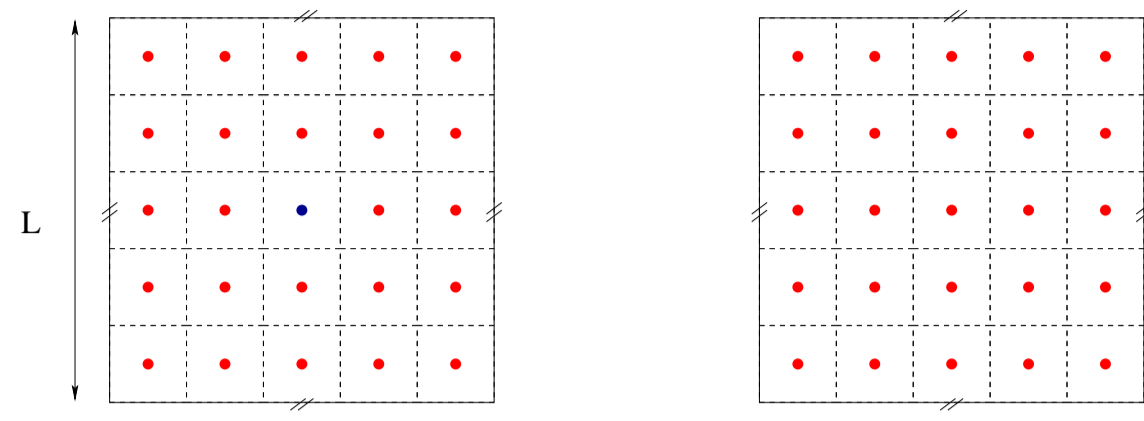


Thermodynamic limits for crystals



Ground state density matrices and energies:

$$\begin{array}{cc} I_{sc,L,\mu}^\nu & I_{sc,L,\mu}^0 \\ \gamma_L^\nu & \gamma_L^0 \end{array}$$

Do we have

$$\begin{array}{l} Q_L^\nu = \gamma_L^\nu - \gamma_L^0 \longrightarrow Q^\nu ? \\ \mathcal{E}_L^\nu = I_{sc,L,\mu}^\nu - I_{sc,L,\mu}^0 \longrightarrow \mathcal{E}^\nu ? \end{array}$$

Drawbacks of the supercell model:

- Spurious interactions between the defect and its periodic images,
- Inaccuracies for charged defects (jellium background).

Our approach : define a new model by passing to the thermodynamic limit in the supercell model.

γ_{per}^0 is the density matrix of the perfect crystal in the thermodynamic limit. It verifies the *self-consistent equation*

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

with

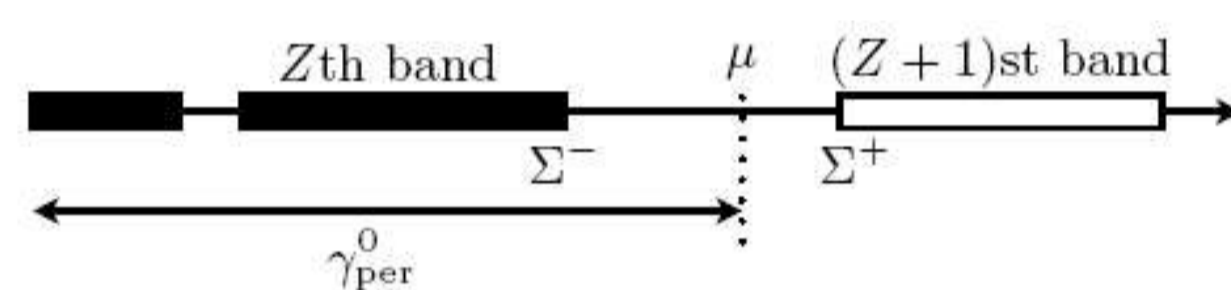
$$\begin{array}{l} H_{per}^0 = -\frac{1}{2}\Delta + \Phi_{per}, \\ -\Delta\Phi_{per} = 4\pi(\rho_{per}^0 - \rho_{per}^{muc}), \quad \Phi_{per} \mathcal{R}\text{-periodic} \end{array}$$

ρ_{per}^0 is the density of the periodic fermi sea and \mathcal{R} the Bravais lattice of the host crystal.

The system is locally neutral so we have on the reference unit cell Ω

$$\int_{\Omega} \rho_{per}^0 = \int_{\Omega} \rho_{per}^{muc} = Z,$$

the Fermi level μ being chosen to ensure this equality.



Spectrum of H_{per}^0 .

Variational approximation

$$L^2(\mathbb{R}^3) = \mathcal{H}_- \oplus \mathcal{H}_+,$$

where $\mathcal{H}_- = \text{Ran}(\gamma_{per}^0)$ and $\mathcal{H}_+ = \text{Ran}(1 - \gamma_{per}^0)$.

Let V_-^h (resp. V_+^h) be a finite-dimensional subspace of \mathcal{H}_- (resp. $\mathcal{H}_+ \cap H^2(\mathbb{R}^3)$)

and $V^h = V_-^h \oplus V_+^h \subset L^2(\mathbb{R}^3)$.

Let $(\phi_1, \dots, \phi_{N_-})$ (resp. $(\phi_{N_-+1}, \dots, \phi_{N_b})$) be an orthonormal basis of V_-^h (resp. V_+^h)

Approximation of Q

$$Q = \sum_{i,j=1}^{N_b} Q_{ij}^h |\phi_i\rangle\langle\phi_j|,$$

with the matrix

$$Q^h \in \mathcal{K}^h = \{Q^h = [Q^h]^T, 0 \leq \mathcal{I} + Q^h \leq 1\},$$

and

$$\mathcal{I} = \begin{bmatrix} 1_{N_-} & 0 \\ 0 & 0_{N_+} \end{bmatrix}.$$

So the associated density is

$$\rho_{Q^h}(r) = \sum_{i,j=1}^{N_b} Q_{ij}^h \phi_i(r) \phi_j(r).$$

The matrix of H_{per}^0 reads

$$H^h = \begin{bmatrix} H^{--} & 0 \\ 0 & H^{++} \end{bmatrix},$$

and for Q it is

$$Q^h = \begin{bmatrix} Q^{--} & Q^{+-} \\ Q^{-+} & Q^{++} \end{bmatrix}.$$

Variational approximation of the problem

Approximation of energy

$$e_{\nu,\mu}^h(Q^h) = \text{tr} \left((H^h - \mu) Q^h \right) - \int_{\mathbb{R}^3} V_{\nu} \rho_{Q^h} + \frac{1}{2} D(\rho_{Q^h}, \rho_{Q^h}),$$

Finite-dimensional problem

$$e_{\nu,\mu}^h = \inf \{ e_{\nu,\mu}^h(Q^h), Q^h \in \mathcal{K}^h \}.$$

This is the problem obtained by expanding the density matrix of the perturbation in a basis of Wannier orbitals.

To generate basis functions of \mathcal{H}_- and \mathcal{H}_+ we use *maximally localized Wannier functions (MLWFs)* (Marzari and Vanderbilt, 1997).

A self-consistent model for crystals with local defects

Theorem One has

$$\lim_{L \rightarrow +\infty} (I_{sc,L,\mu}^\nu - I_{sc,L,\mu}^0) = \inf \left\{ E_{\mu}^\nu(Q) - \int_{\mathbb{R}^3} \nu V_{per}^0, Q \in \mathcal{K} \right\}$$

with the energy functional

$$E_{\mu}^\nu(Q) = \text{tr} (H_{per}^0 Q) - D(\nu, \rho_Q) + \frac{1}{2} D(\rho_Q, \rho_Q) - \mu \text{tr}(Q),$$

$$D(f, g) = \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{f(r)g(r')}{|r-r'|} dr dr',$$

and the variational set

$$\mathcal{K} = \left\{ Q \mid 0 \leq Q + \gamma_{per}^0 \leq 1, \text{tr}((1 + |\nabla|) Q^2 (1 + |\nabla|)) + \text{tr}((1 + |\nabla|) (Q^{++} - Q^{--}) (1 + |\nabla|)) < \infty \right\},$$

where we have introduced $Q^{--} = \gamma_{per}^0 Q \gamma_{per}^0$, $Q^{++} = (1 - \gamma_{per}^0) Q (1 - \gamma_{per}^0)$.

We have the existence of a minimizer \bar{Q} for $\inf \{ E_{\mu}^\nu(Q), Q \in \mathcal{K} \}$ and the uniqueness of its density $\rho_{\bar{Q}} = \bar{\rho}$.

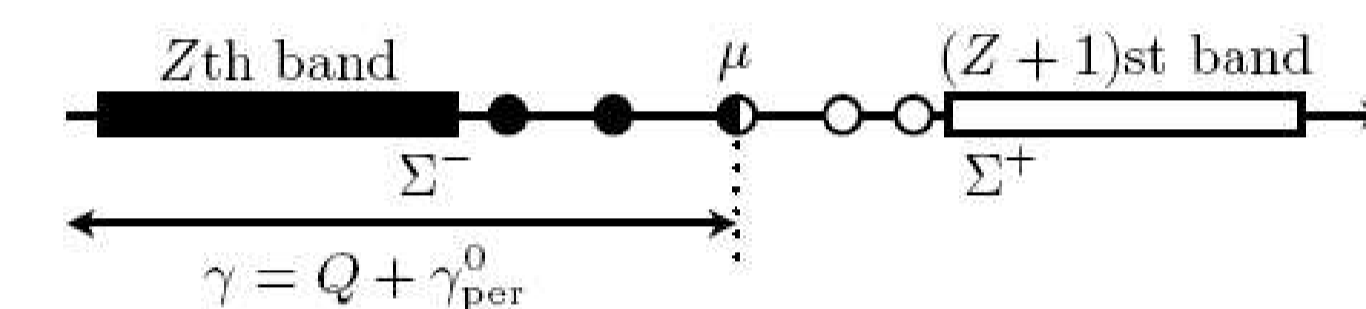
Any solution satisfies the self-consistent equation

$$\bar{Q} = \chi_{(-\infty,\mu]}(H_{\bar{Q}}) - \gamma_{per}^0 + \delta,$$

where

$$H_{\bar{Q}} = -\frac{1}{2}\Delta + \Phi_{per} + (\rho_{\bar{Q}} - \nu) \star \frac{1}{|x|},$$

and where δ is a finite-rank self-adjoint operator on $L^2(\mathbb{R}^3)$ such that $\text{Ran}(\delta) \subset \text{Ker}(H_{\bar{Q}} - \mu)$.



Spectrum of H_Q .



$$\text{tr}(\gamma_L^0) \longrightarrow +\infty \quad \text{when } L \longrightarrow +\infty,$$

$$\text{tr}(\gamma_L^\nu) \longrightarrow +\infty \quad \text{when } L \longrightarrow +\infty.$$

There is no a priori reason why $Q_L^\nu = \gamma_L^\nu - \gamma_L^0$ should be trace-class.

Remark : For any $Q \in \mathcal{K}$, $\int_{\mathbb{R}^3} \rho_Q^2 + D(\rho_Q, \rho_Q) < \infty$.

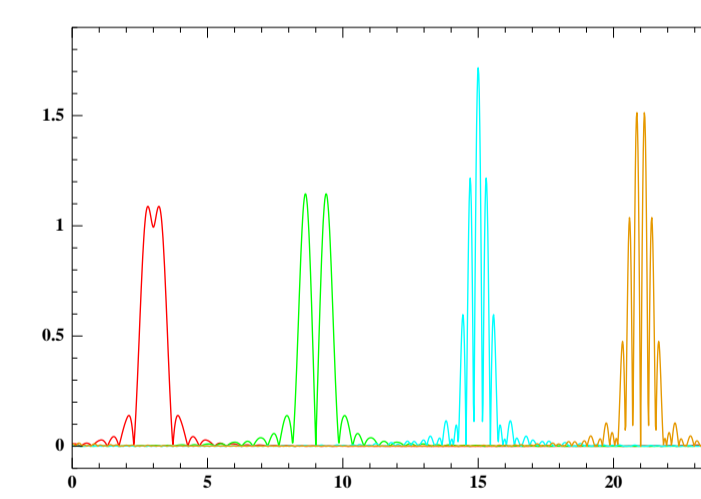
Numerical results

More details can be read in [2].

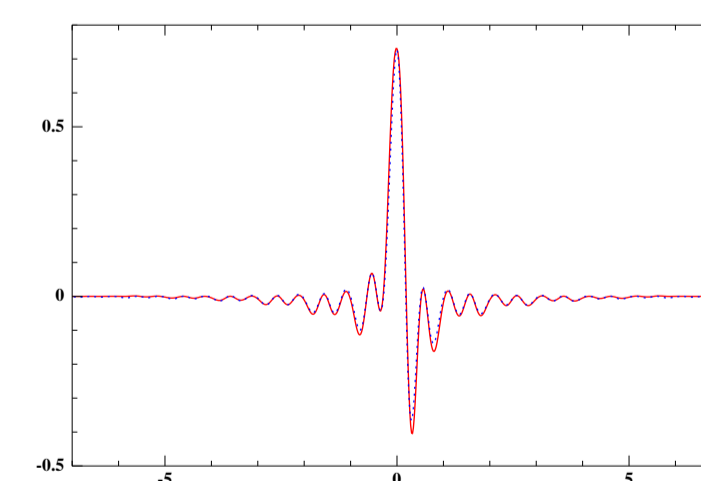
We take the example of a one-dimensional model with Yukawa interaction potential, for which the energy functional is

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

with $D_{\kappa}(f, g) = \frac{A}{2\kappa} \int_{\mathbb{R}} \int_{\mathbb{R}} f(x) e^{-\kappa|x-x'|} g(x') dx dx'$.



Modulus of MLWFs associated with the two occupied bands (left) and with the lowest two virtual bands (right).



Perturbation ρ_{Q^h} of the periodic ground state density with 28 MLWFs (line in red). The reference is a supercell calculation in a basis set of 1224 (dashed line in blue).

Conclusions

- Within the reduced Hartree-Fock model and provided the host crystal is an insulator, we are able to propose a mathematically consistent model for defining the energy of local defects in crystals, obtained as the limit of the supercell model when size of supercell goes to infinity.
- A natural way to discretize this model is to expand the density matrix of the perturbation of the Fermi sea generated by the defect in a basis of Maximally Localized Wannier Functions. Our mathematical analysis is an *a posteriori* rigorous justification of this approach.

[1] E. Cancès, A. Deleurence, M. Lewin (2007) *arXiv : math-ph/0702071*.

[2] E. Cancès, A. Deleurence, M. Lewin (2007) *arXiv : 0706.0794*.

[3] N. Marzari, D. Vanderbilt, *Phys. Rev. B* **56** (1997), 12847.