Time evolution of defects in crystals

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Workshop on “Mathematical and Numerical Analysis of Electronic Structure Models”
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

<table>
<thead>
<tr>
<th>density</th>
<th>electric field</th>
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<tbody>
<tr>
<td>$\nu$</td>
<td>$\mathbf{D}$, div $\mathbf{D} = 4\pi \nu$</td>
</tr>
<tr>
<td>$\delta \rho$</td>
<td>$\mathbf{P}$, div $\mathbf{P} = 4\pi \delta \rho$</td>
</tr>
<tr>
<td>$\rho$</td>
<td>$\mathbf{E}$, div $\mathbf{E} = 4\pi \rho$</td>
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</tbody>
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- **Constitutive equation**: $\varepsilon_M = 3 \times 3$ symmetric real matrix with $\varepsilon_M \geq 1$

\[
\mathbf{D} = \varepsilon_M \mathbf{E} \quad \iff \quad \mathbf{P} = (\varepsilon_M - 1) \mathbf{E} = (1 - \varepsilon_M^{-1}) \mathbf{D}
\]

- **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,

\[
-\text{div} \left( \varepsilon_M(\omega) \nabla \hat{W}(\omega) \right) = 4\pi \hat{\nu}(\omega)
\]
Outline

Some background material
- Description of perfect crystals
- Crystals with defects: static picture

Time evolution of defects in crystals: effective perturbations
- Response to an effective potential
- Linear response and definition of the polarization
- Static polarization in some adiabatic limit

Time evolution of defects in crystals: nonlinear dynamics
- Well-posedness of the nonlinear Hartree dynamics
- Definition of the macroscopic dielectric permittivity

Some background material
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 \( \psi(x_1, \ldots, x_N) = (N!)^{-1/2} \det(\phi_i(x_j))_{1 \leq i,j \leq N} \),

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

- 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 \( T(\gamma) = \frac{1}{2} \text{Tr}(|\nabla|\gamma|\nabla|) = \frac{1}{2} \sum_{i=1}^{+\infty} n_i \| \nabla \phi_i \|^2_{L^2(\mathbb{R}^3)} \)
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

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

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

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

**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 \( E_{\text{xc}}(\gamma) \)

Euler-Lagrange equations for the Hartree model

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

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

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

$$
\begin{cases}
\gamma^0 = 1_{(-\infty, \varepsilon_F]}(H^0), \\
H^0 = -\frac{1}{2} \Delta + V^0, \\
-\Delta V^0 = 4\pi (\rho^{\text{nuc}} - \rho^0), 
\end{cases}
$$
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 $L^2(\mathbb{R}^3) \rightarrow \bigoplus_{\Gamma^*} L^2_{\text{per}}(\Gamma) \, dq$

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

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

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

\[
\mathcal{F}(A\nu)(q + K) = \sum_{K' \in \mathcal{R}^*} A_{K,K'}(q) \mathcal{F}\nu(q + K')
\]

The Hartree model for crystals (2)

Nonlinear eigenvalue problem

\[
\begin{align*}
\gamma^0_{\text{per}} &= 1_{(-\infty, \varepsilon_F]}(H^0_{\text{per}}), \\
\rho^0_{\text{per}} &= \rho_{\gamma^0_{\text{per}}}, \\
H^0_{\text{per}} &= -\frac{1}{2}\Delta + V^0_{\text{per}}, \\
-\Delta V^0_{\text{per}} &= 4\pi(\rho^{\text{nuc}}_{\text{per}} - \rho^0_{\text{per}}), \\
\int \rho^0_{\text{per}} &= \int \rho^{\text{nuc}}_{\text{per}} = N
\end{align*}
\]

More explicit expressions using the Bloch decomposition

\[
(H^0_{\text{per}})_q = -\frac{1}{2}\Delta - iq \cdot \nabla + \frac{|q|^2}{2} + V^0_{\text{per}} = \sum_{n=1}^{+\infty} \varepsilon_{n,q} |u_{n,q}\rangle \langle u_{n,q}|
\]

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

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

$$\sigma(H) = \bigcup_{n \geq 1} [\Sigma^-, \Sigma^+]$$

$$\Sigma^- = \min_{q \in \Gamma^*} \varepsilon_{n,q}, \quad \Sigma^+ = \max_{q \in \Gamma^*} \varepsilon_{n,q}$$

Assume in the sequel that $g = \Sigma^-_{N+1} - \Sigma^+_N > 0$ (insulator)
Defects in crystals

- **Nuclear charge defect** $\rho^{\text{nuc}}_{\text{per}} + \nu$, expected ground state $\gamma = \gamma^0_{\text{per}} + Q_\nu$

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

$$Q_\nu = \arg\min_{Q \in Q} \left\{ \text{Tr}_0 \left( H^0_{\text{per}} Q \right) - \int_{\mathbb{R}^3} \rho_Q (\nu \ast | \cdot |^{-1}) + \frac{1}{2} D(\rho_Q, \rho_Q) \right\}$$

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

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

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

- Density $\rho_Q \in L^2(\mathbb{R}^3) \cap \mathcal{C}$


Time evolution of defects in crystals: effective perturbations
Defects in a time-dependent setting

**Formal thermodynamic limit:** state $\gamma(t) = \gamma^0_{\text{per}} + Q(t)$, Hamiltonian

$$H^\nu_{\gamma}(t) = H^0_{\text{per}} + \nu_c(\rho Q(t) - \nu(t)),$$

$$\nu_c(\rho) = \rho \star |\cdot|^{-1}$$

and dynamics (von Neumann equation)

$$i \frac{d\gamma}{dt} = [H^\nu_{\gamma}, \gamma]$$

**Classical formulation: nonlinear dynamics**

$$i \frac{dQ(t)}{dt} = [H^0_{\text{per}} + \nu_c(\rho Q(t) - \nu(t)), \gamma^0_{\text{per}} + Q(t)]$$

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

**Mild formulation for an effective potential $\nu(t)$**

$$Q(t) = U_0(t) Q^0 U_0(t)^* - i \int_0^t U_0(t - s)[\nu(s), \gamma^0_{\text{per}} + Q(s)] U_0(t - s)^* \, ds$$
Well-posedness of the mild formulation

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

[CS12, Proposition 1]

The integral equation has a unique solution in $C^0(\mathbb{R}_+, Q)$ for $Q^0 \in Q$ and $v = v_c(\rho)$ with $\rho \in L^1_{\text{loc}}(\mathbb{R}_+, L^2(\mathbb{R}^3) \cap C)$. In addition, $\text{Tr}_0(Q(t)) = \text{Tr}_0(Q^0)$, and, if $-\gamma_0^\text{per} \leq Q^0 \leq 1 - \gamma_0^\text{per}$, then $-\gamma_0^\text{per} \leq Q(t) \leq 1 - \gamma_0^\text{per}$.

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: $\frac{1}{\beta} \|Q\|_Q \leq \|U_0(t)QU_0(t)^*\|_Q \leq \beta \|Q\|_Q$
- commutator estimates with $\gamma_0^\text{per}$: $\|i[v, \gamma_0^\text{per}]\|_Q \leq C_{\text{com}} \|v\|_{C'}$
- commutator estimates in $Q$: $\|i[v_c(\rho), Q]\|_Q \leq C_{\text{com}, Q}\|\rho\|_{L^2 \cap C} \|Q\|_Q$
Dyson expansion and linear response

Response at all orders (formally): 

\[ Q(t) = U_0(t)Q^0U_0(t)^* + \sum_{n=1}^{+\infty} Q_{n,v}(t) \]

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

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

Obtained by plugging the formal decomposition into the integral equation

[CS12, Proposition 5]

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

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

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

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

- **polarization operator** $\chi_0^\eta$:
  \[ L^1(\mathbb{R}, \mathcal{C}') \rightarrow C_b(\mathbb{R}, L^2(\mathbb{R}^3) \cap \mathcal{C}) \]
  \[ v \mapsto \rho Q_{1,v}^\eta \]

- **linear response operator** $\mathcal{E}^\eta = v_c^{1/2} \chi_0 v_c^{1/2}$ 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 $K \in \mathcal{R}^*$,

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

Definition of the polarization (2)

[CS12, Proposition 7]

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

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

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 $\eta \to 0$, the convergence being in $L'({\mathbb{R}} \times {\mathbb{R}^3})$

- Static polarizability ($\omega = 0$) recovered in some **adiabatic** limit
Time evolution of defects in crystals: nonlinear dynamics
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 \(-\gamma_0^{\text{per}} \leq Q^0 \leq 1 - \gamma_0^{\text{per}} \) with \( Q^0 \in \mathcal{Q} \), the dynamics

\[
Q(t) = U_0(t)Q^0U_0(t)^* - i \int_0^t U_0(t-s) \left[ \nu_c(\rho_Q(s) - \nu(s)), \gamma_0^{\text{per}} + Q(s) \right] U_0(t-s)^* ds
\]

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 \(-\gamma_0^{\text{per}} \leq Q(t) \leq 1 - \gamma_0^{\text{per}} \).

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

\[
\mathcal{E}(t, Q) = \text{Tr}_0(H_0^{\text{per}} Q) - D(\rho_Q, \nu(t)) + \frac{1}{2} D(\rho_Q, \rho_Q)
\]

- Classical solution well posed under stronger assumptions on \( Q^0, \nu \)
Macroscopic dielectric permittivity (1)

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

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

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

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

endowed with the scalar product

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

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

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

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

[CS12, Proposition 14]

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

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

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)