# Interacting electrons in semiconductors and nanodevices: a mathematical introduction to Density Functional Theory

Eric CANCES

Ecole des Ponts and INRIA, Paris, France

IPAM, UCLA, April 1st, 2009

In the modelling and simulation of nanosystems, it is often necessary to take into account the interactions between quantum electrons
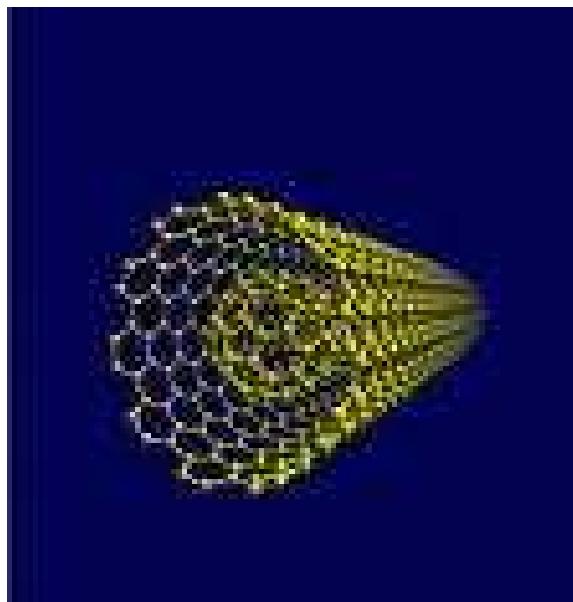
Fullerenes in nanotubes

(University of Tsubuka)
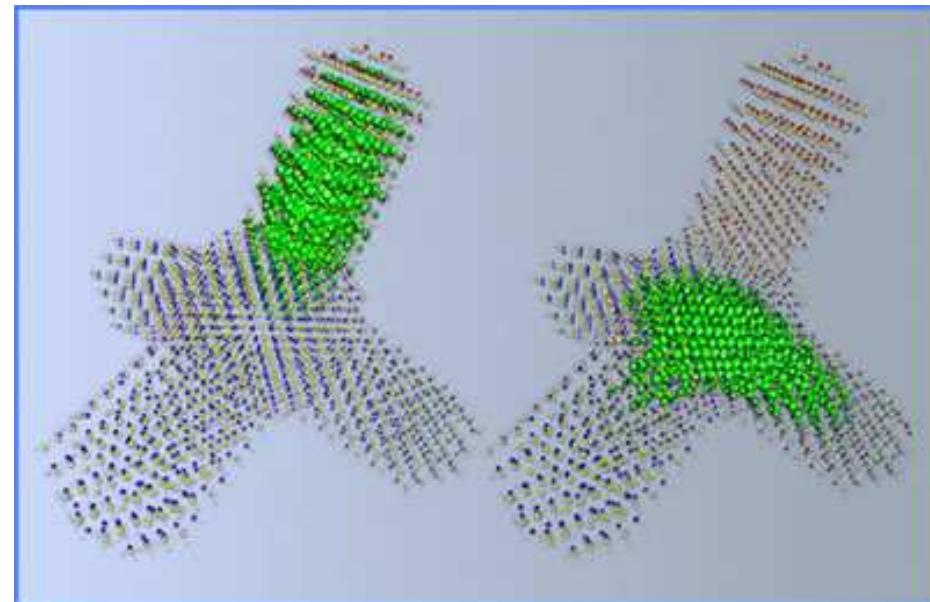
Nano-tetrapods

(Berkeley Lab)

Atomic units: $\hbar = 1$, $m_e = 1$, $e = 1$, $\dfrac{1}{4\pi\varepsilon_0} = 1$

Electrons and nuclei:

Electrons: mass $m_e = 1$, **charge** -1,

Nucleus k : mass $1836 \leq m_k \leq 400\,000$, **charge** $z_k \in \mathbb{N}^*$

Born-Oppenheimer approximation:

M classical point-like nuclei, N quantum elect. in their ground state

$$-\Delta V = 4\pi \left(\sum_{k=1}^{M} z_k \delta_{R_k} - \rho^0 \right)$$

$R_k \in \mathbb{R}^3$ position of the kth nucleus, ρ^0 electronic ground state density

Electronic ground state density (no spin for simplicity)

$$\rho^0(x) = N \int_{\mathbb{R}^{3(N-1)}} |\Psi^0(x, x_2, \cdots, x_N)|^2 \, dx_2 \cdots dx_N$$

where Ψ^0 is the ground state of the electronic Schrödinger equation

$$H_N \Psi^0 = E^0 \Psi^0$$

$$H_N = -\sum_{i=1}^{N} \frac{1}{2} \Delta_{x_i} - \sum_{i=1}^{N} \sum_{k=1}^{M} \frac{z_k}{|x_i - \mathbf{R}_k|} + \sum_{1 \leq i < j \leq N} \frac{1}{|x_i - x_j|}$$

- Pauli principle

$$\forall i < j, \qquad \Psi^0(\cdots, x_j, \cdots, x_i, \cdots) = -\Psi^0(\cdots, x_i, \cdots, x_j, \cdots)$$

- Normalization condition

$$\int_{\mathbb{R}^{3N}} |\Psi^0(x_1, \cdots, x_N)|^2 \, dx_1 \cdots dx_N = 1$$

1. **A short introduction to DFT (Density Functional Theory)**

   One of the most popular models in Physics

2. **Electronic structures of perfect crystals**

   I. Catto, C. Le Bris and P.-L. Lions, *Ann. IHP* 2001

3. **Electronic structures of crystals with local defects**

   E.C., A. Deleurence and M. Lewin, *Comm. Math. Phys.* 2008

   E.C., A. Deleurence and M. Lewin, *J. Phys.: Cond. Matter* 2008

4. **From micro and macro: the example of dielectric permittivity**

   E.C. and M. Lewin, submitted (arXiv 0903.1944)

1 - A short introduction to DFT

For a system of N non-interacting electrons: $H_N = \sum_{i=1}^{N} h_{x_i}$

$$h = -\frac{1}{2}\Delta - \sum_{k=1}^{M} \frac{z_k}{|\cdot - R_k|} \quad \textbf{on} \quad L^2(\mathbb{R}^3)$$

ε_F

ε_F

N=5   N=6
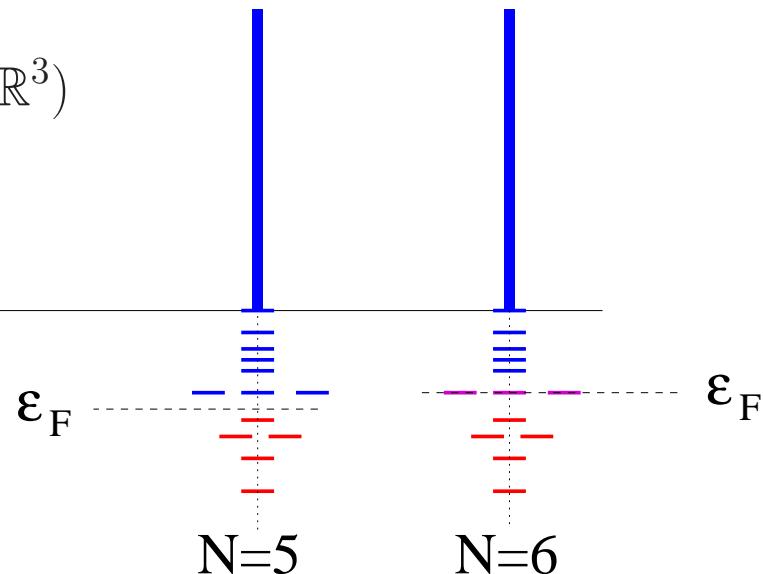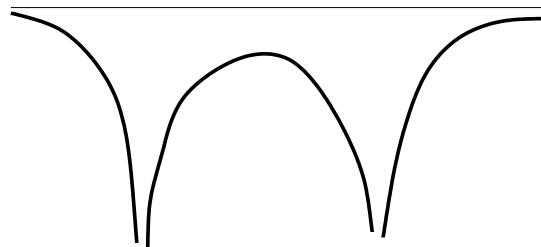
$$h\phi_i = \varepsilon_i\phi_i, \quad \int_{\mathbb{R}^3} \phi_i\phi_j = \delta_{ij}, \quad \varepsilon_1 < \varepsilon_2 \leq \varepsilon_3 \leq ... \text{ negative eigenvalues of } h$$

$$E^0 = \sum_{i=1}^{N} \varepsilon_i, \qquad \Psi^0(x_1, \cdots, x_N) = \frac{1}{\sqrt{N!}}\det(\phi_i(x_j)), \qquad \rho^0(x) = \sum_{i=1}^{N} |\phi_i(x)|^2$$

For non-interacting electrons, $E^0 = \displaystyle\sum_{i=1}^{N} \varepsilon_i$ and $\rho^0(x) = \displaystyle\sum_{i=1}^{N} |\phi_i(x)|^2$ with

$$
\begin{cases}
-\dfrac{1}{2}\Delta\phi_i + V^{\mathrm{ne}}\phi_i = \varepsilon_i\phi_i \\[2em]
\displaystyle\int_{\mathbb{R}^3} \phi_i\phi_j = \delta_{ij} \\[2em]
\varepsilon_1 < \varepsilon_2 \leq \cdots \leq \varepsilon_N \quad \textbf{lowest } N \textbf{ eigenvalues of } h = -\tfrac{1}{2}\Delta + V^{\mathrm{ne}}
\end{cases}
$$

$\longrightarrow$ **Linear eigenvalue problem**

$$
V^{\mathrm{ne}}(x) = -\sum_{k=1}^{M} \frac{z_k}{|x - R_k|}
$$

To deal with very large systems, it is convenient to introduce the
ground state density matrix

$$\gamma^0(x, x') = \sum_{i=1}^{N} \phi_i(x)\phi_i(x') \qquad \text{'insulating' case}$$

$\gamma^0(x, x')$ is the integral kernel of the rank-N orthogonal projector

$$\gamma^0 = \sum_{i=1}^{N} |\phi_i\rangle\langle\phi_i| \qquad \text{i.e.} \qquad \gamma^0\phi = \sum_{i=1}^{N} (\phi_i, \phi)_{L^2}\, \phi_i$$

From γ^0, one can compute the ground state density

$$\rho^0(x) = \gamma^0(x, x) \qquad (\text{note that } \mathrm{Tr}(\gamma^0) = N)$$

and the electronic ground state energy

$$E^0 = \mathrm{Tr}\left(\left(-\frac{1}{2}\Delta + V^{\mathrm{ne}}\right)\gamma^0\right) = \mathrm{Tr}\left(-\frac{1}{2}\Delta\gamma^0\right) + \int_{\mathbb{R}^3} \rho^0 V^{\mathrm{ne}}$$

When the Fermi level is a degenerate eigenvalue ('metals')

$$\gamma^0 = \sum_i n_i |\phi_i\rangle\langle\phi_i| \qquad \text{with} \qquad \begin{vmatrix} n_i = 1 \text{ if } \varepsilon_i < \varepsilon_{\text{F}}, \\ 0 \leq n_i \leq 1 \text{ if } \varepsilon_i = \varepsilon_{\text{F}}, \\ n_i = 0 \text{ if } \varepsilon_i > \varepsilon_{\text{F}}, \end{vmatrix} \qquad \sum_i n_i = N$$

and we still have

$$E^0 = \text{Tr}\left(\left(-\frac{1}{2}\Delta + V^{\text{ne}}\right)\gamma^0\right), \qquad \rho^0(x) = \gamma^0(x, x)$$

γ^0 is a positive self-adjoint operator s.t.

$0 \leq \gamma^0 \leq 1$ (all eigenvalues between 0 and 1)

$\text{Tr}(\gamma^0) = N$

ε_{F}

N=6
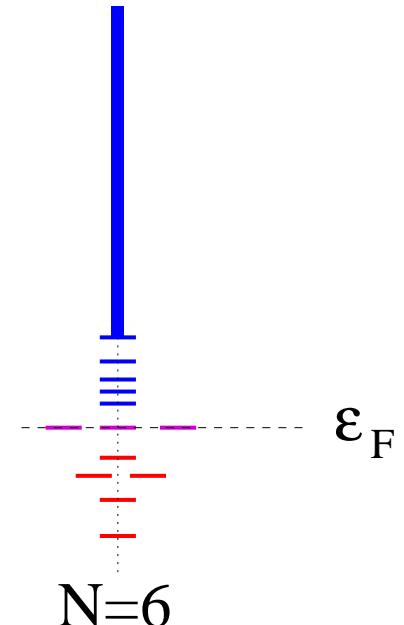
Density matrix formulation of the (non-interacting) GS problem

E^0 (resp. γ^0) is the minimum (resp. a minimizer) to

$$\inf \left\{ E(\gamma), \quad \gamma \in \mathcal{S}(L^2(\mathbb{R}^3)), \quad 0 \leq \gamma \leq 1, \quad \mathrm{Tr}(\gamma) = N, \quad \mathrm{Tr}(-\Delta\gamma) < \infty \right\}$$

$$E(\gamma) = \mathrm{Tr}(H\gamma) = \mathrm{Tr}\left(-\frac{1}{2}\Delta\gamma\right) + \int_{\mathbb{R}^3} \rho_\gamma V^{\mathrm{ne}}, \qquad \rho_\gamma(x) = \gamma(x, x)$$

The minimization set $\mathcal{C}_N$ is convex and any $\gamma \in \mathcal{C}_N$ can be written as

$$\gamma = \sum_{i=1}^{+\infty} m_i |\psi_i\rangle\langle\psi_i|$$

$$\int_{\mathbb{R}^3} \psi_i \psi_j = \delta_{ij}, \qquad 0 \leq m_i \leq 1, \qquad \sum_{i=1}^{+\infty} m_i = N, \qquad \psi_i \in H^1(\mathbb{R}^3)$$

The case of interacting electrons

In the Kohn-Sham model, the ground state energy, density and KS density matrix are obtained by solving

$$\inf \left\{ E^{\mathrm{KS}}(\gamma), \quad \gamma \in \mathcal{S}(L^2(\mathbb{R}^3)), \quad 0 \leq \gamma \leq 1, \quad \mathbf{Tr}(\gamma) = N, \quad \mathbf{Tr}(-\Delta\gamma) < \infty \right\}$$

$$E^{\mathrm{KS}}(\gamma) = \mathbf{Tr}\left(-\frac{1}{2}\Delta\gamma\right) + \int_{\mathbb{R}^3} \rho_\gamma V^{\mathrm{ne}} + \frac{1}{2}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \frac{\rho_\gamma(x)\rho_\gamma(x')}{|x-x'|}\,dx\,dx' + E^{\mathrm{xc}}[\rho_\gamma]$$

$$V^{\mathrm{ne}}(x) = -\sum_{k=1}^{M} \frac{z_k}{|x-\mathbf{R}_k|} \qquad \rho_\gamma(x) = \gamma(x,x)$$

E^{xc} : exchange-correlation functional

Hohenberg-Kohn theorem: existence of an exact XC functional

Prototypical approximate XC functional: $E_{\mathrm{X}\alpha}^{\mathrm{xc}}[\rho] = -C_{\mathrm{X}} \int_{\mathbb{R}^3} \rho^{4/3}(x)\,dx$

Kohn-Sham equations ('insulating' case)

$$
\begin{cases}
\gamma^0 = \sum_{i=1}^{N} |\phi_i\rangle\langle\phi_i| = 1_{(-\infty,\varepsilon_{\mathrm{F}}]}(H_{\rho^0}), \qquad \rho^0(x) = \gamma^0(x,x) = \sum_{i=1}^{N} |\phi_i(x)|^2 \\[2em]
H_{\rho^0}\phi_i = \varepsilon_i\phi_i \\[2em]
\displaystyle\int_{\mathbb{R}^3} \phi_i\phi_j = \delta_{ij} \\[2em]
\varepsilon_1 < \varepsilon_2 \le \cdots \le \varepsilon_N \quad \text{lowest } N \text{ eigenvalues of } H_{\rho^0} \\[2em]
H_{\rho^0} = -\dfrac{1}{2}\Delta + V_{\rho^0}^{\mathrm{KS}}, \qquad V_{\rho^0}^{\mathrm{KS}} = V^{\mathrm{ne}} + \rho^0 \star |\cdot|^{-1} - \dfrac{4}{3}C_{\mathrm{X}}\rho^{0\,1/3}
\end{cases}
$$

ε_{F}

N=5
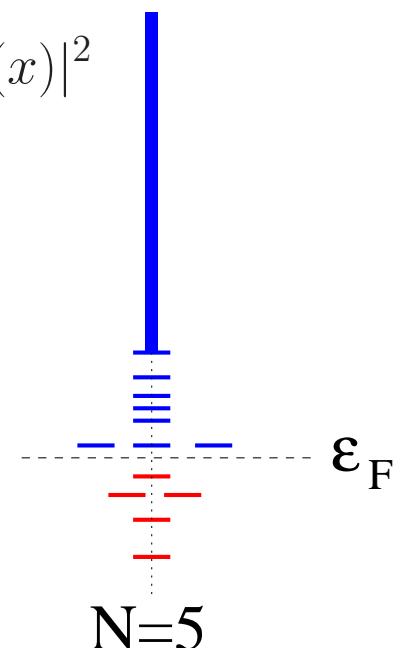
$\longrightarrow$ **Nonlinear eigenvalue problem**

2 - Electronic structure of perfect crystals

Reference model: reduced Hartree-Fock (Kohn-Sham with $E^{\mathrm{xc}} = 0$)

Existence of a ground state density matrix for neutral molecules

Uniqueness of the ground state density

Bulk limit for the perfect crystal
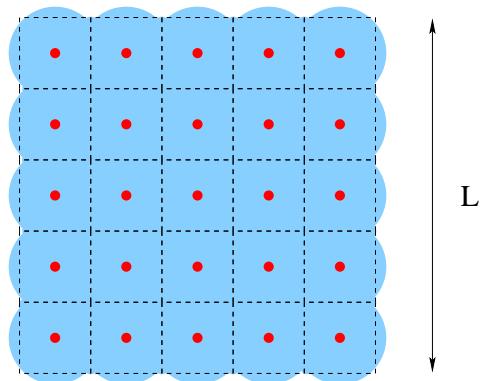
$$\left\{ \begin{array}{l} \rho_L^{\text{nuc}} = \displaystyle\sum_{\mathbf{R} \in \mathcal{R} \cap \Lambda_L} z\delta(\cdot - \mathbf{R}) \\[2em] zL^3 \text{ electrons} \end{array} \right. \qquad \longrightarrow \qquad \left| \begin{array}{l} E_L^0 \quad \text{the ground state total energy} \\[1.5em] \rho_L^0 \quad \text{the (unique) ground state density} \\[1.5em] \gamma_L^0 \quad \text{a ground state density matrix} \end{array} \right.$$

Catto-Le Bris-Lions (Ann. IHP 2001)

$$\lim_{L \to \infty} \frac{E_L^0}{L^3} = E_{\text{per}}^0, \qquad \rho_L^0 \xrightarrow[L \to \infty]{\text{in some sense}} \rho_{\text{per}}^0$$

Besides, E_{per}^0 and ρ_{per}^0 can be computed by solving some periodic reduced Hartree-Fock problem $(\star)$ posed on the set of $\mathcal{R}$-periodic density matrices

$$\forall (x, x') \in \mathbb{R}^3 \times \mathbb{R}^3, \quad \forall \mathbf{R} \in \mathcal{R}, \quad \gamma(x + \mathbf{R}, x' + \mathbf{R}) = \gamma(x, x')$$

E.C.-Deleurence-Lewin (Comm. Math. Phys. 2008)
The solution γ_{per}^0 to $(\star)$ is unique and

$$\gamma_L^0 \xrightarrow[L \to \infty]{\text{in some sense}} \gamma_{\text{per}}^0$$

Periodic mean-field Hamilonian

$$H_{\text{per}}^0 = -\frac{1}{2}\Delta + V_{\text{per}}^0$$

where V_{per}^0 denotes the periodic electrostatic potential generated by the periodic charge density $\rho_{\text{per}}^{\text{tot}} = \rho_{\text{per}}^0 - \rho_{\text{per}}^{\text{nuc}}$

$$\begin{cases} -\Delta V_{\text{per}}^0 = 4\pi \left(\rho_{\text{per}}^0 - \rho_{\text{per}}^{\text{nuc}} \right) \\[2em] V_{\text{per}}^0 \ \mathcal{R}\text{-periodic} \\[2em] \displaystyle\int_\Gamma V_{\text{per}}^0 = 0 \qquad \Gamma: \textbf{periodic cell} \end{cases}$$

$$\gamma_{\mathrm{per}}^{0} = 1_{(-\infty,\varepsilon_{\mathrm{F}}]}(H_{\mathrm{per}}^{0}) \qquad H_{\mathrm{per}}^{0} = -\frac{1}{2}\Delta + V_{\mathrm{per}}^{0}$$

z = 2

Insulator / Semiconductor

z = 3

Conductor

Conduction bands

Band gap

Valence bands

ε_{F}

γ

ε_{F}
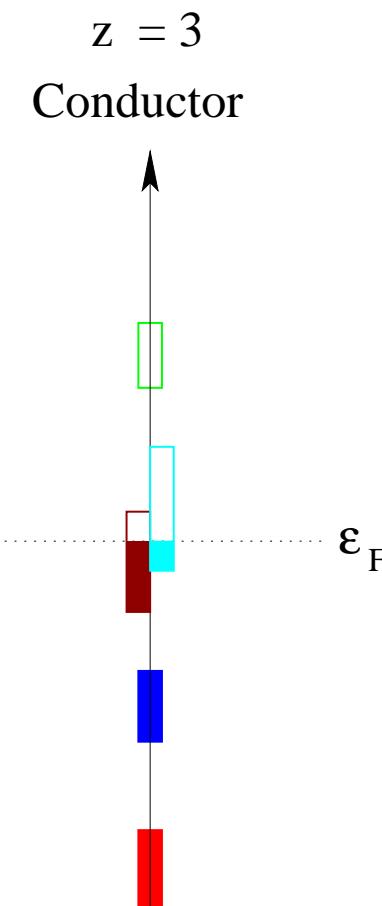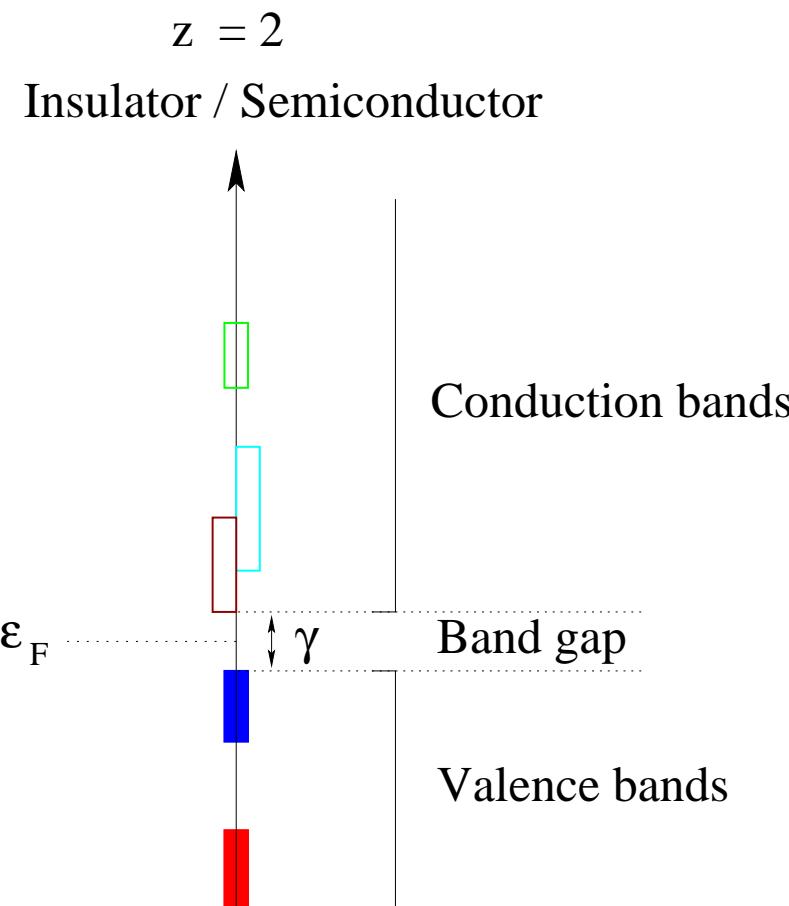
3 - Electronic structure of crystals with local defects

Example of a crystal with a local defect

Impurity with relaxation of the host crystal
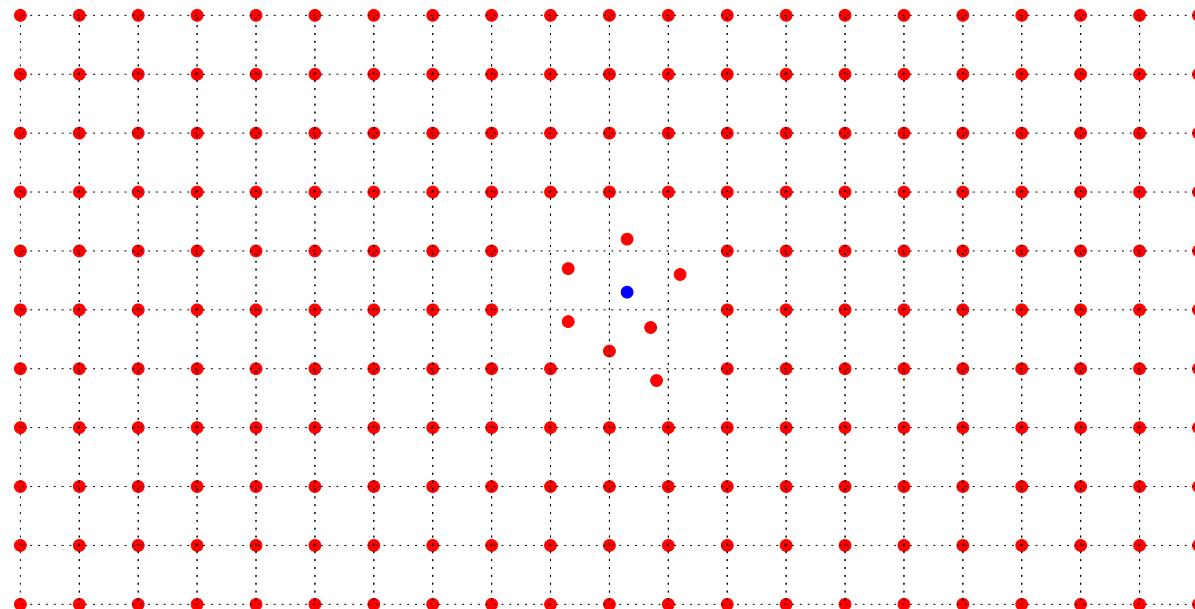
Supercell model (artificial - BvK - periodic boundary conditions)
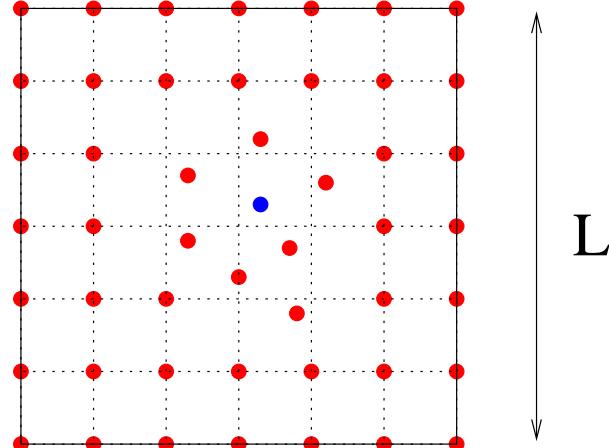
Drawbacks of the supercell model:
- spurious interactions between the defect and its periodic images
- inaccuracies for charged defects (e.g. jellium background)

Alternative: defect = pseudo-molecule embedded in the host crystal

$$\rho^{\mathrm{nuc}} = \rho_{\mathrm{per}}^{\mathrm{nuc}} + m \qquad\qquad \gamma^0 = \gamma_{\mathrm{per}}^0 + Q^{m,\varepsilon_{\mathrm{F}}} \qquad\qquad \rho^0 = \rho_{\mathrm{per}}^0 + \rho^{m,\varepsilon_{\mathrm{F}}}$$

Nuclear charge of the pseudo-molecule (u: relaxation field)

$$m(x) = z'\delta(x - u(0)) - z\delta(x) + \sum_{\mathbf{R}\in\mathcal{R}\setminus\{0\}} z\left(\delta(x - (\mathbf{R} + u(\mathbf{R}))) - \delta(x - \mathbf{R})\right)$$

Compute directly: $Q^{m,\varepsilon_{\mathrm{F}}}$ and $\rho^{m,\varepsilon_{\mathrm{F}}}$

Nucleus of charge z

Nucleus of charge z'
(impurity)

Ghost nucleus of charge –z
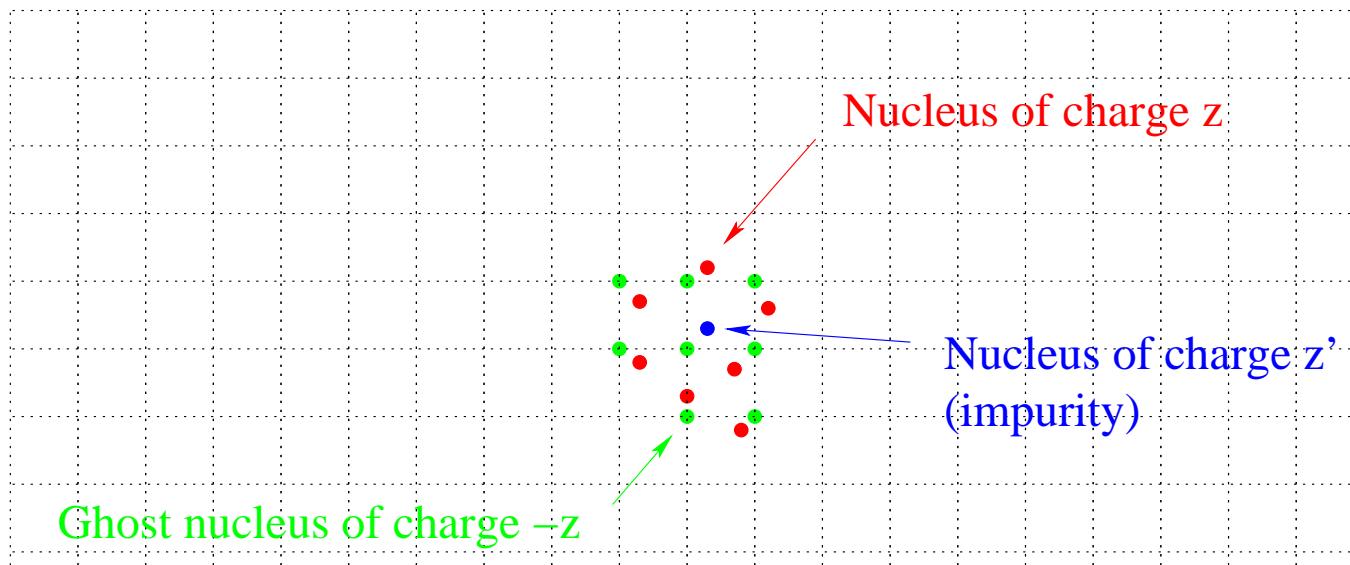
Bulk limit of the supercell model, with and without defect

$$E_{\text{sc},L}^{m,\varepsilon_{\text{F}}}, \rho_{\text{sc},L}^{m,\varepsilon_{\text{F}}}, \gamma_{\text{sc},L}^{m,\varepsilon_{\text{F}}} \qquad E_{\text{sc},L}^{0}, \rho_{\text{sc},L}^{0}, \gamma_{\text{sc},L}^{0} \qquad \varepsilon^{m,\varepsilon_{\text{F}}}, \rho^{m,\varepsilon_{\text{F}}}, Q^{m,\varepsilon_{\text{F}}}$$
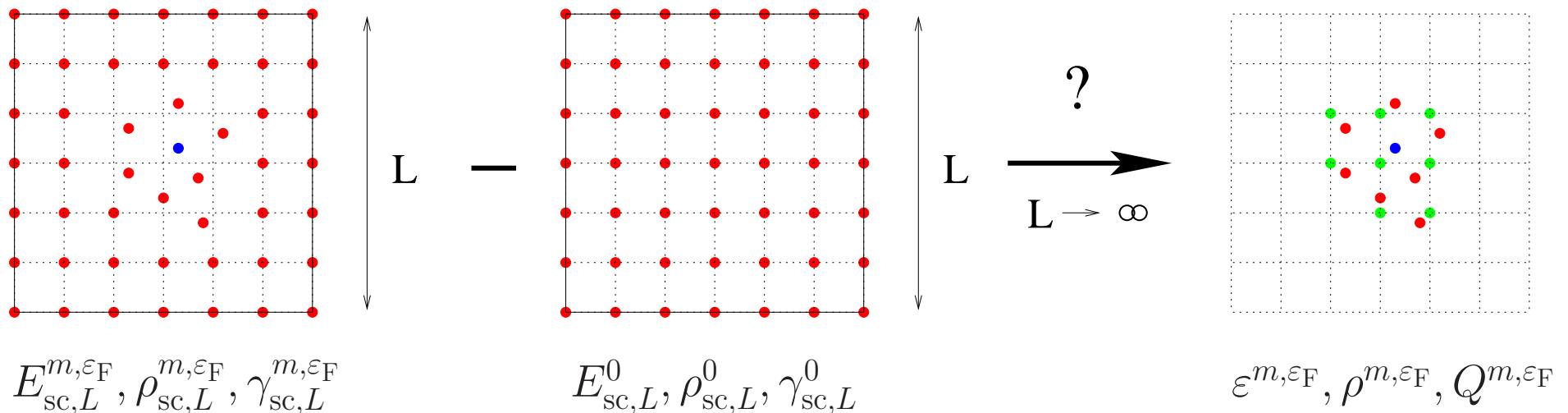
Theorem (E.C.-Deleurence-Lewin, Comm. Math. Phys. 2008). Assume that the host crystal is an insulator or a semiconductor. Then

1. $(\rho_{\text{sc},L}^{0}, \gamma_{\text{sc},L}^{0})$ converges to $(\rho_{\text{per}}^{0}, \gamma_{\text{per}}^{0})$ when L goes to infinity

2. $E_{\text{sc},L}^{m,\varepsilon_{\text{F}}} - E_{\text{sc},L}^{0}$ has a finite limit $\varepsilon^{m,\varepsilon_{\text{F}}}$

- A self-adjoint operator Q on $L^2(\mathbb{R}^3)$ is called **trace-class** if

$$Q = \sum_{i=1}^{+\infty} \lambda_i |\phi_i\rangle\langle\phi_i| \qquad \text{with} \qquad \sum_{i=1}^{+\infty} |\lambda_i| < \infty$$

If Q is trace-class then

$$\rho_Q(x) = Q(x,x) = \sum_{i=1}^{+\infty} \lambda_i |\phi_i(x)|^2 \in L^1(\mathbb{R}^3)$$

and

$$\int_{\mathbb{R}^3} \rho_Q = \text{Tr}(Q) = \sum_{i=1}^{+\infty} \lambda_i = \sum_{n\in\mathbb{N}} \langle e_n |Q| e_n \rangle$$

for any orthonormal basis $(e_n)_{n\in\mathbb{N}}$ of $L^2(\mathbb{R}^3)$.

- A self-adjoint operator Q on $L^2(\mathbb{R}^3)$ is called **Hilbert-Schmidt** if

$$Q = \sum_{i=1}^{+\infty} \lambda_i |\phi_i\rangle\langle\phi_i| \qquad \text{with} \qquad \sum_{i=1}^{+\infty} |\lambda_i|^2 < \infty$$

3. $\rho_{\mathrm{sc},L}^{m,\varepsilon_{\mathrm{F}}} - \rho_{\mathrm{sc},L}^{0}$ converges to $\rho^{m,\varepsilon_{\mathrm{F}}} \in L^2(\mathbb{R}^3)$

4. $\gamma_{\mathrm{sc},L}^{m,\varepsilon_{\mathrm{F}}} - \gamma_{\mathrm{sc},L}^{0}$ converges to some Hilbert-Schmidt operator $Q^{m,\varepsilon_{\mathrm{F}}}$ (u.t.e.)

5. $\rho^{m,\varepsilon_{\mathrm{F}}}$ is the density associated with $Q^{m,\varepsilon_{\mathrm{F}}}$ in the sense that

$$\forall W \text{ regular compactly supported,} \quad \mathrm{Tr}(WQ^{m,\varepsilon_{\mathrm{F}}}) = \int_{\mathbb{R}^3} \rho_{Q^{m,\varepsilon_{\mathrm{F}}}}(x)W(x)dx$$

6. Let $H_{\rho^{m,\varepsilon_{\mathrm{F}}}} = H_{\mathrm{per}}^{0} + (\rho^{m,\varepsilon_{\mathrm{F}}} - m) \star |\cdot|^{-1}$ be the mean-field electronic Hamiltonian of the crystal with the defect. If $\varepsilon_{\mathrm{F}} \notin \sigma(H_{\rho^{m,\varepsilon_{\mathrm{F}}}})$, then

$$\gamma^{0} = \gamma_{\mathrm{per}}^{0} + Q^{m,\varepsilon_{\mathrm{F}}} = 1_{(-\infty,\varepsilon_{\mathrm{F}}]}(H_{\rho^{m,\varepsilon_{\mathrm{F}}}})$$
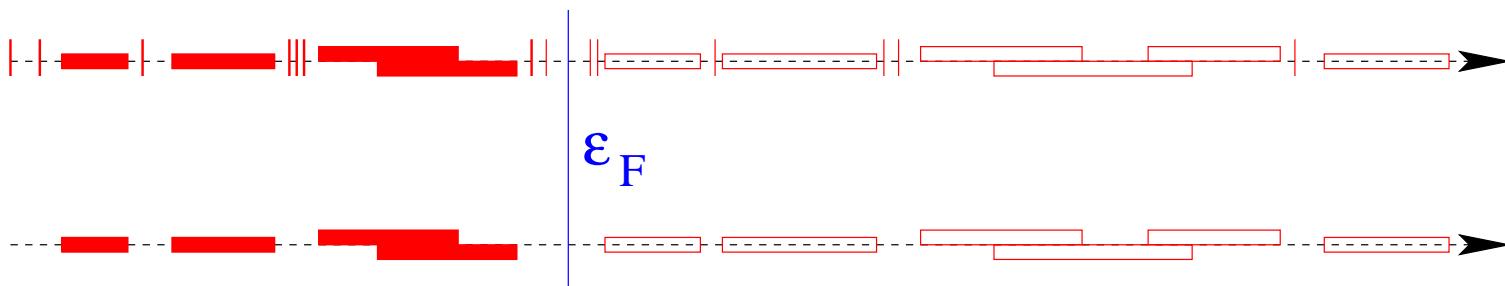
7. Denoting by $\mathcal{H}_- = \mathrm{Ran}(\gamma^0_{\mathrm{per}})$ and $\mathcal{H}_+ = \mathrm{Ran}(1 - \gamma^0_{\mathrm{per}})$ the occupied and virtual spaces of the host crystal, there exists

- an orthonormal basis $(\phi_i^-)_{i > N_-}$ of $\mathcal{H}_-$
- an orthonormal basis $(\phi_i^+)_{i > N_+}$ of $\mathcal{H}_+$

such that in the orthonormal basis $((\phi_i^-), (\phi_i^+))$ of $L^2(\mathbb{R}^3) = \mathcal{H}_- \widehat{\oplus} \mathcal{H}_+$

$$\gamma^0_{\mathrm{per}} = \left(\begin{array}{c|c} I & 0 \\ \hline 0 & 0 \end{array} \right) \qquad Q^{m,\varepsilon_{\mathrm{F}}} = \left(\begin{array}{c|c|c|c} -I_{N_-} & 0 & 0 & 0 \\ \hline 0 & \mathbf{diag}(-a_1, -a_2, \cdots) & 0 & \mathbf{diag}(b_1, b_2, \cdots) \\ \hline\hline 0 & 0 & I_{N_+} & 0 \\ \hline 0 & \mathbf{diag}(b_1, b_2, \cdots) & 0 & \mathbf{diag}(a_1, a_2, \cdots) \end{array} \right)$$

with

$$0 \le a_i < 1, \qquad \sum_{i=1}^{+\infty} a_i < +\infty, \qquad b_i = \sqrt{a_i(1 - a_i)}$$

$$\mathrm{Tr}([Q^{m,\varepsilon_{\mathrm{F}}}]^{++} + [Q^{m,\varepsilon_{\mathrm{F}}}]^{--}) = N_+ - N_-$$

8. $Q^{m,q}$ is a minimizer (and $\rho^{m,q}$ is the unique minimizing density) to some variational problem posed on the set of those Q's satisfying

$$
Q = \left(
\begin{array}{c|c}
\begin{array}{c} Q^{--} \leq 0 \\ \text{trace-class} \end{array} & \begin{array}{c} Q^{-+} \\ \text{Hilbert-Schmidt} \end{array} \\
\hline
\begin{array}{c} Q^{+-} \\ \text{Hilbert-Schmidt} \end{array} & \begin{array}{c} Q^{++} \geq 0 \\ \text{trace-class} \end{array}
\end{array}
\right), \qquad
\begin{array}{l}
Q^* = Q \\
0 \leq \gamma^0_{\text{per}} + Q \leq 1 \\
|\nabla| Q^{++} |\nabla| \text{ trace-class} \\
|\nabla| Q^{--} |\nabla| \text{ trace-class}
\end{array}
$$

In addition (E.C. and M. Lewin, 2009),

- $Q^{m,q}$ is not trace-class (except possibly when $\int_{\mathbb{R}^3} m = 0$)
  Reminiscent of the renormalization problem in QED
  (see Gravejat, Lewin, Séré for a mathematical analysis)
- $\rho^{m,q}$ is not an integrable function for anisotropic crystals

4 - Macroscopic dielectric permittivity

Let us insert a charge distribution $\rho_{\rm f}$ in the perfect crystal

For simplicity, we assume that

1. there are no electrons in $\rho_{\rm f}$

2. the nuclear configuration remains unchanged (no relaxation)

The total charge density then reads

$$\rho = \left(\rho_{\rm per}^{\rm nuc} - \rho_{\rm per}^{0}\right) + \left(\rho_{\rm f} - \rho^{\rho_{\rm f}, \varepsilon_{\rm F}}\right)$$

and the total charge electrostatic potential is given by

$$V = V_{\rm per}^{0} + \left(\rho_{\rm f} - \rho^{\rho_{\rm f}, \varepsilon_{\rm F}}\right) \star \left|\,\cdot\,\right|^{-1}$$

What is the "macroscopic limit" of this equation?

Theorem. Let $\rho_{\mathrm{f}} \in L^1(\mathbb{R}^3) \cap L^2(\mathbb{R}^3)$.

For $\eta > 0$, we denote by $\rho_{\mathrm{f}}^\eta(x) = \eta^3 \rho_{\mathrm{f}}(\eta x)$ and by

$$V_\eta(x) = \eta^{-1} \left[V_{\mathrm{per}}^0 + \left(\rho_{\mathrm{f}}^\eta - \rho^{\rho_{\mathrm{f}}^\eta, \varepsilon_{\mathrm{F}}} \right) \star |\cdot|^{-1} \right] \left(\eta^{-1} x \right).$$

When η goes to zero, V_η converges in $\mathcal{S}'(\mathbb{R}^3)$ to the unique solution in $\left\{ V \in L^6(\mathbb{R}^3) \,|\, \nabla V \in L^2(\mathbb{R}^3) \right\}$ of the elliptic equation

$$-\mathrm{div}\left(\varepsilon_{\mathrm{M}} \nabla V \right) = 4\pi \rho_{\mathrm{f}}$$

where ε_{M} is a $3{\times}3$ symmetrix matrix depending only on the electronic structure of the host crystal

ε_{M} is the electronic contribution to the macroscopic dielectric permittivity given by the Adler-Wiser formula

Calculation of ε_{M}

$\mathcal{R}$ direct lattice, Γ periodic cell
$\mathcal{R}^*$ dual lattice, Γ^* first Brillouin zone

Ex.: cubic lattice $\mathcal{R} = \mathbb{Z}^3$, $\Gamma = (0,1]^3$, $\mathcal{R}^* = 2\pi\mathbb{Z}^3$, $\Gamma^* = (-\pi,\pi]^3$

Bloch-Floquet decomposition of a function $f \in L^2(\mathbb{R}^3)$

$$f(x) = \fint_{\Gamma^*} f_q(x)\, e^{iq\cdot x} dq$$

where the functions $f_q \in L^2_{\mathrm{per}}(\Gamma)$ are defined by

$$f_q(x) = \sum_{R \in \mathcal{R}} f(x+R)e^{-iq\cdot(x+R)}$$

Besides

$$\|f\|^2_{L^2(\mathbb{R}^3)} = \fint_{\Gamma^*} \|f_q\|^2_{L^2_{\mathrm{per}}(\Gamma)}\, dq.$$

Bloch-Floquet decomposition of $H_{\text{per}}^0 = -\dfrac{1}{2}\Delta + V_{\text{per}}^0$

$$
f = \fint_{\Gamma^*} f_q(x)\, e^{iq\cdot x} dq \qquad\Rightarrow\qquad H_{\text{per}}^0 = \fint_{\Gamma^*} \left[(H_{\text{per}}^0)_q f_q \right](x)\, e^{iq\cdot x}
$$

The operator

$$
(H_{\text{per}}^0)_q = -\frac{1}{2}\Delta - iq\cdot\nabla + \frac{|q|^2}{2} + V_{\text{per}}
$$

is self-adjoint on $L_{\text{per}}^2(\Gamma)$ and has a compact resolvent. It can therefore be diagonalized in an orthonormal basis set of $L_{\text{per}}^2(\Gamma)$

$$
(H_{\text{per}}^0)_q = \sum_{n=1}^{+\infty} \varepsilon_{n,q} |u_{n,q}\rangle\langle u_{n,q}| \qquad \langle u_{n,q}|u_{n',q}\rangle = \delta_{nn'}
$$

In fact,

$$
\sigma(H_{\text{per}}^0) = \bigcup_{n=1}^{+\infty} \left[\min_{q\in\Gamma^*} \varepsilon_{n,q},\ \max_{q\in\Gamma^*} \varepsilon_{n,q} \right]
$$

Explicit expression of ε_{M} (Adler-Wiser formula)

$$\varepsilon_{\mathrm{M}} = 1 + L - \sum_{K,K' \in \mathcal{R}^* \setminus \{0\}} \beta_K [C^{-1}]_{K,K'} \beta_{K'}^*$$

with

$$\forall k \in \mathbb{R}^3, \quad k^T L k = \frac{1}{\pi^2} \sum_{n=1}^{N} \sum_{n'=N+1}^{+\infty} \int_{\Gamma^*} \frac{\left| \langle (k \cdot \nabla_x) u_{n,q}, u_{n',q} \rangle_{L^2_{\mathrm{per}}(\Gamma)} \right|^2}{\left(\varepsilon_{n',q} - \varepsilon_{n,q} \right)^3} \, dq$$

(N is the number of electrons per unit cell)

and similar expressions for the vectors $\beta_K \in \mathbb{R}^3$ ($K \in \mathcal{R}^* \setminus \{0\}$) and for the coefficients $C_{K,K'} \in \mathbb{C}$ ($K, K' \in \mathcal{R}^* \setminus \{0\}$) of the matrix C

Conclusions and open questions

Conclusions

1. Using rigorous bulk limit arguments, we have obtained a variational model for computing the electronic ground state of insulating and semiconducting crystals with local defects

    $\longrightarrow$ Quid for metals?

2. Hierarchical variational approximations of the modification $Q^{m,\varepsilon_{\mathrm{F}}}$ of the density matrix can be computed using a (possibly enriched) basis of Maximally Localized Wannier Functions of the host crystal (E.C., A. Deleurence and M. Lewin, J. Phys.: Cond. Mat. 2008)

    $\longrightarrow$ Accurary? - Linear scaling? - Sublinear scaling?

3. Ongoing work and future research projects:

  (a) exchange-correlation (LDA, GGA, Hartree-Fock exchange)

  (b) nuclear relaxation, finite temperature

  (c) defects on surfaces, extended defects (dislocations, junctions)

  (d) interaction between defects, stochastic distributions of defects

  (e) excited states

  (f) time-dependent models (TDDFT)

  (g) optimal control of electronic wave packets