Un modèle non linéaire pour la description d'un défaut dans un cristal quantique

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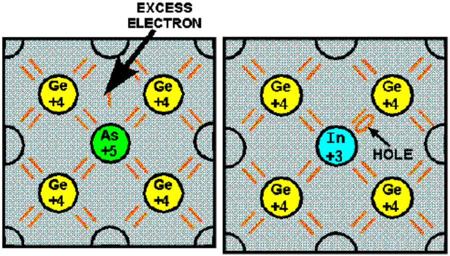
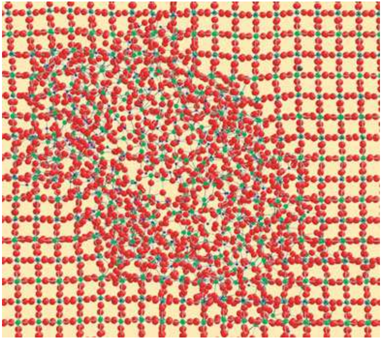
Introduction

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

- **electronics and optics:** doped semi-conductors, quantum dots,...
- **material science:** storage of radioactive waste,...



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.

Introduction

System of interest:

- infinitely many classical **fixed** nuclei (perturb. of periodic structure);
- infinitely many quantum electrons.

Difficulties:

- infinitely many electrons $\to$ *variable = operator of infinite rank*;
- nonlinear model $\to$ *lack of compactness at infinity*;
- long range of Coulomb potential $\to$ *divergences*;
- two scales.

References:

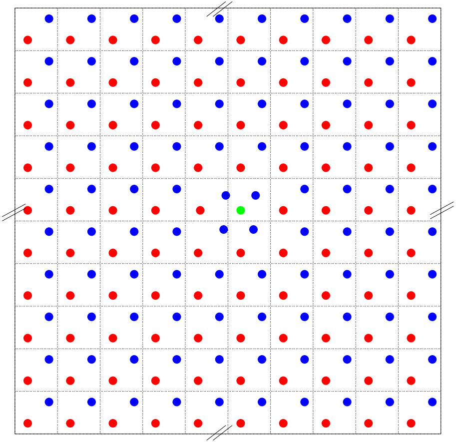
[CDL1] Cancès, Deleurence & M.L. *Comm. Math. Phys.* **281** (2008).

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

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

Supercell method

Main method at present: supercell method.



The supercell model

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

Methodology

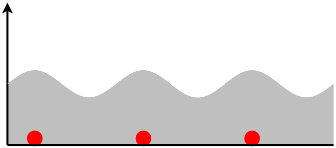
Finite system — model for N electrons

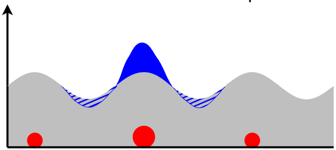
$E_{\text{per}}(N) = \bar{e}N + o(N)$

$E_{\text{def}}(N) = E_{\text{per}}(N) + c + o(1)$

thermodynamic limit $N \to \infty$

Infinite periodic system	**Infinite perturbed system**
ground state γ^0_{per}	ground state $\gamma = \gamma^0_{\text{per}} + Q$





[CLL] Catto, Le Bris & Lions. *Ann. I. H. Poincaré* **18** (2001).
[HLSo] Hainzl, M.L. & Solovej. *Comm. Pure Applied Math.* **76** (2007).
[CDL1] Cancès, Deleurence & M.L. *Comm. Math. Phys.* **281** (2008).

Reduced Hartree-Fock model for a finite system

Electrons (=fermions). Spin neglected for simplicity.

- **Hartree-Fock state:** a *density matrix* $\gamma \in \mathcal{B}(L^2(\mathbb{R}^3))$ s.t. $0 \leq \gamma \leq 1$.

$\mathrm{tr}(\gamma) = \int \rho_\gamma =$ nb of particles in the system.

Density of charge: $\rho_\gamma(x) = \gamma(x,x)$ s.t. $\mathrm{tr}(\gamma V) = \int \rho_\gamma V$.

Example: $\gamma = \sum_{i=1}^{N} |\varphi_i\rangle\langle\varphi_i| \quad \left[\longleftrightarrow \Psi(x_1, ..., x_N) = (N!)^{-1/2} \det(\varphi_i(x_j)) \right]$.

- **Reduced Hartree-Fock energy:**

Ext. elec. field $V_{\rm ext} = -\mu * \frac{1}{|x|}$, where $\mu =$ charge distrib. of nuclei.

$$\mathcal{E}^{\mu}_{\rm rHF}(\gamma) := \mathrm{tr}\left(\frac{-\Delta}{2}\gamma\right) + \int_{\mathbb{R}^3} V_{\rm ext}\, \rho_\gamma + \frac{1}{2} \iint_{\mathbb{R}^6} \frac{\rho_\gamma(x)\rho_\gamma(y)}{|x-y|} dx\, dy$$

Rmk. Not a quantitative model: exchange-correlation missing.

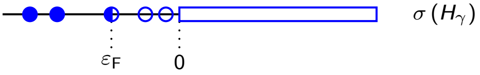
Reduced Hartree-Fock model for a finite system

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

- **Minimizers under constraint** $\operatorname{tr}(\gamma) = N$ ($\exists$, e.g., when $N \leq \int \mu$)

$$\begin{cases} \gamma = \chi_{(-\infty,\varepsilon_{\rm F})}\left(H_\gamma\right) + \delta, & \\ H_\gamma = -\dfrac{\Delta}{2} + V_\gamma, & \text{(mean-field / Fock operator)} \\ -\Delta V_\gamma = 4\pi(\rho_\gamma - \mu) & \text{(Self-Consistent Field)} \end{cases}$$

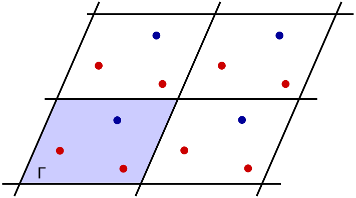
where $0 \leq \delta \leq \chi_{\{\varepsilon_{\rm F}\}}(H_\gamma)$ and $\varepsilon_{\rm F}$=Lagrange multiplier=Fermi level.



Rmk. If $\delta \equiv 0$, may be rewritten as $\left(\frac{-\Delta}{2} + \left(\sum_{i=1}^N |\varphi_i|^2 - \mu\right) * \frac{1}{|x|}\right)\varphi_i = \lambda_i\varphi_i$, for $i = 1 \ldots N$.

[Sol] Solovej. Appendix of *Invent. Math.* **104** (1991).

Periodic Fermi sea I



Discrete subgroup $\mathcal{L} \subset \mathbb{R}^3$, compact fundamental domain Γ.

Nuclei: $\mu = \mu_{\rm per} = \sum_{z \in \mathcal{L}} \chi(\cdot - z)$

where $\chi \geq 0$, $\int \chi \in \mathbb{N} \setminus \{0\}$ support in Γ.

- **Thermodynamic limit:** retain nuclei in a box $C_L = [-L/2; L/2)^3$. Electrons in the whole space [CLL] or in C_L, with chosen BC [CDL1]. Impose neutrality: $N = \int_{C_L} \mu_{\rm per}$.

As $L \to \infty$, γ_L CV to the **unique** **$\mathcal{L}$-periodic sol. of**

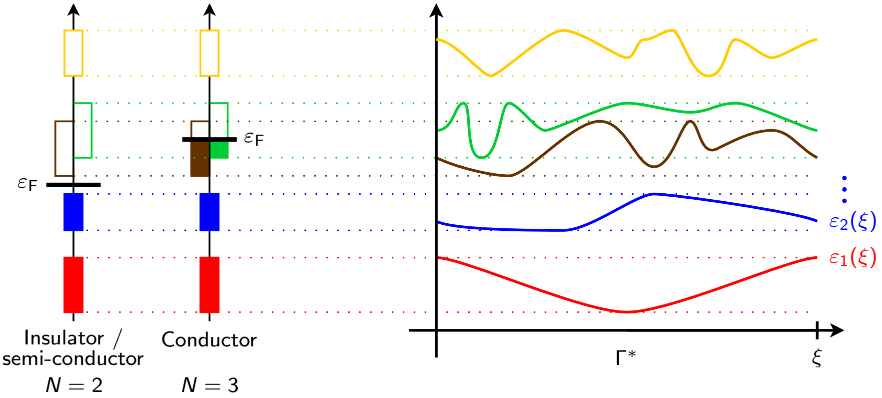
$$\begin{cases} \gamma^0_{\rm per} = \chi_{(-\infty, \varepsilon_F)}\left(H^0_{\rm per}\right), \\ H^0_{\rm per} = -\dfrac{\Delta}{2} + V^0_{\rm per}, \\ -\Delta V^0_{\rm per} = 4\pi\left(\rho_{\gamma^0_{\rm per}} - \mu_{\rm per}\right), \quad \text{with } \displaystyle\int_\Gamma \left(\rho_{\gamma^0_{\rm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

Periodic Fermi sea II

Bloch-Floquet transform: $H^0_{\rm per}$ commutes with all translations $\{\tau_z\}_{z\in\mathcal{L}}$.

$$H^0_{\rm per} \simeq \fint_{\Gamma^*}^{\oplus} H^0_{\rm per}(\xi), \qquad H^0_{\rm per}(\xi) = \frac{1}{2}(-i\nabla+\xi)^2 + V^0_{\rm per} \quad \text{on } L^2_{\rm per}(\Gamma)$$

Brillouin zone: $\Gamma^* = \{\xi \in \mathbb{R}^3 \ : \ |\xi\cdot x| \leq \pi, \ \forall x \in \Gamma\}$.



Assumption: insulator in the following.

Introducing a defect

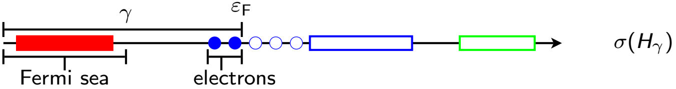
Take $\mu = \mu_{\rm per} + \nu$ where $\nu=$'local defect'. **Goal:** construct solution of

$$\begin{cases} \gamma = \chi_{(-\infty,\varepsilon_{\rm F})}(H_\gamma) + \delta, \\ H_\gamma = -\Delta/2 + V_\gamma, \\ -\Delta V_\gamma = 4\pi\big(\rho_\gamma - \mu_{\rm per} - \nu\big) \end{cases}$$

with $\varepsilon_{\rm F} \in$ gap. Meaning of ρ_γ ? Correct functional setting ?

- **Idea [CIL,HLSS]:** write everything relatively to $\gamma^0_{\rm per}$.

$$(\star) \qquad \begin{cases} Q = \gamma - \gamma^0_{\rm per} = \chi_{(-\infty,\varepsilon_{\rm F})}(H_\gamma) - \chi_{(-\infty,\varepsilon_{\rm F})}\left(H^0_{\rm per}\right) + \delta, \\ H_\gamma = H^0_{\rm per} + W_Q, \\ -\Delta W_Q = 4\pi\big(\rho_Q - \nu\big). \end{cases}$$



[CIL] Chaix, Iracane + Chaix, Iracane & Lions. *J. Phys. B* **22** (1989).
[HLSS] Hainzl, M.L., Séré & Solovej. *J. Phys. A* **76** (2007).

Functional analysis setting

• **Schatten classes:**

Let A= self-adjoint compact operator, $A = \sum_i \lambda_i |\varphi_i\rangle\langle\varphi_i|$ ($\lambda_i \to 0$).

- A Hilbert-Schmidt ($A \in \mathfrak{S}_2$) when $\sum_i |\lambda_i|^2 < \infty$.
- A trace-class ($A \in \mathfrak{S}_1$) when $\sum_i |\lambda_i| < \infty$.
  Then $\mathrm{tr}(A) = \sum_i \lambda_i = \sum_k \langle e_k, Ae_k\rangle$ for any orth. basis $\{e_k\}$.
  Density $\rho_A(x) = \sum_i \lambda_i |\varphi_i(x)|^2 \in L^1(\mathbb{R}^3)$.

The sum $\sum_k \langle e_k, Ae_k\rangle$ can CV for one basis and not for other ones!

• **Generalization [HLSé]:** A is $\gamma^0_{\rm per}$-trace-class ($A \in \mathfrak{S}_1^0$) when $A \in \mathfrak{S}_2$ and $A^{--} = \gamma^0_{\rm per} A \gamma^0_{\rm per}$, $A^{++} = (\gamma^0_{\rm per})^\perp A (\gamma^0_{\rm per})^\perp \in \mathfrak{S}_1$. Define $\mathrm{tr}_0(A) = \mathrm{tr}(A^{--} + A^{++})$.

$$A = \begin{pmatrix} A^{--} & A^{-+} \\ A^{+-} & A^{++} \end{pmatrix}$$

• **Notation:** $D(f,g) = \iint_{\mathbb{R}^6} \frac{f(x)g(y)}{|x-y|}\,dx\,dy = 4\pi \int_{\mathbb{R}^3} \frac{\overline{\hat{f}(k)}\hat{g}(k)}{|k|^2}\,dk$ and $\mathcal{C} := \{f \ : \ D(f,f) < \infty\}$.

[HLSé] Hainzl, M.L. & Séré. *Commun. Math. Phys.* **257** (2005).

Existence of bound states

Theorem (Existence of bound states [CDL1])

For all ε_F in the gap and ν such that $\nu * |\cdot|^{-1} \in L^2(\mathbb{R}^3) + \mathcal{C}'$, there exists at least one solution Q to Eq. $(\star)$, such that $(1-\Delta)^{1/2} Q \in \mathfrak{S}_2$, $(1-\Delta)^{1/2} Q^{\pm\pm} (1-\Delta)^{1/2} \in \mathfrak{S}_1$ and $\rho_Q \in L^2(\mathbb{R}^3) \cap \mathcal{C}$.

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 thermo. limit'.

If ε_F is fixed in the gap and ν is small enough, then $\varepsilon_F \notin \sigma(H_Q)$, hence $\delta \equiv 0$ and Q is unique. Furthermore one has $\mathrm{tr}_0(Q) = 0$.

Variational proof [CIL,HLSS]: formally

$$\text{“}\mathcal{E}_{\rm rHF}^{\mu_{\rm per}+\nu}(\gamma) - \mathcal{E}_{\rm rHF}^{\mu_{\rm per}+\nu}(\gamma^0_{\rm per})\text{”} = \mathrm{tr}\left(H^0_{\rm per} Q\right) - \iint_{\mathbb{R}^6} \frac{\rho_Q(x)\nu(y)}{|x-y|}\,dx\,dy + \frac{1}{2}\iint_{\mathbb{R}^6} \frac{\rho_Q(x)\rho_Q(y)}{|x-y|}\,dx\,dy := \mathcal{F}^\nu(Q).$$

Variational interpretation

$$\mathcal{F}^\nu(Q) - \varepsilon_{\rm F}{\rm tr}_0 Q = {\rm tr}_0(H^0_{\rm per} - \varepsilon_{\rm F})Q - D(\nu,\rho_Q) + \frac{1}{2}D(\rho_Q,\rho_Q).$$

Note $0 \leq \gamma \leq 1 \iff -\gamma^0_{\rm per} \leq Q \leq (\gamma^0_{\rm per})^\perp \iff Q^2 \leq Q^{++} - Q^{--}$

$$\Rightarrow {\rm tr}_0(H^0_{\rm per} - \varepsilon_{\rm F})Q = {\rm tr}|H^0_{\rm per} - \varepsilon_{\rm F}|(Q^{++} - Q^{--}) \geq {\rm tr}|H^0_{\rm per} - \varepsilon_{\rm F}|Q^2 \geq 0.$$

Theorem (Variational interpretation [CDL1])

For all $\varepsilon_{\rm F}$ in the gap, $\mathcal{F} - \varepsilon_{\rm F}{\rm tr}_0$ is strongly continuous and convex on

$$\mathcal{K} := \{Q = Q^* \ :\ -\gamma^0_{per} \leq Q \leq (\gamma^0_{per})^\perp,\ (1-\Delta)^{1/2}Q \in \mathfrak{S}_2,$$
$$(1-\Delta)^{1/2}Q^{\pm\pm}(1-\Delta)^{1/2} \in \mathfrak{S}_1\}.$$

Minimizers $Q \in \mathcal{K}$ are exactly the solutions of $(\star)$. Any such Q also minimizes the pb

$$(\star\star) \qquad E^\nu(q) = \inf_{R\in\mathcal{K},\ {\rm tr}_0(R)=q} \mathcal{F}^\nu(R) \quad \text{where} \quad q = {\rm tr}_0(Q).$$

One has $E^\nu(q) < E^\nu(q-q') + E^0(q')$ for all $q' \neq q$ and any minimizing sequence for $(\star\star)$ is precompact in $\mathcal{Q}$.

Properties of bound states

Theorem (Properties of bound states [CL])

*Fix $\varepsilon_{\rm F} \in$ gap. Assume $\nu \in L^1(\mathbb{R}^3)\cap L^2(\mathbb{R}^3)$ is small enough with $\int_{\mathbb{R}^3}\nu \neq 0$. Then Q is **not** trace-class. If $\mathcal{L}$ is anisotropic, then ρ_Q is **not** in $L^1(\mathbb{R}^3)$.*

Reason: $\rho_Q = -\mathcal{L}(\rho_Q-\nu)+o(\rho_Q-\nu)$. $\mathcal{L}$ can be explicitely computed.

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

$L\geq 0$ is given by the *Adler-Wiser formula* [Adl,Wis]

$$k^TLk = \frac{8\pi}{|\Gamma|}\sum_{n=1}^{N}\sum_{n'=N+1}^{+\infty}\fint_{\Gamma^*}\frac{\left|\left\langle (k\cdot\nabla_x)u_{n,q},u_{n',q}\right\rangle_{L^2_{\rm per}(\Gamma)}\right|^2}{\left(\epsilon_{n',q}-\epsilon_{n,q}\right)^3}\,dq,$$

where $\epsilon_{n,q}, u_{n,q}$ = eigenvalues/vectors of Bloch Hamiltonian $H^0_{\rm per}(q)$.

Always $L\neq 0$; for anisotropic materials, $L\neq cI_3$.

[CL] Cancès & M.L. *Arch. Rat. Mech. Anal.* (2010).
[Adl] Adler, *Phys. Rev.* **126** (1962). [Wis] Wiser, *Phys. Rev.* **129** (1963).

Dielectric permittivity

Theorem (Homogenization limit [CL])

Fix $\varepsilon_{\rm F} \in$ *gap and take* $\nu_\eta = \eta^3\nu(\cdot\eta)$. *Let* $V_\eta = (\rho_{\bar{Q}_\eta} - \nu_\eta) * |\cdot|^{-1}$. *Then* $W_\eta(x) = \eta^{-1}V_\eta(x/\eta)$ *CV weakly in* $\mathcal{C}'$ *as* $\eta \to 0$ *to the unique sol. of*

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

where $\varepsilon_{\rm M}$ *is a* 3×3 *symmetric matrix* $\neq I_3$, *the (electronic contribution to the) macroscopic dielectric tensor of the perfect crystal.*

Explanation: $\rho_Q = -\mathcal{L}(\rho_Q - \nu) + o(\rho_Q - \nu) \Rightarrow \nu - \rho_Q = (1+\mathcal{L})^{-1}\nu + \cdots$.
$\varepsilon_{\rm M}$ obtained from strong limit of $U_\eta^*(1+\mathcal{L})^{-1}U_\eta$, U_η = dilation unitary operator.

Calculation: $\tilde{\varepsilon} := v_c^{1/2}(1+\mathcal{L})v_c^{-1/2}$ where $v_{\rm c}(\nu) := \nu * |\cdot|^{-1}$. Bloch matrix $\Rightarrow$ $\{\tilde{\varepsilon}_{K,K'}(q)\}_{K,K'\in(2\pi\mathbb{Z})^3}$, $q \in [-\pi,\pi)^3$. $\lim_{\eta\to 0}\tilde{\varepsilon}_{0,0}(\sigma\eta) = 1 + \sigma^T L\sigma$, $\lim_{\eta\to 0}\tilde{\varepsilon}_{0,K'}(\sigma\eta) = \beta_{K'}\cdot\sigma$, $\lim_{\eta\to 0}\tilde{\varepsilon}_{K,K'}(\sigma\eta) = C_{K,K'}$. Then [BarRes86]:

$$\varepsilon_{\rm M} = 1 + L - \sum_{K,K'\in(2\pi\mathbb{Z})^3\setminus\{0\}} \beta_K [C^{-1}]_{K,K'}\beta_{K'}^*$$

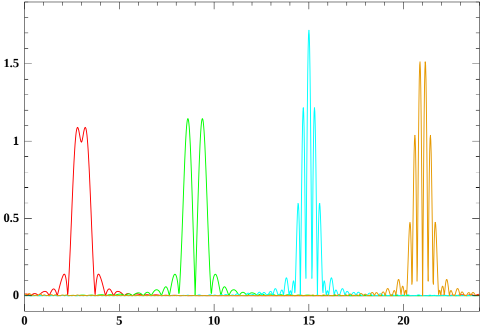
[BarRes86] Baroni and Resta, *Phys. Rev. B* **33** (1986).

Numerics I

Two different scales:

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

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

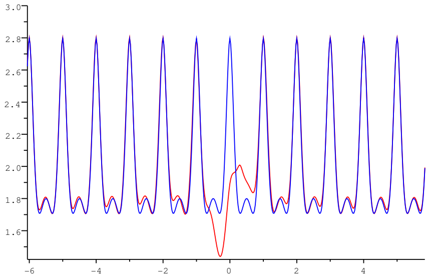


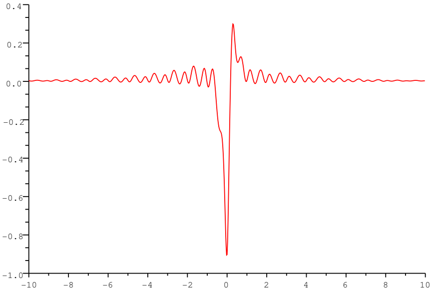
Modulus of the Maximally Localized Wannier Orbitals [MV] for the first two bands (red and green), the 3rd and 4th bands (blue and orange).

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

Numerics II

Comp. 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

- Possible to describe an **infinite quantum system perturbed locally**:
  - use perfect system as reference;
  - variational (as soon as the perturbation is localized enough);
  - divergences;
  - well-behaved associated numerical methods.

- **Perspectives**:
  - simulations on real systems;
  - theory of realistic models;
  - time-dependent setting;
  - relaxation of nuclei;
  - correlation? metals?