Charge screening in the Thomas-Fermi-von Weiszäcker model

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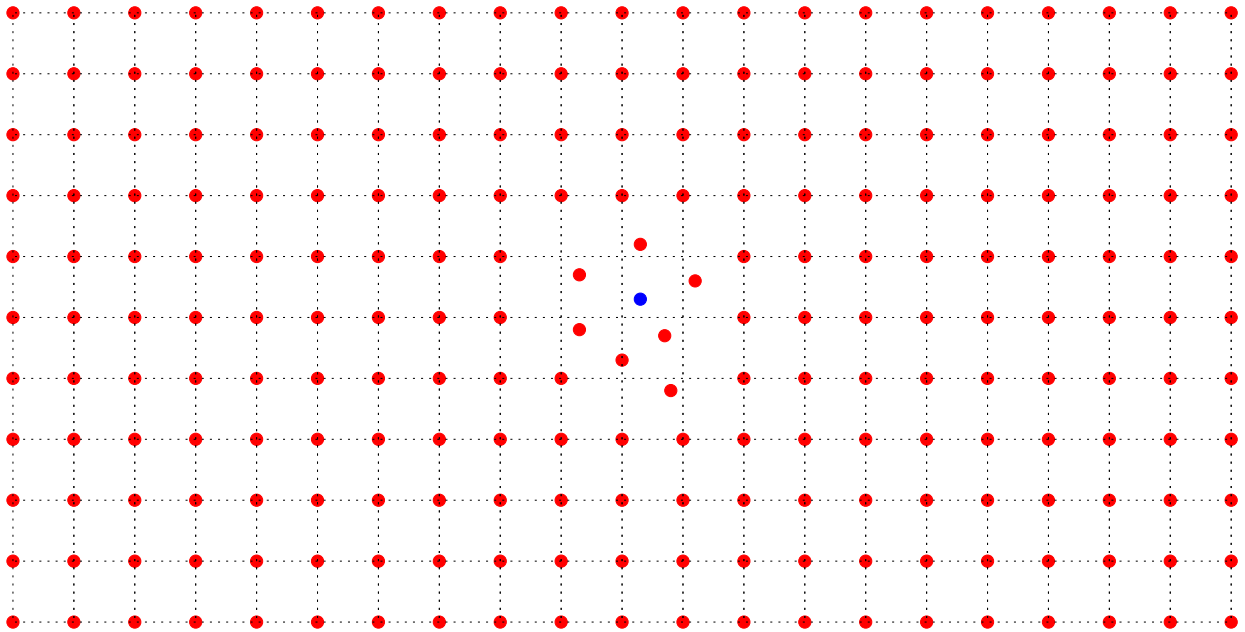
Model for a periodic crystal with a local defect

Impurity with relaxation of the host crystal



- Thomas-Fermi model: Lieb-Simon 1977
- reduced Hartree-Fock model: Cancès-Deleurence-Lewin 2008
- Thomas-Fermi-von Weiszäcker (TFW) ?

Outline

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TFW model for finite systems

Orbital-free DFT: the energy functional is an explicit functional of the electronic density

Approximations of the electronic ground state energy and density are obtained by solving

$$\inf\left\{\mathcal{E}_{\rho^{\mathrm{nuc}}}(\rho),\quad \rho\geq 0,\quad \int_{\mathbb{R}^3}\rho = N,\quad \sqrt{\rho}\in H^1(\mathbb{R}^3)\right\}$$

Thomas-Fermi-von Weizsäcker model

$$\begin{aligned}\mathcal{E}^{\mathrm{TFW}}_{\rho^{\mathrm{nuc}}}(\rho) &= C_{\mathrm{W}}\int_{\mathbb{R}^3}|\nabla\sqrt{\rho}|^2 + C_{\mathrm{TF}}\int_{\mathbb{R}^3}\rho^{5/3} \qquad \text{(kinetic energy)}\\ &\quad + \frac{1}{2}D\left(\rho-\rho^{\mathrm{nuc}},\rho-\rho^{\mathrm{nuc}}\right) \qquad \text{(Coulomb energy)}\end{aligned}$$

Coulomb space

Coulomb space and Coulomb energy functional

$$\mathcal{C} := \{\rho \quad | \quad D(\rho,\rho) < \infty\}$$

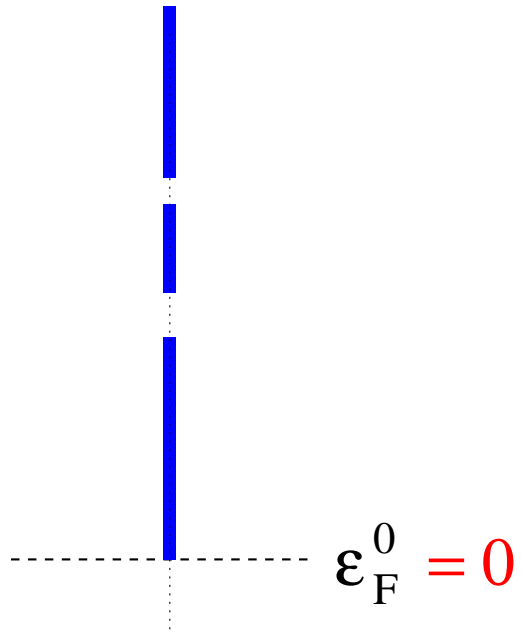
$$\forall \rho_1, \rho_2 \in L^{6/5}(\mathbb{R}^3),\ D(\rho_1,\rho_2) = \int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \frac{\rho_1(x)\,\rho_2(y)}{|x-y|}\,dx\,dy$$

TFW model for perfect crystals

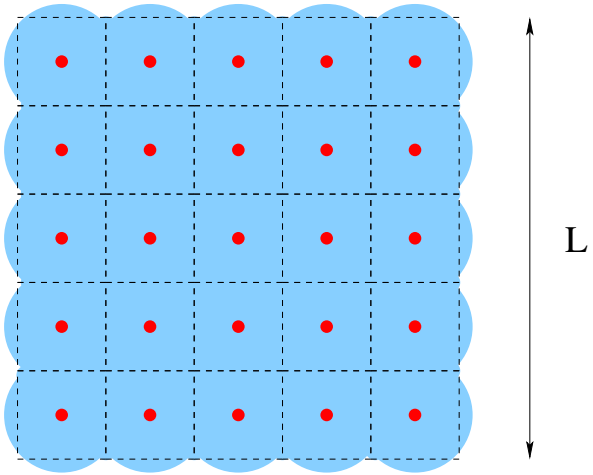
$\rho^{\mathrm{nuc}} \longrightarrow \rho^{\mathrm{nuc}}_{\mathrm{per}}$

Periodic lattice: $\mathcal{R}$ (example: cubic lattice $\mathcal{R} = a\mathbb{Z}^3$)
Unit cell: Γ (example for the cubic lattice $\mathcal{R} = a\mathbb{Z}^3$: $\Gamma = [-a/2, a/2)^3$)

$$
\begin{cases}
u^0_{\mathrm{per}} = \sqrt{\rho^0_{\mathrm{per}}} \\
H^0_{\mathrm{per}}\, u^0_{\mathrm{per}} = \epsilon^0_{\mathrm{F}}\, u^0_{\mathrm{per}} = 0, \\
\int_\Gamma |u^0_{\mathrm{per}}|^2 = \int_\Gamma \rho^{\mathrm{nuc}}_{\mathrm{per}} \\
H^0_{\mathrm{per}} = -C_{\mathrm{W}}\Delta + \frac{5}{3} C_{\mathrm{TF}} (\rho^0_{\mathrm{per}})^{2/3} + V^0_{\mathrm{per}} \\
-\Delta V^0_{\mathrm{per}} = 4\pi \left(\rho^0_{\mathrm{per}} - \rho^{\mathrm{nuc}}_{\mathrm{per}}\right)
\end{cases}
$$



Bulk limit for the perfect crystal



$$\begin{cases} \rho_L^{\mathrm{nuc}} = \sum_{\mathbf{R}\in\mathbb{Z}^3\cap\Lambda_L} z\delta(\cdot-\mathbf{R}) \\ \\ zL^3 \text{ electrons} \end{cases} \longrightarrow \rho_L^0 \text{ the (unique) ground state density}$$

Theorem (Catto-Le Bris-Lions, Springer 1998)

$$\rho_L^0 \underset{L\to\infty}{\overset{\text{in some sense}}{\longrightarrow}} \rho_{\mathrm{per}}^0$$

$$0 < a \leq u_{\mathrm{per}}^0(x) \leq b < +\infty \quad \forall x \in \mathbb{R}^3$$

Case of a local defect in a perfect crystal

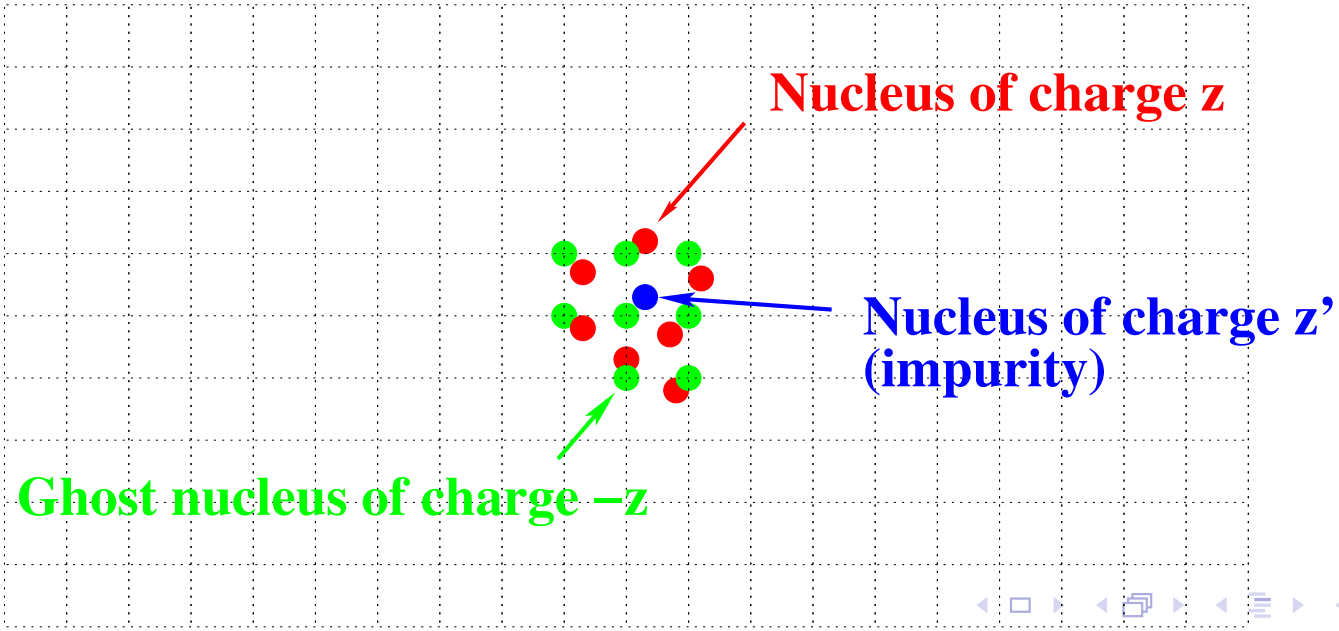
Defect = quasi-molecule embedded in the host crystal

$$\rho^{\mathrm{nuc}}(\mathbf{r}) = \rho^{\mathrm{nuc}}_{\mathrm{per}}(\mathbf{r}) + m(\mathbf{r}),\ \rho^{0}(\mathbf{r}) = \rho^{0}_{\mathrm{per}}(\mathbf{r}) + \rho_m(\mathbf{r}),\ \sqrt{\rho^{0}(\mathbf{r})} = u^{0}_{\mathrm{per}}(\mathbf{r}) + v_m(\mathbf{r})$$

Charge of the defect: $Q = \int_{\mathbb{R}^3} \rho^0_m$ with
$\rho^0_m = m - \rho_m = m - (2u^0_{\mathrm{per}} v_m + v_m^2)$

Goal: find a model to directly compute the function $v_m(\mathbf{r})$

Nuclear charge distribution $m(\mathbf{r})$ of the quasi-molecule



Outline

Formal argument for crystals with defects

Same argument as in (E. Cancès, A. Deleurence and M. Lewin, 2008).

Test density ρ, $\sqrt{\rho} = u^0_{\rm per} + v \geq 0$

$$\mathcal{E}^{\rm TFW}_{\rho^{\rm nuc}_{\rm per}+m}((u^0_{\rm per}+v)^2) - \mathcal{E}^{\rm TFW}_{\rho^{\rm nuc}_{\rm per}}((u^0_{\rm per})^2) = \mathcal{E}^m(v) - \int_{\mathbb{R}^3} m V^0_{\rm per}$$

and

$$\mathcal{E}^m(v) := \langle H^0_{\rm per} v, v\rangle_{H^{-1}(\mathbb{R}^3),H^1(\mathbb{R}^3)}$$

$$+\tfrac{1}{2} D\left(2u^0_{\rm per}v + v^2 - m, 2u^0_{\rm per}v + v^2 - m\right)$$

$$+C_{\rm TF}\int_{\mathbb{R}^3}\left(|u^0_{\rm per}+v|^{10/3} - |u^0_{\rm per}|^{10/3} - \tfrac{5}{3}|u^0_{\rm per}|^{4/3}(2u^0_{\rm per}v + v^2)\right)$$

Variational model for local defects

Tentative variational model for local defects (justified by thermodynamic limit arguments)

$$I^m = \inf \{\mathcal{E}^m(v),\ v \in \mathcal{Q}_+\} \tag{1}$$

$$\mathcal{Q}_+ := \left\{v \in L^2(\mathbb{R}^3) \mid \nabla v \in (L^2(\mathbb{R}^3))^3,\ v \geq -u^0_{\rm per},\ u^0_{\rm per} v \in \mathcal{C}\right\}$$

where $\mathcal{C}$ denotes the Coulomb space. The set $\mathcal{Q}_+$ is a closed convex subset of the Hilbert space $\mathcal{Q} := \left\{v \in L^2(\mathbb{R}^3) \mid \nabla v \in (L^2(\mathbb{R}^3))^3,\ u^0_{\rm per} v \in \mathcal{C}\right\}$

Theorem (E. Cancès-V.E., 2010). Let $m \in \mathcal{C}$. Then,

1. Well-posedness of the problem

   Problem (1) has a unique minimizer v_m, and there exists a positive constant $C_0 > 0$ such that

$$\forall m \in \mathcal{C}, \quad \|v_m\|_{\mathcal{Q}} \leq C_0 \left(\|m\|_{\mathcal{C}} + \|m\|^2_{\mathcal{C}}\right).$$

Charge of local defects

2. Local defects are always neutral

Let $\rho^0_m = m - (2u^0_{\rm per} v_m + v_m^2)$ (total density of charge of the defect) and $\Phi^0_m = \rho^0_m \star |\cdot|^{-1}$ (Coulomb potential generated by ρ^0_m). It holds

$$
\begin{array}{lcl}
v_m \in H^2(\mathbb{R}^3) & \Rightarrow & v_m(\mathbf{r}) \longrightarrow_{|\mathbf{r}|\to\infty} 0 \\
\Phi^0_m \in L^2(\mathbb{R}^3) & \Rightarrow & \Phi^0_m \text{ cannot decay as } \frac{Q}{|\mathbf{r}|} \text{ with } Q \neq 0 \\
\lim_{\epsilon\to 0} \frac{1}{|B_\epsilon|} \int_{B_\epsilon} |\widehat{\rho^0_m}(\mathbf{k})|\, d\mathbf{k} = 0 & \Rightarrow & Q = \int_{\mathbb{R}^3} \rho^0_m(\mathbf{r})\, d\mathbf{r} = 0 \quad \text{if } \rho^0_m \in L^1(\mathbb{R}^3)
\end{array}
$$

Compactness of minimizing sequences

3. Any minimizing sequence for (1) converges to v_m in $\mathcal{Q}$

4. For any $q \in \mathbb{R}$, there exists a minimizing sequence $(v^k_{m,q})_{k\in\mathbb{N}}$ for (1) consisting of functions of $\mathcal{Q}_+ \cap L^1(\mathbb{R}^3)$ such that

$$\forall k \in \mathbb{N}, \quad \int_{\mathbb{R}^3} \left(2u^0_{\rm per} v^k_{m,q} + |v^k_{m,q}|^2\right) = \int_{\mathbb{R}^3} \left(|u^0_{\rm per} + v^k_{m,q}|^2 - |u^0_{\rm per}|^2\right) = q$$

Special case of a homogeneous host crystal

Theorem (E. Cancès-V.E., 2010). Consider the case when $\forall x \in \mathbb{R}^3,\ \rho^{\mathrm{nuc}}_{\mathrm{per}}(x) = \rho^0_{\mathrm{per}}(x) = \alpha^2$ and $u^0_{\mathrm{per}}(x) = \alpha$ (homogeneous host crystal)

For each $m \in \mathcal{C}$, the unique solution v_m to (1) reads

$$v_m = g \star m + \widetilde{r}_2(m)$$

where $\widetilde{r}_2(m) \in L^1(\mathbb{R}^3)$ with $\|\widetilde{r}_2(m)\|_{L^1(\mathbb{R}^3)} \leq C_0 \left(\|m\|^2_{\mathcal{C}} + \|m\|^8_{\mathcal{C}}\right)$ and where $g \in L^1(\mathbb{R}^3)$ is characterized by its Fourier transform

$$\widehat{g}(k) = \frac{1}{(2\pi)^{3/2}} \frac{4\pi\alpha}{|k|^4 + \frac{20}{9}\alpha^{4/3}|k|^2 + 8\pi\alpha^2}$$

For each $m \in L^1(\mathbb{R}^3) \cap \mathcal{C}$, it holds $v_m \in L^1(\mathbb{R}^3) \cap L^2(\mathbb{R}^3)$ and

$$\int_{\mathbb{R}^3} \rho^0_m = \int_{\mathbb{R}^3} (m - (2u^0_{\mathrm{per}} v_m + v_m^2)) = 0$$

Outline

Thermodynamic limit

Defect problem in a supercell of size L^3

Theorem (E. Cancès-V.E., 2010).

1. Thermodynamic limit with a charge constraint

   For $q \in \mathbb{R}$, let $v_{m,q,L}$ be the solution of the defect problem in a supercell of size L^3 (denoted Γ_L) with the constraint

   $$\int_{\Gamma_L} \left(m - \left(2u^0_{\mathrm{per}} v_{m,q,L} + v^2_{m,q,L}\right)\right) = q.$$

   Then $(v_{m,q,L})_{L\in\mathbb{N}^*}$ converges to v_m, the unique solution of (1).

2. Thermodynamic limit without a charge constraint

   Let $v_{m,L}$ be the solution of the defect problem in a supercell of size L^3 (denoted Γ_L) witout any charge constraint. Then $(v_{m,q,L})_{L\in\mathbb{N}^*}$ converges to v_m, the unique solution of (1) and

   $$\int_{\Gamma_L} \left(m - \left(2u^0_{\mathrm{per}} v_{m,q,L} + v^2_{m,q,L}\right)\right) \underset{L\to\infty}{\longrightarrow} 0.$$

Outline

TFW: case of atoms and molecules

(J.P. Solovej, 1990)
TFW theory for a molecule: K nuclei at positions $R_1, \cdots, R_K \in \mathbb{R}^3$ and with nuclear charges $z_1, \cdots, z_K \geq 0$.

$$\rho^{\mathrm{nuc}} = \sum_{k=1}^{K} z_k \delta_{R_k}, \quad Z = \sum_{k=1}^{K} z_k.$$

$$I(z_1, \cdots, z_K; N) = \inf \left\{ \mathcal{E}^{\mathrm{TFW}}_{\rho^{\mathrm{nuc}}}(\rho),\ \sqrt{\rho} \in H^1(\mathbb{R}^3),\ \int_{\mathbb{R}^3} \rho \leq N \right\} \qquad (2)$$

There exists $N_c(z_1, \cdots, z_K) > Z$ such that for all $N \leq N_c(z_1, \cdots, z_K)$, the variational problem (2) has a unique minizer $\rho_{(z_1, \cdots z_K; N)}$.

$$Q_c(z_1, \cdots, z_K) = Z - N_c(z_1, \cdots z_K) < 0$$

is the maximal (negative) ionization the molecule can achieve.

Limit as the charge of the nuclei tends to ∞

$$z' = (z_1, \cdots z_L), \quad z'' = (z_{L+1}, \cdots, z_K)$$

Theorem (J.P. Solovej, 1990).
There exists $Q_\infty(z'') < 0$ such that

$$\lim_{z' \to \infty} Q_c(z) = Q_\infty(z'').$$

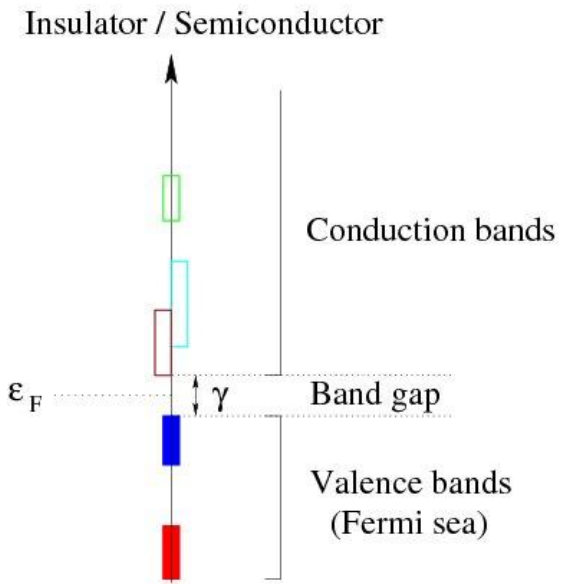
Charge screening in the Hartree model

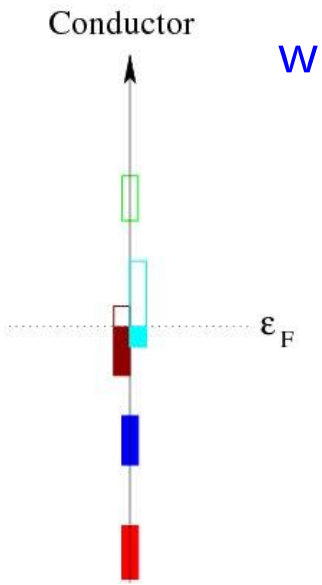
(E. Cancès, A. Deleurence and M. Lewin, 2008)

Hartree model for perfect crystal:

$$H^0_{\rm per} = -\frac{1}{2}\Delta + V^0_{\rm per} \qquad \gamma^0_{\rm per} = 1_{(-\infty,\epsilon_{\rm F}]}(H^0_{\rm per}) \quad \text{(orthogonal projector)}$$

Assumption: The periodic crystal is a semiconductor.





Hartree model for crystals with local defects

$$\begin{aligned} \rho^{\rm nuc} &= \rho^{\rm nuc}_{\rm per} + m \\ \gamma^0 &= \gamma^0_{\rm per} + Q^{m,\epsilon_{\rm F}} \\ \rho^0 &= \rho^0_{\rm per} + \rho^{m,\epsilon_{\rm F}} \end{aligned}$$

Conclusions and open problems

A variational problem was proposed in order to model local defects in periodic crystals in the framework of the TFW theory (justified by thermodynamic limit arguments).

- Defects are fully screened for the TF and TFW models. Is it the case for any orbital-free DFT models?
- A-priori decay of the solution v_m ?
- Quid for the TFWD model?