Supercell method for the computation of energies of crystals

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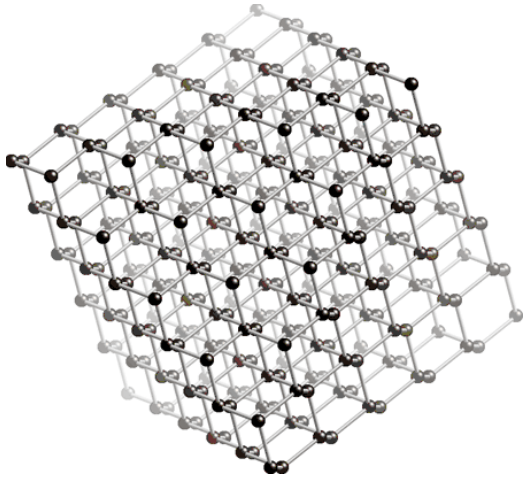
Goals:

- Define and compute numerically the energy per cell of a crystal.
- Define and compute numerically the energy of a local defect inside a crystal.

What is a crystal?



- A periodic arrangement of (fixed) nuclei on a lattice.
  Modeled by a periodic density charge μ_{per}, or by a periodic potential V_{per}.
- An arrangement of moving electrons around these nuclei.

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

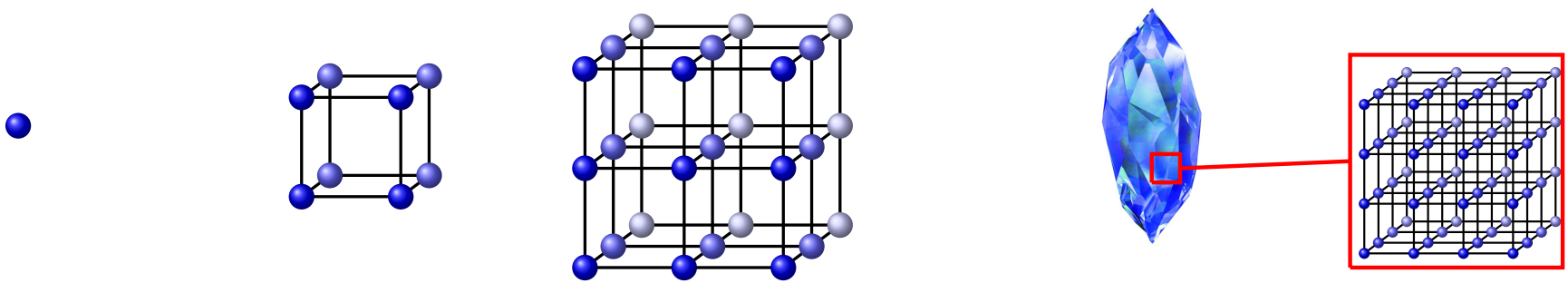
Remarks

- The number of electrons is infinite.
- There is no Schrödinger-like equations *a priori*.

The thermodynamic limit

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 characterise the limit?

The thermodynamic limit for different models

Model	Existence of the limit	Characterisation of the limit
Schrödinger[1,2]	yes	no
non-interacting Schrödinger	yes	yes
DFT	no	(yes ?)
reduced-HF (rHF) [3]	yes	yes
Hartree-Fock (HF) [3]	maybe	(yes ?)

Remarks

The main difficulty for the Existence/Characterisation is to prove that the *final solution* is periodic.
This is the case for the rHF/non-interacting model: the model is convex.
Otherwise, symmetry breaking may happen (periodic problem, non periodic minimiser).

Speed of convergence?

We expect a very slow speed of convergence: the edge effects only vanish at the limit.

Idea

If the *final solution* is periodic, perform a periodic thermodynamic limit.

[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).

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

The non-interacting (linear) case

Notations for the crystal

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

Unit cell: $\Gamma = [-a/2, a/2)^3$.
Reciprocal unit cell: $\Gamma^* = [-\pi/a, \pi/a)^3$.

Supercell: $\Gamma_L := L\Gamma$.

The Hamiltonian we wish to study

(mean field) potential: $V_{\text{per}} \in L^2_{\text{per}}(\Gamma)$.

Non-interacting Hamiltonian:

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

Number of electrons per cell: $N \in \mathbb{N}^*$.

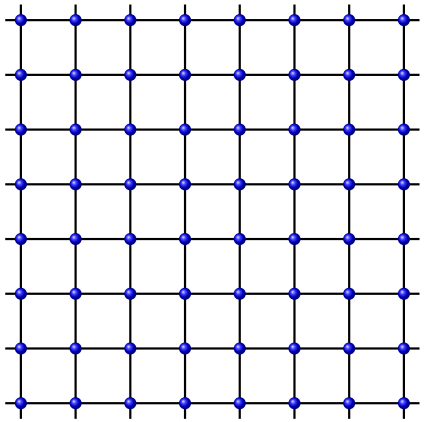
Questions

- How to define the energy per cell?
- How to compute it?

Idea: Perform a periodic thermodynamic limit.

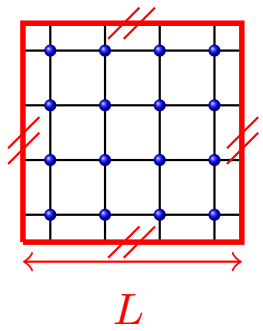
The supercell model

Full model



$\approx$

Supercell model



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

Supercell Hamiltonian

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

Number of electrons = NL^3.

Roadmap

- Compute the total energy E^L of the supercell.
- Define the energy per cell as the limit of $L^{-3}E^L$ when $L \to \infty$.

1-body Hamiltonian

$$h_1 := -\frac{1}{2}\Delta^L + V_{\text{per}} \quad \text{self-adjoint operator acting on} \quad \mathcal{H}_1 = L^2(\Gamma_L).$$

Fact: h_1 is compact resolvent ($\Longrightarrow$ discrete spectrum).

- $\varepsilon_1 \leq \ldots \leq \varepsilon_N$ the smallest eigenvalues.
- $u_1, \ldots, u_N \in \mathcal{H}_1$ the corresponding normalised eigenvectors.

N-body non-interacting Hamiltonian

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

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:

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

The minimiser is $\gamma_N := \mathbb{1}\left(H_N \leq \varepsilon_N\right)$, and satisfies $\mathrm{Tr}_{\mathcal{H}_1}(\gamma_N) = N$.

In our case

Supercell minimiser

$$\gamma^L := \mathbb{1}\left(H^L < \varepsilon_F^L\right) \quad \text{where } \varepsilon_F^L \text{ is chosen so that } \quad \frac{1}{L^3}\mathrm{Tr}_{L^2_{\mathrm{per}}(\Gamma_L)}\left[\gamma^L\right] = N.$$

Supercell energy per unit cell

$$I^L := \frac{1}{L^3}E^L = \frac{1}{L^3}\mathrm{Tr}_{L^2_{\mathrm{per}}(\Gamma_L)}\left[H^L\gamma^L\right].$$

In the thermodynamic limit, we expect

Exact minimiser

$$\gamma_{\mathrm{per}} \quad \text{of the form} \quad \gamma_{\mathrm{per}} := \mathbb{1}\left(H_{\mathrm{per}} < \varepsilon_F\right) \quad \text{where } \varepsilon_F \text{ is chosen so that } \quad \underline{\mathrm{Tr}}\,(\gamma) = N.$$

Exact energy per cell

$$I_{\mathrm{per}} = \underline{\mathrm{Tr}}\,\left[H_{\mathrm{per}}\gamma_{\mathrm{per}}\right].$$

Trace per cell

$$\underline{\mathrm{Tr}}\,\text{“}\,\text{”} := \lim_{L\to\infty}\frac{1}{L^3}\mathrm{Tr}_{L^2_{\mathrm{per}}(\Gamma_L)}.$$

Questions

- Does the sequence $L^{-3}E_L$ converge to I_{per} as $L \to \infty$?
- What is the speed of convergence?

Lemma

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

$$\left|I^L - I_{\mathrm{per}}\right| \leq Ce^{-\alpha L}.$$

The Bloch-Floquet transform

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

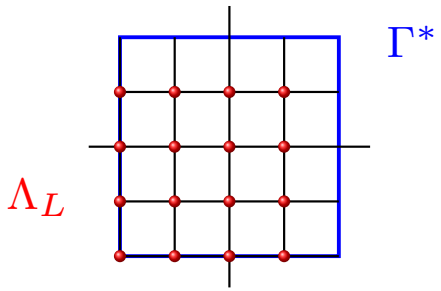
Fibers

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

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

3D case

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



Supercell set of translations : $\mathcal{R}_L := \mathcal{R} \cap \Gamma_L$.

(Supercell) Bloch-Floquet transform for functions

$$f \in L^2(\Gamma_L) = \bigoplus_{\mathbf{Q} \in \Lambda_L} f_{\mathbf{Q}} \quad \text{with} \quad f_{\mathbf{Q}} \in L^2_{\mathbf{Q}}.$$

(Supercell) Bloch fibers

$$f_{\mathbf{Q}}(\mathbf{x}) := \sum_{\mathbf{R} \in \mathcal{R}_L} \mathrm{e}^{\mathrm{i}\mathbf{Q}\cdot\mathbf{R}} f(\mathbf{x} - \mathbf{R}) = \sum_{\mathbf{R} \in \mathcal{R}_L} \mathrm{e}^{\mathrm{i}\mathbf{Q}\cdot\mathbf{R}} \tau_{\mathbf{R}} f(\mathbf{x}).$$

Bloch-Floquet for operators

Lemma

Let $A^L : L^2_{\mathrm{per}}(\Gamma_L) \to L^2_{\mathrm{per}}(\Gamma_L)$ be such that $\tau_{\mathbf{R}} A^L = A^L \tau_{\mathbf{R}}$ for all $\mathbf{R} \in \mathcal{R}$. Then, the operator A^L is block-diagonal with respect to the $L^2_{\mathbf{Q}}$ decomposition.

Proof

$$\left[A^L f\right]_{\mathbf{Q}}(\mathbf{x}) = \sum_{\mathbf{R} \in \mathcal{R}_L} \mathrm{e}^{\mathrm{i}\mathbf{Q}\cdot\mathbf{R}} \tau_{\mathbf{R}} \left(A^L f\right)(\mathbf{x}) = \sum_{\mathbf{R} \in \mathcal{R}_L} \mathrm{e}^{\mathrm{i}\mathbf{Q}\cdot\mathbf{R}} A^L (\tau_{\mathbf{R}} f)(\mathbf{x})$$

$$= A^L \left(\sum_{\mathbf{R} \in \mathcal{R}_L} \mathrm{e}^{\mathrm{i}\mathbf{Q}\cdot\mathbf{R}} \tau_{\mathbf{R}} f \right)(\mathbf{x}) = A^L \left(f_{\mathbf{Q}}\right)(\mathbf{x}).$$

In other words, writing $\widetilde{A^L_{\mathbf{Q}}} : L^2_{\mathbf{Q}} \to L^2_{\mathbf{Q}}$, we have

$$A^L = \begin{pmatrix} \widetilde{A^L_{\mathbf{Q}_0}} & 0 & \cdots & 0 \\ 0 & \widetilde{A^L_{\mathbf{Q}_1}} & 0 & 0 \\ \vdots & \vdots & \vdots & \vdots \\ 0 & \dots & 0 & \widetilde{A^L_{\mathbf{Q}_{L^3}}} \end{pmatrix}$$

(Bloch transform = block-decomposition).

Covariance

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

"Twisted" Bloch transform

$$A^L_{\mathbf{Q}} := S_{-\mathbf{Q}} \widetilde{A^L_{\mathbf{Q}}} S_{\mathbf{Q}}, \quad : L^2_{\mathrm{per}}(\Gamma) \to L^2_{\mathrm{per}}(\Gamma).$$

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

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

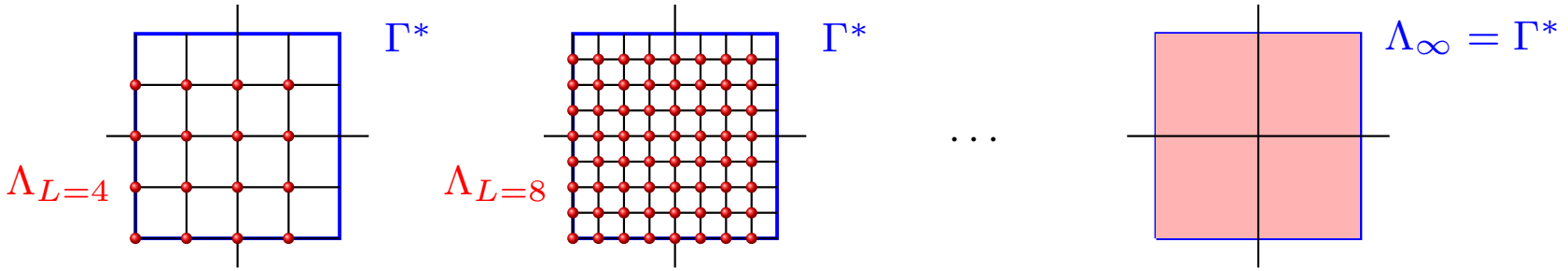
Example: The periodic Hamiltonian

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

Bloch transform

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

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



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

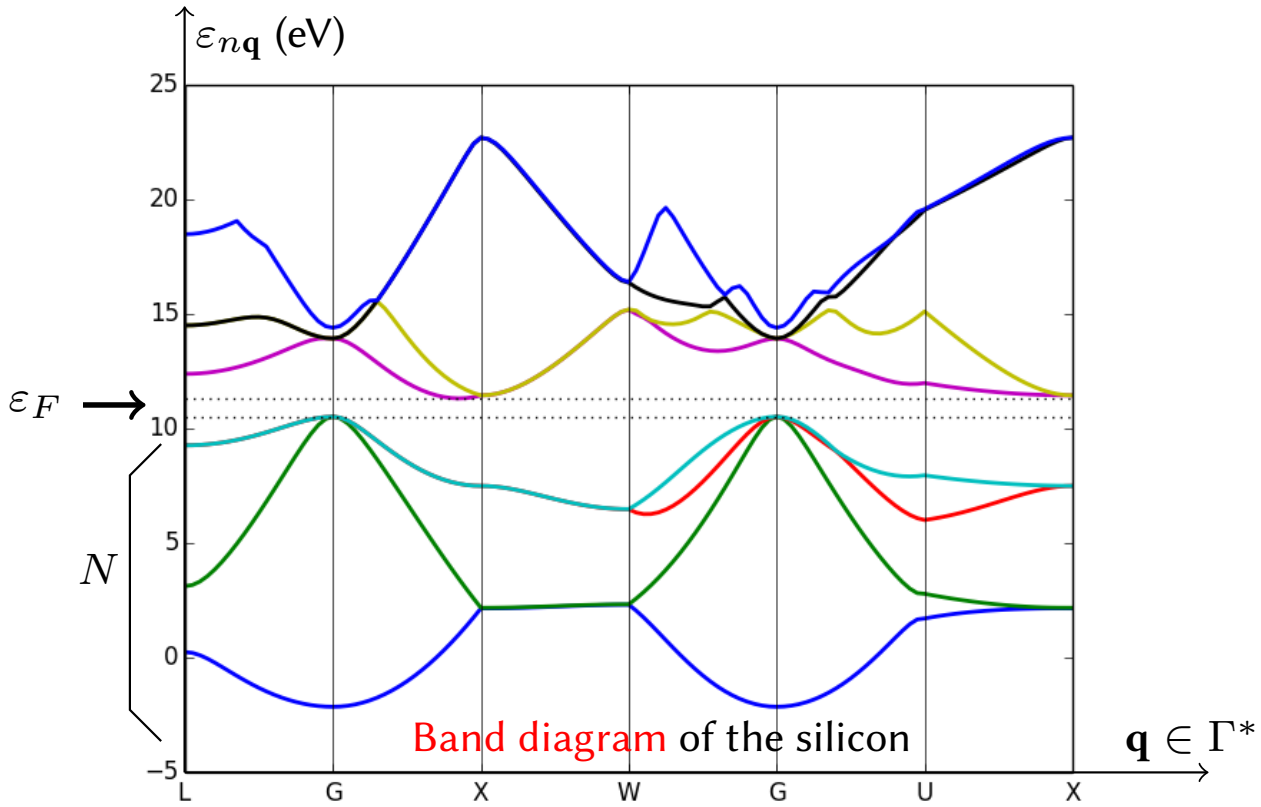
Trace per unit volume

$$\underline{\mathrm{Tr}}_L(A) = \frac{1}{L^3}\sum_{\mathbf{Q}\in\Lambda_L} A_{\mathbf{Q}} \xrightarrow[L\to\infty]{} \underline{\mathrm{Tr}}(A) := \fint_{\Gamma^*} A_{\mathbf{q}}\mathrm{d}\mathbf{q}.$$

Supercell model $\Longleftrightarrow$ Regular sampling of Γ^*.

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: The system is insulating if there exists a gap $g > 0$ such that

$$\forall \mathbf{q} \in \Gamma^*, \quad \varepsilon_{N,\mathbf{q}} + \frac{g}{2} \leq \varepsilon_F \leq \varepsilon_{N+1,\mathbf{q}} - \frac{g}{2}.$$

Full Hamiltonian

One-body density

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

Energy per unit cell (update)

$$I_{\rm per} = \underline{\mathrm{Tr}} \left(H_{\rm per} \gamma_{\rm per} \right) = \fint_{\Gamma^*} \mathrm{Tr}_{L^2_{\rm per}(\Gamma)} \left(H_{\mathbf{q}} \gamma_{\mathbf{q}} \right) \mathrm{d}\mathbf{q} = \fint_{\Gamma^*} \left(\sum_{n=1}^{N} \varepsilon_{n\mathbf{q}} \right) \mathrm{d}\mathbf{q}$$

Supercell model

Supercell one-body density

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

Supercell energy per unit cell (update)

$$I^L = \underline{\mathrm{Tr}} \left(H^L \gamma^L \right) = \frac{1}{L^3} \sum_{\mathbf{Q} \in \Lambda_L} \mathrm{Tr}_{L^2_{\rm per}(\Gamma)} \left(H_{\mathbf{Q}} \gamma_{\mathbf{Q}} \right) = \frac{1}{L^3} \sum_{\mathbf{Q} \in \Lambda_L} \left(\sum_{n=1}^{N} \varepsilon_{n\mathbf{Q}} \right).$$

Error for the energy

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

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

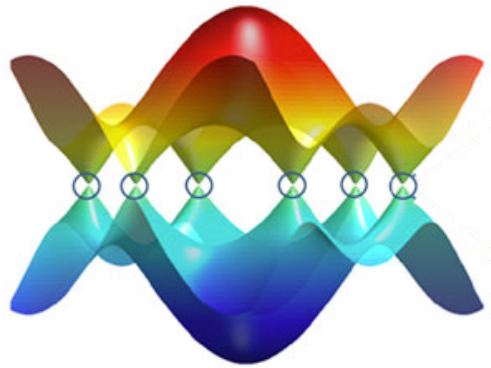
Tools in complex analysis

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 ([4,5,6])

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 to the fact that $|\gamma_{\mathrm{per}}(\mathbf{x}, \mathbf{y})| \leq C\mathrm{e}^{-\alpha|\mathbf{x}-\mathbf{y}|}$.

[4] W. Kohn, Phys. Rev. 115 (1959).

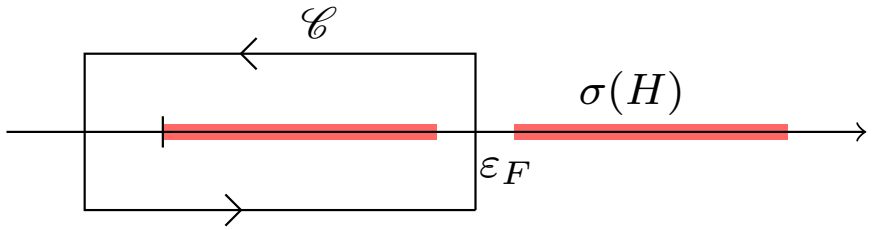
[5] J. Des Cloizeaux, Phys. Rev. 135 (1964).

[6] 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.

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)

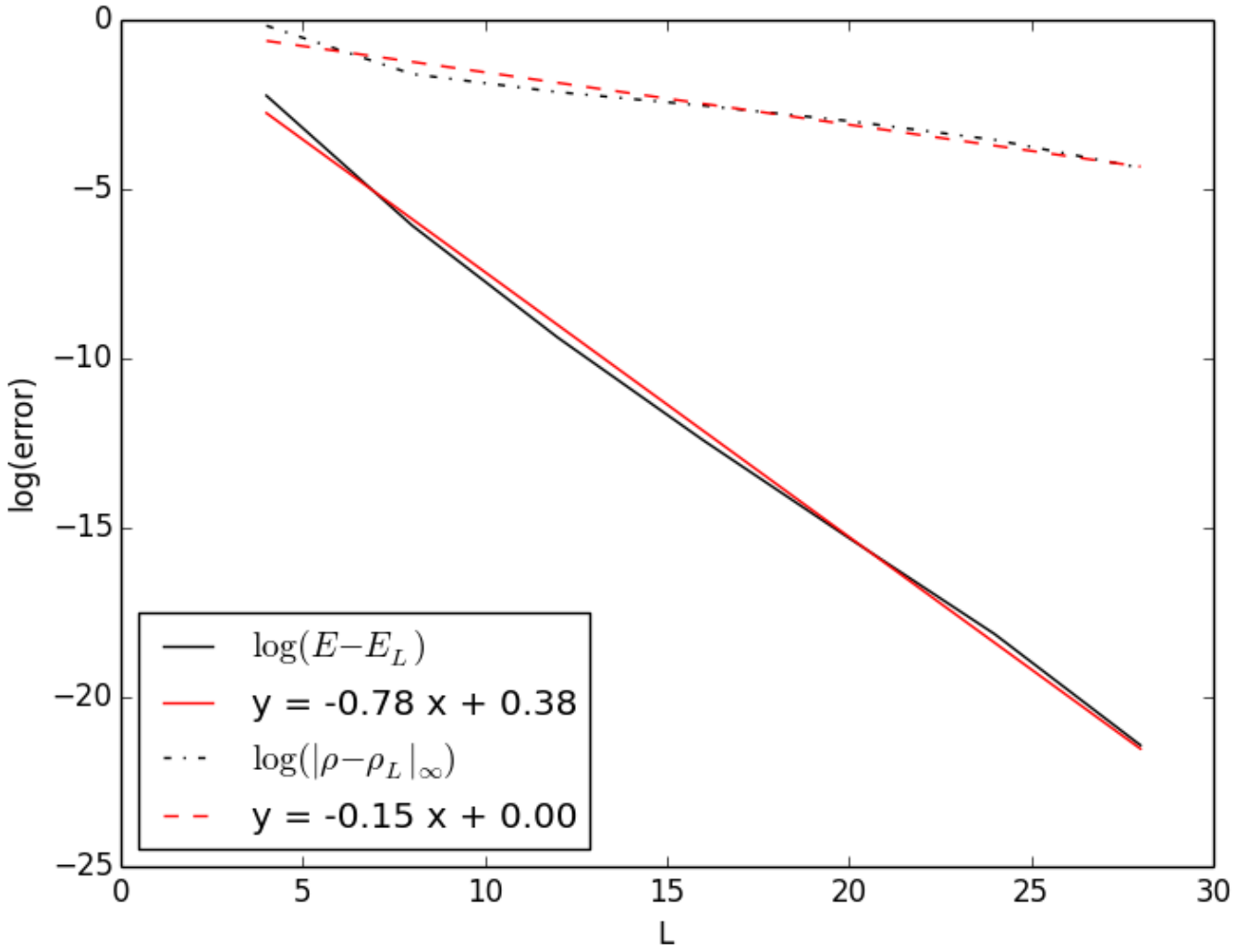
In the insulating case, there exists $C \in \mathbb{R}^+$ and $\alpha > 0$ such that, for all $L \in \mathbb{N}^*$,

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

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

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 define an "interacting" model?

Take an effective model (DFT, HF, ...), and perform a (periodic) thermodynamic limit.

Problem: symmetry breaking

Lemma (current work with Mathieu Lewin and Faizan Nazar)

Let

$$I^\alpha(L) := \frac{1}{L^3} \inf \left\{ \mathrm{Tr}_{L^2(\Gamma_L)}(-\Delta\gamma) + \int_{\Gamma_L} V_{\mathrm{per}}\rho_\gamma + D_L(\rho_\gamma,\rho_\gamma) - \alpha \int_{\Gamma_L} \rho_\gamma^{4/3}, \quad \gamma \in \mathcal{P}(\Gamma_L) \right\},$$

then, for $\alpha > \alpha_c$, it holds that $I^\alpha(2) < I^\alpha(1)$.

Idea

Enforce the 1-periodicity (for instance using convexity) $\Longrightarrow$ reduced Hartree-Fock (rHF).

Recall the non-interacting case

Non-interacting energy as a minimisation problem

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

Set of one-body density matrices

$$\mathcal{P}_{\mathrm{per}} = \left\{\gamma \in \mathcal{S}(L^2(\mathbb{R}^3)),\ 0 \le \gamma \le 1,\ \forall \mathbf{R} \in \mathcal{R},\ \tau_{\mathbf{R}}\gamma = \gamma\tau_{\mathbf{R}}\right\}.$$

Set of supercell one-body density matrices

$$\mathcal{P}_{\mathrm{per}} = \left\{\gamma \in \mathcal{S}(L^2_{\mathrm{per}}(\Gamma_L)),\ 0 \le \gamma \le 1,\ \forall \mathbf{R} \in \mathcal{R},\ \tau_{\mathbf{R}}\gamma = \gamma\tau_{\mathbf{R}}\right\}.$$

Charge density: $\mu_{\rm per}$

reduced Hartree-Fock

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

with ($\mu_{\rm per}$ is the charge density)

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

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

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

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

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

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 $\gamma^L \in \mathcal{P}^L$ cannot be compared.

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.

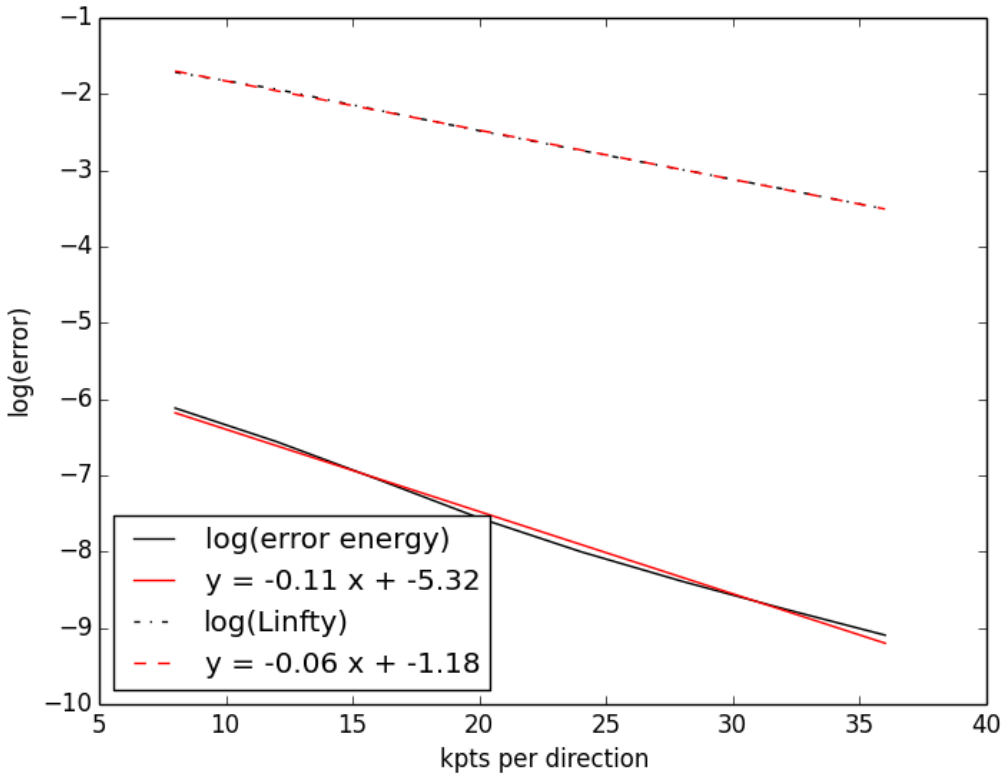
$\Longrightarrow$ Construct test functions from $\rho_{\gamma_{\mathrm{per}}}$ and ρ_{γ^L}, and use the results for the linear case.

Lemma (DG, Salma Lahbabi)

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

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

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



Rates of convergence for the reduced Hartree-Fock model.

Crystals with local defects

General picture

Perfect crystal

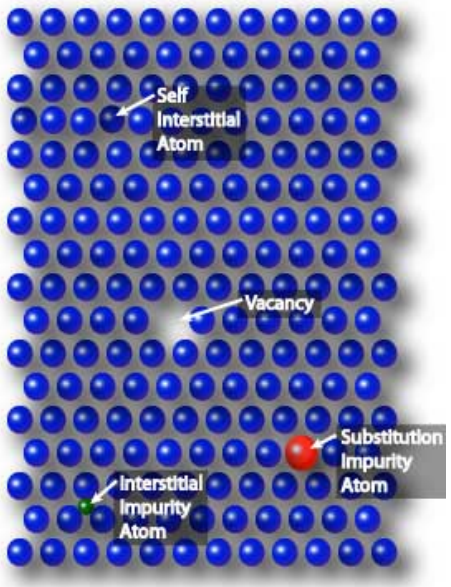
$$H_{\rm per} = -\frac{1}{2}\Delta + V_{\rm per} \quad \text{acting on} \quad L^2_{\rm per}(\Gamma).$$

Local defect (charge)

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

Crystal with local defect

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



Local defects

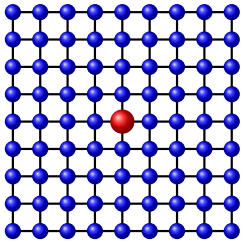
How to define the energy of the defect?

- 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.

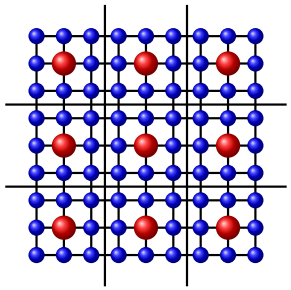
Supercell thermodynamic limit

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 $\mathcal{J}_\nu^L$ have limit as $L \to \infty$? Yes in rHF[7]: $\mathcal{J}_\nu$.
- Can we characterize the limit? Yes, as a minimization problem.
- What is the speed of convergence of $\mathcal{J}_\nu^L \to \mathcal{J}_\nu$?

[7] 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 $\nu \in L^2_{\rm per}(\Gamma)$ 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.

Comments

- Recover the term predicted by Leslie and Gillan[8], and by Makov and Payne[9].
- 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.

[8] M. Leslie and M.J. Gillan. J. Phys. C 18 (1985).

[9] 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.

Work in progress (see Antoine Levitt's talk)

- 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.