The Kohn-Sham model for crystals with local defects

Eric CANCES

Ecole des Ponts and INRIA, Paris, France

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Joint work with A. Deleurence and M. Lewin

Outline of the talk

1. Density matrix formulation of DFT

2. Electronic structures of crystals with local defects

3. Some related works

1 - Density matrix formulation of DFT

Extended Kohn-Sham model (Valone '80, Lieb '83, Dreizler and Gross '90)

- **Obtained by constrained minimization on mixed quantum states**

$$\inf_{\Psi \text{ N}-\text{body pure state}} \langle \Psi | H_N | \Psi \rangle = \inf_{\Gamma \text{N}-\text{body mixed state}} \mathbf{Tr}(H_N \Gamma_N)$$

- **Always provides the exact ground state energy and density (with the exact exchange-correlation functional)**
- **Identical to the Kohn-Sham model in most cases (when the ground-state density is pure state non-interacting V-representable)**
- **0-temperature limit of the finite temperature Kohn-Sham model**
- **The extended Kohn-Sham model is convex!**

Orbital formulation of the extended Kohn-Sham model

In the extended Kohn-Sham model, the ground state energy and density are obtained by solving

$$\inf\left\{\mathcal{E}^{\mathrm{KS}}(\{\phi_i\},\{n_i\}),\quad \phi_i\in H^1(\mathbb{R}^3),\quad \int_{\mathbb{R}^3}\phi_i^*\phi_j=\delta_{ij},\quad 0\le n_i\le 1,\quad \sum_{i=1}^{+\infty}n_i=N\right\}$$

where

$$\mathcal{E}^{\mathrm{KS}}(\{\phi_i\},\{n_i\})=\frac{1}{2}\sum_{i=1}^{+\infty}n_i\int_{\mathbb{R}^3}|\nabla\phi_i|^2+\int_{\mathbb{R}^3}\rho V^{\mathrm{ne}}+\frac{1}{2}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}\,d\mathbf{r}'+E^{\mathrm{xc}}[\rho]$$

with

$$V^{\mathrm{ne}}(\mathbf{r})=-\sum_{k=1}^{M}\frac{z_k}{|\mathbf{r}-\mathbf{R}_k|}\qquad \rho(\mathbf{r})=\sum_{i=1}^{+\infty}n_i|\phi_i(\mathbf{r})|^2$$

$(\phi_i)_{i\ge1}$**: molecular orbitals,** $(n_i)_{i\ge1}$**: occupation numbers**
$E^{\mathrm{xc}}[\rho]$**: exchance-correlation functional**

Kohn-Sham density matrices

$$\gamma(\mathbf{r},\mathbf{r}') = \sum_{i=1}^{+\infty} n_i \phi_i(\mathbf{r})\phi_i(\mathbf{r}')^* \qquad \gamma(\mathbf{r},\mathbf{r}) = \sum_{i=1}^{+\infty} n_i |\phi_i(\mathbf{r})|^2 = \rho_\gamma(\mathbf{r})$$

$(\phi_i)_{i\geq 1}$: **orbitals** $\qquad \langle \phi_i | \phi_j \rangle := \int_{\mathbb{R}^3} \phi_i(\mathbf{r})^* \, \phi_j(\mathbf{r}) \, d\mathbf{r} = \delta_{ij}$

$(n_i)_{i\geq 1}$: **occupation numbers** $\qquad 0 \leq n_i \leq 1, \quad \sum_{i=1}^{+\infty} n_i = N$

$\longrightarrow$ **Good for numerics (linear scaling algorithms)**

$\longrightarrow$ **And also good for mathematical studies (bulk limits)**

$\gamma(\mathbf{r},\mathbf{r}')$ is the integral kernel of the self-adjoint operator

$$\gamma = \sum_{i=1}^{+\infty} n_i |\phi_i\rangle\langle\phi_i|$$

$$\gamma = \gamma^\dagger, \qquad 0 \leq \gamma \leq 1, \qquad \mathbf{Tr}(\gamma) = N$$

Density matrix formulation of the (extended) Kohn-Sham LDA model

The ground state energy, density and KS density matrix are obtained by solving

$$\inf\left\{E^{\mathrm{KS}}(\gamma),\quad \gamma=\gamma^{\dagger},\quad 0\le\gamma\le 1,\quad \mathbf{Tr}(\gamma)=N,\quad \mathbf{Tr}(-\Delta\gamma)<\infty\right\}$$

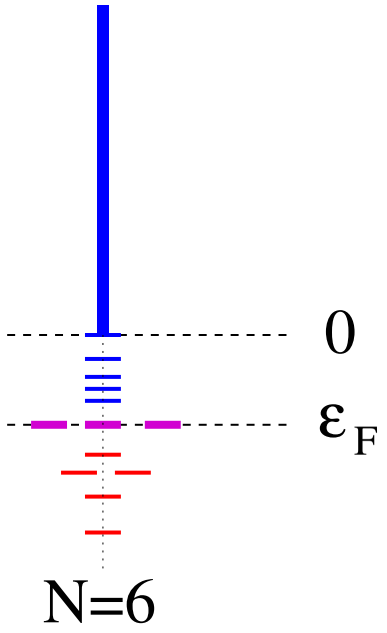
$$E^{\mathrm{KS}}(\gamma)=\mathbf{Tr}\left(-\frac{1}{2}\Delta\gamma\right)+\int_{\mathbb{R}^3}\rho_\gamma V^{\mathrm{ne}}+\frac{1}{2}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\frac{\rho_\gamma(\mathbf{r})\rho_\gamma(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}\,d\mathbf{r}'+E^{\mathrm{xc}}[\rho_\gamma]$$

$$V^{\mathrm{ne}}(\mathbf{r})=-\sum_{k=1}^{M}\frac{z_k}{|\mathbf{r}-\mathbf{R}_k|}\qquad \rho_\gamma(\mathbf{r})=\gamma(\mathbf{r},\mathbf{r})$$

Prototypical approximate XC functional: $E^{\mathrm{xc}}_{\mathrm{X}\alpha}[\rho]=-C_{\mathrm{X}}\displaystyle\int_{\mathbb{R}^3}\rho^{4/3}(\mathbf{r})\,d\mathbf{r}$

Theorem (A. Anantharaman, E.C., Ann. IHP 2009). **If $N \leq Z = \sum_{k=1}^{M} z_k$, then the extended Kohn-Sham LDA problem has a minimizer. Any minimizer γ^0 satisfies the extended Kohn-Sham equations**

$$\begin{cases} \gamma^0 = \displaystyle\sum_{i=1}^{+\infty} n_i |\phi_i\rangle\langle\phi_i|, \qquad \rho^0(\mathbf{r}) = \gamma^0(\mathbf{r},\mathbf{r}) = \sum_{i=1}^{+\infty} n_i |\phi_i(\mathbf{r})|^2 \\ H_{\rho^0}\phi_i = \varepsilon_i \phi_i \\ \langle\phi_i|\phi_j\rangle = \delta_{ij} \\ \left| \begin{array}{l} n_i = 1 \text{ if } \varepsilon_i < \varepsilon_{\rm F}, \\ 0 \leq n_i \leq 1 \text{ if } \varepsilon_i = \varepsilon_{\rm F}, \\ n_i = 0 \text{ if } \varepsilon_i > \varepsilon_{\rm F}, \end{array} \right. \qquad \displaystyle\sum_{i=1}^{+\infty} n_i = N \quad \textbf{(Aufbau principle)} \\ H_{\rho^0} = -\frac{1}{2}\Delta + V_{\rho^0}^{\rm KS}, \qquad V_{\rho^0}^{\rm KS} = V^{\rm ne} + \rho^0 \star |\cdot|^{-1} + V_{\rho^0}^{\rm xc} \end{cases}$$



2 - Electronic structures of crystals with local defects

Reference model for the mathematical analysis: Hartree
(Kohn-Sham with $E^{\rm xc} = 0$)

Existence of a ground state density matrix for neutral systems
Uniqueness of the ground state density (Solovej, Invent. Math. 1991)

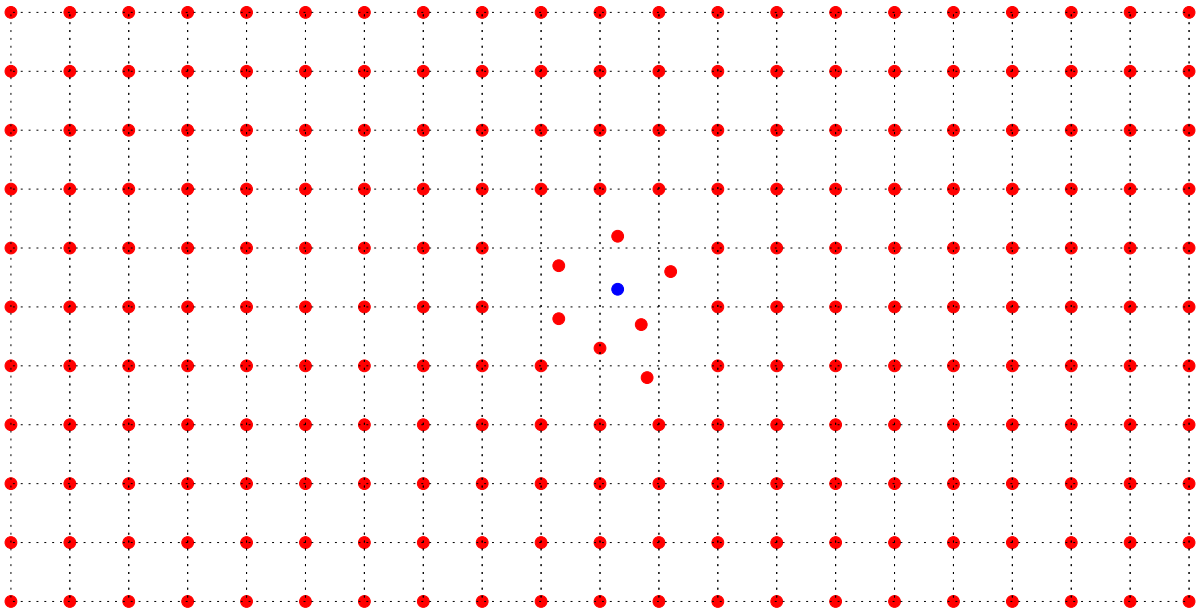
E.C., A. Deleurence and M. Lewin, Comm. Math. Phys. 2008
E.C. and M. Lewin, Arch. Ration. Mech. Anal. 2009

The resulting embedding model can be used for Kohn-Sham calculations

E.C., A. Deleurence and M. Lewin, J. Phys.: Cond. Mat. 2008

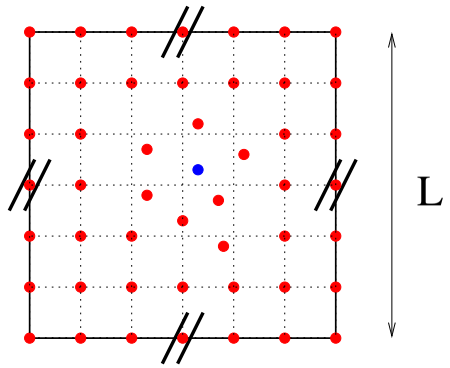
Example of a crystal with a local defect

Impurity with relaxation of the host crystal

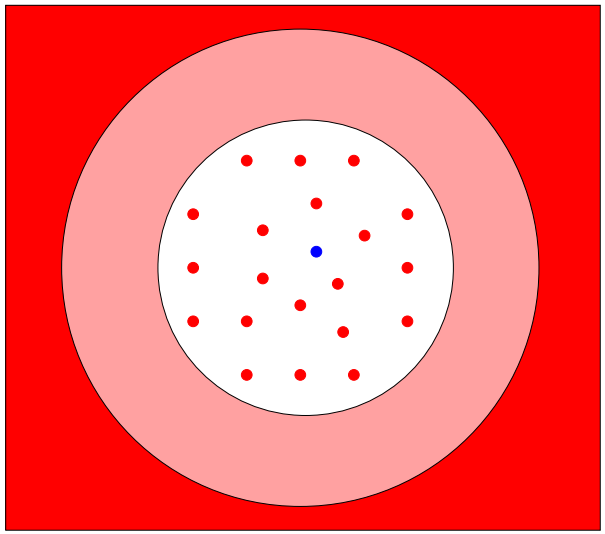


Usual approaches

- **Supercell model**
- **Perturbative methods, Green functions**
- **Phenomenological embedding methods**



Supercell



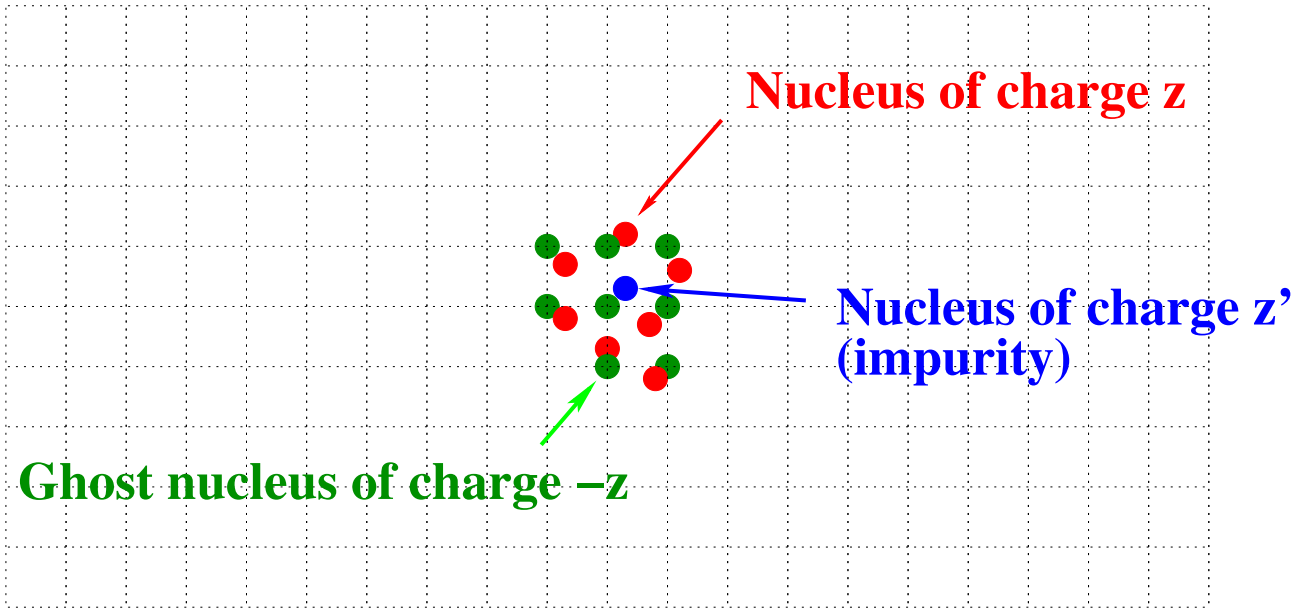
Phenomenological embedding

Defect = quasi-molecule embedded in the host crystal

$$\rho^{\mathrm{nuc}} = \rho^{\mathrm{nuc}}_{\mathrm{per}} + m \qquad \gamma^{0} = \gamma^{0}_{\mathrm{per}} + Q^{m,\varepsilon_{\mathrm{F}}} \qquad \rho^{0} = \rho^{0}_{\mathrm{per}} + \rho^{m,\varepsilon_{\mathrm{F}}}$$

Goal: **find a way to directly compute $Q^{m,\varepsilon_{\mathrm{F}}}$ and $\rho^{m,\varepsilon_{\mathrm{F}}}$**

Nuclear charge m of the quasi-molecule



The Hartree model for perfect crystals

Consider an $\mathcal{R}$-periodic nuclear distribution $\rho^{\mathrm{nuc}}_{\mathrm{per}}$ such that $\int_{\mathrm{UC}} \rho^{\mathrm{nuc}}_{\mathrm{per}} = z$. Then

1. the $\mathcal{R}$-periodic GS electronic density ρ^0_{per} is unique and $\int_{\mathrm{UC}} \rho^0_{\mathrm{per}} = z$

2. the mean-field Hamiltonian is the periodic Schrödinger operator

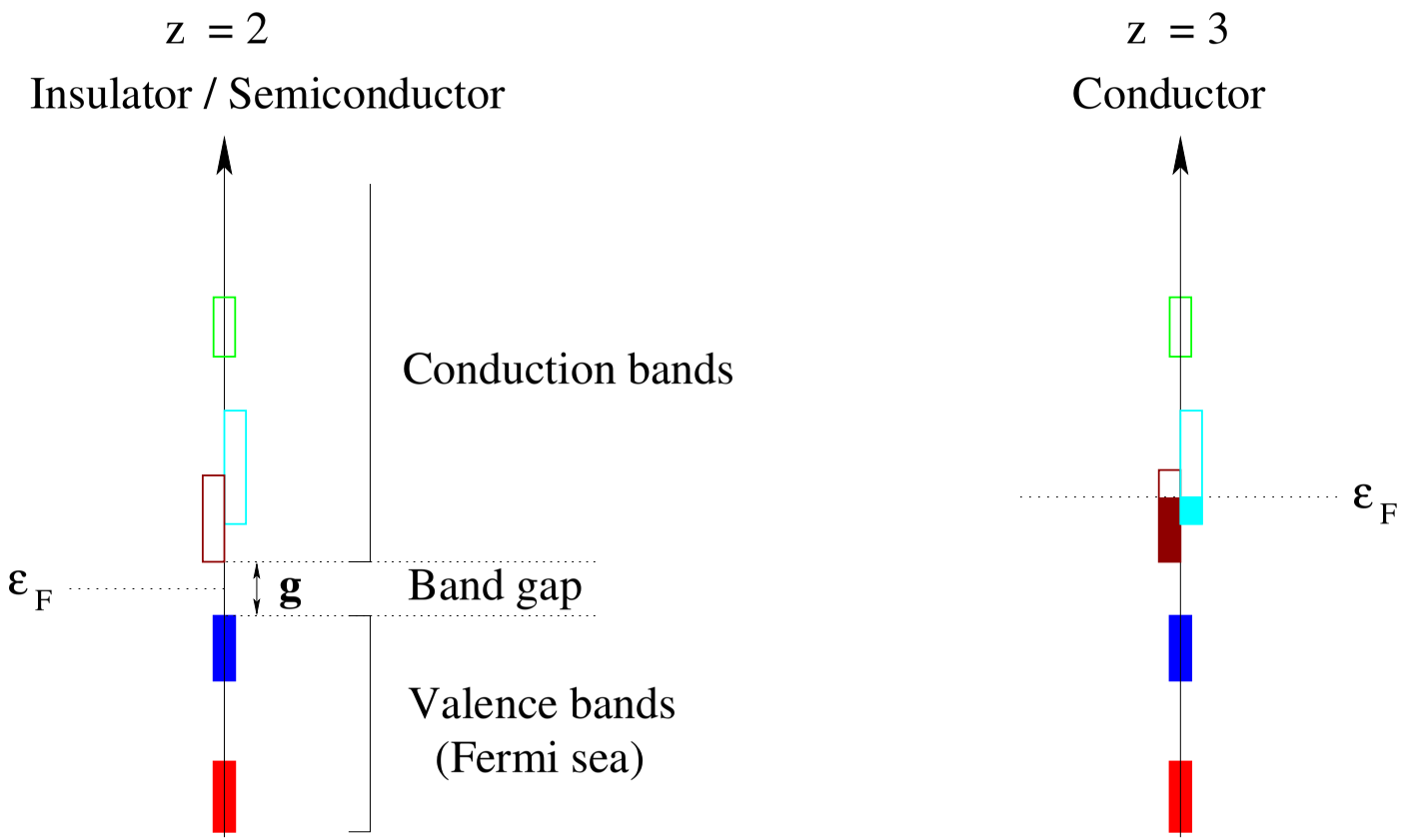
$$H^0_{\mathrm{per}} = -\frac{1}{2}\Delta + V^0_{\mathrm{per}}$$

where V^0_{per} denotes the periodic electrostatic potential generated by the periodic charge density $\rho^{\mathrm{tot}}_{\mathrm{per}} = \rho^0_{\mathrm{per}} - \rho^{\mathrm{nuc}}_{\mathrm{per}}$

$$\begin{cases} -\Delta V^0_{\mathrm{per}} = 4\pi \left(\rho^0_{\mathrm{per}} - \rho^{\mathrm{nuc}}_{\mathrm{per}}\right) \\ \\ V^0_{\mathrm{per}} \ \mathcal{R}\text{-periodic} \end{cases}$$

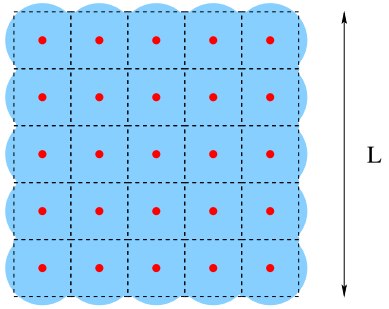
3. the GS density matrix $\gamma^0_{\rm per}$ is unique and it is an orthogonal projector

$$\gamma^0_{\rm per} = 1_{(-\infty,\varepsilon_{\rm F}]}(H^0_{\rm per}) \qquad \rho^0_{\rm per}(\mathbf{r}) = \gamma^0_{\rm per}(\mathbf{r},\mathbf{r})$$



Mathematical justification of the Hartree model for perfect crystals

Thermodynamic limit (bulk limit) argument

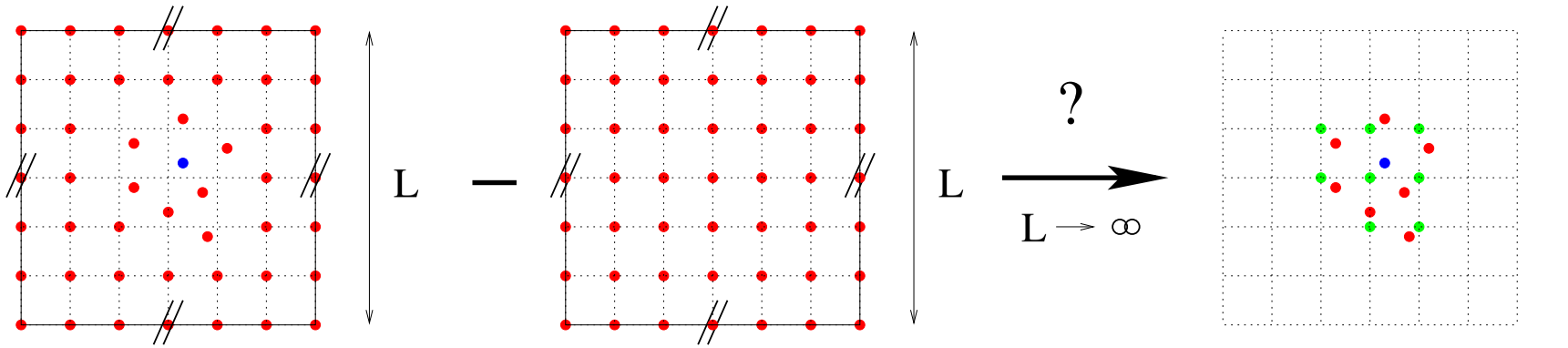


$$\begin{cases} \rho_L^{\rm nuc} = \displaystyle\sum_{\mathbf{R}\in\mathcal{R}\cap\Lambda_L} z\delta(\cdot-\mathbf{R}) \\ \\ zL^3 \text{ electrons} \end{cases} \longrightarrow \left| \begin{array}{ll} E_L^0 & \text{the ground state total energy} \\ \\ \rho_L^0 & \text{the (unique) ground state density} \\ \\ \gamma_L^0 & \text{a ground state density matrix} \end{array} \right.$$

Theorem (Catto-Le Bris-Lions, Ann. IHP 2001)

$$\lim_{L\to\infty} \frac{E_L^0}{L^3} = E_{\rm per}^0, \qquad \rho_L^0 \overset{\text{in some sense}}{\underset{L\to\infty}{\longrightarrow}} \rho_{\rm per}^0, \qquad \gamma_L^0 \overset{\text{in some sense}}{\underset{L\to\infty}{\longrightarrow}} \gamma_{\rm per}^0$$

Thermodynamic limit of the supercell model, with and without defect



$E^{m,\varepsilon_{\rm F}}_{{\rm sc},L}, \rho^{m,\varepsilon_{\rm F}}_{{\rm sc},L}, \gamma^{m,\varepsilon_{\rm F}}_{{\rm sc},L}$ $\quad$ $E^{0}_{{\rm sc},L}, \rho^{0}_{{\rm sc},L}, \gamma^{0}_{{\rm sc},L}$ $\quad$ $\varepsilon^{m,\varepsilon_{\rm F}}, \rho^{m,\varepsilon_{\rm F}}, Q^{m,\varepsilon_{\rm F}}$

Theorem (E.C.-Deleurence-Lewin, Comm. Math. Phys. 2008). Assume that the host crystal is an insulator or a semiconductor. Then

1. $(\rho^{0}_{{\rm sc},L}, \gamma^{0}_{{\rm sc},L})$ **converges to** $(\rho^{0}_{\rm per}, \gamma^{0}_{\rm per})$ **when** L **goes to infinity**

2. $E^{m,\varepsilon_{\rm F}}_{{\rm sc},L} - E^{0}_{{\rm sc},L}$ **has a finite limit** $\varepsilon^{m,\varepsilon_{\rm F}}$

- **A self-adjoint operator Q on $L^2(\mathbb{R}^3)$ is called trace-class if**

$$Q = \sum_{i=1}^{+\infty} \lambda_i |\phi_i\rangle\langle\phi_i| \qquad \textbf{with} \qquad \langle\phi_i|\phi_j\rangle = \delta_{ij}, \qquad \sum_{i=1}^{+\infty} |\lambda_i| < \infty$$

If Q is trace-class then

$$\rho_Q(\mathbf{r}) = Q(\mathbf{r},\mathbf{r}) = \sum_{i=1}^{+\infty} \lambda_i |\phi_i(\mathbf{r})|^2 \in L^1(\mathbb{R}^3)$$

and for any orthonormal basis $(e_n)_{n\in\mathbb{N}}$ of $L^2(\mathbb{R}^3)$,

$$\int_{\mathbb{R}^3} \rho_Q = \mathbf{Tr}(Q) = \sum_{i=1}^{+\infty} \lambda_i = \sum_{n\in\mathbb{N}} \langle e_n|Q|e_n\rangle = \textbf{ charge of } Q$$

- **A self-adjoint operator Q on $L^2(\mathbb{R}^3)$ is called Hilbert-Schmidt if**

$$Q = \sum_{i=1}^{+\infty} \lambda_i |\phi_i\rangle\langle\phi_i| \qquad \textbf{with} \qquad \langle\phi_i|\phi_j\rangle = \delta_{ij}, \qquad \sum_{i=1}^{+\infty} |\lambda_i|^2 < \infty$$

3. $\rho_{\mathrm{sc},L}^{m,\varepsilon_{\mathrm{F}}} - \rho_{\mathrm{sc},L}^{0}$ **converges to** $\rho^{m,\varepsilon_{\mathrm{F}}} \in L^2(\mathbb{R}^3)$

4. $\gamma_{\mathrm{sc},L}^{m,\varepsilon_{\mathrm{F}}} - \gamma_{\mathrm{sc},L}^{0}$ **converges to some Hilbert-Schmidt operator** $Q^{m,\varepsilon_{\mathrm{F}}}$ **(u.t.e.)**

5. $\rho^{m,\varepsilon_{\mathrm{F}}}$ **is the density associated with** $Q^{m,\varepsilon_{\mathrm{F}}}$ **in some weak sense**

Theorem (E.C. and M. Lewin, ARMA 2009). As a consequence of the long-range of the Coulomb potential

- $Q^{m,\varepsilon_{\mathrm{F}}}$ **is not trace-class (except possibly when** $\displaystyle\int_{\mathbb{R}^3} m = 0$**)**

  Reminiscent of the renormalization problem in QED
  (see Gravejat, Lewin, Séré for a mathematical analysis)

- $\rho^{m,\varepsilon_{\mathrm{F}}}$ **is not an integrable function for anisotropic crystals**

There exist two orthonormal bases $(\phi_n)_{n\in\mathbb{N}}$ **and** $(\psi_n)_{n\in\mathbb{N}}$ **of** $L^2(\mathbb{R}^3)$ **such that**

$$\sum_{n=0}^{+\infty} \langle \phi_n | Q^{m,\varepsilon_{\mathrm{F}}} | \phi_n \rangle \quad \neq \quad \sum_{n=0}^{+\infty} \langle \psi_n | Q^{m,\varepsilon_{\mathrm{F}}} | \psi_n \rangle \quad \neq \quad \lim_{R\to+\infty} \int_{|\mathbf{r}|<R} \rho^{m,\varepsilon_{\mathrm{F}}}(\mathbf{r})\, d\mathbf{r}$$

Definitions of the "bare" and "renormalized" charges of the defect

There exists

- **an orthonormal basis** $(\phi_i^-)_{i>N_-}$ **of** $\mathcal{H}_- = \mathbf{Ran}(\gamma^0_{\rm per})$
- **an orthonormal basis** $(\phi_i^+)_{i>N_+}$ **of** $\mathcal{H}_+ = \mathbf{Ran}(1-\gamma^0_{\rm per})$

such that in the orthonormal basis $((\phi_i^-),(\phi_i^+))$ **of** $L^2(\mathbb{R}^3) = \mathcal{H}_- \oplus \mathcal{H}_+$

$$\gamma^0_{\rm per} = \left(\begin{array}{c||c} I & 0 \\ \hline\hline 0 & 0 \end{array}\right) \qquad Q^{m,\varepsilon_{\rm F}} = \left(\begin{array}{c|c||c|c} -I_{N_-} & 0 & 0 & 0 \\ \hline 0 & \mathbf{diag}(-a_1,-a_2,\cdots) & 0 & \mathbf{diag}(b_1,b_2,\cdots) \\ \hline\hline 0 & 0 & I_{N_+} & 0 \\ \hline 0 & \mathbf{diag}(b_1,b_2,\cdots) & 0 & \mathbf{diag}(a_1,a_2,\cdots) \end{array}\right)$$

with

$$0 \le a_i < 1, \qquad \sum_{i=1}^{+\infty} a_i < +\infty, \qquad b_i = \sqrt{a_i(1-a_i)}$$

$$\boxed{\mathbf{Tr}_0(Q^{m,\varepsilon_{\rm F}}) := \mathbf{Tr}([Q^{m,\varepsilon_{\rm F}}]^{++} + [Q^{m,\varepsilon_{\rm F}}]^{--}) = N_+ - N_- = \text{"bare" charge of } Q^{m,\varepsilon_{\rm F}}}$$

We can prove that for an isotropic crystal, there exists $\varepsilon_\mu > \varepsilon_{\mathrm{M}} > 1$ (ε_{M}: macroscopic dielectric permittivity of the host crystal) such that if the Coulomb energy of m is small enough, then

- **$\mathbf{Tr}_0(Q^{m,\varepsilon_{\mathrm{F}}}) = 0$ so that the "bare" charge of the defect is**

$$q_{\text{"bare"}} = \int_{\mathbb{R}^3} m - \mathbf{Tr}_0(Q^{m,\varepsilon_{\mathrm{F}}}) = \int_{\mathbb{R}^3} m$$

- **if $\rho_{Q^{m,\varepsilon_{\mathrm{F}}}} \in L^1(\mathbb{R}^3)$, then $\displaystyle\int_{\mathbb{R}^3} \rho_{Q^{m,\varepsilon_{\mathrm{F}}}} = \frac{\varepsilon_\mu - 1}{\varepsilon_\mu} \int_{\mathbb{R}^3} m$, and the "observed" or "renormalized" charge of the defect is**

$$q_{\text{"renormalized"}} = \int_{\mathbb{R}^3} m - \int_{\mathbb{R}^3} \rho_{Q^{m,\varepsilon_{\mathrm{F}}}} = \frac{1}{\varepsilon_\mu} \int_{\mathbb{R}^3} m$$

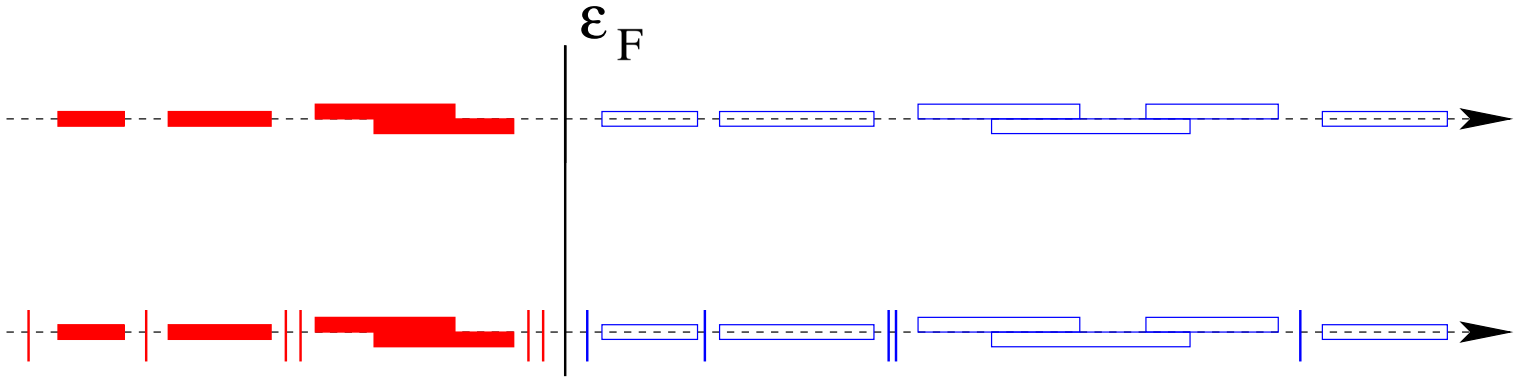
Characterization of $Q^{m,\varepsilon_{\mathrm{F}}}$

Let $\widetilde{H}_{\rho^{m,\varepsilon_{\mathrm{F}}}}$ be the Hartree Hamiltonian of the crystal with the local defect

$$\widetilde{H}_{\rho^{m,\varepsilon_{\mathrm{F}}}} = H^0_{\mathrm{per}} - V_m^{\mathrm{Coulomb}} + V_{\rho^{m,q}}^{\mathrm{Coulomb}}$$

$Q^{m,q}$ satisfies the Dyson-like self-consistent embedding equation

$$Q^{m,q} = 1_{(-\infty,\varepsilon_F]}(\widetilde{H}_{\rho^{m,q}}) - 1_{(-\infty,\varepsilon_F]}(H^0_{\mathrm{per}})$$



Can $Q^{m,\varepsilon}$ be obtained by minimizing some energy functional on some variational set?

Variational characterization of $Q^{m,\varepsilon_{\rm F}}$

Let $\mathcal{H}_- = \mathbf{Ran}(\gamma^0_{\rm per})$ and $\mathcal{H}_+ = \mathbf{Ran}(1-\gamma^0_{\rm per})$. Then $L^2(\mathbb{R}^3) = \mathcal{H}_- \oplus \mathcal{H}_+$ and

$$\gamma^0_{\rm per} \;=\; \left(\begin{array}{c|c} I & 0 \\ \hline 0 & 0 \end{array}\right) \qquad H^0_{\rm per} - \varepsilon_{\rm F} \;=\; \left(\begin{array}{c|c} [H^0_{\rm per} - \varepsilon_{\rm F}]^{--} \leq 0 & 0 \\ \hline 0 & [H^0_{\rm per} - \varepsilon_{\rm F}]^{++} \geq 0 \end{array}\right)$$

$Q^{m,\varepsilon_{\rm F}}$ is a minimizer (and $\rho^{m,\varepsilon_{\rm F}}$ is the unique minimizing density) to

$$\inf\left\{\mathcal{E}^m_{\varepsilon_{\rm F}}(Q),\ Q \in \mathcal{Q}\right\}$$

$$\mathcal{E}^m_{\varepsilon_{\rm F}}(Q) = \mathbf{Tr}_0((H^0_{\rm per} - \varepsilon_{\rm F})Q) - \int_{\mathbb{R}^3} \rho_Q V_m^{\rm Coulomb} + \frac{1}{2}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \frac{\rho_Q(x)\,\rho_Q(x')}{|x-x'|}\,dx\,dx'$$

$$Q = \left(\begin{array}{c|c} Q^{--} \leq 0 & Q^{-+} \\ \textbf{trace-class} & \textbf{Hilbert-Schmidt} \\ \hline Q^{+-} & Q^{++} \geq 0 \\ \textbf{Hilbert-Schmidt} & \textbf{trace-class} \end{array}\right), \qquad \begin{array}{l} Q^* = Q \\ 0 \leq \gamma^0_{\rm per} + Q \leq 1 \\ |\nabla|Q^{++}|\nabla|,\ |\nabla|Q^{--}|\nabla| \ \textbf{trace-class} \end{array}$$

Conclusion

1. **Using rigorous bulk limit arguments, we have obtained a (non-trivial) variational model for computing the electronic ground state of insulating and semiconducting crystals with local defects.**

   This model takes into account the screening effect in insulators and semi-conductors in an implicit (but exact) way.

   Homogeneous electron gas: Franck, Lewin, Lieb, Seiringer 2011

   $\longrightarrow$ **Quid for real metals?**

2. **Hierarchical variational approximations of the modification $Q^{m,\varepsilon_{\rm F}}$ of the density matrix can be computed using a (possibly enriched) basis of Maximally Localized Wannier Functions of the host crystal (E.C., A. Deleurence and M. Lewin, J. Phys.: Cond. Mat. 2008)**

   $\longrightarrow$ **Accurary? - Linear scaling? - Sublinear scaling?**

3 - Some related works

Time-dependent models (TDDFT) - Macroscopic limit

$\longrightarrow$ Talk by G. Stoltz

Orbital-free models for local defects in crystals

Defects are always neutral in the Thomas-Fermi-von Weizsäcker theory

$\longrightarrow$ Poster by V. Ehrlacher

Mean-field models for crystals with randomly distributed defects (doped semiconductors), alloys, amorphous materials

$\longrightarrow$ Poster by S. Lahbabi