The microscopic origin of the macroscopic dielectric permittivity of crystals

Gabriel STOLTZ

stoltz@cermics.enpc.fr

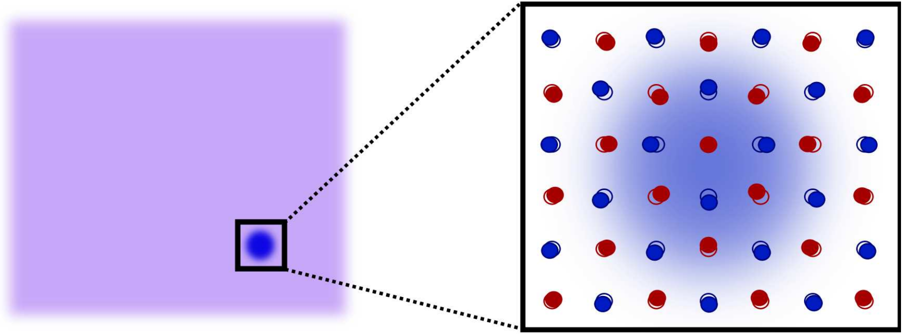
(CERMICS, Ecole des Ponts & MICMAC team, INRIA Rocquencourt)

Work in collaboration with E. Cancès and M. Lewin

Séminaire "Problèmes Spectraux en Physique Mathématique"

Microscopic origin of macroscopic dielectric properties (1)

In a dielectric material, the presence of an electric field causes the nuclear and electronic charges to slightly separate, inducing a local electric dipole



This generates an induced response inside the material (reorganization of the electronic density), screening the applied field

Microscopic origin of macroscopic dielectric properties (2)

- **Dielectric material:** can polarize in presence of external fields

	density	electric field
external	ν	$\mathbf{D}$, div $\mathbf{D} = 4\pi\nu$
polarization	$\delta\rho$	$\mathbf{P}$, div $\mathbf{P} = 4\pi\delta\rho$
total	ρ	$\mathbf{E}$, div $\mathbf{E} = 4\pi\rho$

$$\mathbf{D} = \mathbf{E} + \mathbf{P}$$

- **Constitutive equation:** $\varepsilon_{\mathrm{M}} = 3 \times 3$ symmetric real matrix with $\varepsilon_{\mathrm{M}} \geqslant 1$

$$\mathbf{D} = \varepsilon_{\mathrm{M}}\mathbf{E} \iff \mathbf{P} = (\varepsilon_{\mathrm{M}} - 1)\mathbf{E} = (1 - \varepsilon_{\mathrm{M}}^{-1})\mathbf{D}$$

- **Time-dependent fields:** the response of the material is not instantaneous, but given by a convolution with some response function. With $\mathbf{E}(t) = -\nabla W(t)$ where $W(t)$ is the macroscopic potential,

$$-\mathrm{div}\left(\varepsilon_{\mathrm{M}}(\omega)\nabla\widehat{W}(\omega)\right) = 4\pi\,\widehat{\nu}(\omega)$$

Another motivation: Opto-electronical properties

- Photovoltaic effet: convert light into electric current/voltage
  - Mechanism: promotion of valence electrons into excited states
  - Compute band gaps in photovoltaic materials
  - Need for methods going beyond standard ground-state approaches

- Reference numerical approach: GW method → horrible equations...
  - Dyson equation $G(12) = G^{(0)}(12) + \int d(34) G^{(0)}(13)\Sigma(34)G(42)$
  - Self-energy $\Sigma(12) = \mathrm{i} \int d(34) W(1^+3) G(14)\Gamma(42;3)$
  - **Screened interaction** $\boxed{W(12) = v(12) + \int d(34) W(13) P(34) v(42)}$
  - Irreducible polarization $P(12) = -\mathrm{i} \int d(34) G(23) G(42) \Gamma(34;1)$
  - Vertex function $\Gamma(12;3) = \delta(12)\delta(13) + \int d(4567) \dfrac{\delta \Sigma(12)}{\delta G(45)} G(46) G(75) \Gamma(67;3)$

Outline

Some background material

- Description of perfect crystals
- Crystals with defects: static picture

Time evolution of defects in crystals

- Response to an effective potential
- Well-posedness of the nonlinear Hartree dynamics
- Frequency dependent macroscopic dielectric permittivity

[CS12] E. Cancès and G. Stoltz, *Ann. I. H. Poincare-An.* **29**(6) (2012) 887-925

[CLS11] E. Cancès, M. Lewin and G. Stoltz, in *Numerical Analysis of Multiscale Computations*, B. Engquist, O. Runborg, Y.-H. R. Tsai. (Eds.), Lect. Notes Comput. Sci. Eng. **82** (2011)

[CL10] E. Cancès and M. Lewin, *Arch. Rational Mech. Anal* **197**(1) 139-177 (2010)

Elements of electronic structure theory

Some elements on trace-class operators

- Compact self-adjoint operator $A = \sum_{i=1}^{+\infty} \lambda_i \, |\phi_i\rangle \langle \phi_i|$ with $\lambda_i \to 0$

- The operator A is called trace-class ($A \in \mathfrak{S}_1$) if $\sum_{i=1}^{+\infty} |\lambda_i| < \infty$. Its density

$\rho_A(x) = \sum_{i=1}^{+\infty} \lambda_i |\phi_i(x)|^2$ belongs to $L^1(\mathbb{R}^3)$ and

$$\mathrm{Tr}(A) := \sum_{i=1}^{+\infty} \lambda_i = \sum_{i=1}^{+\infty} \langle e_i | A | e_i \rangle = \int_{\mathbb{R}^3} \rho_A$$

- A is Hilbert-Schmidt ($A \in \mathfrak{S}_2$) if $A^* A \in \mathfrak{S}_1$, *i.e.* $\sum_{i \geqslant 1} |\lambda_i|^2 < \infty$. If A is

self-adjoint, its integral kernel is in $L^2(\mathbb{R}^3 \times \mathbb{R}^3)$

$$A(x,y) = \sum_{i \geqslant 1} \lambda_i \, \overline{\phi_i(x)} \phi_i(y).$$

Density operators for a finite system of N electrons in $\mathbb{R}^3$

- Bounded, self-adjoint operator on $L^2(\mathbb{R}^3)$ such that $0 \leqslant \gamma \leqslant 1$ and $\mathrm{Tr}(\gamma) = N$. In some orthonormal basis of $L^2(\mathbb{R}^3)$,

$$\gamma = \sum_{i=1}^{+\infty} n_i |\phi_i\rangle\langle\phi_i|, \qquad 0 \leqslant n_i \leqslant 1, \qquad \sum_{i=1}^{+\infty} n_i = N$$

- For the Slater determinant $\psi(x_1, \dots, x_N) = (N!)^{-1/2} \mathrm{det}(\phi_i(x_j))_{1 \leqslant i,j \leqslant N}$,

$$\gamma_\psi = \sum_{i=1}^{N} |\phi_i\rangle\langle\phi_i|$$

- **Electronic density** $\rho_\gamma(x) = \displaystyle\sum_{i=1}^{+\infty} n_i |\phi_i(x)|^2$ with $\rho_\gamma \geqslant 0$ and $\displaystyle\int_{\mathbb{R}^3} \rho_\gamma = N$.
- **Kinetic energy** $T(\gamma) = \dfrac{1}{2}\mathrm{Tr}(|\nabla|\gamma|\nabla|) = \dfrac{1}{2}\displaystyle\sum_{i=1}^{+\infty} n_i \|\nabla\phi_i\|^2_{L^2(\mathbb{R}^3)}$

The Hartree model for finite systems

- **Hartree energy** $E_{\rho^{\rm nuc}}^{\rm Hartree}(\gamma) = \mathrm{Tr}\left(-\frac{1}{2}\Delta\gamma\right) + \frac{1}{2} D(\rho_\gamma - \rho^{\rm nuc}, \rho_\gamma - \rho^{\rm nuc})$

where

$$D(f,g) = \int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \frac{f(x)\, g(x')}{|x-x'|}\, dx\, dx' = 4\pi \int_{\mathbb{R}^3} \frac{\overline{\widehat{f}(k)}\, \widehat{g}(k)}{|k|^2}\, dk$$

is the classical Coulomb interaction, defined for $f,g \in L^{6/5}(\mathbb{R}^3)$, but which can be extended to

$$\mathcal{C} = \left\{ f \in \mathscr{S}'(\mathbb{R}^3) \;\middle|\; \widehat{f} \in L^1_{\rm loc}(\mathbb{R}^3),\ |\cdot|^{-1}\widehat{f}(\cdot) \in L^2(\mathbb{R}^3) \right\}$$

Variational formulation

$$\inf\left\{ E_{\rho^{\rm nuc}}^{\rm Hartree}(\gamma),\ \gamma \in \mathcal{S}(L^2(\mathbb{R}^3)),\ 0 \leqslant \gamma \leqslant 1,\ \mathrm{Tr}(\gamma) = N,\ \mathrm{Tr}(-\Delta\gamma) < \infty \right\}$$

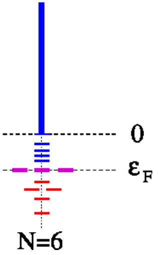
- More general models of density functional theory: correction term $E_{\rm xc}(\gamma)$

[Sol91] J.-P. Solovej, *Invent. Math.*, 1991

Euler-Lagrange equations for the Hartree model

Nonlinear eigenvalue problem, ε_{F} Lagrange multiplier of $\mathrm{Tr}(\gamma) = N$

$$
\left\{
\begin{array}{l}
\gamma^0 = \displaystyle\sum_{i=1}^{+\infty} n_i |\phi_i\rangle\langle\phi_i|, \qquad \rho^0(x) = \displaystyle\sum_{i=1}^{+\infty} n_i |\phi_i(x)|^2, \\
H^0 \phi_i = \varepsilon_i \phi_i, \qquad \langle \phi_i, \phi_j \rangle = \delta_{ij}, \\
n_i = \left\{ \begin{array}{cl} 1 & \text{if } \varepsilon_i < \varepsilon_{\mathrm{F}} \\ \in [0,1] & \text{if } \varepsilon_i = \varepsilon_{\mathrm{F}} \\ 0 & \text{if } \varepsilon_i > \varepsilon_{\mathrm{F}} \end{array} \right. \qquad \displaystyle\sum_{i=1}^{+\infty} n_i = N, \\
H^0 = -\dfrac{1}{2}\Delta + V^0, \\
-\Delta V^0 = 4\pi(\rho^0 - \rho^{\mathrm{nuc}}).
\end{array}
\right.
$$



When $\varepsilon_N < \varepsilon_{N+1}$ (gap): $\left\{ \begin{array}{l} \gamma^0 = 1_{(-\infty,\varepsilon_{\mathrm{F}}]}(H^0), \\ H^0 = -\dfrac{1}{2}\Delta + V^0, \\ -\Delta V^0 = 4\pi(\rho^0 - \rho^{\mathrm{nuc}}), \end{array} \right.$

The Hartree model for crystals (1)

- **Thermodynamic limit**, periodic nuclear density $\rho_{\rm per}^{\rm nuc}$, lattice $\mathcal{R} \simeq (a\mathbb{Z})^3$

with unit cell Γ, reciprocal lattice $\mathcal{R}^* \simeq \left(\frac{2\pi}{a}\mathbb{Z}\right)^3$ with unit cell Γ^*

- **Bloch-Floquet transform:** unitary $L^2(\mathbb{R}^3) \to \fint_{\Gamma^*}^{\oplus} L^2_{\rm per}(\Gamma)\, dq$

$$f_q(x) = \sum_{R \in \mathcal{R}} f(x+R)\, \mathrm{e}^{-\mathrm{i}q\cdot(x+R)} = \frac{(2\pi)^{3/2}}{|\Gamma|} \sum_{K \in \mathcal{R}^*} \widehat{f}(q+K)\, \mathrm{e}^{\mathrm{i}K\cdot x}$$

- Any operator commuting with the spatial translations τ_R $(R \in \mathcal{R})$ can be decomposed as $(Af)_q = A_q f_q$, and $\sigma(A) = \overline{\bigcup_{q\in\Gamma^*} \sigma(A_q)}$
- Bloch matrices: $A_{K,K'}(q) = \langle e_K, A_q e_{K'} \rangle_{L^2_{\rm per}(\Gamma)}$, $e_K(x) = |\Gamma|^{-1/2}\mathrm{e}^{\mathrm{i}K\cdot x}$

$$\mathcal{F}(Av)(q+K) = \sum_{K' \in \mathcal{R}^*} A_{K,K'}(q) \mathcal{F}v(q+K')$$

[CLL01] I. Catto, C. Le Bris, and P.-L. Lions, *Ann. I. H. Poincaré-An*, 2001
[CDL08] E. Cancès, A. Deleurence and M. Lewin, *Commun. Math. Phys.*, 2008

The Hartree model for crystals (2)

Nonlinear eigenvalue problem

$$\begin{cases} \gamma_{\rm per}^0 = 1_{(-\infty,\varepsilon_{\rm F}]}(H_{\rm per}^0), \qquad \rho_{\rm per}^0 = \rho_{\gamma_{\rm per}^0}, \\ H_{\rm per}^0 = -\dfrac{1}{2}\Delta + V_{\rm per}^0, \\ -\Delta V_{\rm per}^0 = 4\pi(\rho_{\rm per}^0 - \rho_{\rm per}^{\rm nuc}), \qquad \displaystyle\int_\Gamma \rho_{\rm per}^0 = \int_\Gamma \rho_{\rm per}^{\rm nuc} = N \end{cases}$$

More explicit expressions using the Bloch decomposition

$$\left(H_{\rm per}^0\right)_q = -\frac{1}{2}\Delta - \mathrm{i}q\cdot\nabla + \frac{|q|^2}{2} + V_{\rm per}^0 = \sum_{n=1}^{+\infty} \varepsilon_{n,q}|u_{n,q}\rangle\langle u_{n,q}|$$

$$\left(\gamma_{\rm per}^0\right)_q = \sum_{n=1}^{+\infty} 1_{\{\varepsilon_{n,q}\leqslant\varepsilon_{\rm F}\}}|u_{n,q}\rangle\langle u_{n,q}|$$

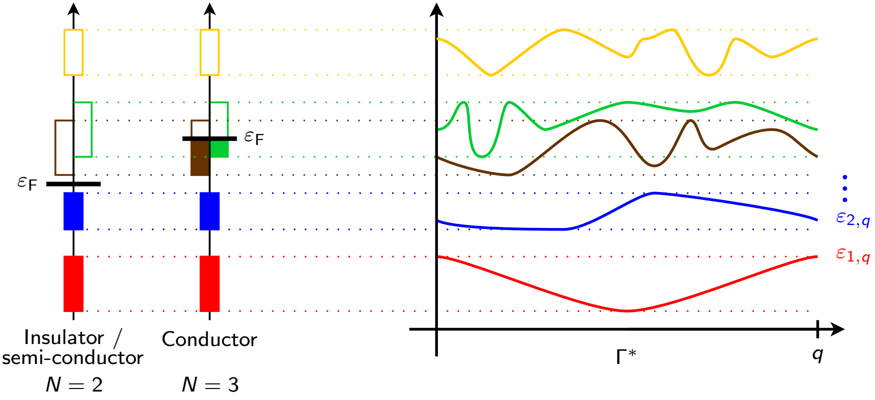
Fermi level obtained from $N = \dfrac{1}{|\Gamma^*|}\displaystyle\sum_{n=1}^{+\infty}\left|\{q\in\Gamma^* \mid \varepsilon_{n,q}\leqslant\varepsilon_{\rm F}\}\right|$

The Hartree model for crystals (3)

The spectrum of the periodic Hamiltonian is composed of bands

$$\sigma(H) = \bigcup_{n \geq 1} \left[\Sigma_n^-, \Sigma_n^+ \right], \qquad \Sigma_n^- = \min_{q \in \overline{\Gamma^*}} \varepsilon_{n,q}, \quad \Sigma_n^+ = \max_{q \in \overline{\Gamma^*}} \varepsilon_{n,q}$$

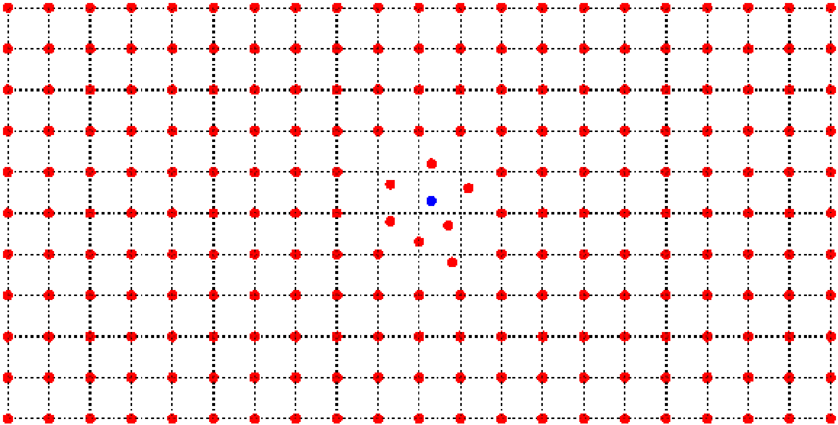
Assume in the sequel that $g = \Sigma_{N+1}^- - \Sigma_N^+ > 0$ (insulator)



Defects in crystals

Local defects (1)

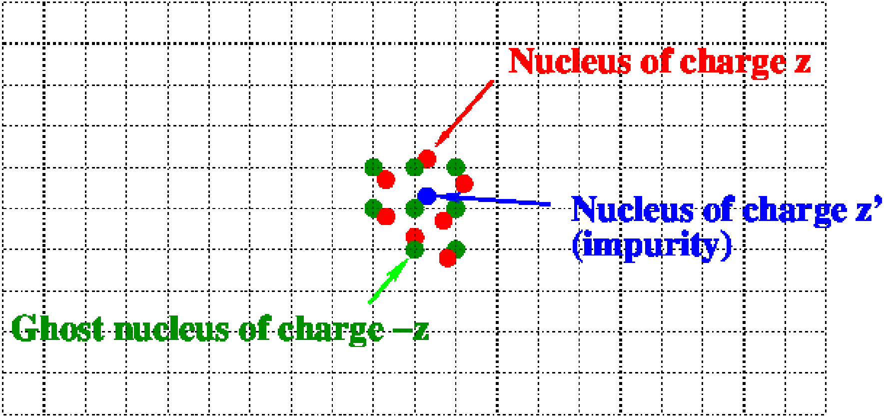
- Local perturbation: nuclear charge defect $\rho^{\rm nuc}_{\rm per} + \nu$



- Expected ground state $\gamma = \gamma^0_{\rm per} + Q_\nu$ with Q_ν "local"

Local defects (2)

- Local perturbation: nuclear charge defect $\rho_{\mathrm{per}}^{\mathrm{nuc}} + \nu$



- Expected ground state $\gamma = \gamma_{\mathrm{per}}^0 + Q_\nu$ with Q_ν "local"

Defects in crystals (1)

- A thermodynamic limit shows that Q_ν can be thought of as some defect state embedded in the periodic medium

$$Q_\nu = \underset{\substack{Q \in \mathcal{Q} \\ -\gamma^0_{\rm per} \leqslant Q \leqslant 1-\gamma^0_{\rm per}}}{\operatorname{argmin}} \left\{ \mathrm{Tr}_0\left(H^0_{\rm per} Q\right) - \int_{\mathbb{R}^3} \rho_Q(\nu \star |\cdot|^{-1}) + \frac{1}{2} D(\rho_Q, \rho_Q) \right\}$$

where, defining $Q^{--} = \gamma^0_{\rm per} Q \gamma^0_{\rm per}$ and $Q^{++} = (1-\gamma^0_{\rm per}) Q (1-\gamma^0_{\rm per})$,

$$\mathcal{Q} = \left\{ Q^* = Q,\ (1-\Delta)^{1/2} Q \in \mathfrak{S}_2,\ (1-\Delta)^{1/2} Q^{\pm\pm} (1-\Delta)^{1/2} \in \mathfrak{S}_1 \right\}$$

- Generalized trace $\mathrm{Tr}_0(Q) = \mathrm{Tr}(Q^{++}) + \mathrm{Tr}(Q^{--})$
- Density $\rho_Q \in L^2(\mathbb{R}^3) \cap \mathcal{C}$

[HLS05] C. Hainzl, M. Lewin, and E. Séré, *Commun. Math. Phys.*, 2005 (and subsequent works)
[CDL08] E. Cancès, A. Deleurence and M. Lewin, *Commun. Math. Phys.*, 2008
[CL10] E. Cancès and M. Lewin, *Arch. Rational Mech. Anal.*, 2010

Defects in crystals (2)

Definition of the embedding energy

$$\mathrm{Tr}_0((H^0_{\rm per} - \varepsilon_{\rm F})Q) := \mathrm{Tr}(|H^0_{\rm per} - \varepsilon_{\rm F}|^{1/2}(Q^{++} - Q^{--})|H^0_{\rm per} - \varepsilon_{\rm F}|^{1/2})$$

[CL, Theorem 1]

Let ν such that $(\nu \star |\cdot|^{-1}) \in L^2(\mathbb{R}^3) + \mathcal{C}'$. Then, there exists at least one minimizer $Q_{\nu,\varepsilon_{\rm F}}$, and all the minimizers share the same density $\rho_{\nu,\varepsilon_{\rm F}}$. In addition, $Q_{\nu,\varepsilon_{\rm F}}$ is solution to the self-consistent equation

$$Q_{\nu,\varepsilon_{\rm F}} = 1_{(-\infty,\varepsilon_{\rm F})}\left(H^0_{\rm per} + (\rho_{\nu,\varepsilon_{\rm F}} - \nu) \star |\cdot|^{-1}\right) - 1_{(-\infty,\varepsilon_{\rm F}]}\left(H^0_{\rm per}\right) + \delta,$$

where δ is a finite-rank self-adjoint operator on $L^2(\mathbb{R}^3)$ such that $0 \leqslant \delta \leqslant 1$ and $\mathrm{Ran}(\delta) \subset \mathrm{Ker}\left(H^0_{\rm per} + (\rho_{\nu,\varepsilon_{\rm F}} - \nu) \star |\cdot|^{-1} - \varepsilon_{\rm F}\right)$.

When ν is sufficiently small, $\delta = 0$ and the minimizer is unique.

Time evolution of defects in crystals: effective perturbations

The time-dependent Hartree dynamics

- Finite system described by the density matrix $\gamma(t)$, von Neumann equation

$$\mathrm{i}\frac{d\gamma(t)}{dt} = \left[H^0_{\gamma(t)}, \gamma(t)\right], \qquad H^0_\gamma = -\frac{1}{2}\Delta + V_{\mathrm{nuc}} + v_{\mathrm{c}}(\rho_\gamma)$$

- When a perturbation $v(t)$ is added, the dynamics is modified as

$$\mathrm{i}\frac{d\gamma(t)}{dt} = \left[H^0_{\gamma(t)} + v(t), \gamma(t)\right],$$

- **Formal thermodynamic limit:** state $\gamma(t) = \gamma^0_{\mathrm{per}} + Q(t)$ and dynamics

$$\mathrm{i}\frac{d\gamma}{dt} = \left[H^v_\gamma, \gamma\right], \qquad H^v_\gamma(t) = H^0_{\mathrm{per}} + v_{\mathrm{c}}(\rho_Q(t) - \nu(t))$$

[Chadam76] J. M. Chadam, The time-dependent Hartree-Fock equations with Coulomb two-body interaction, *Commun. Math. Phys.* **46** (1976) 99–104
[Arnold96] A. Arnold, Self-consistent relaxation-time models in quantum mechanics, *Commun. Part. Diff. Eq.* **21**(3-4) (1996) 473–506

Defects in a time-dependent setting: the dynamics

Classical formulation: nonlinear dynamics

$$\mathrm{i}\frac{dQ(t)}{dt} = \left[H^0_{\mathrm{per}} + v_{\mathrm{c}}(\rho_{Q(t)} - \nu(t)), \gamma^0_{\mathrm{per}} + Q(t)\right]$$

Denote $U_0(t) = \mathrm{e}^{-\mathrm{i}tH^0_{\mathrm{per}}}$ the free evolution.

Mild formulation for an effective potential $v(t)$

$$Q(t) = U_0(t) Q^0 U_0(t)^* - \mathrm{i}\int_0^t U_0(t-s)[v(s), \gamma^0_{\mathrm{per}} + Q(s)] U_0(t-s)^* \, ds$$

Mild formulation for the nonlinear dynamics

Replace $v(s)$ by $v_{\mathrm{c}}(\rho_{Q(s)} - \nu(s))$ in the above formula

Well-posedness of the mild formulation

If initially $Q(0) \in \mathcal{Q}$, the Banach space allowing to describe local defects in crystals, does $Q(t) \in \mathcal{Q}$?

[CS12, Proposition 1]

The integral equation has a unique solution in $C^0(\mathbb{R}_+, \mathcal{Q})$ for $Q^0 \in \mathcal{Q}$ and $v = v_{\rm c}(\rho)$ with $\rho \in L^1_{\rm loc}(\mathbb{R}_+, L^2(\mathbb{R}^3) \cap \mathcal{C})$.
In addition, $\mathrm{Tr}_0(Q(t)) = \mathrm{Tr}_0(Q^0)$, and, if $-\gamma^0_{\rm per} \leqslant Q^0 \leqslant 1 - \gamma^0_{\rm per}$, then $-\gamma^0_{\rm per} \leqslant Q(t) \leqslant 1 - \gamma^0_{\rm per}$.

This result is based on a series of technical results

- boundedness of the potential: $v \in L^1_{\rm loc}(\mathbb{R}_+, L^\infty(\mathbb{R}^3))$
- stability of time evolution: $\dfrac{1}{\beta}\|Q\|_{\mathcal{Q}} \leqslant \|U_0(t) Q U_0(t)^*\|_{\mathcal{Q}} \leqslant \beta \|Q\|_{\mathcal{Q}}$
- commutator estimates with $\gamma^0_{\rm per}$: $\left\|\mathrm{i}[v, \gamma^0_{\rm per}]\right\|_{\mathcal{Q}} \leqslant C_{\rm com} \|v\|_{\mathcal{C}'}$
- commutator estimates in $\mathcal{Q}$: $\|\mathrm{i}[v_{\rm c}(\varrho), Q]\|_{\mathcal{Q}} \leqslant C_{\rm com,\mathcal{Q}} \|\varrho\|_{L^2 \cap \mathcal{C}} \|Q\|_{\mathcal{Q}}$

Dyson expansion and linear response

Response at all orders (formally): $Q(t) = U_0(t)Q^0U_0(t)^* + \sum_{n=1}^{+\infty} Q_{n,v}(t)$

$$Q_{1,v}(t) = -\mathrm{i}\int_0^t U_0(t-s)\left[v(s), \gamma^0_{\mathrm{per}} + U_0(s)Q^0U_0(s)^*\right] U_0(t-s)^*\,ds,$$

$$Q_{n,v}(t) = -\mathrm{i}\int_0^t U_0(t-s)\left[v(s), Q_{n-1,v}(s)\right] U_0(t-s)^*\,ds \quad \text{for } n \geqslant 2$$

Obtained by plugging the formal decomposition into the integral equation

[CS12, Proposition 5]

Under the previous assumptions, $Q_{n,v} \in C^0(\mathbb{R}_+, \mathcal{Q})$ with $\mathrm{Tr}_0(Q_{n,v}(t)) = 0$,

$$\|Q_{n,v}(t)\|_{\mathcal{Q}} \leqslant \beta \frac{1 + \|Q^0\|_{\mathcal{Q}}}{n!}\left(C\int_0^t \|\rho(s)\|_{L^2\cap\mathcal{C}}\,ds\right)^n.$$

The formal expansion therefore converges in $\mathcal{Q}$, uniformly on any compact subset of $\mathbb{R}_+$, to the unique solution in $C^0(\mathbb{R}_+, \mathcal{Q})$ of the integral equation.

Definition of the polarization (1)

- **Aim:** Justify the Adler-Wiser formula for the polarization matrix
- **Damped linear response:** standard linear response as $\eta \to 0$

$$Q^{\eta}_{1,v}(t) = -\mathrm{i} \int_{-\infty}^{t} U_0(t-s) \left[v(s), \gamma^0_{\mathrm{per}} \right] U_0(t-s)^* \mathrm{e}^{-\eta(t-s)} \, ds$$

- polarization operator $\chi^{\eta}_0 : \begin{cases} L^1(\mathbb{R}, \mathcal{C}') & \to & C^0_{\mathrm{b}}(\mathbb{R}, L^2(\mathbb{R}^3) \cap \mathcal{C}) \\ v & \mapsto & \rho_{Q^{\eta}_{1,v}} \end{cases}$
- linear response operator $\mathscr{E}^{\eta} = v_{\mathrm{c}}^{1/2} \chi_0 v_{\mathrm{c}}^{1/2}$ acting on $L^1(\mathbb{R}, L^2(\mathbb{R}^3))$

$$\langle f_2, \mathscr{E}^{\eta} f_1 \rangle_{L^2(L^2)} = \int_{\mathbb{R}} \langle \mathcal{F}_t f_2(\omega), \mathscr{E}^{\eta}(\omega) \mathcal{F}_t f_1(\omega) \rangle_{L^2(\mathbb{R}^3)} \, d\omega$$

- Bloch decomposition: for a.e. $(\omega, q) \in \mathbb{R} \times \Gamma^*$ and any $K \in \mathcal{R}^*$,

$$\mathcal{F}_{t,x} \left(\mathscr{E}^{\eta} f \right) (\omega, q+K) = \sum_{K' \in \mathcal{R}^*} \mathscr{E}^{\eta}_{K,K'}(\omega, q) \, \mathcal{F}_{t,x} f(\omega, q+K')$$

[Adler62] S. L. Adler, *Phys. Rev.*, 1962
[Wiser63] N. Wiser, *Phys. Rev.*, 1963

Definition of the polarization (2)

[CS12, Proposition 7]

The Bloch matrices of the damped linear response operator $\mathscr{E}^\eta$ read

$$\mathscr{E}^\eta_{K,K'}(\omega,q) = \frac{\mathbf{1}_{\Gamma^*}(q)}{|\Gamma|} \frac{|q+K'|}{|q+K|} T^\eta_{K,K'}(\omega,q),$$

where the continuous functions $T^\eta_{K,K'}$ are uniformly bounded:

$$T^\eta_{K,K'}(\omega,q) = \sum \fint_{\Gamma^*} \frac{\langle u_{m,q'}, \mathrm{e}^{-\mathrm{i}K\cdot x} u_{n,q+q'}\rangle_{L^2_{\rm per}} \langle u_{n,q+q'}, \mathrm{e}^{\mathrm{i}K'\cdot x} u_{m,q'}\rangle_{L^2_{\rm per}}}{\varepsilon_{n,q+q'} - \varepsilon_{m,q'} - \omega - \mathrm{i}\eta} \, dq'$$

(the sum is over $1 \leqslant n \leqslant N < m$ and $1 \leqslant m \leqslant N < n$)

- The Bloch matrices of the standard linear response are recovered as $\eta \to 0$, the convergence being in $\mathscr{S}'(\mathbb{R}\times\mathbb{R}^3)$
- Static polarizability recovered in some adiabatic limit

Time evolution of defects in crystals: nonlinear dynamics

Time-dependent Hartree dynamics for defects

Well-posedness of the mild formulation

For $\nu \in L^1_{\rm loc}(\mathbb{R}_+, L^2(\mathbb{R}^3)) \cap W^{1,1}_{\rm loc}(\mathbb{R}_+, \mathcal{C})$, and $-\gamma^0_{\rm per} \leqslant Q^0 \leqslant 1 - \gamma^0_{\rm per}$ with $Q^0 \in \mathcal{Q}$, the dynamics

$$Q(t) = U_0(t) Q^0 U_0(t)^* - \mathrm{i} \int_0^t U_0(t-s) \Big[v_{\rm c}(\rho_{Q(s)} - \nu(s)), \gamma^0_{\rm per} + Q(s) \Big] U_0(t-s)^* ds$$

has a unique solution in $C^0(\mathbb{R}_+, \mathcal{Q})$. For all $t \geq 0$, $\mathrm{Tr}_0(Q(t)) = \mathrm{Tr}_0(Q^0)$ and $-\gamma^0_{\rm per} \leqslant Q(t) \leqslant 1 - \gamma^0_{\rm per}$.

• Idea of the proof: (i) short time existence and uniqueness by a fixed-point argument; (ii) extension to all times by controlling the energy

$$\mathcal{E}(t, Q) = \mathrm{Tr}_0(H^0_{\rm per} Q) - D(\rho_Q, \nu(t)) + \frac{1}{2} D(\rho_Q, \rho_Q)$$

• Classical solution well posed under stronger assumptions on Q^0, ν

Macroscopic dielectric permittivity (1)

Starting from $Q^0 = 0$, the nonlinear dynamics can be rewritten as

$$Q(t) = Q_{1,v_c(\rho_Q - \nu)}(t) + \widetilde{Q}_{2,v_c(\rho_Q - \nu)}(t)$$

In terms of electronic densities: $\left[(1+\mathcal{L})(\nu - \rho_Q)\right](t) = \nu(t) - r_2(t)$

Properties of the operator $\mathcal{L}$

For any $0 < \Omega < g$, the operator $\mathcal{L}$ is a non-negative, bounded, self-adjoint operator on the Hilbert space

$$\mathscr{H}_\Omega = \left\{ \varrho \in L^2(\mathbb{R}, \mathcal{C}) \,\middle|\, \mathrm{supp}(\mathcal{F}_{t,x}\varrho) \subset [-\Omega, \Omega] \times \mathbb{R}^3 \right\},$$

endowed with the scalar product

$$\langle \varrho_2, \varrho_1 \rangle_{L^2(\mathcal{C})} = 4\pi \int_{-\Omega}^{\Omega} \int_{\mathbb{R}^3} \frac{\overline{\mathcal{F}_{t,x}\varrho_2(\omega,k)}\mathcal{F}_{t,x}\varrho_1(\omega,k)}{|k|^2} \, d\omega \, dk.$$

Hence, $1 + \mathcal{L}$, considered as an operator on $\mathscr{H}_\Omega$, is invertible.

Macroscopic dielectric permittivity (2)

- **Linearization:** given $\nu \in \mathscr{H}_\Omega$, find ρ_ν such that $(1+\mathcal{L})(\nu - \rho_\nu) = \nu$
- **Homogenization limit:** spread the charge as $\nu_\eta(t,x) = \eta^3 \nu(t, \eta x)$ and consider the rescaled potential

$$W_\nu^\eta(t,x) = \eta^{-1} v_{\mathrm{c}}(\nu_\eta - \rho_{\nu_\eta})\left(t, \eta^{-1} x\right)$$

When $\mathcal{L} = 0$, the potential is $W_\nu^\eta = v_{\mathrm{c}}(\nu)$

[CS12, Proposition 14]

The rescaled potential W_ν^η converges weakly in $\mathcal{H}_\Omega$ to the unique solution W_ν in $\mathcal{H}_\Omega$ to the equation

$$-\mathrm{div}\Big(\varepsilon_{\mathrm{M}}(\omega) \nabla \left[\mathcal{F}_t W_\nu\right](\omega, \cdot)\Big) = 4\pi \left[\mathcal{F}_t \nu\right](\omega, \cdot)$$

where $\varepsilon_{\mathrm{M}}(\omega)$ (for $\omega \in (-g, g)$) is a smooth mapping with values in the space of symmetric 3×3 matrices, and satisfying $\varepsilon_{\mathrm{M}}(\omega) \geqslant 1$.

- The matrix $\varepsilon_{\mathrm{M}}(\omega)$ can be expressed using the Bloch decomposition

Perspectives

Perspectives and open issues

- Metallic systems (no gap: many estimates break down)
- Longtime behavior of the defect
- Influence of electric and magnetic fields (rather than a local perturbation as was the case here)
- Interaction of electronic defects with phonons (lattice vibrations)
- GW methods (the polarization matrix enters the definition of the self-energy)