High-order integration methods for Brillouin Zone integration

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Some motivations

Main objective: Numerical simulation of materials

Some properties

- *Mechanical properties*
  elastic constants
- *Thermic properties*
  specific heat
- *Electric properties*
  conductivity
- *Magnetic properties*
  susceptibility
- *Optical properties*
  conductivity

Ok, but why numerics ?

- Cheaper, faster
- Fundamental research
- Material design

Cost of a 2 nm^2 electronic chip ?

$30,000

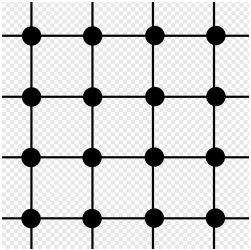
What is a material ?

Infinite periodic crystal $\Longrightarrow$ **Physical space:** $\mathbb{R}^d$, **Lattice:** $\mathcal{R} \equiv \mathbb{Z}^d$

Infinite number of electrons $\Longrightarrow$ **Fixed electronic density:** $\rho(\mathbf{x})$

Too complicated ?

Reduce the dimension !



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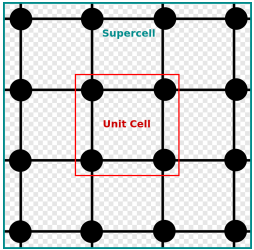


Schrödinger equation

Further simplifications

- Born-Oppenheimer approximation
- e-e interaction neglected
- Finite basis of localized functions: **Wannier functions**

Time Independent Schrödinger Equation

Let $H(\mathbf{R}, \mathbf{R}')$ be the Hamiltonian between two sites of $\mathcal{R}$. It is a Hermitian matrix of $\mathbb{C}^{M\times M}$ with $\mathcal{R}$-periodicity which verifies

$$H(\mathbf{R}, \mathbf{R}')\psi_n = E_n\psi_n \qquad \text{(TISE)}$$

where the E_n and ψ_n are the eigenvalues and eigenvectors of $H(\mathbf{R}, \mathbf{R}')$.

Bloch's theorem

Reciprocal lattice

$$\mathcal{R}^* = 2\pi/\mathcal{R} \tag{1}$$

Brillouin zone ($\mathcal{R}^*$ unit cell)

$$\mathcal{B} \equiv [-\pi, \pi]^d \tag{2}$$

Bloch's transform

Solutions to (TISE) can be expanded in a basis of planewaves modulated by $\mathcal{R}$-periodic functions called **Bloch waves**.
For $\mathbf{k} \in \mathcal{B}$,

$$\psi_{n\mathbf{k}}(\mathbf{R}) = \mathrm{e}^{i\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}} \tag{3}$$

where $\forall \mathbf{R} \in \mathcal{R}$, $u_{n\mathbf{k}}(\mathbf{r} + \mathbf{R}) = u_{n\mathbf{k}}(\mathbf{r})$.

Bloch transform

Main Idea: Study the system using these Bloch waves Using the Bloch theorem

Bloch transform and Schrödinger equation (again ?)

$\forall \mathbf{k} \in \mathcal{B}$,

$$H_{\mathbf{k}} = \sum_{\mathbf{R} \in \mathcal{R}_L} \mathrm{e}^{i\mathbf{k}\cdot\mathbf{R}} H(\mathbf{0}, \mathbf{R}) \in \mathbb{C}^{M \times M} \tag{4}$$

$\forall \mathbf{k} \in \mathcal{B}$,

$$H_{\mathbf{k}} u_{n\mathbf{k}} = \varepsilon_{n\mathbf{k}} u_{n\mathbf{k}} \tag{TISE2}$$

where the $\varepsilon_{n\mathbf{k}}$ are **bands** and the set of all bands is the **band structure** of the system.

Remark:

- Bloch's transform (among other many great things): *Théorie Spectrale et Mécanique Quantique, Ed. 2024*, Mathieu Lewin
- Other derivations of Bloch's Theorem: *Convergence rates of supercell calculations in the reduced Hartree–Fock model,* , David Gontier, Salma Lahbabi

A band structure example

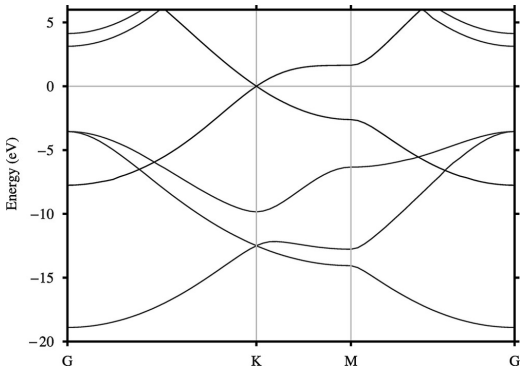


Figure 1: Band structure of graphene taken from "The Physics of Graphene"

Brillouin Zone Integration

Bulk properties

Bulk properties of our system can be written as two types of integrals

$$I(E) = \frac{1}{|\mathcal{B}|} \sum_n \int_{\mathcal{B}} f(H_{\mathbf{k}}) \delta(E - \varepsilon_{n\mathbf{k}}) \mathrm{d}\mathbf{k}$$

$$F(E) = \frac{1}{|\mathcal{B}|} \sum_n \int_{\mathcal{B}} f(H_{\mathbf{k}}) \mathbb{1}(E - \varepsilon_{n\mathbf{k}}) \mathrm{d}\mathbf{k}$$

where f is a continuous function of $H_{\mathbf{k}}$.

We restrict ourselves to $I(E)$ where $f = 1$, the

Density Of States (DOS)

What is the DOS ?

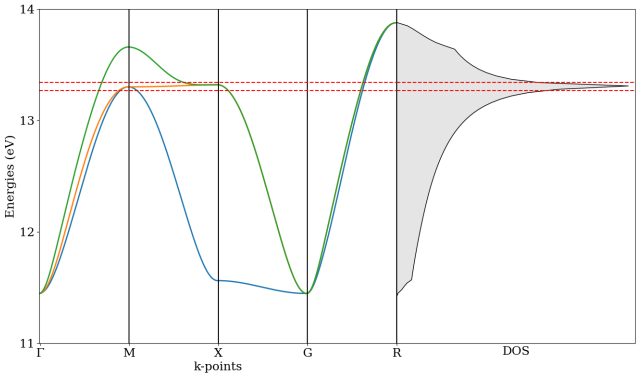
$$D(E) = \frac{1}{|\mathcal{B}|} \sum_{n=1}^{M} \int_{\mathcal{B}} \delta(E - \varepsilon_{n\mathbf{k}}) \mathrm{d}\mathbf{k}$$

$$D(E) = \frac{1}{|\mathcal{B}|} \sum_{n=1}^{M} \int_{S_n(E)} \frac{1}{|\nabla \varepsilon_{n\mathbf{k}}|} \mathrm{d}\sigma(\mathbf{k})$$

where $S_n(E) = \{\mathbf{k} \in \mathcal{B}, \varepsilon_{n\mathbf{k}} = E\}$

Issues

- Not well-defined
- Singular function of E
- Not easily computable



Smearing and Periodic Trapezoidal Rule

Main Idea: Smooth the Dirac with a regular kernel $K_\eta \underset{\eta \to 0^+}{\longrightarrow} \delta$

Smearing

Formally:

$$D(E) = \lim_{\eta \to 0^+} (D * K_\eta)(E) = \lim_{\eta \to 0^+} D_\eta(E) \tag{5}$$

Many choices, but the most natural one is the **Lorentzian**:

$$K_\eta(E) = \frac{1}{\pi} \frac{\eta}{E^2 + \eta^2} = -\frac{1}{\pi} \mathrm{Im} \left(\frac{1}{E + i\eta} \right) \tag{6}$$

Why ?

- Simple expression, simple to compute
- At fixed $\eta \Leftrightarrow$ Trace of the Green's function

Smearing

Final Formula

$$D(E) = -\frac{1}{\pi} \lim_{\eta \to 0^+} \mathrm{Im} \left(\sum_n \int_{\mathcal{B}} \frac{1}{E + i\eta - \varepsilon_{n\mathbf{k}}} \mathrm{d}\mathbf{k} \right)$$

$$D_{N,\eta}(E) = -\frac{1}{\pi} \mathrm{Im} \left(\frac{1}{N^d} \sum_{\mathbf{k} \in \mathcal{B}_N} \mathrm{Tr} \left(\frac{1}{E + i\eta - H_{\mathbf{k}}} \right) \right)$$

where

$$\mathcal{B}_N = \left\{ \frac{2\pi}{N} \mathbf{n} - \pi, \mathbf{n} \in \mathbb{Z}^d, 0 \leq n_i \leq N-1, i \in \{1, \ldots, d\} \right\} \tag{7}$$

Take away

- Computes an approximated DOS
- System dependent: hard to automatically tune
- Error in $\mathcal{O}(N^{-1})$

Smeared DOS also have a physical meaning and are of use to physicists and chemists.

Linear Tetrahedron

Main Idea: Interpolate linearly the bands in tetrahedra.
Reminder:

$$D(E) = \frac{1}{|\mathcal{B}|} \sum_{n=1}^{M} \int_{S_n(E)} \frac{1}{|\nabla \varepsilon_{n\mathbf{k}}|} \mathrm{d}\sigma(\mathbf{k}) \tag{8}$$

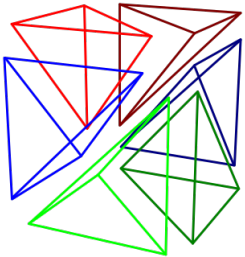


Figure 2: Tetrahedral decomposition of a cube (taken from Wikipedia)

Take away

- Explicit formula for the approximated DOS in all dimensions
- Easy to compute from the formulas
- Performs badly for convex or concave functions
- Error in $\mathcal{O}(N^{-2})$

Brillouin Contour Deformation (BCD)

Main idea: Regularize the integrand using contour deformation

Lemma

Let I be a $\mathcal{R}^*$-periodic function, analytic in an open set $U = \mathbb{R}^d + i[-\eta, \eta]^d$. Then, for all $\mathcal{R}^*$-periodic and continuously differentiable functions $\mathbf{h}(\mathbf{k}) : \mathbb{R}^d \to [-\eta, \eta]^d$, we have

$$\int_{\mathcal{B}} I(\mathbf{k}) \mathrm{d}\mathbf{k} = \int_{\mathcal{B}} I(\mathbf{k} + i\mathbf{h}(\mathbf{k})) \det(\mathbf{1} + i\mathbf{h}'(\mathbf{k})) \mathrm{d}\mathbf{k}$$

In our case for $\eta = 0$,

$$D(E) = -\frac{1}{\pi} \mathrm{Im} \left(\frac{1}{|\mathcal{B}|} \sum_{n=1}^{M} \int_{\mathcal{B}} \frac{1}{E - \varepsilon_{\mathbf{k}+i\mathbf{h}(\mathbf{k})}} \det\left(\mathbf{1} + i\mathbf{h}'(\mathbf{k})\right) \mathrm{d}\mathbf{k} \right) \tag{9}$$

Remark

- Cauchy theorem to prove the lemma
- Regular integrand for whatever $\eta \geq 0$

Examples of deformation

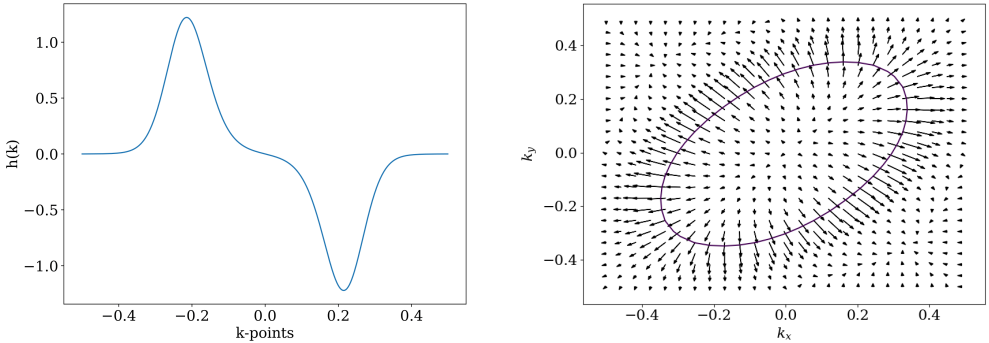


Figure 3: 1D and 2D deformations (for monatomic chain and graphene)

Some insights on the BCD

Reminder:

$$D(E) = -\frac{1}{\pi}\mathrm{Im}\left(\frac{1}{|\mathcal{B}|}\sum_{n=1}^{M}\int_{\mathcal{B}}\frac{1}{E-\varepsilon_{\mathbf{k}+i\mathbf{h}(\mathbf{k})}}\det\left(\mathbf{1}+i\mathbf{h}'(\mathbf{k})\right)\mathrm{d}\mathbf{k}\right) \tag{10}$$

Discretization:

$$D_N(E) = -\frac{1}{\pi N^d}\mathrm{Im}\left(\sum_{\mathbf{k}\in\mathcal{B}_N}\mathrm{Tr}\left(\frac{1}{E-H_{\mathbf{k}+i\mathbf{h}(\mathbf{k})}}\right)\det\left(\mathbf{1}+i\mathbf{h}'(\mathbf{k})\right)\right) \tag{11}$$

Remark:

- The integrand is analytic almost everywhere on the complex space
- How to compute a fitting deformation ?
- Discretization using the trapezoidal rule on $\mathcal{B}_N$

Benchmark results: 1D Monatomic Chain

Main idea: Benchmark our methods on multiple systems in all dimensions.
1D Monatomic Chain: Toy model, everything is computable explicitly

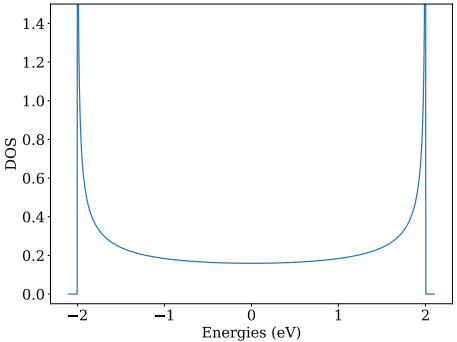


Figure 4: DOS of the 1D monatomic chain

Benchmark results: 1D Monatomic Chain

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1D Monatomic Chain: Toy model, everything is computable explicitly

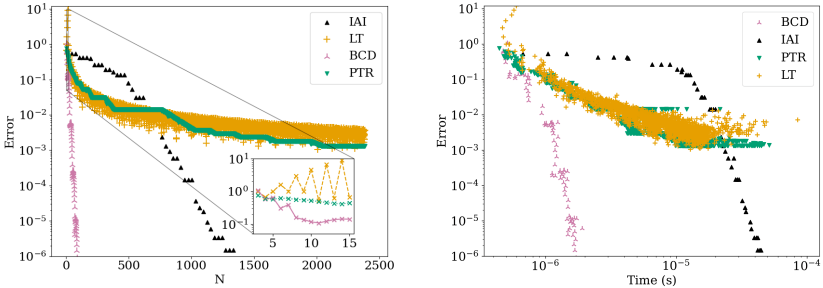

Figure 5: Relative error (ℓ^∞) and computation time for the 1D monatomic chain

Benchmark results: $SrVO_3$

Strontium Vanadate ($SrVO_3$): Realistic material, non-explicit Hamiltonian

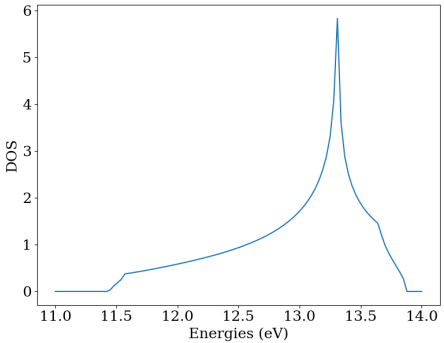

Figure 6: DOS of the $SrVO_3$

Benchmark results: $SrVO_3$

Strontium Vanadate ($SrVO_3$): Realistic material, non-explicit Hamiltonian

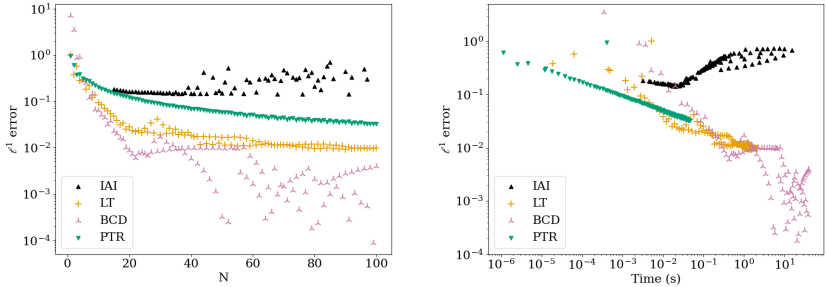

Figure 7: Relative error (ℓ^1) and computation time for the $SrVO_3$

Conclusion

BCD is overall the best-method for the computation of both smeared and non-smeared DOS.

- Low reliability on its internal parameters
- Exponential convergence
- Good for a black-box approach

Thanks for your attention !

How to compute a good deformation ?

Our integrand is analytic in the upper complex space and we want to continue it analytically in the lower complex space.
For $E = \varepsilon_{n\mathbf{k}_0}$, we have near k_0:

$$L_\eta(E - \varepsilon_{n\mathbf{k}+i\mathbf{h}(\mathbf{k})}) = \frac{1}{\pi}\mathrm{Im}\left(\frac{1}{E - \varepsilon_{n\mathbf{k}+i\mathbf{h}(\mathbf{k})} + i\eta}\right) = \frac{1}{\eta\pi}\frac{1}{1 + \frac{(E-\varepsilon_{n\mathbf{k}+i\mathbf{h}(\mathbf{k})})^2}{\eta^2}} \tag{12}$$

Thus for small $(E - \varepsilon_{n\mathbf{k}+i\mathbf{h}(\mathbf{k})})/\eta$ we have near k_0

$$\varepsilon_{n\mathbf{k}+i\mathbf{h}(\mathbf{k})} - E \approx \nabla\varepsilon_{n\mathbf{k}_0} \cdot (\mathbf{k} + i\mathbf{h}(\mathbf{k}) - \mathbf{k}_0) \tag{13}$$

Therefore to have negative imaginary part near the real axis we need

$$\nabla\varepsilon_{n\mathbf{k}_0} \cdot \mathbf{h}(\mathbf{k}) < 0 \tag{14}$$

Thus we chose

$$\mathbf{h}(\mathbf{k}) = -\alpha\left(\mathrm{Tr}\left(\partial_i H_{\mathbf{k}}\chi\left(\frac{H_{\mathbf{k}} - E}{\Delta E}\right)\right)\right)_{i\in\{1,\dots,d\}} \tag{15}$$