

# The microscopic origin of the macroscopic dielectric permittivity of crystals

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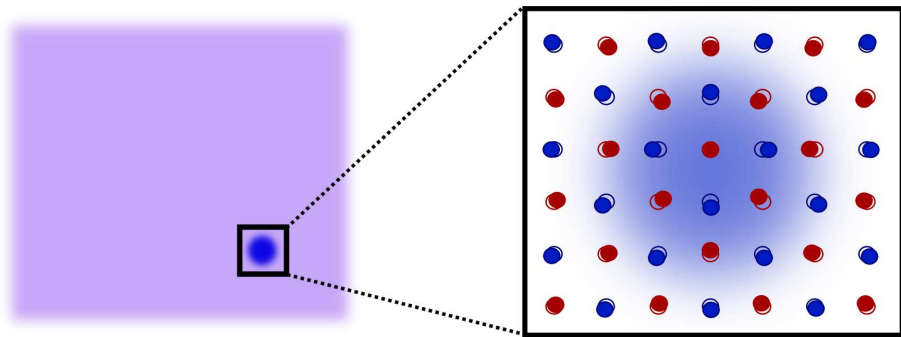
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*Work in collaboration with E. Cancès and M. Lewin*

GDRE ConEDP Meeting 2013

# 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	$\nu$	$\mathbf{D}$ , $\text{div } \mathbf{D} = 4\pi\nu$
polarization	$\delta\rho$	$\mathbf{P}$ , $\text{div } \mathbf{P} = 4\pi\delta\rho$
total	$\rho$	$\mathbf{E}$ , $\text{div } \mathbf{E} = 4\pi\rho$

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

- **Constitutive equation:**  $\epsilon_M = 3 \times 3$  symmetric real matrix with  $\epsilon_M \geq 1$

$$\mathbf{D} = \epsilon_M \mathbf{E} \iff \mathbf{P} = (\epsilon_M - 1)\mathbf{E} = (1 - \epsilon_M^{-1})\mathbf{D}$$

- **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,

$$-\text{div} \left( \epsilon_M(\omega) \nabla \widehat{W}(\omega) \right) = 4\pi \widehat{\nu}(\omega)$$

# 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  $\Sigma(12) = i \int d(34)W(1^+3)G(14)\Gamma(42; 3)$
  - **Screened interaction**  $W(12) = v(12) + \int d(34)W(13)P(34)v(42)$
  - Irreducible polarization  $P(12) = -i \int d(34)G(23)G(42)\Gamma(34; 1)$
  - Vertex function  $\Gamma(12; 3) = \delta(12)\delta(13) + \int d(4567) \frac{\delta\Sigma(12)}{\delta G(45)} G(46)G(75)\Gamma(67; 3)$

## 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. Poincaré-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  $\lambda_i \rightarrow 0$
- 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.  $\sum_{i \geq 1} |\lambda_i|^2 < \infty$ . If  $A$  is self-adjoint, its integral kernel is in  $L^2(\mathbb{R}^3 \times \mathbb{R}^3)$

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

# 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  $0 \leq \gamma \leq 1$  and  $\text{Tr}(\gamma) = N$ . In some orthonormal basis of  $L^2(\mathbb{R}^3)$ ,

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

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

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

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



# The Hartree model for finite systems

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

where

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

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

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

## Variational formulation

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

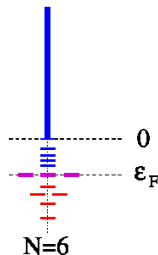
- More general models of density functional theory: correction term  $E_{\text{xc}}(\gamma)$

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

# Euler-Lagrange equations for the Hartree model

**Nonlinear** eigenvalue problem,  $\varepsilon_F$  Lagrange multiplier of  $\text{Tr}(\gamma) = N$

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



When  $\varepsilon_N < \varepsilon_{N+1}$  (gap):

$$\left\{ \begin{array}{l} \gamma^0 = 1_{(-\infty, \varepsilon_F]}(H^0), \\ H^0 = -\frac{1}{2}\Delta + V^0, \\ -\Delta V^0 = 4\pi(\rho^{\text{nuc}} - \rho^0), \end{array} \right.$$

# The Hartree model for crystals (1)

- **Thermodynamic limit**, periodic nuclear density  $\rho_{\text{per}}^{\text{nuc}}$ , lattice  $\mathcal{R} \simeq (a\mathbb{Z})^3$  with unit cell  $\Gamma$ , reciprocal lattice  $\mathcal{R}^* \simeq \left(\frac{2\pi}{a}\mathbb{Z}\right)^3$  with unit cell  $\Gamma^*$

- **Bloch-Floquet transform**: unitary  $L^2(\mathbb{R}^3) \rightarrow \int_{\Gamma^*}^{\oplus} L^2_{\text{per}}(\Gamma) dq$

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

- Any operator **commuting with the spatial translations**  $T_R$  ( $R \in \mathcal{R}$ ) can be decomposed as  $(Af)_q = A_q f_q$ , and  $\sigma(A) = \bigcup_{q \in \Gamma^*} \sigma(A_q)$

- **Bloch matrices**:  $A_{K,K'}(q) = \langle e_K, A_q e_{K'} \rangle_{L^2_{\text{per}}(\Gamma)}$ ,  $e_K(x) = |\Gamma|^{-1/2} e^{iK \cdot x}$

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

[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

$$\left\{ \begin{array}{l} \gamma_{\text{per}}^0 = \mathbf{1}_{(-\infty, \varepsilon_F]}(H_{\text{per}}^0), \quad \rho_{\text{per}}^0 = \rho \gamma_{\text{per}}^0, \\ H_{\text{per}}^0 = -\frac{1}{2}\Delta + V_{\text{per}}^0, \\ -\Delta V_{\text{per}}^0 = 4\pi(\rho_{\text{per}}^{\text{nuc}} - \rho_{\text{per}}^0), \quad \int_{\Gamma} \rho_{\text{per}}^0 = \int_{\Gamma} \rho_{\text{per}}^{\text{nuc}} = N \end{array} \right.$$

More explicit expressions using the Bloch decomposition

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

$$(\gamma_{\text{per}}^0)_q = \sum_{n=1}^{+\infty} \mathbf{1}_{\{\varepsilon_{n,q} \leq \varepsilon_F\}} |u_{n,q}\rangle \langle u_{n,q}|$$

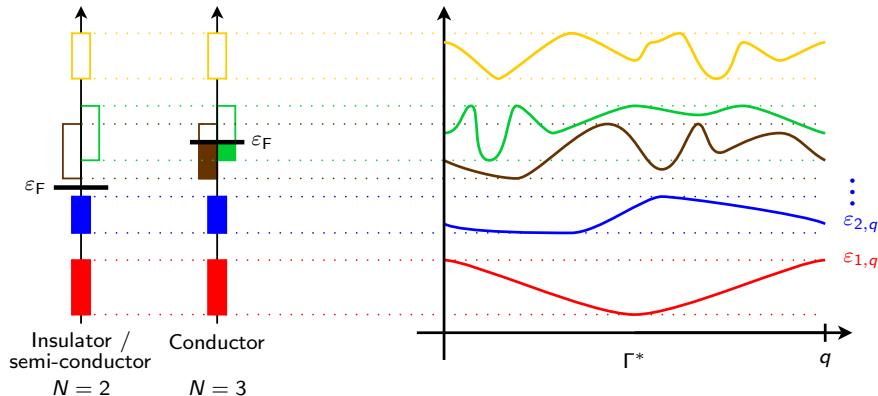
$$\text{Fermi level obtained from } N = \frac{1}{|\Gamma^*|} \sum_{n=1}^{+\infty} |\{q \in \Gamma^* \mid \varepsilon_{n,q} \leq \varepsilon_F\}|$$

# The Hartree model for crystals (3)

The spectrum of the periodic Hamiltonian is composed of bands

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

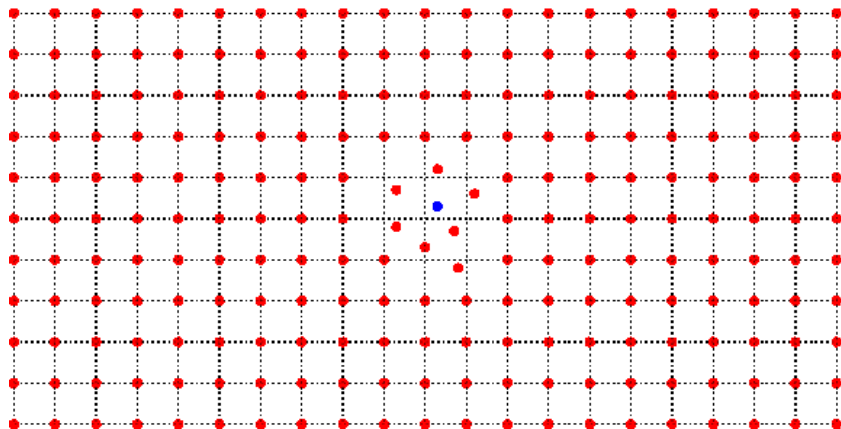
Assume in the sequel that  $g = \Sigma_{N+1}^- - \Sigma_N^+ > 0$  (insulator)



# Defects in crystals

# Local defects (1)

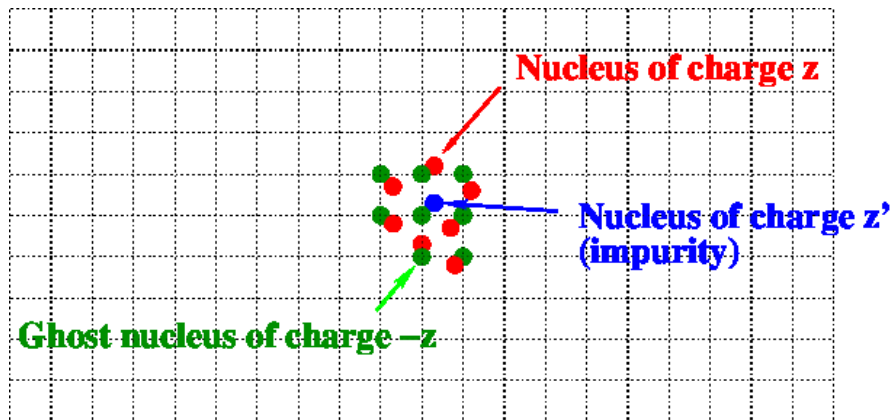
- Local perturbation: nuclear charge defect  $\rho_{\text{per}}^{\text{nuc}} + \nu$



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

## Local defects (2)

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



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



# Defects in crystals (1)

- A thermodynamic limit shows that  $Q_\nu$  can be thought of as some defect state **embedded in the periodic medium**

$$Q_\nu = \operatorname{argmin}_{\substack{Q \in \mathcal{Q} \\ -\gamma_{\text{per}}^0 \leq Q \leq 1 - \gamma_{\text{per}}^0}} \left\{ \operatorname{Tr}_0 (H_{\text{per}}^0 Q) - \int_{\mathbb{R}^3} \rho_Q(\nu \star |\cdot|^{-1}) + \frac{1}{2} D(\rho_Q, \rho_Q) \right\}$$

where, defining  $Q^{--} = \gamma_{\text{per}}^0 Q \gamma_{\text{per}}^0$  and  $Q^{++} = (1 - \gamma_{\text{per}}^0) Q (1 - \gamma_{\text{per}}^0)$ ,

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

- Generalized trace  $\operatorname{Tr}_0(Q) = \operatorname{Tr}(Q^{++}) + \operatorname{Tr}(Q^{--})$
- 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**

$$\mathrm{Tr}_0((H_{\mathrm{per}}^0 - \varepsilon_F)Q) := \mathrm{Tr}(|H_{\mathrm{per}}^0 - \varepsilon_F|^{1/2}(Q^{++} - Q^{--})|H_{\mathrm{per}}^0 - \varepsilon_F|^{1/2})$$

[CL, Theorem 1]

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

$$Q_{\nu, \varepsilon_F} = \mathbf{1}_{(-\infty, \varepsilon_F)} (H_{\mathrm{per}}^0 + (\rho_{\nu, \varepsilon_F} - \nu) \star |\cdot|^{-1}) - \mathbf{1}_{(-\infty, \varepsilon_F]} (H_{\mathrm{per}}^0) + \delta,$$

where  $\delta$  is a finite-rank self-adjoint operator on  $L^2(\mathbb{R}^3)$  such that  $0 \leq \delta \leq 1$  and  $\mathrm{Ran}(\delta) \subset \mathrm{Ker}(H_{\mathrm{per}}^0 + (\rho_{\nu, \varepsilon_F} - \nu) \star |\cdot|^{-1} - \varepsilon_F)$ .

When  $\nu$  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

$$i \frac{d\gamma(t)}{dt} = \left[ H_{\gamma(t)}^0, \gamma(t) \right], \quad H_{\gamma}^0 = -\frac{1}{2} \Delta + V_{\text{nuc}} + v_c(\rho_{\gamma})$$

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

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

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

$$i \frac{d\gamma}{dt} = \left[ H_{\gamma}^v, \gamma \right], \quad H_{\gamma}^v(t) = H_{\text{per}}^0 + v_c(\rho_Q(t) - \nu(t))$$

[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

$$i \frac{dQ(t)}{dt} = [H_{\text{per}}^0 + v_c(\rho_{Q(t)} - \nu(t)), \gamma_{\text{per}}^0 + Q(t)]$$

Denote  $U_0(t) = e^{-itH_{\text{per}}^0}$  the free evolution.

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

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

Mild formulation for the **nonlinear** dynamics

Replace  $v(s)$  by  $v_c(\rho_{Q(s)} - \nu(s))$  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  $v = v_c(\rho)$  with  $\rho \in L^1_{\text{loc}}(\mathbb{R}_+, L^2(\mathbb{R}^3) \cap \mathcal{C})$ .

In addition,  $\text{Tr}_0(Q(t)) = \text{Tr}_0(Q^0)$ , and, if  $-\gamma_{\text{per}}^0 \leq Q^0 \leq 1 - \gamma_{\text{per}}^0$ , then  $-\gamma_{\text{per}}^0 \leq Q(t) \leq 1 - \gamma_{\text{per}}^0$ .

This result is based on a series of technical results

- boundedness of the potential:  $v \in L^1_{\text{loc}}(\mathbb{R}_+, L^\infty(\mathbb{R}^3))$
- stability of time evolution:  $\frac{1}{\beta} \|Q\|_{\mathcal{Q}} \leq \|U_0(t)QU_0(t)^*\|_{\mathcal{Q}} \leq \beta \|Q\|_{\mathcal{Q}}$
- commutator estimates with  $\gamma_{\text{per}}^0$ :  $\|i[v, \gamma_{\text{per}}^0]\|_{\mathcal{Q}} \leq C_{\text{com}} \|v\|_{\mathcal{C}'}$
- commutator estimates in  $\mathcal{Q}$ :  $\|i[v_c(\varrho), Q]\|_{\mathcal{Q}} \leq C_{\text{com}, \mathcal{Q}} \|\varrho\|_{L^2 \cap \mathcal{C}} \|Q\|_{\mathcal{Q}}$

## Dyson expansion and linear response

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

$$Q_{1,v}(t) = -i \int_0^t U_0(t-s) [v(s), \gamma_{\text{per}}^0 + U_0(s)Q^0 U_0(s)^*] U_0(t-s)^* ds,$$
$$Q_{n,v}(t) = -i \int_0^t U_0(t-s) [v(s), Q_{n-1,v}(s)] U_0(t-s)^* ds \quad \text{for } n \geq 2$$

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  $\text{Tr}_0(Q_{n,v}(t)) = 0$ ,

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

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  $\eta \rightarrow 0$

$$Q_{1,v}^\eta(t) = -i \int_{-\infty}^t U_0(t-s) [v(s), \gamma_{\text{per}}^0] U_0(t-s)^* e^{-\eta(t-s)} ds$$

- **polarization** operator  $\chi_0^\eta : \begin{cases} L^1(\mathbb{R}, \mathcal{C}') & \rightarrow C_b^0(\mathbb{R}, L^2(\mathbb{R}^3) \cap \mathcal{C}) \\ v & \mapsto \rho_{Q_{1,v}^\eta} \end{cases}$
- linear response operator  $\mathcal{E}^\eta = v_c^{1/2} \chi_0^\eta v_c^{1/2}$  acting on  $L^1(\mathbb{R}, L^2(\mathbb{R}^3))$

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

- **Bloch decomposition:** for a.e.  $(\omega, q) \in \mathbb{R} \times \Gamma^*$  and any  $K \in \mathcal{R}^*$ ,  
$$\mathcal{F}_{t,x}(\mathcal{E}^\eta f)(\omega, q + K) = \sum_{K' \in \mathcal{R}^*} \mathcal{E}_{K,K'}^\eta(\omega, q) \mathcal{F}_{t,x} f(\omega, q + K')$$

[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  $\mathcal{E}^\eta$  read

$$\mathcal{E}_{K,K'}^\eta(\omega, q) = \frac{\mathbf{1}_{\Gamma^*}(q)}{|\Gamma|} \frac{|q + K'|}{|q + K|} T_{K,K'}^\eta(\omega, q),$$

where the continuous functions  $T_{K,K'}^\eta$  are uniformly bounded:

$$T_{K,K'}^\eta(\omega, q) = \sum \int_{\Gamma^*} \frac{\langle u_{m,q'}, e^{-iK \cdot x} u_{n,q+q'} \rangle_{L^2_{\text{per}}} \langle u_{n,q+q'}, e^{iK' \cdot x} u_{m,q'} \rangle_{L^2_{\text{per}}}}{\varepsilon_{n,q+q'} - \varepsilon_{m,q'} - \omega - i\eta} dq'$$

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

- The Bloch matrices of the standard linear response are recovered as  $\eta \rightarrow 0$ , the convergence being in  $\mathcal{S}'(\mathbb{R} \times \mathbb{R}^3)$
- 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  $\nu \in L^1_{\text{loc}}(\mathbb{R}_+, L^2(\mathbb{R}^3)) \cap W^{1,1}_{\text{loc}}(\mathbb{R}_+, \mathcal{C})$ , and  $-\gamma_{\text{per}}^0 \leq Q^0 \leq 1 - \gamma_{\text{per}}^0$  with  $Q^0 \in \mathcal{Q}$ , the dynamics

$$Q(t) = U_0(t)Q^0U_0(t)^* - i \int_0^t U_0(t-s) \left[ v_{\mathcal{C}}(\rho_{Q(s)} - \nu(s)), \gamma_{\text{per}}^0 + Q(s) \right] U_0(t-s)^* ds$$

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

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

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

- **Classical** solution well posed under stronger assumptions on  $Q^0, \nu$

# Macroscopic dielectric permittivity (1)

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

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

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

## 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

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

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  $\mathcal{H}_\Omega$ , is invertible.

## Macroscopic dielectric permittivity (2)

- **Linearization:** given  $\nu \in \mathcal{H}_\Omega$ , find  $\rho_\nu$  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

$$W_\nu^\eta(t, x) = \eta^{-1} v_c(\nu_\eta - \rho_{\nu_\eta})(t, \eta^{-1} x)$$

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

### [CS12, Proposition 14]

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

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

where  $\varepsilon_M(\omega)$  (for  $\omega \in (-g, g)$ ) is a smooth mapping with values in the space of symmetric  $3 \times 3$  matrices, and satisfying  $\varepsilon_M(\omega) \geq 1$ .

- The matrix  $\varepsilon_M(\omega)$  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)