Habilitation à diriger les recherches

Antoine Levitt

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http://antoine.levitt.fr/soutenance.pdf
http://antoine.levitt.fr/HDR.pdf

Structure of the HDR

Chapter I. Results obtained

Chapter II. Introduction to electronic structure

Chapter III. Periodic quantum systems

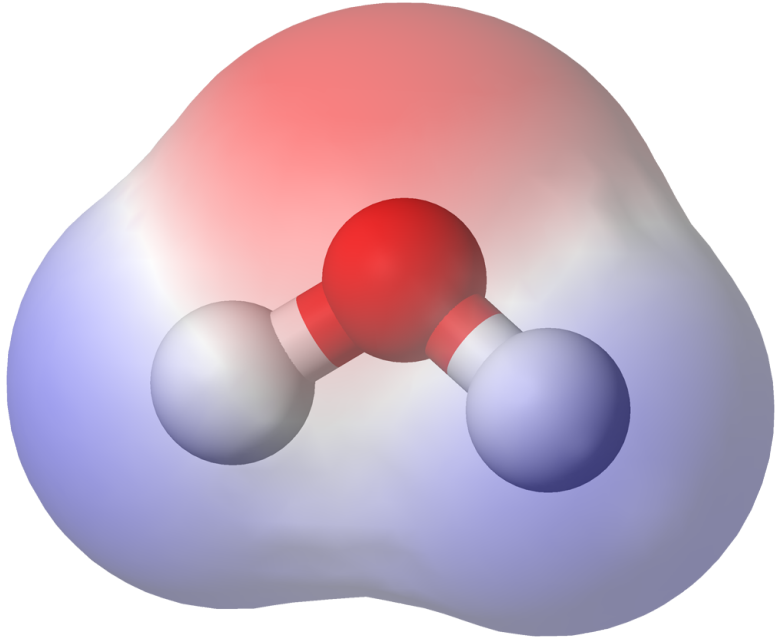
Chapter IV. Wannier functions

Chapter V. Iterative methods

Perspectives

Electronic structure theory

- The behavior of "ordinary" matter is driven by the behavior of nuclei and electrons
- Nuclei can be considered point particles, but electrons must be modeled with quantum mechanics



Water is a good solvent because its electron distribution gives it a dipole moment

The Schrödinger equation (1926)

In atomic units (no spin):

$$i\partial_t \psi = H\psi$$

$$H = \sum_{n=1}^{N} \left(\underbrace{-\frac{1}{2}\Delta_{x_n}}_{\text{Kinetic}} + \underbrace{V_{\text{ext}}(x_n)}_{\text{El-nucl Coulomb}} \right) + \sum_{n=1}^{N} \sum_{m \neq n} \underbrace{\frac{1}{|x_n - x_m|}}_{\text{El-el Coulomb}}$$

- $|\psi(t, x_1, \ldots, x_N)|^2$: probability of finding electrons at positions $x_1, \ldots, x_N$
- Electrons are fermions: ψ changes sign under coordinate permutation
- Stationary states $H\psi = E\psi$. Lowest E is the **ground state**
- Entanglement because of el-el interaction: the state of an electron depends parametrically on the state of all other electrons!
- Complexity explosion
  - Conceptual: the wave function is too rich to be directly useful
  - Computational: solve a PDE in dimension $3N$

Need for approximations (1929)

$$i\partial_t \psi = H\psi$$
$$\psi(t) \in L^2(\mathbb{R}^{3N})$$

Dirac:

- "The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known...
- ...and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble.
- It therefore becomes desirable that **approximate** practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation."

An approximation: KSDFT (1965)

Kohn-Sham density functional theory for the ground state

$$\begin{cases} -\frac{1}{2}\Delta\phi_n + V_{\mathrm{ext}}\phi_n + V_{\mathrm{HXC}}[\rho]\phi_n = \lambda_n\phi_n, \quad \langle\phi_n,\phi_m\rangle_{L^2(\mathbb{R}^3)} = \delta_{mn} \\ \rho(x) = \sum_{n=1}^{N} |\phi_n(x)|^2 \\ V_{\mathrm{HXC}}[\rho] = \frac{1}{|x|} * \rho + V_{\mathrm{XC}}[\rho] \end{cases}$$

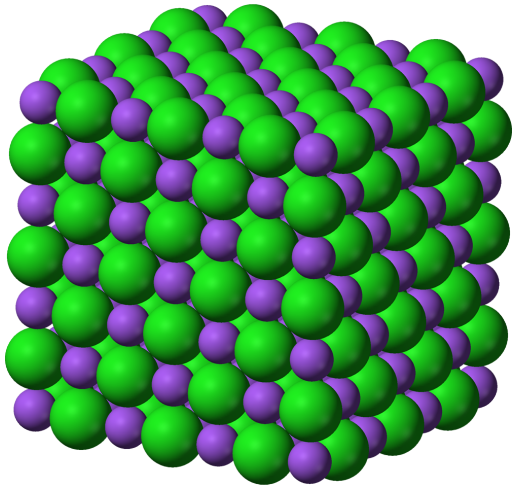
- V_{XC} is an approximation of the true exchange-correlation potential; e.g. LDA: $(V_{\mathrm{XC}}[\rho])(x) = v_{\mathrm{xc}}(\rho(x))$
- N nonlinear coupled PDEs in dimension 3
- Aufbau principle: $\{\lambda_n\}_{n=1,\dots,N}$ are the lowest eigenvalues of

$$H_\rho = -\frac{1}{2}\Delta + V_{\mathrm{ext}} + V_{\mathrm{HXC}}[\rho]$$

- Equivalent reformulation with density matrices $\gamma = \sum_{n=1}^{N} |\phi_n\rangle\langle\phi_n|$:

$$\boxed{\gamma = \mathbb{1}(H_{\rho_\gamma} \leq \varepsilon_F)}$$

DFT for crystals



A perfect crystal is defined by

- Lattice $\mathcal{R} \subset \mathbb{R}^3$
- $\mathcal{R}$-periodic atomic potential V_{ext}
- N electrons per unit cell: γ is an infinite-rank projector, $\underline{\mathrm{Tr}}(\gamma) = N$

$$\boxed{\gamma = \mathbb{1}(H_{\rho_\gamma} \leq \varepsilon_F)}$$

Subtleties of thermodynamic limit: Coulomb non-summability, symmetry breaking, fractional occupations [Catto/Le Bris/Lions '01]

Bloch theory, insulators and conductors

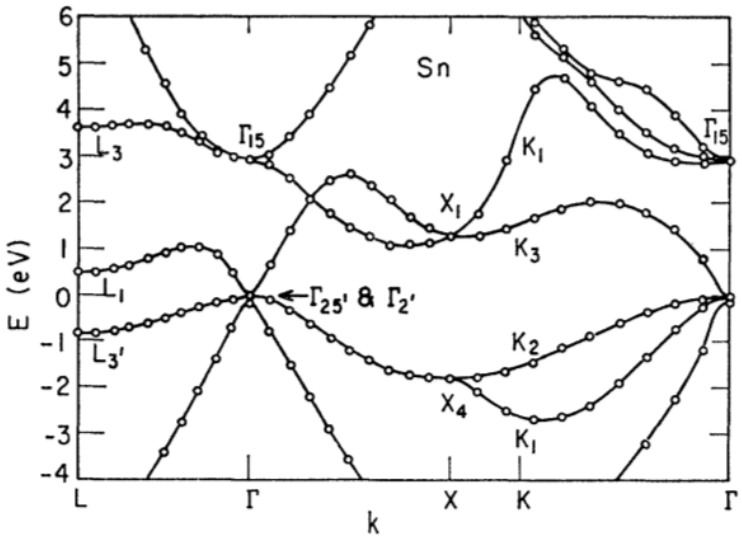
- H_{ρ_γ} is a **periodic** operator, can be studied using Bloch theory
- Generalized eigenvectors: Bloch waves

$$\psi_{nk}(x) = e^{ik\cdot x} u_{nk}(x)$$

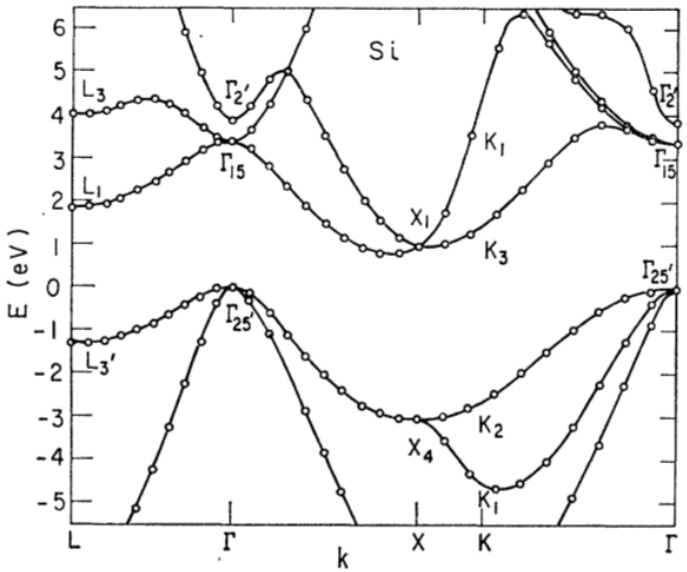
where the u_{nk} are periodic functions satisfying

$$\left(\frac{1}{2}(-i\nabla + k)^2 + V_{\text{ext}} + V_{\text{HXC}}[\rho_\gamma]\right) u_{nk} = \varepsilon_{nk} u_{nk}$$

- $k \mapsto \varepsilon_{nk}$: dispersion relation/band structure
- $\mathcal{R}^*$-periodic: plot in the Brillouin zone $\mathcal{B} = \mathbb{R}^3 \setminus \mathcal{R}^*$



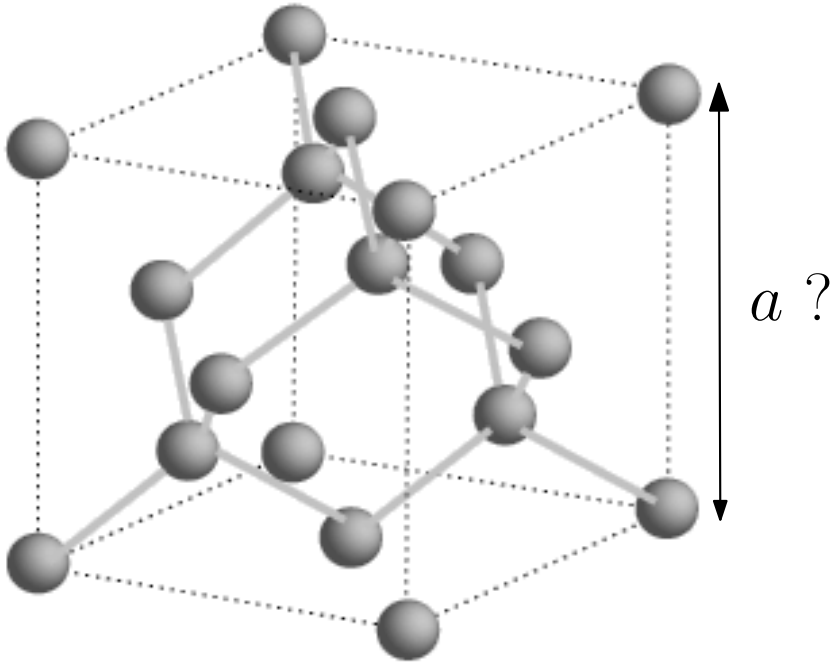
Tin (metal)



Silicon (semiconductor)

Crystal properties

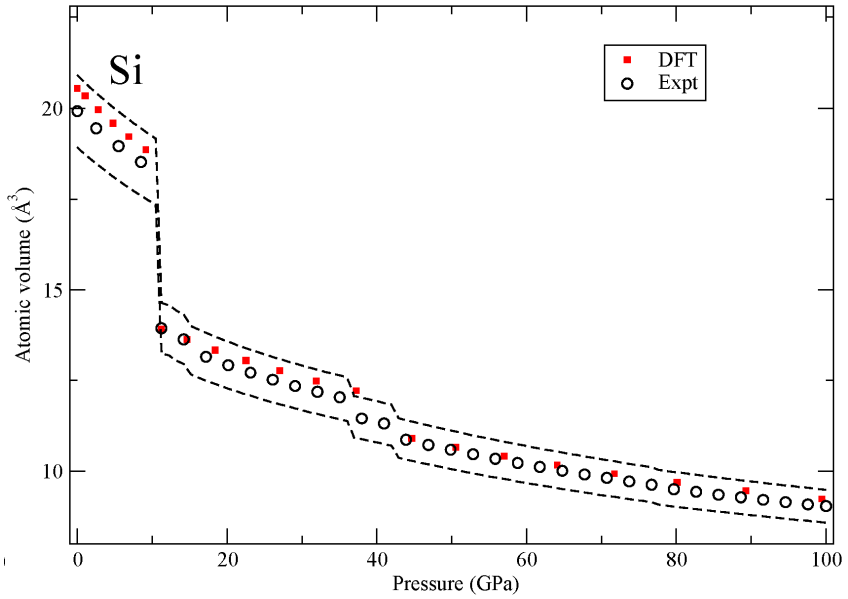
DFT gives access to $E(a)$, energy per unit volume

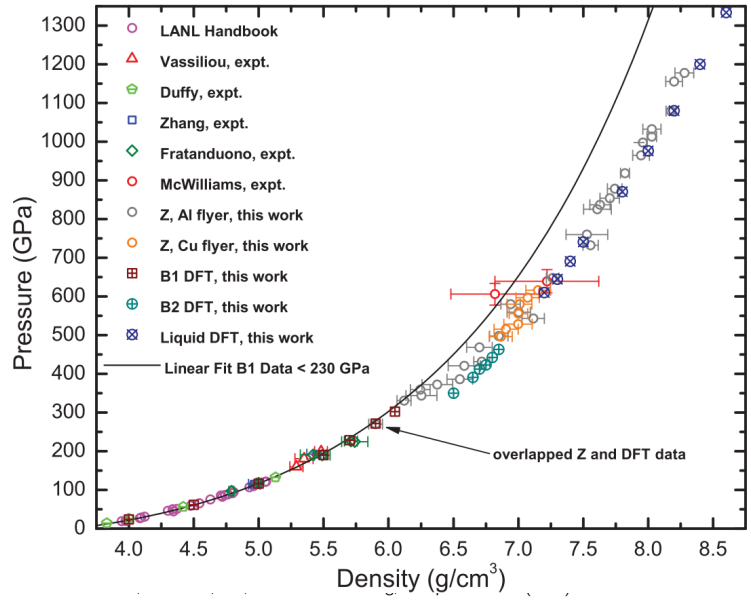


- Lattice constant: $\arg\min E(a)$
- Pressure: related to $\frac{dE}{da}$
- Young's modulus (speed of sound): related to $\frac{d^2E}{da^2}$
- Anharmonic effects: $\frac{d^3E}{da^3}$
- Many other static and dynamic properties, purely ab initio

DFT in practice

- Methodological developments since the '90s (pseudopotentials, numerical methods, HPC...): routinely solved for hundreds of atoms
- Workhorse of condensed matter physics and quantum chemistry



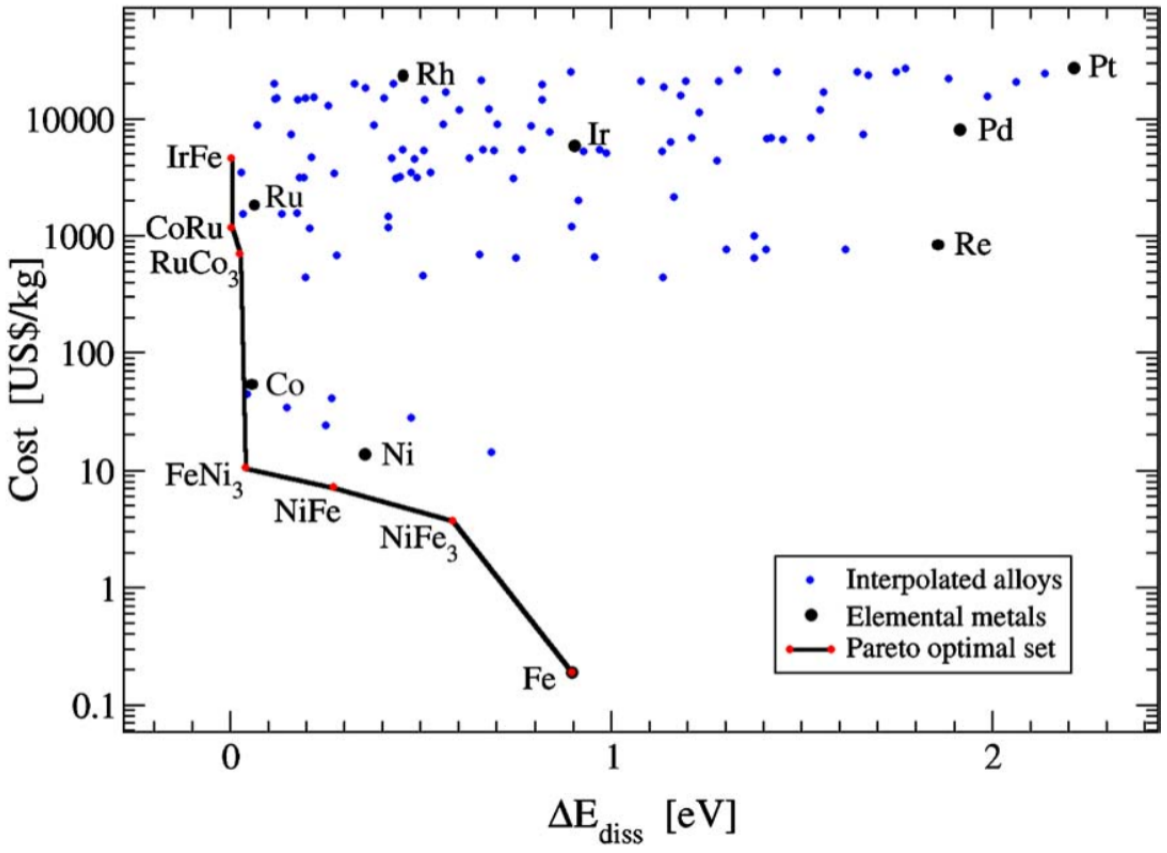


Equation of state of MgO, Root, Seth, et al., Physical Review Letters 115.19 (2015).

... but severe deficiencies (excited states, strongly correlated materials)

Applications

From fundamental physics to practical applications



Dissociation energy of adsorbed CO, Andersson, Martin P., et al. Journal of Catalysis 239.2 (2006)

Electronic structure for mathematicians

- Complex equations
- Need for reliable, automatic, accurate and fast methods
- Involves many branches of mathematics

Analysis	Computing	"Pure" math
PDEs	Linear algebra	Probability
Spectral theory	Optimization	Group theory
Complex analysis	Numerical analysis	Topology
Nonlinear analysis	HPC	Differential geometry

- Underexplored mathematically

Keyword	Web of Science	MathSciNet	Ratio
Maxwell equations	19,459	2,055	10%
Boltzmann equation	24,519	2,268	10%
Navier Stokes	47,341	9,436	20%
Density Functional Theory	142,374	171	0.1%

Mathematicians for electronic structure

- Applied mathematics: rigorous results on structure, asymptotics, numerical methods.
- Informs the choice of numerical methods that are robust, adaptive and free of divergences ("two infinities": mesh and box size)
- Main difficulty: pre-asymptotic regime often dictated by physics more than mathematics...

My work:
Physics, mathematical analysis, numerical analysis, implementation

Strongly linked concepts, radically different language and viewpoints

- Ultraviolet/infrared divergence, Sobolev spaces, preconditioning
- Self-energy, Feshbach-Schur map, block inversion
- Dyson expansion, fixed-point theorem, Neumann series
- ...

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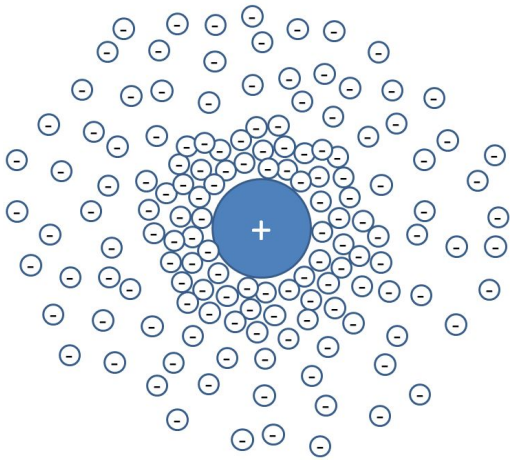
Screening



Phenomenologically, response to a point charge $V_{\text{ext}} = \frac{Q}{|x|}$:

System	V_{eff}	Features
Vacuum	$\frac{Q}{\lvert x\rvert}$	No screening
Insulator/semiconductor	$\frac{Q}{\varepsilon_r \lvert x\rvert}$	Partial screening
Uniform electron gas (Thomas-Fermi)	$\propto \frac{Qe^{-k_{\text{TF}}\lvert x\rvert}}{\lvert x\rvert}$	Full screening
Uniform electron gas (Lindhard)	$\propto \frac{Q\cos(2k_{\text{F}}\lvert x\rvert)}{\lvert x\rvert^3}$	Friedel oscillations

Goal: understand this mathematically

Full screening

Introduce a defect potential V_{def} into a periodic background $(H_{\mathrm{per}}, \varepsilon_F)$:

$$\gamma_{\mathrm{def}} = \mathbb{1}\left(H_{\mathrm{per}} + V_{\mathrm{eff}} - \varepsilon_F\right) - \mathbb{1}\left(H_{\mathrm{per}} - \varepsilon_F\right)$$
$$V_{\mathrm{eff}} = V_{\mathrm{def}} + V_{\mathrm{H}\cancel{\mathrm{xc}}}[\rho_{\gamma_{\mathrm{def}}}]$$

- For finite temperature T: replace $\mathbb{1}(x \leq \varepsilon_F)$ with the Fermi-Dirac function

$$f_T(x - \varepsilon_F) = \frac{1}{1 + e^{\frac{x-\varepsilon_F}{T}}}$$

- For insulators (with a gap) at $T = 0$, partial screening studied in [Cancès/Lewin '10]; full screening known in Thomas-Fermi models

Theorem (A. Levitt, ARMA, 2020)

Assume that V_{per} is L^2_{per}, $\varepsilon_F \in \mathbb{R}$, $T > 0$. Then for V_{def} small enough in $\Delta^{-1}H^{-2}(\mathbb{R}^3)$, there is a (locally unique) solution of the defect problem, and $V_{\mathrm{eff}} \in L^2(\mathbb{R}^3)$.

Sketch of proof

Linearized equation (implicit function theorem):

$$V_{\text{eff}} = V_{\text{def}} + v_c \chi_0 V_{\text{eff}} + O\left(\|V_{\text{eff}}\|^2\right)$$

where

- $v_c = \frac{1}{|x|} * \cdot = -4\pi\Delta^{-1}$ is a multiplication by $\frac{4\pi}{|q|^2}$ in Fourier space: singular at small q (long range)
- χ_0 is the independent-particle susceptibility operator: derivative at 0 of the map

$$F : V \mapsto \rho\Big(f_T\left(H_{\text{per}} + V - \varepsilon_F\right) - f_T\left(H_{\text{per}} - \varepsilon_F\right)\Big)$$

Therefore

$$V_{\text{eff}} \approx \varepsilon^{-1} V_{\text{def}}$$

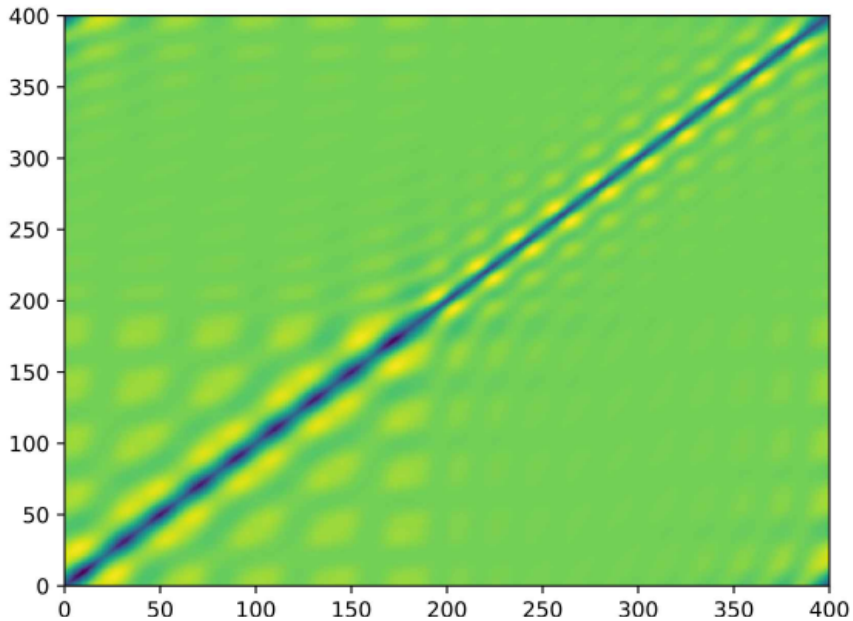
where

$$\boxed{\varepsilon = 1 - v_c \chi_0}$$

$v_c \geq 0$, $\chi_0 \leq 0$: ε invertible. Properties (function spaces)?

Sketch of proof

$\chi_0(x, x')$ for a 1D metal-insulator junction



"Homogenized" behavior of χ_0 for a periodic system:

$$\lim_{R\to\infty} \frac{\left\langle \phi\left(\frac{\cdot}{R}\right), \chi_0\, \phi\left(\frac{\cdot}{R}\right)\right\rangle}{\left\langle \phi\left(\frac{\cdot}{R}\right), \phi\left(\frac{\cdot}{R}\right)\right\rangle} = -D$$

the density of states per unit volume at the Fermi level, for $\phi \in C_c^\infty(\mathbb{R}^3)$.

- For insulators, $D = 0 \Rightarrow \varepsilon^{-1} = O(1)$: partial screening
- For conductors, $D \neq 0 \Rightarrow \varepsilon^{-1} = O(|q|^2)$: full screening

□

SCF iterations

How to solve

$$V_{\mathrm{eff}} = V_{\mathrm{def}} + v_{\mathrm{c}} F(V_{\mathrm{eff}})$$

in practice? Damped SCF iteration

$$V_{n+1} = V_n + \alpha(V_{\mathrm{def}} + v_{\mathrm{c}} F(V_n) - V_n)$$

Jacobian of this iteration at convergence:

$$J_\alpha = 1 - \alpha(1 - v_{\mathrm{c}}\chi_0) = 1 - \alpha\varepsilon$$

Local convergence OK for α small enough but $v_{\mathrm{c}} = \frac{4\pi}{|q|^2}$: rate dependent on box size for metals
For metals: Kerker preconditioning $\alpha \to \beta \frac{|q|^2}{|q|^2 + 4\pi D}$.

Theorem (A. Levitt, ARMA, 2020)

In the above setup, the Kerker-preconditioned SCF iteration is well-defined and locally convergent in $L^2(\mathbb{R}^3)$ for $\beta > 0$ small enough.

Preconditioner = metric : mathematical analysis = numerical analysis

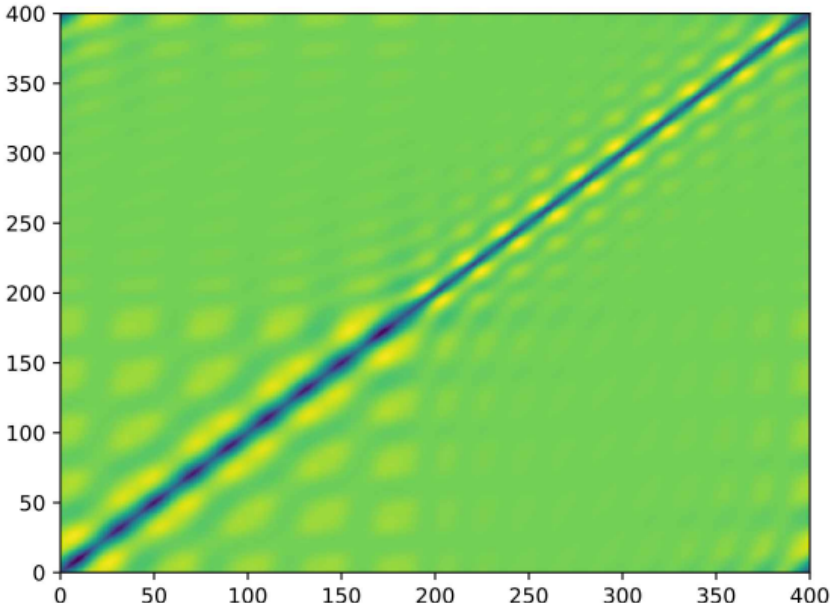
What to do for heterogeneous systems?

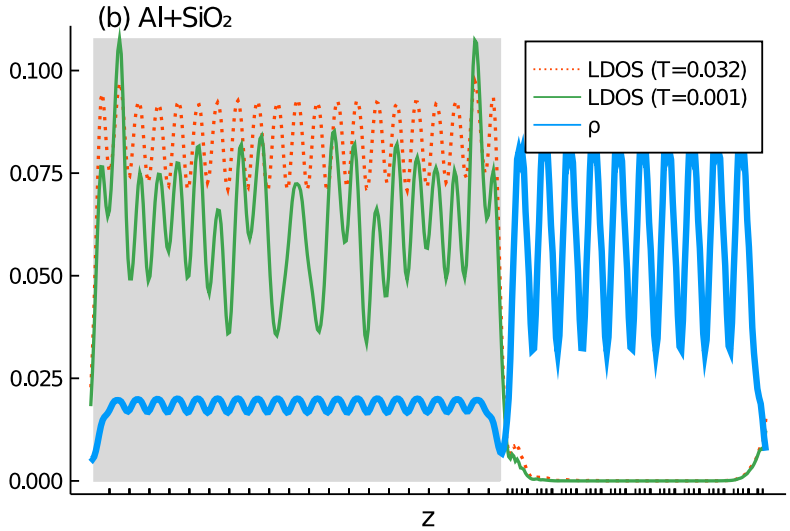
Local density of states based preconditioning

M. Herbst, A. Levitt. (not in the HDR)
Black-box inhomogeneous preconditioning for self-consistent field iterations in density functional theory.
Submitted, 2020.

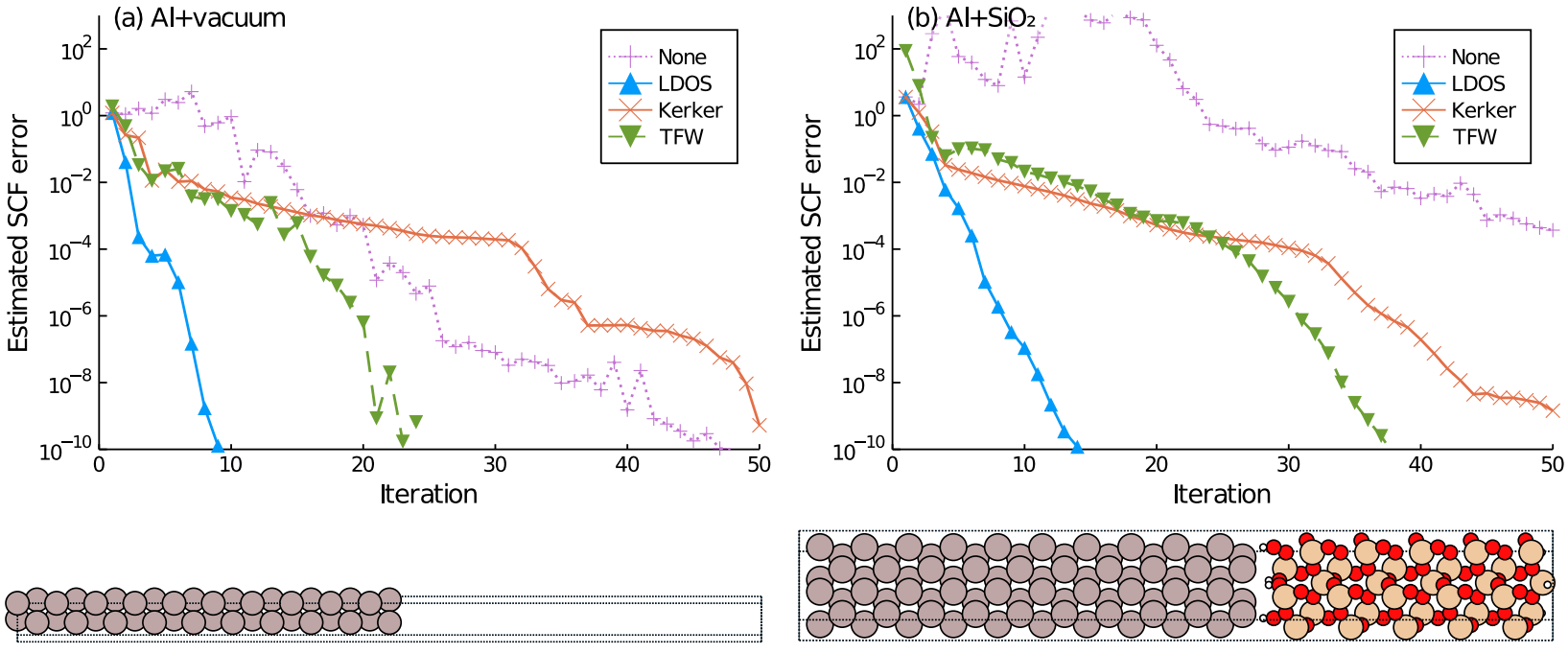
"Mass lumping"

$$\int \chi_0(x,x')V(x')dx' \approx V(x)\int \chi_0(x,x')dx'$$
$$= V(x)\,\mathrm{LDOS}(x)$$





Local density of states based preconditioning



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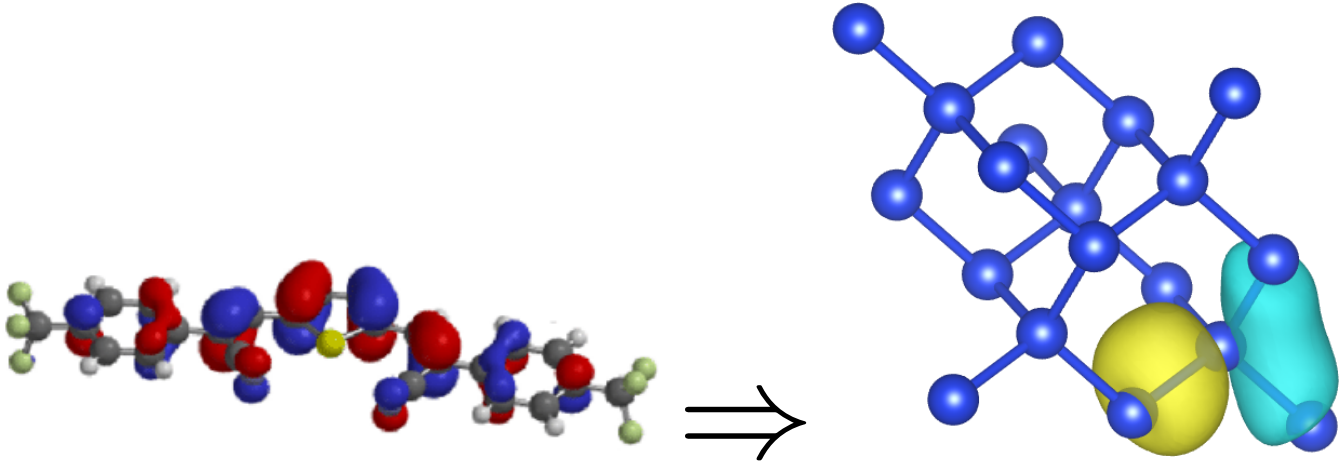
Wannier functions



Orbitals ϕ_n coming from DFT computations are delocalized over the whole system

Need localized orbitals for

- Physical interpretation (polarization, bonding...)
- Band structure interpolation
- Sparsifying computations

Wannier functions for periodic crystals

Assume an insulator, with occupied Bloch waves

$$\psi_{nk}(x) = e^{ik\cdot x} u_{nk}(x)$$

for $n = 1, \ldots, N$, $k \in \mathcal{B}$. Define Wannier functions by

$$w_{n0}(x) = \frac{1}{|\mathcal{B}|} \int_{\mathcal{B}} \psi_{nk}(x) dk \qquad w_{nR}(x) = w_{n0}(x - R), R \in \mathcal{R}$$

- $\{w_{nR}\}_{n=1,\ldots,N,R\in\mathcal{R}}$ is an orthogonal basis of the occupied subspace
- Localization of $w_{n0} \Leftrightarrow$ smoothness and periodicity of $k \mapsto \psi_{nk}$
- ψ_{nk} is only determined up to a phase
- ψ_{nk} cannot be chosen smooth at eigenvalue crossings

Generalized Wannier functions $\widetilde{w}_{nR}$ with

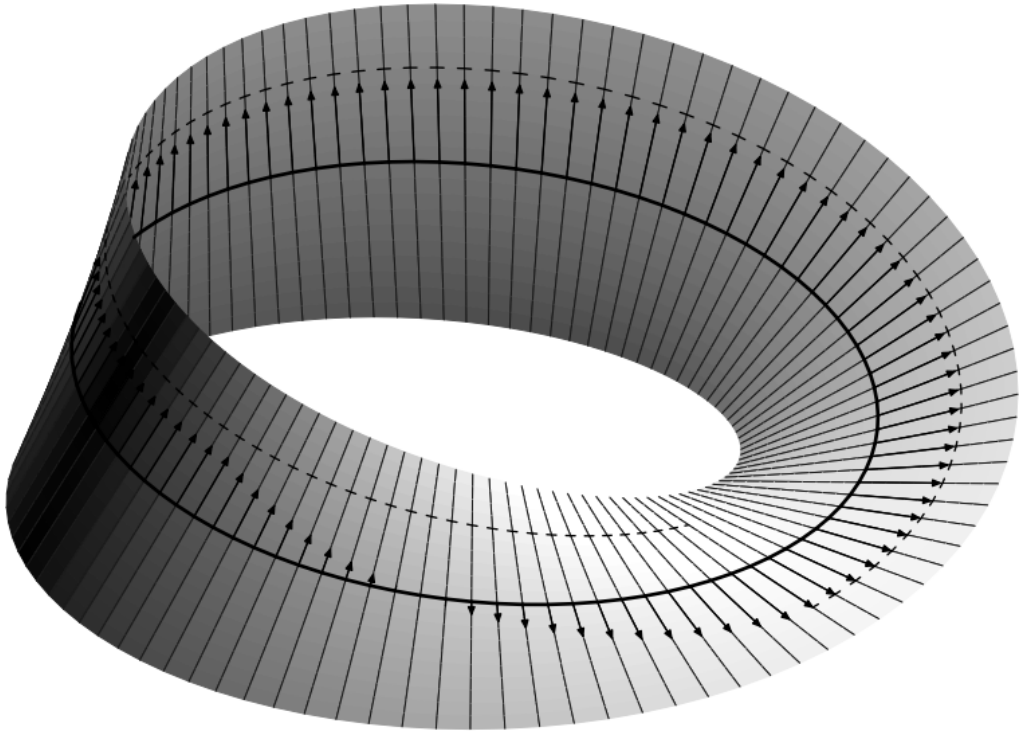
$$\widetilde{\psi}_{nk}(x) = \sum_{m=1}^{N} \psi_{nk}(x) U_{mn}(k)$$

Can we find $U_{mn}(k)$ so that $\widetilde{\psi}_{nk}$ is smooth and $\mathcal{R}^*$-periodic?

A detour through topology

Can we find a smooth and periodic basis of $\mathrm{Span}\{\psi_{1k}, \ldots, \psi_{Nk}\}$?

Asking for smooth and periodic bases is dangerous...



Existence depends on the vanishing of topological invariants

Topology and Wannier functions

Theorem (G. Panati, '07)

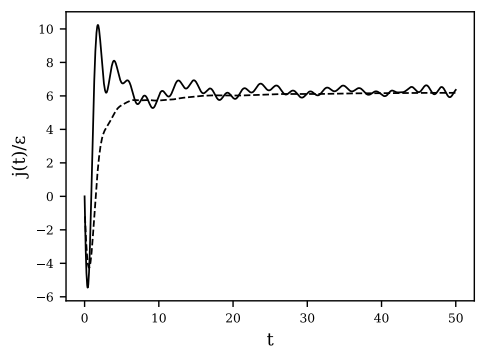
Assume that V is continuous and periodic in $\mathbb{R}^d$, $d \leq 3$, and

$$\inf_{k \in \mathcal{B}} \varepsilon_{N+1,k} > \sup_{k \in \mathcal{B}} \varepsilon_{N,k}.$$

Then there exists exponentially-localized Wannier functions $\{w_{nR}, n = 1, \ldots, N, R \in \mathcal{R}\}$.

Proof: the symmetry $H_{-k} = \overline{H_k}$ implies the vanishing of the appropriate topological invariants (Chern class) □

Symmetry broken with magnetic fields $\Rightarrow$ non-existence of localized Wannier functions, quantum Hall effect (Nobel prize '85)



Hall current in the Haldane model, [Cancès/Fermanian/Levitt/Siraj-Dine, submitted '20]

Numerical methods for finding Wannier functions

In practice, how to compute localized Wannier functions?

Marzari-Vanderbilt scheme ('97)

Starting from a physically reasonable initial guess, optimize the total variance iteratively

$$\Omega = \sum_{n=1}^{N} \left(\int |x|^2 |w_{n0}(x)|^2 dx - \left| \int x |w_{n0}(x)|^2 dx \right|^2 \right)$$

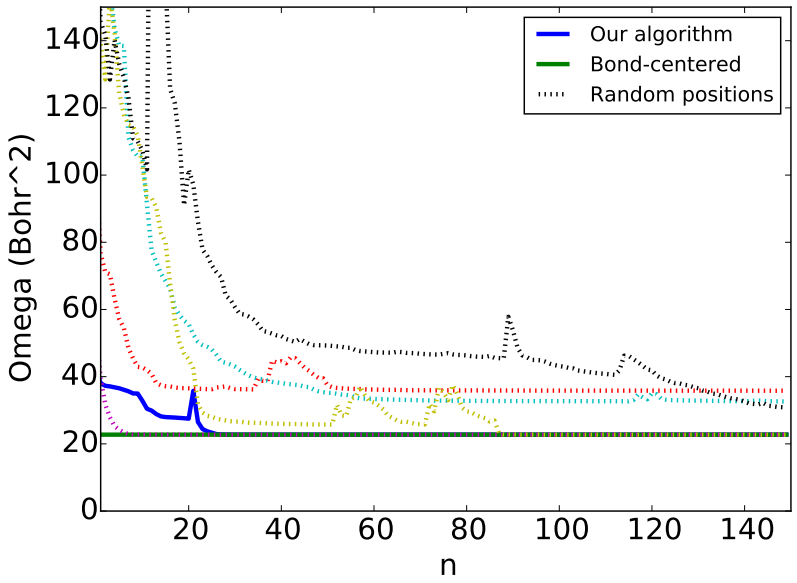
Problem:

- Need manual guess for the initial Wannier functions
- Non-convex optimization problem
- Topological vortices if the initial guess is not good enough

Automated Wannier functions

E. Cancès, A. Levitt, G. Panati, and G. Stoltz.
Robust determination of maximally localized Wannier functions.
Physical Review B, 2017.

Numerical construction of Wannier functions following the theoretical proof of existence.



Great for simple materials with small unit cells, not so much for others...

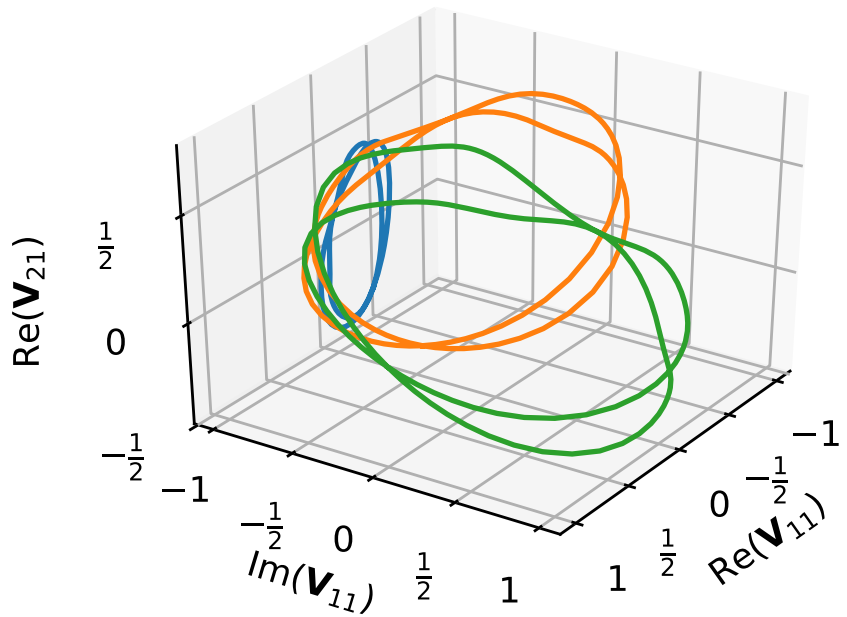
Wannier functions for topological insulators

D. Gontier, A. Levitt, and S. Siraj-Dine.
Numerical construction of Wannier functions through homotopy.
Journal of Mathematical Physics, 2019.

Extension of the previous methodology to spin-orbit coupling (topological insulators).

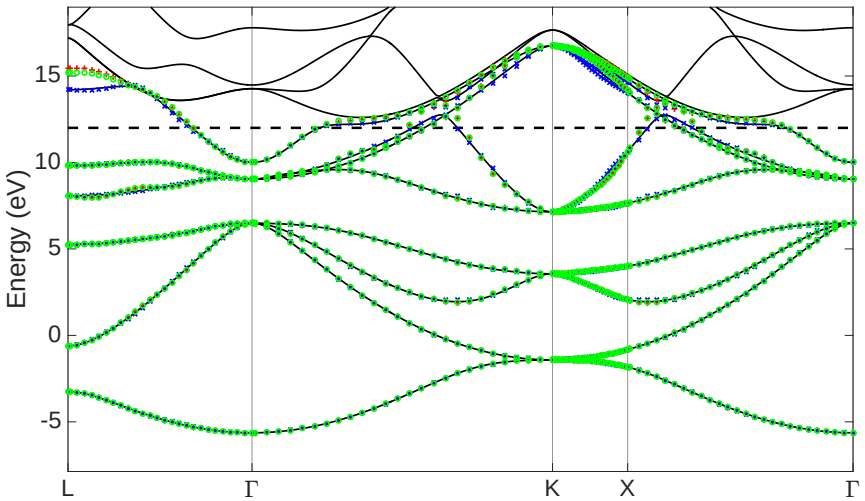
Numerical homotopy problem

Given a loop $[0,1] \ni k \mapsto V(k) \in \mathrm{SU}(N)$, deform it to a point in $\mathrm{SU}(N)$



Wannier functions for metals

[Souza/Marzari/Vanderbilt '01]



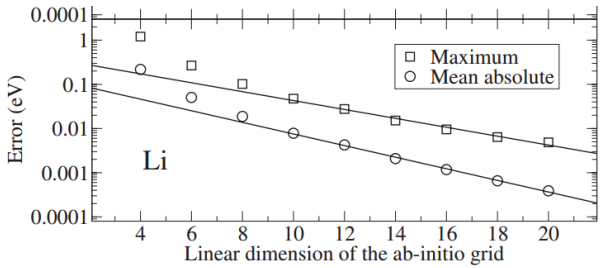


FIG. 6. Convergence of the Wannier-interpolated band energies as a function of the linear dimensions $N_0^{1/3}$ of the *ab initio* **q**-point grid. We plot the maximum error (squares) and mean absolute error

How does this work?

Theorem (H. Cornean, D. Gontier, A. Levitt, D. Monaco, AHP '19)

Under generic conditions, even without a gap there exists an almost-exponentially localized orthonormal family $\{w_{nR}, n = 1, \dots, N+1, R \in \mathcal{R}\}$ *spanning a superset of the space spanned by the first* N *bands.*

but the ones found in practice are only algebraically localized [Damle/Levitt/Lin, SIAM MMS '19]

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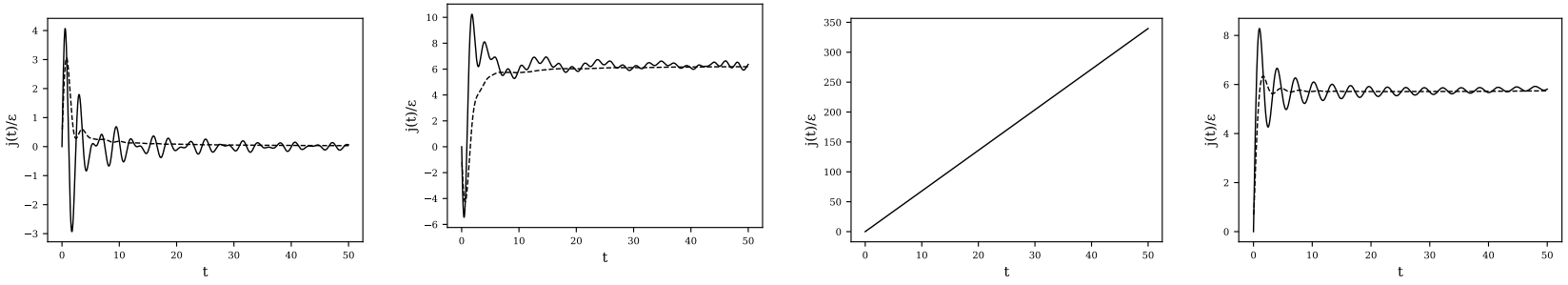
Perspectives: mathematical physics

- Transport properties of electrons in crystals



(a) Normal insulator phase.

(b) Chern insulator phase, transverse current.

(c) Metallic phase.

(d) Graphene.

Figure: Current response to a constant electric field as a function of time in the linear response regime [Cancès/Fermanian/Levitt/Siraj-Dine submitted '20]

- Towards imperfect crystals: impurities, electron-phonon coupling
- Plasmons (with É. Cancès, J. Sabin)
- ...

Perspectives: numerical analysis

- Brillouin zone integration (with É. Cancès, V. Ehrlacher, D. Gontier, D. Lombardi)
- Approximation of response functions above the ionization threshold (with M-S. Dupuy, S. Behr)
- Direct minimization vs SCF (with É. Cancès, G. Kemlin)
- A posteriori error analysis (with É. Cancès, G. Dusson, M. Herbst, G. Kemlin)

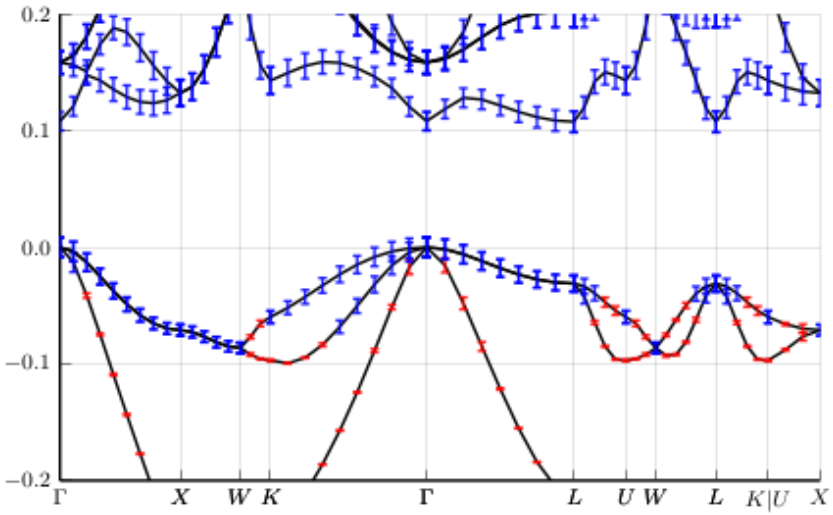
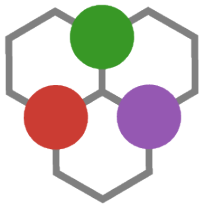


Figure: Band structure of Silicon (without electronic interaction) with fully guaranteed error bars [Cancès/Herbst/Levitt, Faraday Discussions '20]

- ...

Perspectives: algorithms

With M. Herbst



DFTK

`https://dftk.org`

- Robust and efficient SCF
- Approximating $\varepsilon = 1 - (v_c + K_{XC})\chi_0$ and understanding its three sources of ill-conditioning:
  - Coulomb interaction
  - XC-induced electronic phase transitions (e.g. ferromagnetism)
  - Large modes of χ_0 (e.g. localized states)
- Multiple solutions of Kohn-Sham equations (bifurcation analysis)
- (Time-dependent) linear response
- DFTK development (HPC, automatic differentiation...)
- ...