Electrons in a crystal (periodic Schrödinger operator)

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- A few words about INRIA Matherials team and CERMICS.
- What is a crystal ?
- Ilibert spaces and the periodic Schrödinger operator.
- Bloch Floquet theory and numerical implementation.
- Inverse spectral problem and numerical results.

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- CERMICS (Centre d'Enseignement et de Recherche en Mathématiques, Informatique et Calcul Scientifique) is a laboratory of École des Ponts ParisTech, hosting joint research teams with INRIA and University of Marne-la-Vallée.
- Some members of Matherials team: Claude Lebris, **Eric Cancès**, **Tony Lelièvre**, Gabriel Stoltz, Mathias Rousset, **Virginie Ehrlacher**, Frédéric Legoll, Antoine Levitt... PhD students and postdocs.



- Main research topics : Analysis of numerical methods for quantum chemistry and physics, statistical physics, molecular dynamics, homogenization and related problems.
- My PhD work is on mathematical (deterministic and stochastic) methods for the simulation of photovoltaic processes.

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Figure: rock crystals, crystal skull, Gallium metal, CIGS photovoltaic cells.

A crystal is a solid material composed of an infinite number of atoms that are arranged periodically in space.





The study of the states of electrons in the crystal (electronic structure) enables to understand the macroscopic behavior of the solid. For example, electrical, optical or magnetic properties depend very strongly on this electronic structure.



Understanding the optoelectronical properties of a photovoltaic cell is crucial to improve its efficiency.

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The band theory allow to determine the admissible energy states of the electrons in a crystalline material. The band structure accounts for the electric conductivity of the material (conductor, semiconductor or insulator).



• Let a, b, c be a basis of $\mathbb{R}^3.$ We define the Bravais lattice $\mathcal R$ and the admissible unit cell Γ as follows :

$$\mathcal{R} := \{ \textit{ma} + \textit{nb} + \textit{pc}, \quad \textit{m}, \textit{n}, \textit{p} \in \mathbb{Z} \}, \quad \Gamma := \{ \alpha\textit{a} + \beta\textit{b} + \gamma\textit{c}, \quad \alpha, \beta, \gamma \in [0, 1)^3 \}.$$

• Let \mathbf{a}^* , \mathbf{b}^* , \mathbf{c}^* be the unique basis of \mathbb{R}^3 that satisfies

 $a \cdot a^* = b \cdot b^* = c \cdot c^* = 2\pi, \quad a \cdot b^* = a \cdot c^* = b \cdot a^* = b \cdot c^* = c \cdot a^* = c \cdot b^* = 0.$

 \bullet We define the dual lattice \mathcal{R}^* as follows

$$\mathcal{R}^* := \{ ma^* + nb^* + pc^*, \quad m, n, p \in \mathbb{Z} \}.$$

• The first Brillouin zone Γ^* is defined as the set of points of \mathbb{R}^3 that are closer to (0,0,0) than any other point in the dual lattice \mathcal{R}^* (Wigner-Seitz cell of \mathcal{R}^*).

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Bravais lattice and Brillouin zone -2-



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Hilbert spaces and operators

Let \mathcal{H} be a Hilbert space. An operator on \mathcal{H} is a linear map $A : D(A) \to \mathcal{H}$ defined on a linear subspace $D(A) \subset \mathcal{H}$ that is dense in \mathcal{H} . D(A) is called the domain of A. Useful Hilbert spaces (which appear naturally in quantum physics) are:

$$\begin{split} L^2(\mathbb{R}^3) &:= \left\{ f: \mathbb{R}^3 \to \mathbb{R} \quad | \quad \int_{\mathbb{R}^3} |f(x)|^2 dx < \infty \right\} \\ L^2_{loc}(\mathbb{R}^3) &:= \left\{ f: \mathbb{R}^3 \to \mathbb{R} \quad | \quad \int_K |f(x)|^2 dx < \infty, \quad \forall K \subset \mathbb{R}^3 \text{ compact} \right\} \\ L^2_{per}(\Gamma) &= \left\{ f \in L^2_{loc}(\mathbb{R}^3), \quad f(x+R) = f(x), \quad \forall R \in \mathcal{R}, \forall x \in \mathbb{R}^3 \right\} \\ H^2(\mathbb{R}^3) &:= \left\{ f: \mathbb{R}^3 \to \mathbb{R} \quad | \quad f, Df, D^2 f \in L^2(\mathbb{R}^3) \right\} \\ H^2_{loc}(\mathbb{R}^3) &:= \left\{ f: \mathbb{R}^3 \to \mathbb{R} \quad | \quad f, Df, D^2 f \in L^2_{loc}(\mathbb{R}^3) \right\} \\ H^2_{per}(\Gamma) &= \left\{ f \in H^2_{loc}(\mathbb{R}^3), \quad f(x+R) = f(x), \quad \forall R \in \mathcal{R}, \forall x \in \mathbb{R}^3 \right\} \end{split}$$

We consider the periodic Schrödinger operator acting on $L^2(\mathbb{R}^3)$ with domain $H^2(\mathbb{R}^3)$:

$$-rac{1}{2}\Delta+V_{per}$$

where $V_{per} \in L^2_{per}(\Gamma)$ is a real-valued periodic potential with the same periodicity as the one of the lattice \mathcal{R} .

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- Quantum physics => the state of a quantum system of N particles is given by a wavefunction $\psi \in L^2(\mathbb{R}^{3N})$. For $B \subset \mathbb{R}^{3N}$, the quantity $\int_B |\psi(x)|^2$ represents the probability of finding the particles of the system in the region B. In particular $\int_{\mathbb{R}^{3N}} |\psi(x)|^2 = 1$.
- The energy of the system is characterized by an operator defined on $L^2(\mathbb{R}^{3N})$ called the Hamiltonian.
- The general form of the Hamiltonian of a system of N electrons and M nuclei whose positions $(R_j)_{1 \le j \le M} \in \mathbb{R}^3$ are fixed and whose electrical charges are $(z_j)_{1 \le j \le M} \in \mathbb{Z}$ is given by ¹



• The energy of a state characterized by its wavefunction $\psi(x_1, \cdots x_N)$ is given by $\langle \psi | H_{mol} | \psi \rangle$.

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^1 In the atomic units i.e \hbar=m_e=e^2(4\pi\epsilon_0)^{-1}=1
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- Mean-field theory : when $N, M \rightarrow \infty$, the action of electrons and nuclei is averaged.
- This leads to a Hamiltonian of one particle

$${\cal H}=-rac{1}{2}\Delta+V_{per}$$

- One needs hours (days) of explanation to justify rigorously all these simplifications.
- The fundamental state satisfies the eigenvalue equation $H\psi_0 = E_0\psi_0$. Equivalently for the excited states $H\psi_n = E_n\psi_n$.
- We want to analyze the spectrum of the operator *H*.
- The notion of spectrum is a generalization of eigenvalues of finite dimensional matrices.

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The Bloch-Floquet theory allows to characterize the spectrum of H. Indeed,

$$\sigma(H) = \bigcup_{q \in \Gamma^*} \sigma(H_q)$$

where for every point (Bloch vector) of the first Brillouin zone $q \in \Gamma^*$, the operator H_q acts on $L^2_{per}(\Gamma)$ with domain $H^2_{per}(\Gamma)$ and is given by

$$H_q := rac{1}{2}\Delta_x - iq\cdot
abla_x + rac{1}{2}|q|^2 + V_{per}(x).$$

What do we gain by doing this ?

Theorem

For all $q \in \Gamma^*$ the operator H_q has compact resolvent. This implies that there exists a sequence $(\epsilon_n(q))_{n \in \mathbb{N}^*}$ of real non decreasing eigenvalues going to ∞ and an ONB $(e_{n,q})_{n \in \mathbb{N}^*}$ of $L^2_{per}(\Gamma)$ such that

$$\forall n \in \mathbb{N}^*, \quad H_q e_{n,q} = \epsilon_n(q) e_{n,q},$$

$$\sigma(H_q) = \bigcup_{n \in \mathbb{N}^*} \{\epsilon_n(q)\}.$$

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Band diagram and Fermi level

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It follows from the Bloch Floquet theory that

$$\sigma(H) = \bigcup_{q \in \Gamma^*} \bigcup_{n \in \mathbb{N}^*} \{\epsilon_n(q)\} = \bigcup_{n \in \mathbb{N}^*} \bigcup_{q \in \Gamma^*} \{\epsilon_n(q)\}$$

- The function $q \mapsto \epsilon_n(q)$ is called the n^{th} energy band of the crystal.
- The distance $|\min_{q\in\Gamma^*} \epsilon_{n+1}(q) \max_{q\in\Gamma^*} \epsilon_n(q)|$ is called n^{th} band gap.
- Of particular importance is the gap between the valence band and the conduction band. i.e the two closest bands to Femi level.
- If the number of electrons in a unit cell of a crystal is N, then the Fermi Level E_F is defined such that

$$\frac{1}{|\Gamma^*|}\int_{\Gamma^*}\sum_{n\in\mathbb{N}^*}\mathbb{1}_{\epsilon_n(q)\leq E_f}dq=N.$$



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Numerical implementation

- Assume for simplicity that $\mathcal{R} = 2\pi\mathbb{Z}^3$ then $\mathcal{R}^* = \mathbb{Z}^3$, $\Gamma = (0, 2\pi)^3$ and $\Gamma^* = (-1/2, 1/2)^3$.
- Use the Fourier expansion for the periodic potential and truncate at some level $C \in \mathbb{R}^*_+$.

$$V_{per}(x) pprox \sum_{k \in \mathbb{Z}^3, \ |k| \leq C} \hat{v}_k (2\pi)^{-3/2} e^{-ik \cdot x}$$
 where $v_{-k} = v_k^*$

• Discretize the Brillouin zone. $\tilde{\Gamma}^* := \{q_1, q_2, \cdots, q_L\} \subset \Gamma^*$.

 For some cutoff P_c ∈ N^{*}, we consider the approximation space X whose dimension is finite and denoted by P = dim(X).

$$X:= extsf{span}\left\{e_k:=(2\pi)^{-3/2}e^{-ik\cdot x}, \quad |k|\leq extsf{P_c}
ight\}$$

- For every $1 \le j \le L$, discretize the hamiltonian H_{q_j} in the space X. We obtain a hermitian matrix $\tilde{H}_{q_j} \in \mathbb{C}^{P \times P}$: $(\tilde{H}_{q_j})_{kk} = \frac{1}{2}(k+q_j)^2 + \hat{v}_0$, $(\tilde{H}_{q_j})_{kl} = \hat{v}_{k-l}$
- For every $q_j \in \tilde{\Gamma}^*$ solve the discrete eigenvalue problem $\tilde{H}_{q_j}\tilde{e}_{n,q} = \epsilon_n(q)\tilde{e}_{n,q}$.



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• A photovoltaic cell is basically a semiconductor material. Electrons of the valence band are excited through photons (light) and jump to the conduction band.



- To control the efficiency of a solar cell, one must control some properties of its electronic structure. For instance : the position of the gap, its length, the curvature of the bands, etc.
- The crucial term in the Schrödinger operator is the potential V_{per} which describes how the atoms are organized.
- For given M band functions $q \mapsto b_m(q)$ where $1 \le m \le M$, can we find a (or the) periodic potential W such that the M first bands of the operator $-\frac{1}{2}\Delta + W_{per}$ coincide with our target bands $q \mapsto b_m(q)$?
- Our final aim is to predict new types of interesting materials.

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• We introduce the following cost functional

$$\mathcal{J}(W_{per}) = \sum_{1 \leq m \leq M} \frac{1}{|\Gamma^*|} \int\limits_{\Gamma^*} |\epsilon_m(q, W_{per}) - b_m(q)|^2 dq$$

• We seek for the potential W that minimizes this cost. i.e solve the optimization problem

$$W^* \in \underset{W_{per} \in L^2_{per}(\Gamma)}{\operatorname{argmin}} \mathcal{J}(W_{per}) \tag{1}$$

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Proposition (ongoing work for $M \ge 2, d \ge 1$)

If M = 1 and d = 1 (one dimensional crystal) then the problem (1) has a minimizer in $\mathcal{M}_b(\Gamma)$ (the space of bounded measures).



- Non convex optimization \rightarrow existence of numerous local minima \rightarrow some local minima are -physically- interesting though.
- The gradient at each step depends on the solution of the direct problem and is time consuming.

$$\forall r \in \mathbb{Z}^3, \ |r| \leq C, \quad \partial_{\hat{W}_r} \mathcal{J}(W_{per}) = 2 \sum_{m=1}^M \sum_{q \in \Gamma^*} \sum_{|j| \leq P} \sum_{|s| \leq j} \overline{\hat{e}}_{q,m,s} \hat{e}_{q,m,s} \frac{1}{\sqrt{2\pi}} \delta_{r,2s-j} \left(\epsilon_m(q, W_{pe}) - b_m(q) \right)$$

• Speed of convergence depends on the computation of the gradient. One needs to choose carefully *P* and *C* (ongoing work).

"Prediction is very difficult, especially if it's about the future." Niels Bohr.

Thank you for your attention.

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