Numerical methods for Brillouin zone integration

David Gontier

CEREMADE, Université Paris-Dauphine

Oberwolfach
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Joint work with É. Cancès, V. Ehrlacher, A. Levitt, D. Lombardi

Goal:

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

Crystal? modelled by a periodic, non-interacting Hamiltonian.

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

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

Non-interacting Hamiltonian:

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

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

Energy (per cell) of the electrons?

Bloch's transform

Studying $H_{\rm per} \Longleftrightarrow$ studying the family of operators $(H_{\mathbf{k}})_{\mathbf{k}\in\Gamma^*}$, where

$$H_{\mathbf{k}} := \frac{1}{2}(-\mathrm{i}\nabla_{\rm per} + \mathbf{k})^2 + V_{\rm per}, \quad \text{acting on} \quad L^2_{\rm per}(\Gamma).$$

Remark: The operators $H_{\mathbf{k}}$ are compact resolvent:

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

Integrated density of states (IDoS) (we denote by $⨍_{\Gamma^*} := \frac{1}{|\Gamma^*|}\int_{\Gamma^*}$)

$$\mathcal{N}(\varepsilon) := ⨍_{\Gamma^*} \left(\sum_{n>0} \mathbb{1}(\varepsilon_{n\mathbf{k}} \leq \varepsilon) \right) \mathrm{d}\mathbf{k}.$$

Fermi energy:

$$\varepsilon_F \in \mathbb{R} \quad \text{such that} \quad \mathcal{N}(\varepsilon_F) = N.$$

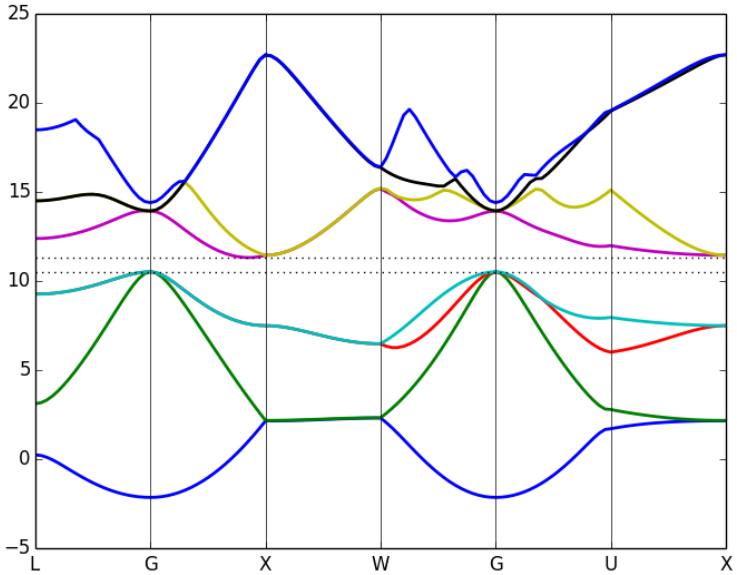
Energy per unit cell

$$E := ⨍_{\Gamma^*} \left(\sum_{n>0} \varepsilon_{n\mathbf{k}} \mathbb{1}(\varepsilon_{n\mathbf{k}} \leq \varepsilon_F) \right) \mathrm{d}\mathbf{k}.$$

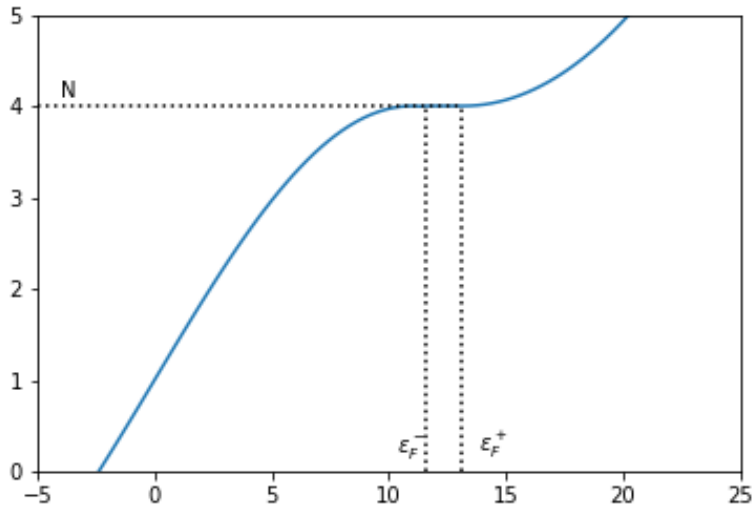
How to perform numerically the Brillouin zone integration $⨍_{\Gamma^*}$?

Here, we assume that we can perfectly compute the eigenvalues $\varepsilon_{n\mathbf{k}}$.

Band diagram of silicon (insulator)

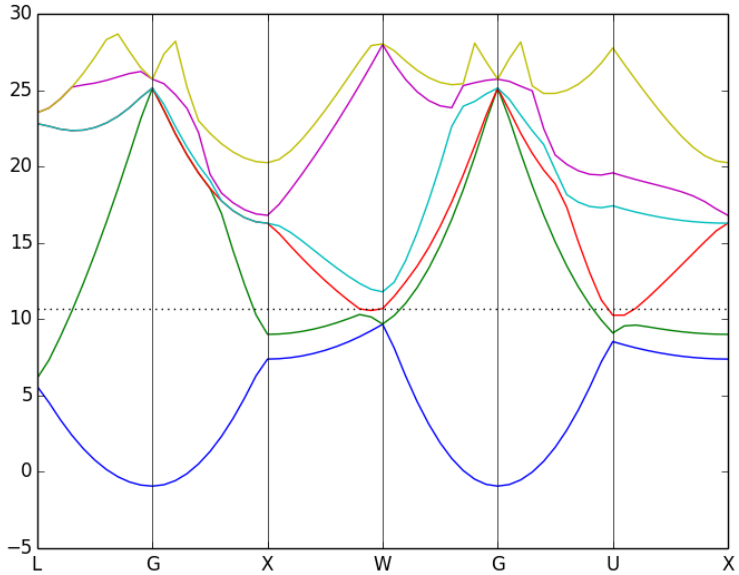


IDoS $\mathcal{N}(\varepsilon)$

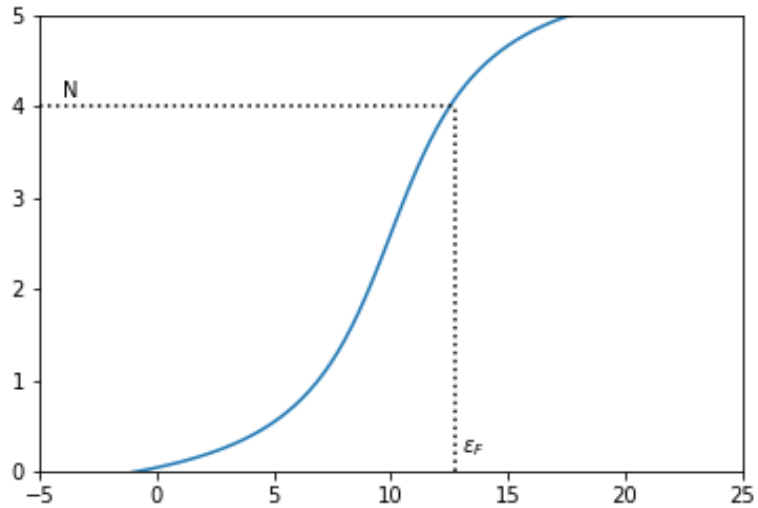


$\mathcal{N}^{-1}(\{N\}) = [\varepsilon_F^-, \varepsilon_F^+]$ is an interval.

Band diagram of aluminium (metal)



IDoS $\mathcal{N}(\varepsilon)$



$\mathcal{N}^{-1}(\{N\}) = \{\varepsilon_F\}$ is unique.

The insulating case

In the insulating case, $\mathbb{1}(\varepsilon_{n\mathbf{k}} < \varepsilon_F) = 1$ if $n \leq N$, and 0 else, hence the energy simplifies into

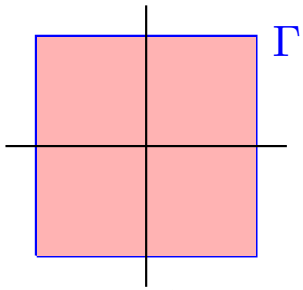
$$E = \fint_{\Gamma^*} \left(\sum_{n=1}^{N} \varepsilon_{n\mathbf{k}} \right) \mathrm{d}\mathbf{k}.$$

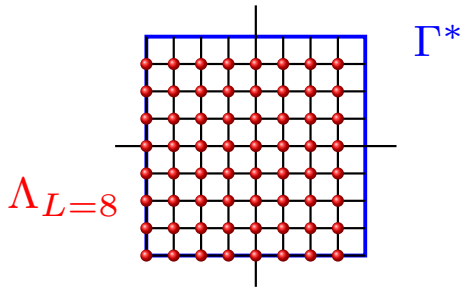
Lemma

The integrand $\mathbf{k} \mapsto \sum_{n=1}^{N} \varepsilon_{n\mathbf{k}}$ is analytic and $\mathcal{R}^*$-periodic. In particular, there exists $C \in \mathbb{R}^+$ and $\alpha > 0$ such that, for all $L \in \mathbb{N}$,

$$\left| \fint_{\Gamma^*} \left(\sum_{n=1}^{N} \varepsilon_{n\mathbf{k}} \right) \mathrm{d}\mathbf{k} - \sum_{\mathbf{K} \in \Lambda_L} \left(\sum_{n=1}^{N} \varepsilon_{n\mathbf{K}} \right) \right| \leq C \mathrm{e}^{-\alpha L} \qquad \textit{(Exponential rate of convergence).}$$

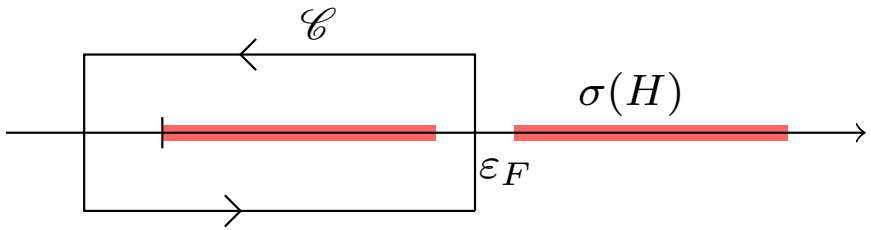
We can approximate the integral with a Riemann sum.





Proof $\mathbf{k} \mapsto H(\mathbf{k})$ is analytic (quadratic), and

$$\sum_{n=1}^{N} \varepsilon_{n\mathbf{k}} = \mathrm{Tr} \left(\oint_{\mathscr{C}} \frac{H_{\mathbf{k}}}{z - H_{\mathbf{k}}} \mathrm{d}z \right).$$



Metallic systems

Problems

- First, we need to compute the Fermi level (extra source of error);
- The integrand is no longer smooth.

Two widely used methods

- Interpolation methods;
- Smearing methods.

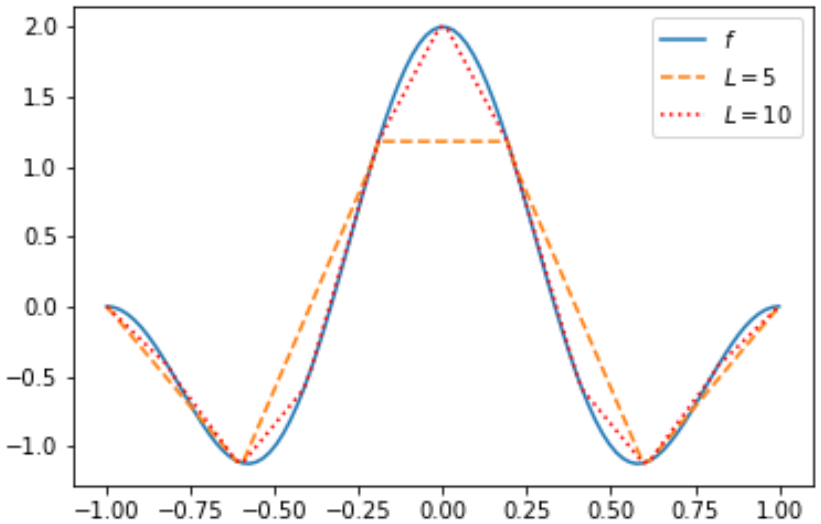
The metallic case. 1/ Interpolation methods

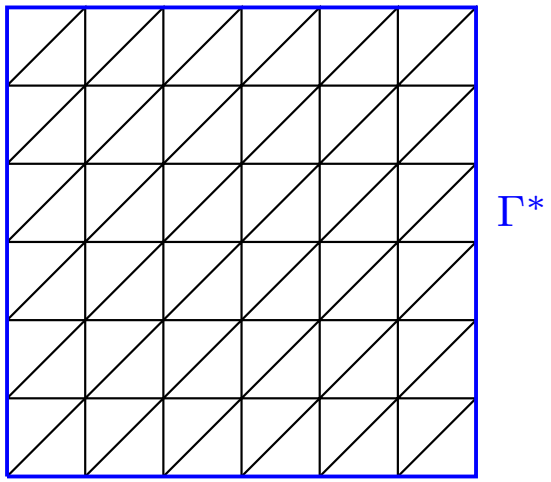
Idea: Approximate $\mathbf{k} \mapsto \varepsilon_{n\mathbf{k}}$ with a simpler function.

A family of linear interpolation operators $\left(\Pi^{L,q}\right)_{L\in\mathbb{N}}$ is of order $(q+1)$ if

$$\forall f \text{ smooth}, \quad \|f - \Pi^{L,q} f\|_\infty \leq \frac{C}{L^{q+1}} \|f^{(q+1)}\|_\infty.$$

Example: the *linear tetrahedron method* ($q = 1$).





division of Γ^* in simplexes (for $d = 2$).

Approximated eigenvalues

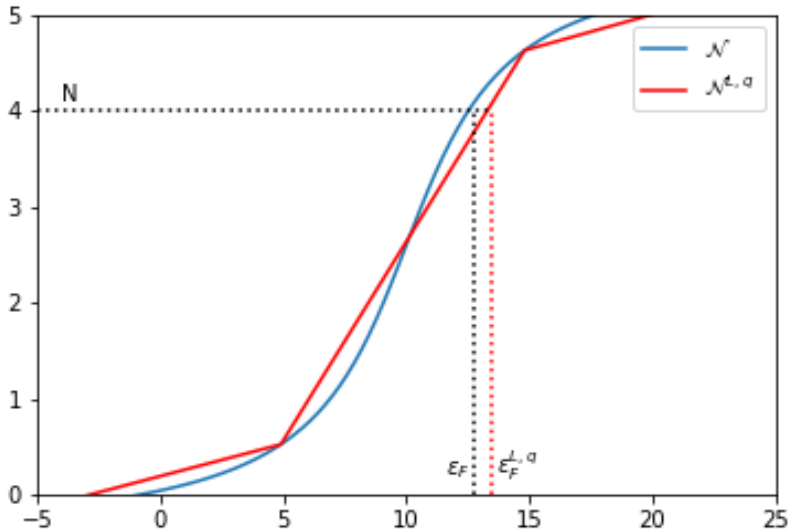
$$\varepsilon_{n\mathbf{k}}^{L,q} := \Pi^{L,q}\left(\varepsilon_{n\mathbf{k}}\right).$$

Approximated integrated density of states

$$\mathcal{N}^{L,q}(\varepsilon) := \fint_{\Gamma^*} \left(\sum_{n>0} \mathbb{1}(\varepsilon_{n\mathbf{k}}^{L,q} \leq \varepsilon) \right) \mathrm{d}\mathbf{k}.$$

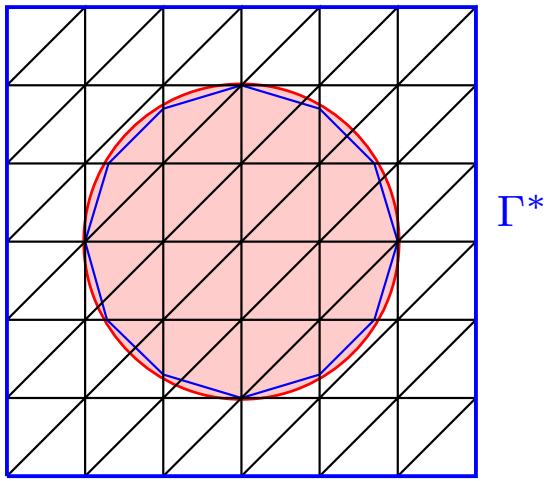
Approximated Fermi energy

$$\varepsilon_F^{L,q} \in \mathbb{R} \quad \text{such that} \quad \mathcal{N}^{L,q}(\varepsilon_F^{L,q}) = N.$$



Approximated energy per unit cell

$$E^{L,p,q} := \fint_{\Gamma^*} \left(\sum_{n>0} \varepsilon_{n\mathbf{k}}^{L,p} \mathbb{1}(\varepsilon_{n\mathbf{k}}^{L,q} \leq \varepsilon_F) \right) \mathrm{d}\mathbf{k}.$$



- $q \Longrightarrow$ the domain of integration (here still a union of simplexes).
- $p \Longrightarrow$ degree of the polynomial to integrate on this domain.

In practice, $p \geq q$. (we can integrate quadratic functions (p=2) on simplexes (q=1)).

Assumptions:

- No band-crossings at the Fermi level;
- No flat bands at the Fermi level ($\nabla_{\mathbf{k}} \varepsilon_{n\mathbf{k}} \neq \mathbf{0}$).

$\Longrightarrow$ The function $\mathcal{N}(\varepsilon)$ is smooth near the Fermi level.

Lemma (Cancès, Ehrlacher, G., Levitt, Lombardi)

Let $\left(\Pi^{L,q}\right)_{L\in\mathbb{N}}$ *and* $\left(\Pi^{L,p}\right)_{L\in\mathbb{N}}$ *be linear interpolation operators of order* $(q+1)$ *and* $(p+1)$ *respectively. Then, under the previous assumptions, there exists* $\delta > 0$ *and* $C \in \mathbb{R}^+$ *such that, for all* $L \in \mathbb{N}$,

$$\max_{\varepsilon\in(\varepsilon_F-\delta,\varepsilon_F+\delta)} \left|\mathcal{N}(\varepsilon) - \mathcal{N}^{L,q}(\varepsilon)\right| \leq \frac{C}{L^{q+1}}, \qquad \left|\varepsilon_F - \varepsilon_F^{L,q}\right| \leq \frac{C}{L^{q+1}},$$

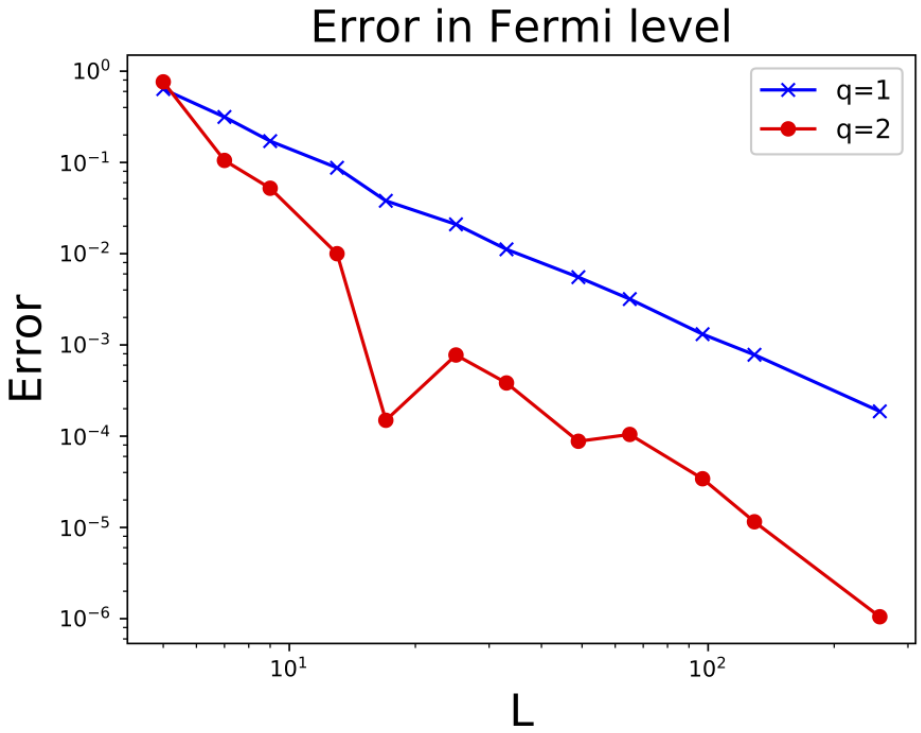
and

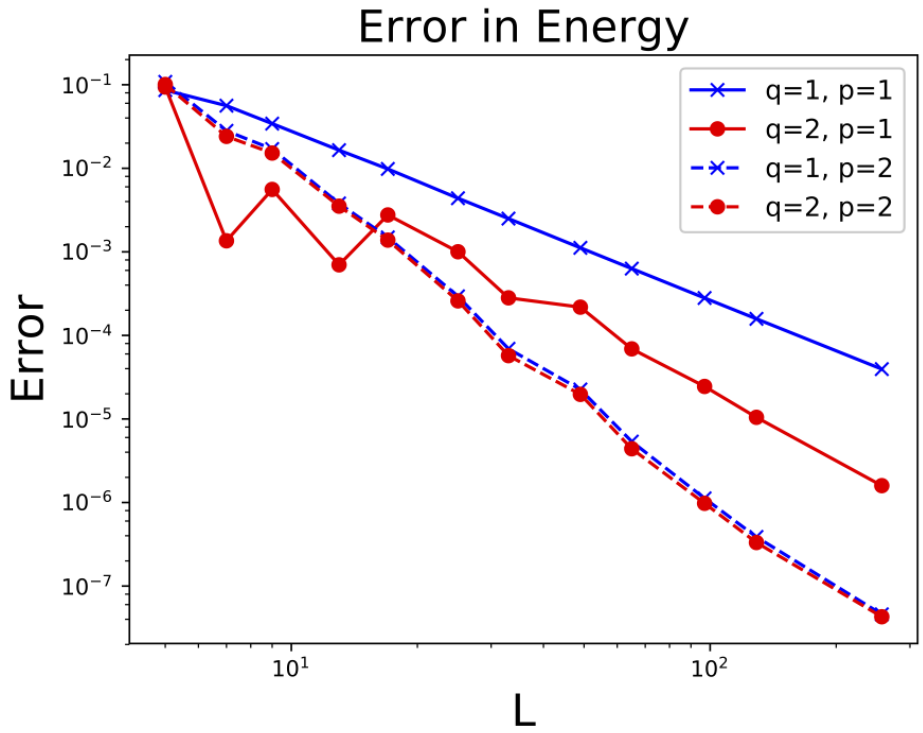
$$\left|E - E^{L,p,q}\right| \leq C\left(\frac{1}{L^{p+1}} + \frac{1}{L^{2q+2}}\right).$$

Remarks:

- The $L^{-(p+1)}$ comes from the *bulk error*, while the $L^{-(2q+2)}$ comes from the *surface error*.
- For tetrahedron methods ($q = 1$), we can choose $p = 3$ (low computational cost, but better precision for the energy). This leads to $O(L^{-4})$ rate of convergence.
- The last result only works for the energy.

Results (toy model, not coming from a Schrödinger operator)





The metallic case. 2/ Smearing methods

Idea: Replace the discontinuous function $f(x) := \mathbb{1}(x < 0)$ by a smooth function f^σ.

Smearing functions

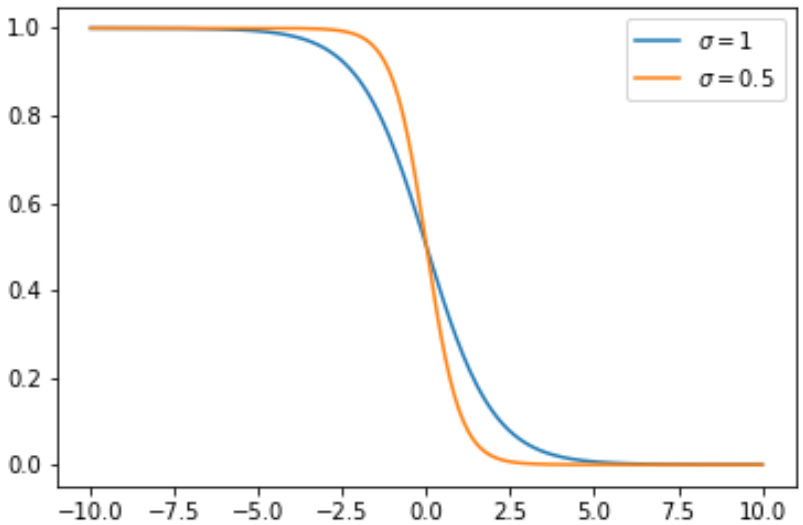
$$f^\sigma(x) := f^1(x/\sigma) \quad \text{where } (f - f^1) \text{ decays exponentially}$$

Definition f^1 is of order $p \in \mathbb{N}$ if

$$\int_{\mathbb{R}} (f - f^1)(x) P(x) \mathrm{d}x = 0 \quad \text{for all polynomials } P \text{ of degree} \leq p,$$

Example: Fermi-Dirac (of order 1)

$$f^\sigma(x) := \frac{1}{1 + \mathrm{e}^{x/\sigma}}.$$



Smeared integrated density of states

$$\mathcal{N}^\sigma(\varepsilon) := \fint_{\Gamma^*} \left(\sum_{n>0} f^\sigma(\varepsilon_{n\mathbf{k}} - \varepsilon) \right) \mathrm{d}\mathbf{k}.$$

Smeared Fermi level

$$\varepsilon_F^\sigma \in \mathbb{R} \quad \text{such that} \quad \mathcal{N}^\sigma(\varepsilon_F^\sigma) = N.$$

Smeared energy per unit cell

$$E^\sigma := \fint_{\Gamma^*} \left(\sum_{n>0} \varepsilon_{n\mathbf{k}} f^\sigma(\varepsilon_{n\mathbf{k}} - \varepsilon_F^\sigma) \right) \mathrm{d}\mathbf{k}.$$

Lemma (Cancès, Ehrlacher, G., Levitt, Lombardi)

Let f^1 be a smearing function of order $p \in \mathbb{N}$. Under the previous assumptions, there exists $\delta > 0$ and $C \in \mathbb{N}^+$ such that, for all $\sigma > 0$,

$$\max_{\varepsilon \in (\varepsilon_F - \delta, \varepsilon_F + \delta)} |\mathcal{N}(\varepsilon) - \mathcal{N}^\sigma(\varepsilon)| \leq C\sigma^{p+1}, \quad |\varepsilon_F - \varepsilon_F^\sigma| \leq C\sigma^{p+1}, \quad \text{and} \quad |E - E^\sigma| \leq C\sigma^{p+1},$$

Idea of the proof

- near the Fermi level, $\mathcal{N}$ is smooth $\Longrightarrow$ perform Taylor expansion;
- far from the Fermi level, $(f - f^\sigma)(\cdot - \varepsilon_F)$ decays exponentially.

Remark: We still need to find a numerical method to approximate $\mathcal{N}^\sigma$, ε_F^σ and E^σ.
Recall that,

$$\mathcal{N}^\sigma(\varepsilon) := \fint_{\Gamma^*} \left(\sum_{n>0} f^\sigma(\varepsilon_{n\mathbf{k}} - \varepsilon) \right) \mathrm{d}\mathbf{k}.$$

Lemma (for the Fermi-Dirac function)

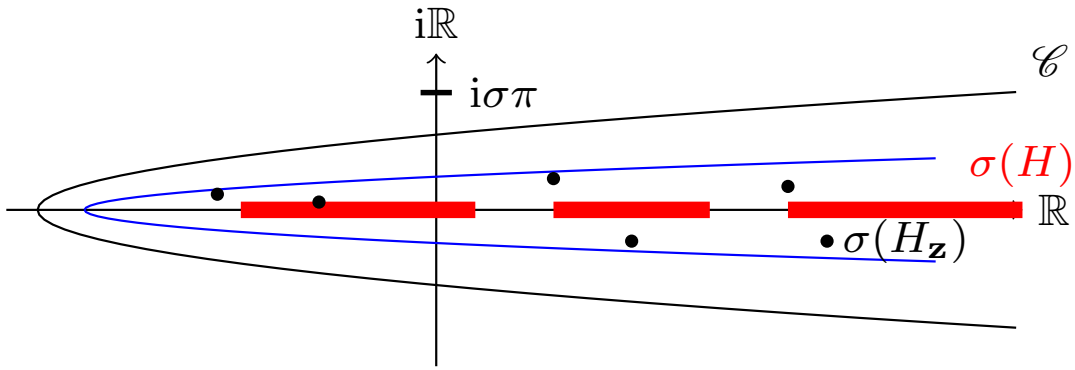
For all ε in a neighbourhood of ε_F, and all $\sigma > 0$, the integrand $\mathbf{k} \mapsto \sum_{n>0} f^\sigma(\varepsilon_{n\mathbf{k}} - \varepsilon)$ is $\mathcal{R}^*$-periodic and analytic in a complex strip of width $(cst \cdot \sigma)$. In particular, there exists $C \in \mathbb{R}^+$ and $\alpha > 0$, such that

$$\left| \fint_{\Gamma^*} \left(\sum_{n>0} f^\sigma(\varepsilon_{n\mathbf{k}} - \varepsilon) \right) \mathrm{d}\mathbf{k} - \sum_{\mathbf{K} \in \Lambda_L} \left(\sum_{n>0} f^\sigma(\varepsilon_{n\mathbf{K}} - \varepsilon) \right) \right| \leq C\sigma^{-(d+1)} \mathrm{e}^{-\alpha\sigma L}.$$

Again, we can approximate the integral with a Riemann sum.

Idea of the proof

$$\sum_{n>0} f^\sigma(\varepsilon_{n\mathbf{k}} - \varepsilon) = \mathrm{Tr}\left(\oint_{\mathscr{C}} \frac{f^\sigma(z)}{z - H_{\mathbf{k}}} \mathrm{d}z \right).$$



Conclusion

Insulators with Riemann sum

$$\boxed{\left|E - E^L\right| \leq C\mathrm{e}^{-\alpha L}.}$$

Metals with interpolation methods of order p and q,

$$\boxed{\left|E - E^{L,p,q}\right| \leq C\left(\frac{1}{L^{p+1}} + \frac{1}{L^{2q+2}}\right).}$$

Metals with smearing methods of order p

$$\left|E - E^{\sigma,L}\right| \leq |E - E^\sigma| + \left|E^\sigma - E^{\sigma,L}\right| \leq C\left(\sigma^{p+1} + \sigma^{-(d+1)}\mathrm{e}^{-\alpha\sigma L}\right).$$

Choosing $\sigma \approx \sigma_L := L^{-1^+}$,

$$\boxed{\left|E - E^{\sigma_L,L}\right| \leq \frac{C}{L^{(p+1)^-}}.}$$

• É. Cancès, V. Ehrlacher, D. Gontier, A. Levitt, D. Lombardi. *Numerical quadrature in the Brillouin zone for periodic Schrödinger operators.* (in preparation, but should be on arXiv very soon).