

Exact embedding of local defects in crystals

Mathieu LEWIN

Mathieu.Lewin@math.cnrs.fr

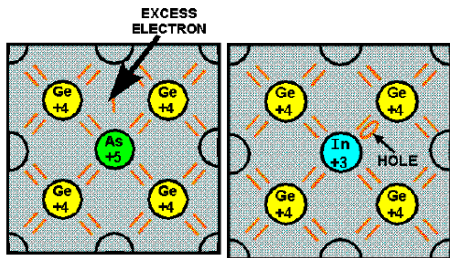
(CNRS & University of Cergy-Pontoise)

joint work with É. Cancès & A. Deleurence (ENPC, Marne-La-Vallée)

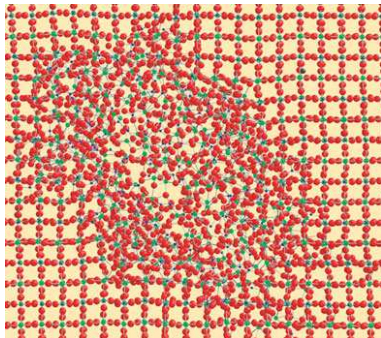
Minneapolis, September 2008

Introduction

Describing the **electronic state of a crystal in presence of a defect** is a major issue in Quantum Chemistry and Physics.



Germanium crystal doped with arsenic or indium.



Structural damage in crystalline zircon (a candidate for storing nuclear waste for over 250 000 years) in the presence of a heavy nucleus.

Farnan et al, *Nature* **445** (2007), 190.

What we want to do:

- construct a model from “first principles”;
- study it from a mathematical point of view;
- provide an efficient numerical method.

Our model should be able to:

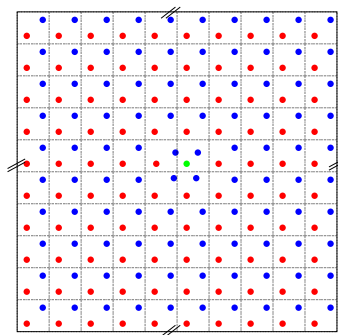
- describe charged defects;
- take the interaction between all electrons into account.

- 1 **Infinitely many particles.** QM very hard in this setting.
 - Only one possibility to construct the model:
 - *thermodynamic (Van Hove) limit.*
 - Mathematical difficulty:
 - *operators (one-body density matrix) of infinite rank.*
- 2 **Two different scales:**
 - *delocalized states* for electrons far from the defect;
 - *localized states* for those close to it.
- 3 **Nonlinearity.**
 - We will not consider the full Schrödinger model.
 - We want to describe interactions between particles
 - resort to *approximate nonlinear model* (Kohn-Sham type).

The super-cell method

At present:

- *Linear empirical models*: not quantitatively predictive;

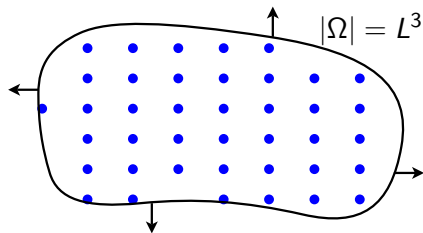


The supercell model

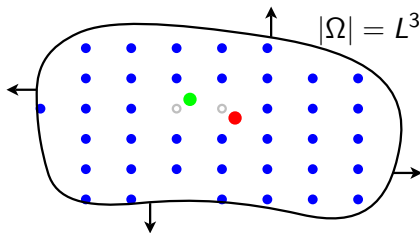
- *Supercell non linear model*: efficient for perfect crystals and only some kind of defects.
 - Spurious interactions between the defect and its periodic images;
 - inaccuracies for charged defects.

The Van Hove Limit

We first choose and fix some DFT-type energy functional $\gamma \mapsto \mathcal{E}(\gamma)$.



$$\gamma_L^0 \rightarrow \gamma_{\text{per}}^0$$
$$\mathcal{E}_L(\gamma_L^0) = \bar{e}L^3 + o(L^3)$$



$$\gamma_L \rightarrow \gamma$$
$$\mathcal{E}_L(\gamma_L) = \bar{e}L^3 + o(L^3)$$
$$\mathcal{E}_L(\gamma_L) - \mathcal{E}_L(\gamma_L^0) = c + o(1)$$

Goal: characterize $(\gamma_{\text{per}}^0, \bar{e})$ and (γ, c) (in a practically useful way).
So far this has only been possible for mean-field type models.

DFT (Kohn-Sham) model

For simplicity:

- perfect crystal = \mathbb{Z}^3 with charge Z at each site;
- $\Omega = C_L := [-L/2, L/2]^3$ with (some) boundary conditions.

$$\mathcal{E}_L^{\rho_{\text{nuc}}}(\gamma) := \text{tr}(T\gamma) + \frac{1}{2} \iint_{(C_L)^2} \frac{(\rho_\gamma - \rho_{\text{nuc}})(x)(\rho_\gamma - \rho_{\text{nuc}})(y)}{|x - y|} dx dy + E_L^{\text{xc}}(\rho_\gamma)$$

- γ = one-body density matrix. Neutral system: $\text{tr}(\gamma) = Z|C_L \cap \mathbb{Z}^3|$;
- $T = -\Delta/2$ = kinetic energy;
- E_L^{xc} = Exchange-correlation fn: $E_L^{\text{xc}}(\rho) = \int_{C_L} F^{\text{xc}}(\rho(x)) dx$ (LDA).
Sometimes in mathematical works, $E_L^{\text{xc}} = 0$ for simplicity; ☹
- we take $\rho_{\text{nuc}} = \rho_{\text{per}} + \nu$ where $\rho_{\text{per}} = Z \sum_{k \in \mathbb{Z}^3} m(\cdot - k)$ and ν = defect.

Periodic Schrödinger Operators I

Lattice $\mathbb{Z}^3 \subset \mathbb{R}^3$. Unit cell: $\Gamma = [-1/2; 1/2)^3$. Brillouin zone: $\Gamma^* = [-\pi; \pi)^3$. τ_z = translation operator by $z \in \mathbb{Z}^3$.

• **Periodic operators:** Let H be a self-adjoint operator on $L^2(\mathbb{R}^3)$ and such that $\tau_z H = H \tau_z$.

$\Rightarrow H$ and $(\tau_z)_{z \in \mathbb{Z}^3}$ can be “diagonalized” simultaneously.

Notice $\sigma(\tau_z) = S^1, \forall z \in \mathbb{Z}^3$. Generalized eigenstates ($\xi \in \Gamma^*$):

$$\begin{aligned} L_\xi^2(\Gamma) &= \left\{ u \in L_{\text{loc}}^2(\mathbb{R}^3), \forall z \in \mathbb{Z}^3, \tau_z u = e^{-iz \cdot \xi} u \right\} \\ &= \left\{ e^{i\xi \cdot x} v(x), v \in L_{\text{per}}^2(\Gamma) \right\}. \end{aligned}$$

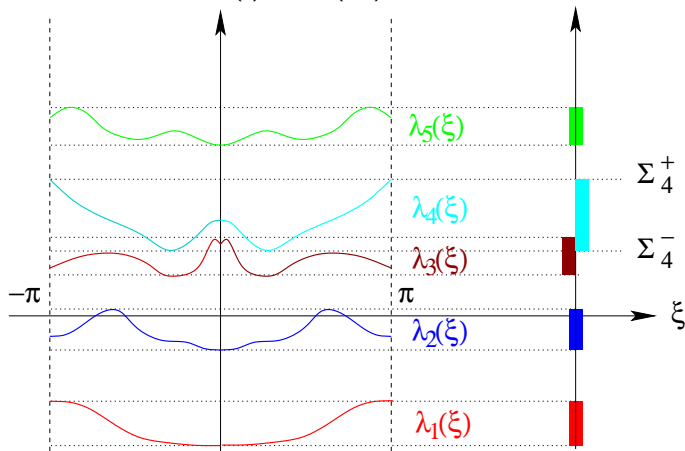
• **Bloch decomposition:** $L^2(\mathbb{R}^3) \simeq \int_{\Gamma^*}^\oplus L_\xi^2(\Gamma)$

$$H \simeq (2\pi)^{-3} \int_{\Gamma^*}^\oplus H_\xi d\xi = \int_{\Gamma^*}^\oplus H_\xi d\xi \implies \sigma(H) = \bigcup_{\xi \in \Gamma^*} (2\pi)^{-3} \sigma(H_\xi)$$

where H_ξ is a self-adjoint operator acting on $L_\xi^2(\Gamma)$.

Periodic Schrödinger Operators II

Example: effective Hamiltonian $H := -\Delta/2 + V_{\text{per}}$ where $V_{\text{per}} \in L^2_{\text{loc}}(\mathbb{R}^3)$ is \mathbb{Z}^3 -periodic. Then $\sigma(H_\xi) = \{\lambda_n(\xi)\}_{n \geq 1}$, with $\lambda_n(\xi) \rightarrow \infty \forall \xi \in \Gamma^*$ and $\lambda_n(\cdot) \in C^0(\Gamma^*)$ continuous \Rightarrow **band spectrum**.



The Perfect Crystal I

Typical behavior: (provided there is *no symmetry breaking*)

- the \mathbb{Z}^3 -periodic GS γ_L^0 is the *unique ground state* of $\mathcal{E}_L^{\rho_{\text{per}}}$ for $L \gg 1$;
- $\gamma_L^0 \rightarrow \gamma_{\text{per}}^0$ where $\gamma_{\text{per}}^0 =$ unique GS of the energy per unit volume;
- $\mathcal{E}_L^{\rho_{\text{per}}}(\gamma_L^0) \sim \bar{e}L^3$ where $\bar{e} =$ GS energy per unit volume.

$$e(\gamma) = \int_{\Gamma^*} \text{tr}_{L_\xi^2(\Gamma)} \left(-\frac{1}{2} \Delta \gamma_\xi \right) d\xi + \\ + \frac{1}{2} \iint_{\Gamma^2} G_1(x-y) (\rho_\gamma - \rho_{\text{per}})(x) (\rho_\gamma - \rho_{\text{per}})(y) dx dy + \int_{\Gamma} F^{\text{xc}}(\rho_\gamma(x)) dx$$

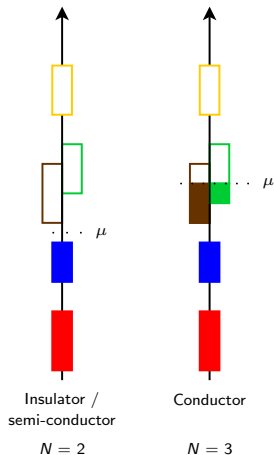
where $G_1(x) = 4\pi \sum_{k \in 2\pi\mathbb{Z}^3 \setminus \{0\}} e^{ik \cdot x} |k|^{-2}$.

$$\bar{e} = \inf_{\substack{\gamma \text{ } \mathbb{Z}^3\text{-per} \\ 0 \leq \gamma \leq 1, \int_{\Gamma} \rho_\gamma = Z}} e(\gamma) = e(\gamma_{\text{per}}^0).$$

[CLL] Catto, Le Bris, Lions, *Ann. I. H. Poincaré* **18** (2001).

[CDL] Cancès, Deleurence, M.L. *Commun. Math. Phys.* **281** (2008).

The Perfect Crystal II



Mean-field (Fock) operator:

$$H_{\text{per}}^0 := -\frac{\Delta}{2} + (\rho_{\text{per}} - \rho_{\gamma_{\text{per}}^0}) * G_1 + \frac{\partial F^{\text{xc}}}{\partial \rho}(\rho_{\gamma_{\text{per}}^0})$$

- $(\lambda_n(\xi))_{\xi \in \Gamma^*} =$ Bloch eigenvalues of H_{per}^0 .

Then γ^0 solves the SCF equation:

$$\gamma_{\text{per}}^0 = \chi_{(-\infty, \mu]}(H_{\text{per}}^0)$$

with $\sum_{n \geq 1} |\{\xi \mid \lambda_n(\xi) \leq \mu\}| = N$.

In the following we will assume that the **perfect crystal is an insulator**.

Formal Derivation of the Energy with the Defect

We formally subtract the (infinite) energy of the Fermi sea γ^0 :

$$\begin{aligned}\mathcal{E}^\nu(Q) &= \mathcal{E}_{\text{KS}}^{\rho_{\text{per}}+\nu}(\gamma) - \mathcal{E}_{\text{KS}}^{\rho_{\text{per}}+\nu}(\gamma_{\text{per}}^0) \\ \text{"="} \text{ tr}(H_{\text{per}}^0 Q) &- \iint \frac{\nu(x)\rho_Q(y)}{|x-y|} dx dy + \frac{1}{2} \iint \frac{\rho_Q(x)\rho_Q(y)}{|x-y|} dx dy + \tilde{E}^{\text{xc}}(Q)\end{aligned}$$

where $Q := \gamma - \gamma_{\text{per}}^0$ and

$$\begin{aligned}\tilde{E}^{\text{xc}}(Q) &= \int \left\{ F^{\text{xc}}(\rho_{\gamma_{\text{per}}^0}(x) + \rho_Q(x)) - F^{\text{xc}}(\rho_{\gamma_{\text{per}}^0}(x)) \right. \\ &\quad \left. - \frac{\partial F^{\text{xc}}}{\partial \rho}(\rho_{\gamma_{\text{per}}^0})(x) \rho_Q(x) \right\} dx.\end{aligned}$$

This idea was used before in the mean-field approx. of QED.

[Cl] Chaix Iracane, *J. Phys. B* **22** (1989).

[HLSS] Hainzl, M.L., Séré, Solovej. *Phys. Rev A* **76** (2007).

Defining the energy

$$\mathcal{E}^\nu(Q) = \text{tr} (H_{\text{per}}^0 Q) - \iint \frac{\nu(x)\rho_Q(y)}{|x-y|} dx dy + \frac{1}{2} \iint \frac{\rho_Q(x)\rho_Q(y)}{|x-y|} dx dy + \tilde{E}^{\text{xc}}(Q)$$

$Q = \gamma - \gamma_{\text{per}}^0$. To be studied:

$$\inf_{\substack{-\gamma_{\text{per}}^0 \leq Q \leq 1 - \gamma_{\text{per}}^0 \\ \text{tr}(Q) = N}} \mathcal{E}^\nu(Q)$$

where N =number of electrons (holes) counted relatively to the Fermi sea.

Defining the energy correctly is not an easy task.

- Q will always be a **Hilbert-Schmidt operator** (equivalence of Fock representations)
- but it is not known whether it is **trace class** \rightarrow how to define the charge $\text{tr}(Q)$???
- In QED, a GS is *never trace-class* \rightarrow **charge renormalization**.

[GLS] Gravejat, M.L., Séré. *Commun. Math. Phys.* (2008).

What we have done

Using techniques of [HLSS], we have

- defined correctly the energy $\mathcal{E}^\nu(Q)$ (in infinite dimension);
- proved the existence of ground states when $F^{\text{xc}} = 0$;
- proved the Van Hove limit $\gamma_L \rightarrow \gamma$ when $F^{\text{xc}} = 0$;
- proposed a general numerical procedure for computing γ ;
- tested it on a simple 1D system.

[CDL] Cancès, Deleurence, M.L. *Commun. Math. Phys.* **281** (2008).

[CDL'] Cancès, Deleurence, M.L. *J. Phys.: Condens. Matter* **20** (2008).

Works in preparation include

- the mathematical extension to LDA functionals;
- numerics on real systems;
- better understanding of trace-class issue.

The Ground State

Let $Q = \gamma - \gamma_{\text{per}}^0$ be a minimizer for \mathcal{E}^ν with charge constraint $\text{tr}(Q) = N$. Then γ solves the SCF equation

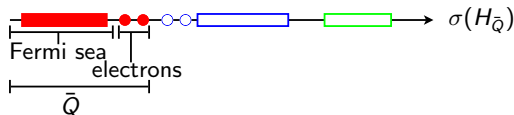
$$\begin{cases} \gamma = \chi_{(-\infty, \mu)}(H_Q), \\ H_Q = H_{\text{per}}^0 + (\rho_Q - \nu) * |\cdot|^{-1} \end{cases}$$

We decompose $Q = \gamma_e + Q_{\text{pol}}$, where $\gamma_e = \chi_{[\Sigma; \mu]}(H_Q) = \sum_{i=1}^N |\varphi_i\rangle\langle\varphi_i|$ and $Q_{\text{pol}} = \chi_{(-\infty; \Sigma)}(H_Q) - \gamma_{\text{per}}^0$. Note $H_Q \varphi_i = \epsilon_i \varphi_i$. Notice

$$H_Q = -\Delta/2 + (\rho_{\gamma_e} - \nu) * |\cdot|^{-1} + V_{\text{pol}} + V_{\text{xc}}$$

where V_{pol} describes the nonlinear polarization of the medium:

$$V_{\text{pol}} = (\rho_{\gamma_{\text{per}}^0} - \rho_{\text{per}}) *_{\Gamma} G_1 + \rho_{Q_{\text{pol}}} * |\cdot|^{-1}.$$



We describe the two different scales separately.

- 1 Computation of an approximation of γ_{per}^0 and H_{per}^0 (discretization of the Brillouin zone + use of, e.g., plane wave basis);
- 2 Construction of a **localized basis** (φ_i) used to discretize the problem with the defect ν ;
- 3 ν being given, computation of the ground state using relaxed constraint algorithms [Can] on \mathcal{E}^ν , in the so-constructed basis.

Main issue: the constraint $-\gamma_{\text{per}}^0 \leq Q \leq 1 - \gamma_{\text{per}}^0$ and H_{per}^0 in \mathcal{E}^ν both require that γ_{per}^0 and H_{per}^0 are well represented in the localized basis.

We say that the basis has to be *compatible* with the previous calculation.

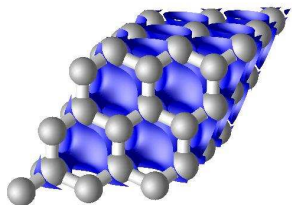
There will be no problem when the localized basis $\{\chi_\mu\}$ satisfies

$$\gamma_{\text{per}}^0 \chi_\mu = 0 \text{ or } \gamma_{\text{per}}^0 \chi_\mu = \chi_\mu, \text{ i.e. in this basis } \gamma_{\text{per}}^0 = \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}.$$

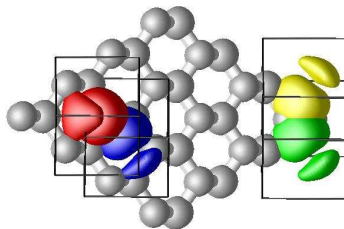
[Can] Cancès, Le Bris *Int. J. Quantum Chem.* **79** (2000). Cancès, *J. Chem. Phys.* **114** (2001). Kudin, Scuseria, Cancès, *J. Chem. Phys.* **116** (2002).

Wannier Functions

Wannier functions: a special Hilbert basis $\{\chi_{n,R}\}_{n \geq 1, R \in \mathbb{Z}^3}$ such that $\chi_{n,R} = \chi_n(\cdot - R)$. Usually each χ_n is uniquely associated with a band.



Bloch functions



Wannier functions

- The Wannier fn only depend on the *perfect crystal*;
- one can retain only the Wannier functions $\chi_{n,R}$ with $R \in B(0, R_0)$ (we assume the defect is located at 0). Increasing R_0 improves the approximation (this is variational).

Wannier Functions

- If n th band is isolated, one can choose χ_n exponentially decaying [Wan]. Can be generalized to *composite bands*.
- *Maximally Localized Wannier functions* [MV] are functions minimizing the criterion

$$\sum_{i=1}^Z (\langle \chi_n, |r|^2 \chi_n \rangle - |\langle \chi_n, r \chi_n \rangle|^2).$$

[Wan] des Cloiseaux. *Phys. Rev.* **135** (1964).

Nenciu. *Commun. Math. Phys.* **91** (1983).

Brouder, Panati, Calandra, Mourougane, Marzari. *PRL* **98** (2007).

[MV] Marzari, Vanderbilt. *Phys. Rev. B* **56** (1997).

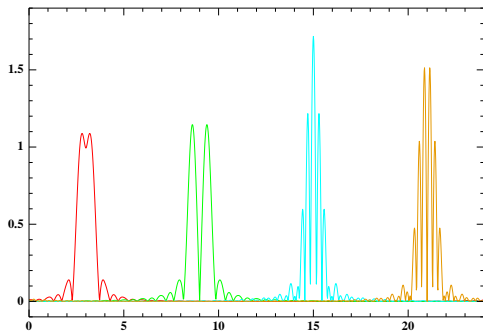
1D Model

1D model with Yukawa interaction potential.

$$E_{1D}(\gamma) = \text{tr} \left(-\frac{1}{2} \frac{d^2 \gamma}{dx^2} \right) - D_\kappa(\rho_{\text{nuc}}, \rho_\gamma) + \frac{1}{2} D_\kappa(\rho_\gamma, \rho_\gamma)$$

with $D_\kappa(f, g) = (A/2\kappa) \int_{\mathbb{R}} \int_{\mathbb{R}} f(x) e^{-\kappa|x-x'|} g(x') dx dx'$,
 $\rho_{\text{nuc}} = Z \sum_{j \in \mathbb{Z}} \delta_j + \nu$ and $\nu = (Z - 1)\delta_{0.25} - Z\delta_0$.

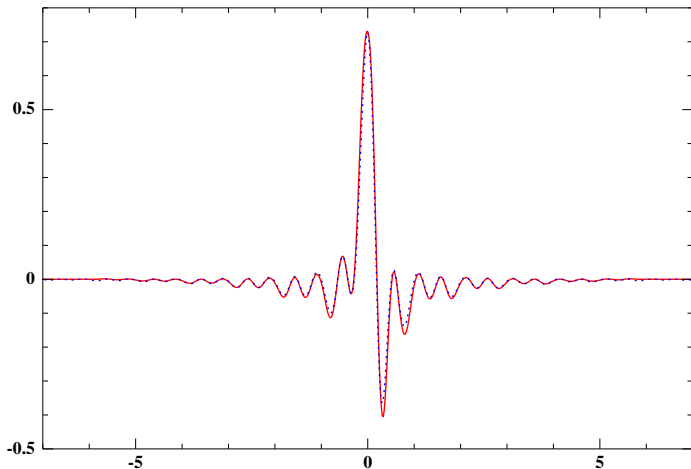
Simulation done with $A = 10$, $\kappa = 5$ and $Z = 2$.



Modulus of the Maximally Localized Wannier Orbitals [MV] for the first two bands (red and green), the 3rd and 4th bands (blue and orange).

Results

Defect: we move one nucleus $0 \rightarrow 0.5$ and lower its charge by one unit.



Perturbation ρ_Q of the periodic ground state density with 28 MLWFs (line in red). The reference is a supercell calculation in a basis set of size 1224 (dashed line in blue).

Conclusion

- A **first principle DFT model** allowing to describe electrons in a crystal with defect.
- **Two “scales”**: electrons of the Fermi sea are delocalized, bound electrons are localized.
- Well-defined for **charged defects**.
- *Numerics*: a **two-step method** which treats in a “compatible way” delocalized and localized electrons.

Perspectives:

- Mathematical properties of minimizers missing.
- Mathematical extension to LDA functionals missing.
- Numerics for real systems in progress.