Charge Screening in Quantum Crystals with Local Defects

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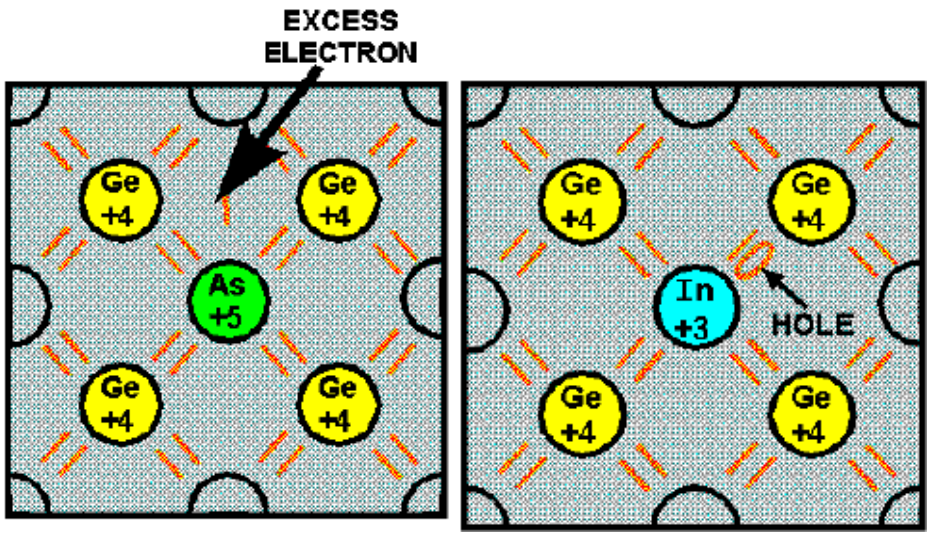
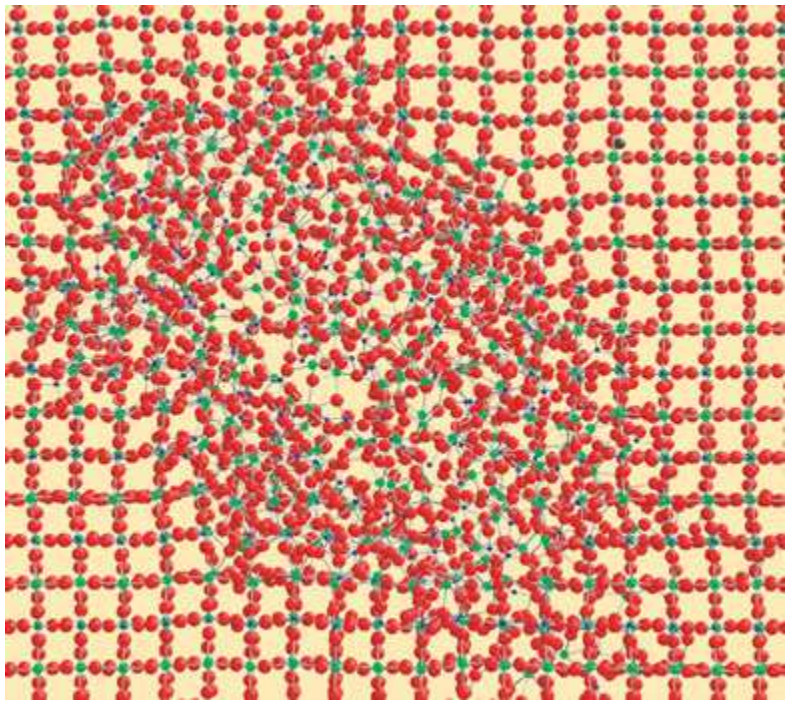
Introduction

Describing the electronic state of a crystal in presence of a defect is a major issue in condensed matter physics



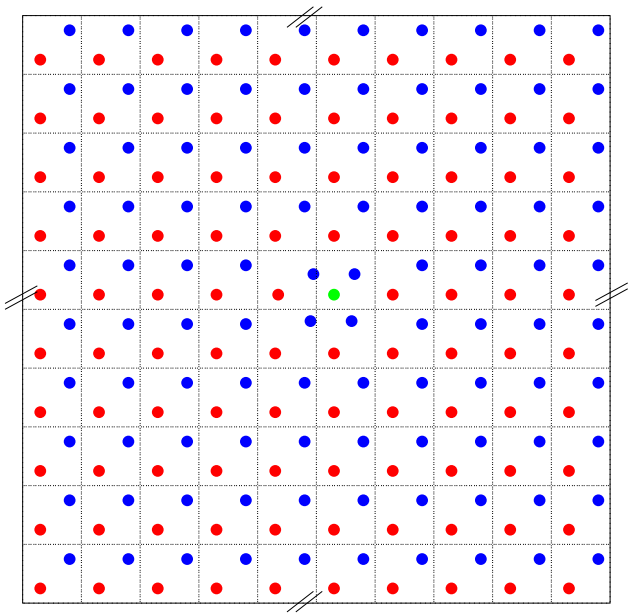
Germanium crystal doped with arsenic or indium.



Structural damage created by displacement of zirconium, silicon and oxygen atoms 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.

Main techniques used at present

- *supercell method* (periodized system in a large box)



The supercell model

  - spurious interactions between the defect and its periodic images
  - inaccuracies for charged defects

- *perturbative methods* (e.g., Green functions expansions)
  - only small defects
- *gluing methods* (models in different regions, pasted together)
  - rather empirical

Our method

- **clamped classical nuclei** with local defect + **quantum electrons**
- **infinite system**, living in the whole space (no boundary effects)
- Kohn-Sham type model for ∞ electrons (mean-field)
- describe the defect as **quasi molecule embedded in perfect crystal**
- $\rightsquigarrow$ **long range effects** (screening), can be seen at macroscopic scale

References:

[CDL1] Cancès, Deleurence & M.L. *Comm. Math. Phys.* **281** (2008).

[CDL2] Cancès, Deleurence & M.L. *J. Phys.: Condens. Matter* **20** (2008).

[CL] Cancès & M.L. *Arch. Rat. Mech. Anal.* **197** (2010).

[Rev] Cancès, M.L. & Stoltz. Proceedings of Workshop "Numerical Analysis of Multiscale Computations" at Banff (Dec. 2009).

Mean-field models

- **State of the quantum electrons:** a *one-particle density matrix*

$$\gamma : L^2(\mathbb{R}^3, \mathbb{C}) \to L^2(\mathbb{R}^3, \mathbb{C}), \qquad \gamma = \gamma^*, \qquad 0 \leq \gamma \leq 1$$

[e^- spin neglected]

Typical example:

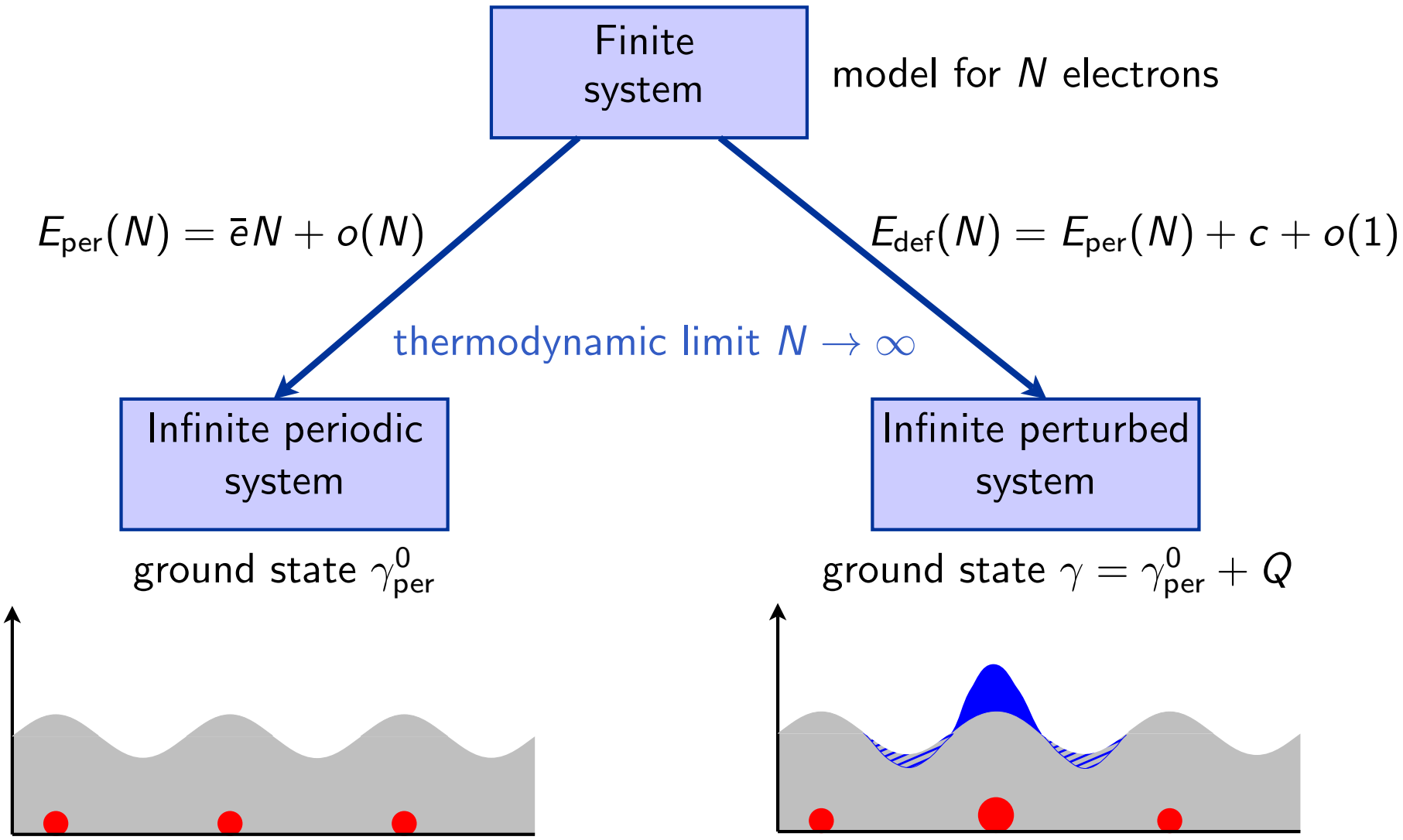
$$\gamma = \sum_{n=1}^{N} |\varphi_n\rangle\langle\varphi_n| \leftrightsquigarrow \text{Hartree-Fock state for } \mathrm{tr}(\gamma) = \int \rho_\gamma = N \text{ electrons}$$

(but *fractional occupation numbers* allowed) $[\rho_\gamma(x) = \gamma(x,x)]$

Crystal: $\gamma =$ operator of infinite rank

- infinite charge, $\mathrm{tr}(\gamma) = \infty$
- infinite energy

Methodology



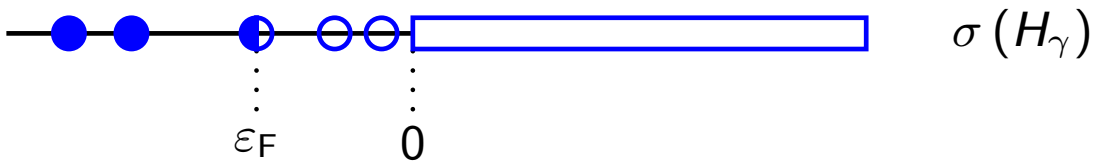
Finite system

- **Kohn-Sham energy**, $\mu =$ external nuclear density

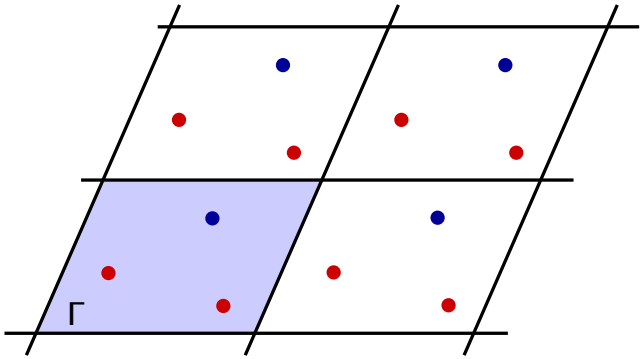
$$\mathcal{E}^{\mu}_{\mathrm{KS}}(\gamma) := \mathrm{tr}\left(\frac{-\Delta}{2}\gamma\right) - \iint_{\mathbb{R}^6} \frac{\mu(x)\rho_\gamma(y)}{|x-y|}dx\,dy + \frac{1}{2}\iint_{\mathbb{R}^6} \frac{\rho_\gamma(x)\rho_\gamma(y)}{|x-y|}dx\,dy + F_{\mathrm{xc}}(\rho_\gamma)$$

- **Eq. for stationary states with** $\mathrm{tr}(\gamma) = N$

$$\begin{cases} \gamma = \chi_{(-\infty,\varepsilon_{\mathrm{F}})}(H_\gamma) + \delta & 0 \le \delta \le \chi_{\{\varepsilon_{\mathrm{F}}\}}(H_\gamma),\ \varepsilon_{\mathrm{F}}=\text{Fermi level} \\ H_\gamma = -\frac{\Delta}{2} + V_\gamma + \frac{\partial}{\partial\rho}F_{\mathrm{xc}}(\rho_\gamma) & \text{(mean-field Fock operator)} \\ -\Delta V_\gamma = 4\pi(\rho_\gamma - \mu) & \text{(self-consistent electrostatic potential)} \end{cases}$$



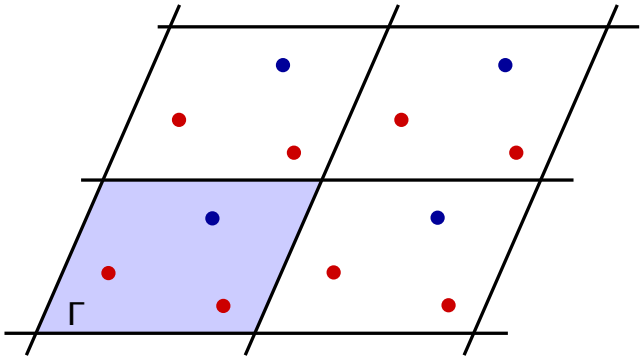
Periodic Fermi sea I



Lattice $\mathcal{L} \subset \mathbb{R}^3$. **Nuclei:** $\mu = \mu_{\rm per} = \sum_{z \in \mathcal{L}} \chi(\cdot - z)$

$\chi \geq 0$ measure supported in Γ

Periodic Fermi sea I



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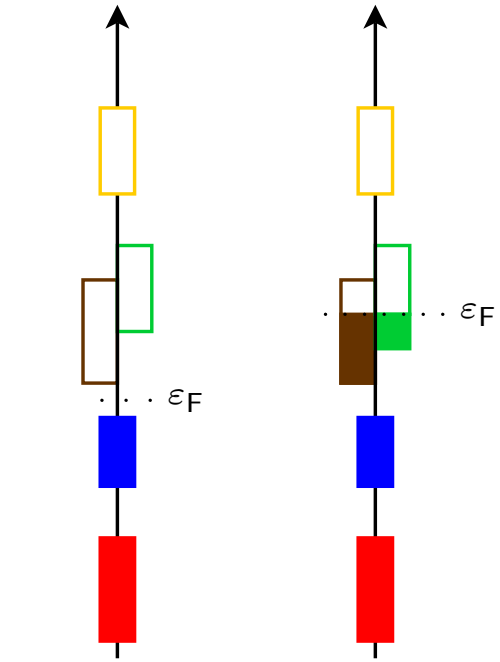
- **Equation for infinite periodic crystal [CLL,CDL1]:**



Insulator / semi-conductor $N = 2$ | Conductor $N = 3$

$$(\star) \quad \begin{cases} \gamma^0_{\rm per} = \chi_{(-\infty,\varepsilon_F)}\left(H^0_{\rm per}\right), \\ H^0_{\rm per} = -\dfrac{\Delta}{2} + V^0_{\rm per} + \dfrac{\partial}{\partial\rho} F_{\rm xc}(\rho_{\gamma^0_{\rm per}}), \\ -\Delta V^0_{\rm per} = 4\pi\left(\rho_{\gamma^0_{\rm per}} - \mu_{\rm per}\right), \\ \displaystyle\int_\Gamma \left(\rho_{\gamma^0_{\rm per}} - \mu_{\rm per}\right) = 0. \end{cases}$$

Note: $\delta \equiv 0$

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

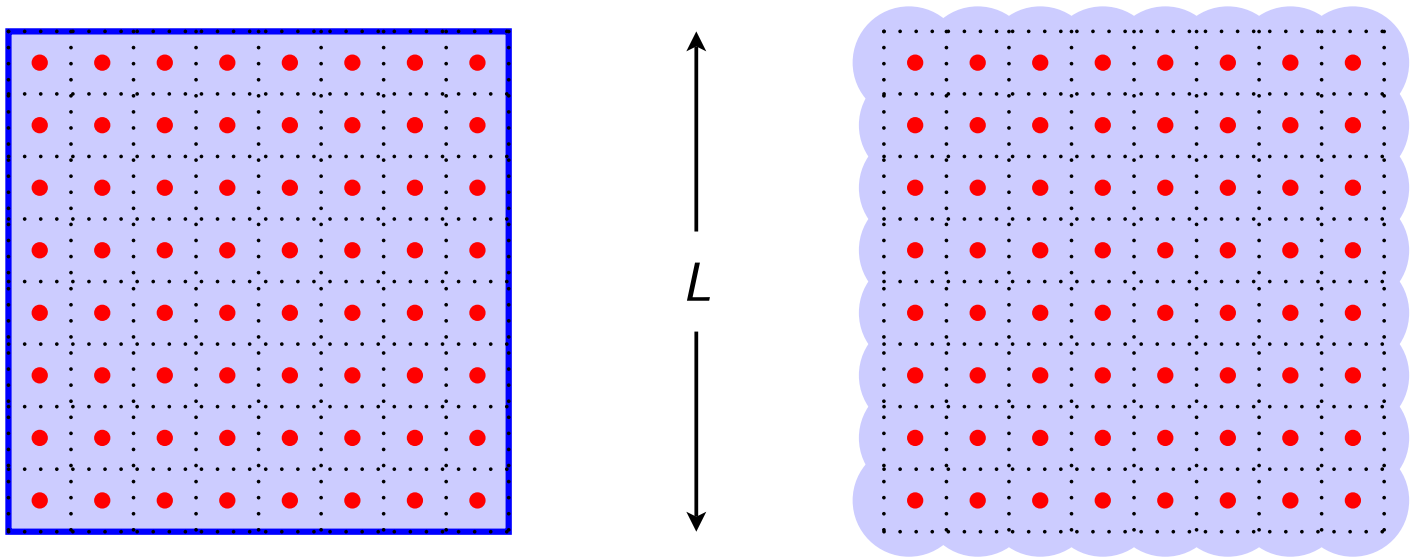
Periodic Fermi sea II

Theorem (Periodic Fermi sea for $F_{\rm xc} \equiv 0$ [CLL,CDL1])

For every $\mathcal{L}$-periodic μ_{per}, there exists a unique periodic solution to $(\star)$.

This state is the one obtained in the thermodynamic limit:

$$\lim_{L\to\infty} \frac{E(L)}{L^3} = \text{energy per unit vol. of } \gamma^0_{per} \quad \text{and} \quad \rho_L \to \rho_{\gamma^0_{per}} \text{ locally}$$

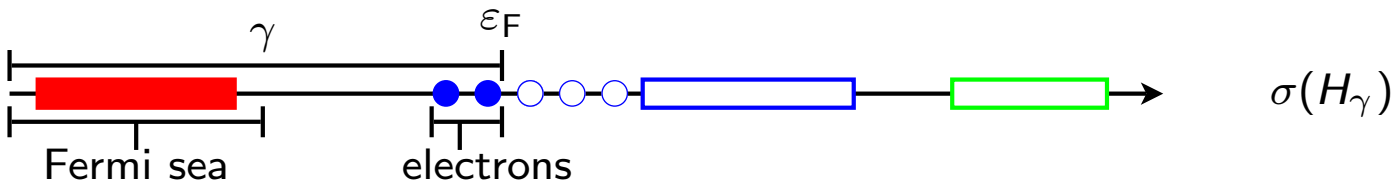


- **Assumption in the following:** insulator

Introducing a defect

Take $\mu = \mu_{\rm per} + \nu$ where ν=local defect (no sign!)

$$\begin{cases} \gamma = \chi_{(-\infty,\varepsilon_{\rm F})}\left(H_\gamma\right) + \delta \\ H_\gamma = -\dfrac{\Delta}{2} + V_\gamma + \dfrac{\partial}{\partial\rho} F_{\rm xc}(\rho_\gamma) \\ -\Delta V_\gamma = 4\pi\left(\rho_\gamma - \mu_{\rm per} - \nu\right) \end{cases}$$



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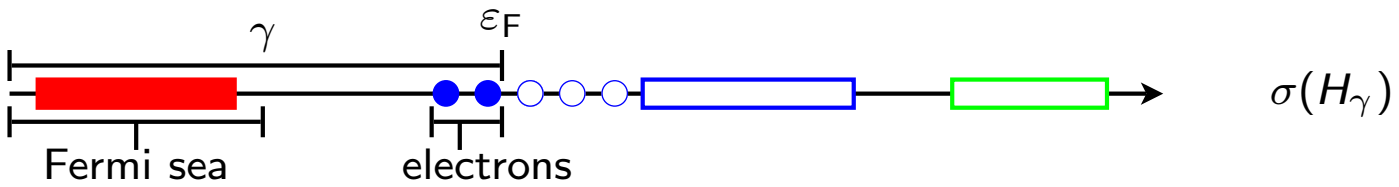

- **Idea:** write everything relatively to $\gamma^0_{\rm per}$

$$(\star\star) \quad \begin{cases} Q = \gamma - \gamma^0_{\rm per} = \chi_{(-\infty,\varepsilon_{\rm F})}\left(H_\gamma\right) - \chi_{(-\infty,\varepsilon_{\rm F})}\left(H^0_{\rm per}\right) + \delta \\ H_\gamma = H^0_{\rm per} + W_Q + G'_{\rm xc}(\rho_Q) \\ -\Delta W_Q = 4\pi\left(\rho_Q - \nu\right), \;\; G'_{\rm xc}(\rho_Q) = \frac{\partial}{\partial\rho} F_{\rm xc}(\rho_{\gamma^0_{\rm per}} + \rho_Q) - \frac{\partial}{\partial\rho} F_{\rm xc}(\rho_{\gamma^0_{\rm per}}) \end{cases}$$

Bound states

Theorem (Existence of bound states for $F_{xc} \equiv 0$ [CDL1,CL])

- *For every ε_F in the gap and ν such that $\nu * |x|^{-1} \in L^2(\mathbb{R}^3) + \dot{H}^1(\mathbb{R}^3)$, there exists at least one solution Q to $(\star\star)$, such that*

$$Q \in \mathfrak{S}_2 \text{ and } Q^{--} = \gamma^0_{per} Q \gamma^0_{per},\ Q^{++} = \left(\gamma^0_{per}\right)^{\perp} Q \left(\gamma^0_{per}\right)^{\perp} \in \mathfrak{S}_1$$

and

$$\rho_Q \in L^2(\mathbb{R}^3) \text{ with } \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\rho_Q(x)\,\rho_Q(y)}{|x-y|}\,dx\,dy < \infty.$$

The associated density ρ_Q is unique, hence so is the mean-field op. H_γ. Only δ can vary among solutions.

- *These states are the ones obtained in the thermodynamic limit.*

Rmk[1]. Nonperturbative, variational, charged defects

Rmk[2]. No mathematical result so far for $F_{xc} \neq 0$ ☹

Method

- **Variational argument:** subtract infinite free energy of Fermi sea

$$\text{“ } \left\{\mathcal{E}_{\rm KS}^{\mu_{\rm per}+\nu}(\gamma) - \varepsilon_{\rm F}\,\mathrm{tr}(\gamma)\right\} - \left\{\mathcal{E}_{\rm KS}^{\mu_{\rm per}+\nu}(\gamma^0_{\rm per}) - \varepsilon_{\rm F}\,\mathrm{tr}(\gamma^0_{\rm per})\right\} \text{ ”}$$

$$= \mathrm{tr}\big((H^0_{\rm per}-\varepsilon_{\rm F})Q\big) - D(\rho_Q,\nu) + \frac{1}{2}D(\rho_Q,\rho_Q) + \underbrace{F_{\rm xc}(\rho_{\gamma^0_{\rm per}}+\rho_Q) - F_{\rm xc}(\rho_{\gamma^0_{\rm per}})}_{:=G_{\rm xc}(\rho_Q)}$$

and minimize w.r.t. $Q = \gamma - \gamma^0_{\rm per}$

- The energy is **bounded from below** (when $F_{\rm xc} \equiv 0$):
  - $\mathrm{tr}\big((H^0_{\rm per} - \varepsilon_{\rm F})Q\big) \geq 0$
  - $-D(\rho_Q,\nu) + \frac{1}{2}D(\rho_Q,\rho_Q) \geq -\frac{1}{2}D(\nu,\nu)$

Effective Charges and Screening

Look at: $(Z = \int_{\mathbb{R}^3} \nu)$

$$\text{total charge of defect} = Z - \underbrace{\text{'charge' of polarized Fermi sea}}_{= \int_{\mathbb{R}^3} \rho_Q \ ???}$$

Rmk. subtracting infinite quantities is dangerous!

$$\sum_{j \geq 0} j - 2 \sum_{j \geq 0} j = \begin{cases} \sum_{j \text{ odd}} j & = +\infty \\ -\sum_{j \geq 0} j & = -\infty \end{cases}$$

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- **bare charge**
  - obtained in the thermodynamic limit
  - often an integer; we expect an overall neutral Fermi sea if small defect
- **microscopic physical charge**
  - seen in perturbation theory $\lambda\nu$ with $\lambda \ll 1$
- **macroscopic physical charge**
  - seen in homogenization limit $\lambda^3\nu(\lambda\cdot)$ with $\lambda \ll 1$

Bare Charge

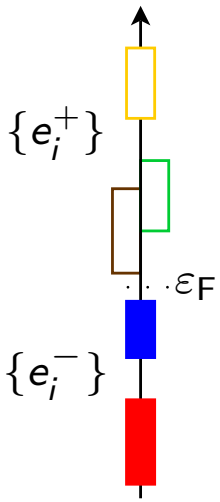
- A compact self-adjoint operator, $A = \sum_i \lambda_i |\varphi_i\rangle\langle\varphi_i|$.

$$A \text{ trace-class } (\in \mathfrak{S}_1) \iff \sum_i |\lambda_i| < \infty$$

Then $\mathrm{tr}(A) := \sum_i \langle e_i, Ae_i\rangle$ CV and does not depend on the basis $\{e_i\}$

Also $\rho_A(x) := \sum_i \lambda_i |\varphi_i(x)|^2 \in L^1(\mathbb{R}^3)$

- $\sum_i \langle e_i, Ae_i\rangle$ can CV for one basis but not for another one!



Bare charge of Fermi sea:

$$\text{“tr”}(Q) := \sum_i \left\langle e_i^+, Qe_i^+ \right\rangle + \sum_i \left\langle e_i^-, Qe_i^- \right\rangle$$

Recall $\displaystyle\int_{\mathbb{R}^3} |\rho_Q|^2 < \infty$ but $\displaystyle\int_{\mathbb{R}^3} |\rho_Q|$ need not be finite

Microscopic Screening

Theorem (Perturbation theory for charged defects [CL])

Fix $\varepsilon_F \in$ gap and take a defect density of the form $\lambda\nu$ with $Z = \int_{\mathbb{R}^3} \nu \neq 0$. For small enough λ, then "tr"$(Q) = 0$ but Q is **not** *trace-class. If $\mathcal{L}$ is anisotropic, then ρ_Q is* **not** *in $L^1(\mathbb{R}^3)$.*

- **Reason:** by perturbation theory, $\rho_Q = \rho_1\lambda + O(\lambda^2)$, where

$$\rho_1 = -\mathcal{L}(\rho_1 - \nu)$$

$\mathcal{L}$ =response function (can be explicitely computed)

$$f \in L^1(\mathbb{R}^3) \Rightarrow \lim_{|k|\to 0} \widehat{\mathcal{L}(f)}(\sigma|k|) = \sigma^T L \sigma \quad \text{for} \quad \sigma \in S^2,$$

where $L \geq 0$, and $L \neq 0$. For anisotropic materials, $L \neq cI_3$

- **Microscopic physical charge of defect:**

$$\frac{\lambda Z}{\varepsilon_\mu} \qquad \text{with } \varepsilon_\mu = 1 + \frac{\mathrm{tr}_{\mathbb{R}^3}(L)}{3} > 1$$

Macroscopic Screening

$$\rho_Q = -\mathcal{L}(\rho_Q - \nu) + o(\rho_Q - \nu) \Longleftrightarrow \nu - \rho_Q = (1+\mathcal{L})^{-1}\nu + o(\rho_Q - \nu).$$

Theorem (Homogenization limit [CL])

Fix $\varepsilon_F \in$ gap and take $\nu_\eta = \eta^3 \nu(\cdot\eta)$. Let $V_\eta = (\nu_\eta - \rho_{Q_\eta}) * |\cdot|^{-1}$. Then $W_\eta(x) = \eta^{-1} V_\eta(x/\eta)$ converges weakly as $\eta \to 0$ to the unique sol. of

$$-div(\varepsilon_M \nabla W) = 4\pi\nu$$

where ε_M is a 3×3 symmetric matrix $\neq I_3$, the macroscopic dielectric tensor of the perfect crystal.

ε_M is given by the *Adler-Wiser formula* [Adl62,Wis63,BarRes86]

- **Macroscopic physical charge for isotropic crystals:**

$$\frac{Z}{\varepsilon_M} \qquad \text{with } 1 < \varepsilon_M < \varepsilon_\mu$$

[Adl62] Adler, *Phys. Rev.* **126** (1962). [Wis63] Wiser, *Phys. Rev.* **129** (1963).
[BarRes86] Baroni and Resta, *Phys. Rev. B* **33** (1986).

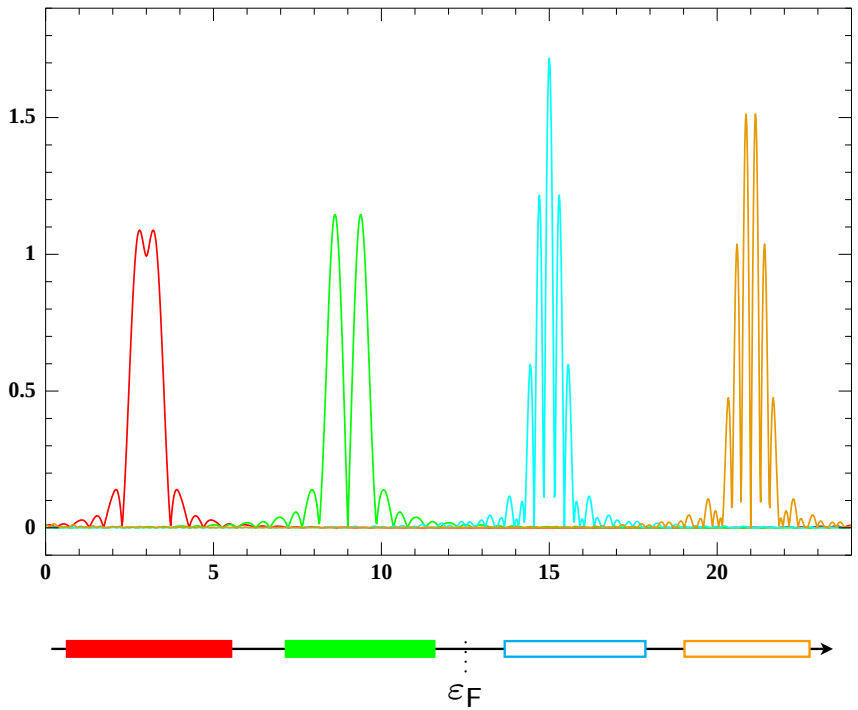
Numerics I

Two different scales:

- use of **Bloch transform** to discretize periodic pb
- use of **localized Wannier basis** for the locally perturbed pb
  Ex: Maximally Localized Wannier functions [MV]

$\rightarrow$ avoid variational collapse

- **1D simulation [CDL2]:** Yukawa potential, $Z = 2$



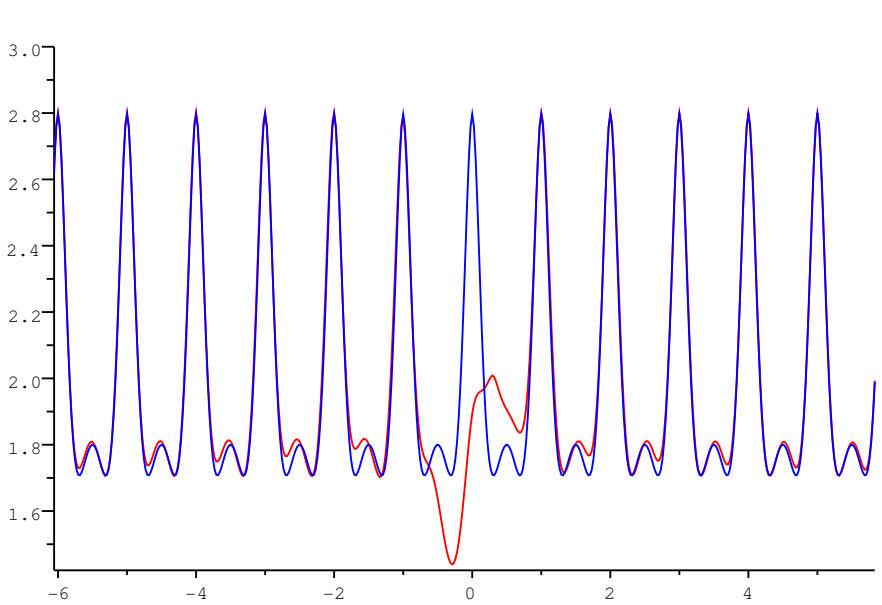
MLWFs: calculated once and for all, independently of defect
Basis very simple to enlarge

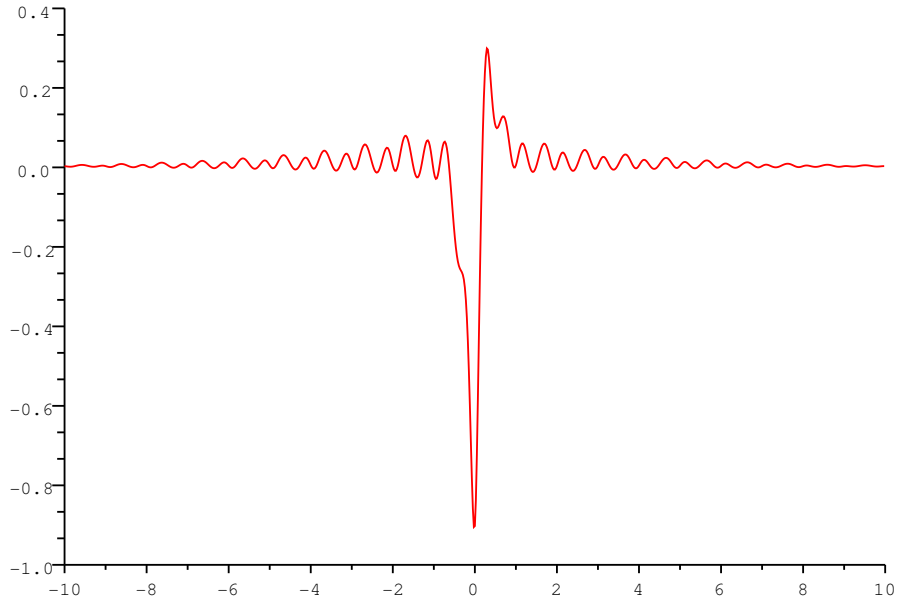
Left: Modulus of the MLWFs corresponding to the 2 filled bands and the first 2 unfilled bands

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

Numerics II

Computation of Q: relaxed constraint algorithms [Can], $\nu = \delta_{0.3} - 2\delta_0$





Polarization of the Fermi sea in the presence of defect, calculated with 28 MLWFs.
As good as supercell calculation in a basis set of size ∼1000.
Left: $\rho_{\gamma^0_{\rm per}}$ and ρ_γ. Right: $\rho_\gamma - \rho_{\gamma^0_{\rm per}}$.

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

Conclusion

- Model in whole space for localized defect
  - use perfect crystal as reference;
  - variational;
  - charge screening.
- Well-behaved computational method
  - two scales;
  - Wannier functions for local perturbation;
  - minimization.
- Extensions
  - $F_{\mathrm{xc}} \neq 0$;
  - numerical tests in 3D;
  - time-dependent setting.