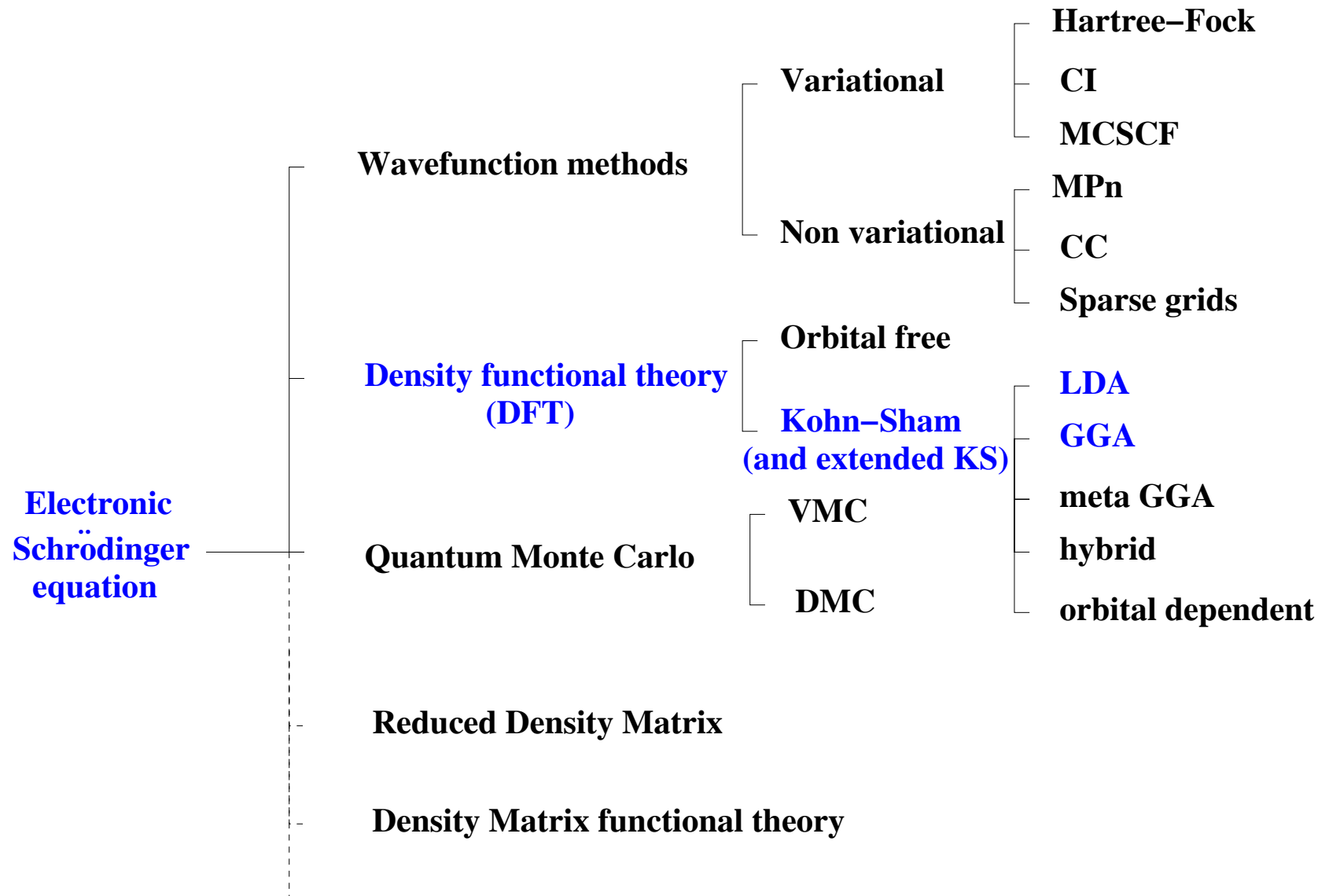


Mathematical aspects of DFT

Eric CANCES

CERMICS - ENPC and INRIA

IMA, Minneapolis, September 2008



1 - Mathematical foundations of DFT

2 - Systems of non-interacting electrons

3 - Kohn-Sham and extended Kohn-Sham models

4 - Bulk (thermodynamic) limits

1 - Mathematical foundations of DFT

Hohenberg-Kohn splitting of the electronic Hamiltonian

$$E^0 = \inf \{ \langle \Psi | H_N | \Psi \rangle, \Psi \in \mathcal{W}_N \}, \quad \mathcal{W}_N = \left\{ \Psi \in \bigwedge_{i=1}^N H^1(\mathbb{R}^3), \|\Psi\|_{L^2} = 1 \right\}$$

$$H_N = H_N^1 + V_{\text{ne}} = H_N^1 + \sum_{i=1}^N V(\mathbf{r}_i)$$

$$H_N^1 = T + V_{\text{ee}} = - \sum_{i=1}^N \frac{1}{2} \Delta_{\mathbf{r}_i} + \sum_{1 \leq i < j \leq N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \quad V(\mathbf{r}) = - \sum_{k=1}^M \frac{z_k}{|\mathbf{r} - \mathbf{R}_k|}$$

Electronic density

$$\Psi \in \mathcal{W}_N \quad \mapsto \quad \rho_\Psi(\mathbf{r}) = N \int_{\mathbb{R}^{3(N-1)}} |\Psi(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N)|^2 d\mathbf{r}_2 \cdots d\mathbf{r}_N$$

 Levy constrained search approach

$$\begin{aligned}
 E^0 &= \inf_{\Psi} \langle \Psi | H_N | \Psi \rangle \\
 &= \inf_{\Psi} \left(\langle \Psi | H_N^1 | \Psi \rangle + \langle \Psi | \left(\sum_{i=1}^N V(\mathbf{r}_i) \right) | \Psi \rangle \right) \\
 &= \inf_{\Psi} \left(\langle \Psi | H_N^1 | \Psi \rangle + \int_{\mathbb{R}^3} \rho_{\Psi} V \right) \\
 &= \inf_{\rho} \inf_{\Psi | \rho_{\Psi} = \rho} \left(\langle \Psi | H_N^1 | \Psi \rangle + \int_{\mathbb{R}^3} \rho_{\Psi} V \right) \\
 &= \inf_{\rho} \left(\inf_{\Psi | \rho_{\Psi} = \rho} \langle \Psi | H_N^1 | \Psi \rangle + \int_{\mathbb{R}^3} \rho V \right) \\
 &= \inf_{\rho} \left(F_{\text{LL}}(\rho) + \int_{\mathbb{R}^3} \rho V \right)
 \end{aligned}$$

Levy-Lieb functional

$$E^0 = \inf \left\{ F_{\text{LL}}(\rho) + \int_{\mathbb{R}^3} \rho V, \quad \rho \in \mathcal{R}_N \right\}$$

$$F_{\text{LL}}(\rho) = \inf \left\{ \langle \Psi | H_N^1 | \Psi \rangle, \quad \Psi \in \mathcal{W}_N \text{ s.t. } \rho_\Psi = \rho \right\}$$

$$\mathcal{R}_N = \left\{ \rho, \quad \exists \Psi \in \mathcal{W}_N \text{ s.t. } \rho_\Psi = \rho \right\} = \left\{ \rho \geq 0, \quad \sqrt{\rho} \in H^1(\mathbb{R}^3), \quad \int_{\mathbb{R}^3} \rho = N \right\}$$

$F_{\text{LL}}(\rho)$ is a “universal” functional of the density

Problem: no easy-to-compute expression of $F_{\text{LL}}(\rho)$ is known

Lieb functional

For any $v \in L^{\frac{3}{2}}(\mathbb{R}^3) + L^\infty(\mathbb{R}^3)$, we can define

$$E(v) = \inf \left\{ \langle \Psi | H_N^1 + \sum_{i=1}^N v(\mathbf{r}_i) | \Psi \rangle, \quad \Psi \in \mathcal{W}_N \right\}$$

and $v \mapsto E(v)$ is a real-valued, concave, continuous function

It holds (Lieb, IJQC 1983)

$$E(v) = \inf \left\{ F_L(\rho) + \int_{\mathbb{R}^3} \rho v, \quad \rho \in L^1(\mathbb{R}^3) \cap L^3(\mathbb{R}^3) \right\}$$

where $F_L(\rho)$ is the convex w-l.s.c. function defined on $L^1(\mathbb{R}^3) \cap L^3(\mathbb{R}^3)$ by

$$F_L(\rho) = \sup \left\{ E(v) - \int_{\mathbb{R}^3} \rho v, \quad v \in L^{\frac{3}{2}}(\mathbb{R}^3) + L^\infty(\mathbb{R}^3) \right\}$$

Physical interpretation of $F_L(\rho)$

Mixed states of N -electron systems are described by N -electron density matrices of the form

$$\Gamma = \sum_{n=1}^{+\infty} p_n |\Psi_n\rangle\langle\Psi_n|, \quad \Psi_n \in \bigwedge_{i=1}^N L^2(\mathbb{R}^3), \quad \langle\Psi_m|\Psi_n\rangle = \delta_{mn}, \quad 0 \leq p_n \leq 1, \quad \sum_{n=1}^{+\infty} p_n = 1$$

the density of Γ being given by

$$\rho_\Gamma(\mathbf{r}) = \sum_{n=1}^{+\infty} p_n \rho_{\Psi_n}(\mathbf{r})$$

Γ is of finite energy if $\sum_{n=1}^{+\infty} p_n \|\nabla\Psi_n\|_{L^2}^2 < \infty$, its energy being then

$$\mathbf{Tr}(H_N\Gamma) = \sum_{n=1}^{+\infty} p_n \langle\Psi_n|H_N|\Psi_n\rangle = \mathbf{Tr}(H_N^1\Gamma) + \int_{\mathbb{R}^3} \rho_\Gamma V$$

Let us denote by \mathcal{D}_N the convex set consisting of the N -electron density matrices of finite energy

$$\{\rho \mid \exists \Gamma \in \mathcal{D}_N \text{ s.t. } \rho_\Gamma = \rho\} = \mathcal{R}_N$$

Therefore

$$\begin{aligned} E^0 &= \inf \{ \mathbf{Tr} (H_N \Gamma), \Gamma \in \mathcal{D}_N \} \\ &= \inf \left\{ \mathbf{Tr} (H_N^1 \Gamma) + \int_{\mathbb{R}^3} \rho_\Gamma V, \Gamma \in \mathcal{D}_N \right\} \\ &= \inf \left\{ \inf \{ \mathbf{Tr} (H_N^1 \Gamma), \Gamma \in \mathcal{D}_N, \rho_\Gamma = \rho \} + \int_{\mathbb{R}^3} \rho V, \rho \in \mathcal{R}_N \right\} \end{aligned}$$

It holds that $F_L(\rho) = \begin{cases} \inf \{ \mathbf{Tr} (H_N^1 \Gamma), \Gamma \in \mathcal{D}_N, \rho_\Gamma = \rho \} & \text{if } \rho \in \mathcal{R}_N \\ +\infty & \text{if } \rho \notin \mathcal{R}_N \end{cases}$

and that F_L is the convex hull of F_{LL} on the convex set \mathcal{R}_N

2 - Systems of non-interacting electrons

Density functional theory for non-interacting electrons

| | Hamiltonian | Levy-Lieb | Lieb |
|-----------------------|-------------|----------------|-------------|
| Interacting e^- | H_N^1 | $F_{LL}(\rho)$ | $F_L(\rho)$ |
| Non-interacting e^- | H_N^0 | $T_{LL}(\rho)$ | $T_J(\rho)$ |

$$H_N^1 = T + V_{ee} = - \sum_{i=1}^N \frac{1}{2} \Delta_{\mathbf{r}_i} + \sum_{1 \leq i < j \leq N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \quad H_N^0 = T = - \sum_{i=1}^N \frac{1}{2} \Delta_{\mathbf{r}_i}$$

Levy-Lieb approach

$$\begin{aligned} T_{\text{LL}}(\rho) &= \inf \{ \langle \Psi | T | \Psi \rangle, \quad \Psi \in \mathcal{W}_N \text{ s.t. } \rho_\Psi = \rho \} \\ &\leq \inf \{ \langle \Psi | T | \Psi \rangle, \quad \Psi \text{ is a Slater determinant s.t. } \rho_\Psi = \rho \} \\ &= \inf \left\{ \sum_{i=1}^N \frac{1}{2} \int_{\mathbb{R}^3} |\nabla \phi_i|^2, \quad \phi_i \in H^1(\mathbb{R}^3), \int_{\mathbb{R}^3} \phi_i \phi_j = \delta_{ij}, \sum_{i=1}^N |\phi_i|^2 = \rho \right\} \\ &= T_{\text{KS}}(\rho) \end{aligned}$$

First order reduced density matrices

Let $\Psi \in \bigwedge_{i=1}^N L^2(\mathbb{R}^3)$ such that $\|\Psi\|_{L^2} = 1$. The first order reduced density matrix associated with Ψ is the function

$$\gamma_{\Psi}(\mathbf{r}, \mathbf{r}') := N \int_{\mathbb{R}^{3(N-1)}} \Psi(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N) \Psi(\mathbf{r}', \mathbf{r}_2, \dots, \mathbf{r}_N) d\mathbf{r}_2 \cdots d\mathbf{r}_N$$

Note that $\rho_{\Psi}(\mathbf{r}) = \gamma_{\Psi}(\mathbf{r}, \mathbf{r})$

The function $\gamma_{\Psi}(\mathbf{r}, \mathbf{r}')$ can be considered as the Green kernel of the operator on $L^2(\mathbb{R}^3)$, also denoted by γ_{Ψ} , and called the first order reduced density operator, defined for all $\phi \in L^2(\mathbb{R}^3)$ by

$$(\gamma_{\Psi}\phi)(\mathbf{r}) = \int_{\mathbb{R}^3} \gamma_{\Psi}(\mathbf{r}, \mathbf{r}') \phi(\mathbf{r}') d\mathbf{r}'$$

The operator γ_Ψ is self-adjoint on $L^2(\mathbb{R}^3)$ and satisfies

$$0 \leq \gamma_\Psi \leq 1 \quad \text{and} \quad \text{Tr}(\gamma_\Psi) = N$$

Therefore, γ_Ψ can be diagonalized as follows: there exists an orthonormal basis $(\phi_i)_{i \geq 1}$ of $L^2(\mathbb{R}^3)$ and a non-increasing sequence $(n_i)_{i \geq 1}$ of real numbers such that

$$\gamma_\Psi = \sum_{i=1}^{+\infty} n_i |\phi_i\rangle \langle \phi_i| \quad \text{with} \quad 0 \leq n_i \leq 1 \quad \text{and} \quad \sum_{i=1}^{+\infty} n_i = N$$

The n_i and the ϕ_i are called respectively the natural occupation numbers and the natural spin-orbitals of the wavefunction Ψ

If in addition Ψ is of finite energy, then all the ϕ_i are in $H^1(\mathbb{R}^3)$ and

$$\langle \Psi | T | \Psi \rangle = \frac{1}{2} \sum_{i=1}^{+\infty} n_i \int_{\mathbb{R}^3} |\nabla \phi_i(\mathbf{r})|^2 d\mathbf{r} = \text{Tr} \left(-\frac{1}{2} \Delta \gamma_\Psi \right)$$

Let $\Gamma \in \mathcal{D}_N$

$$\Gamma = \sum_{n=1}^{+\infty} p_n |\Psi_n\rangle\langle\Psi_n|, \quad \Psi_n \in \bigwedge_{i=1}^N L^2(\mathbb{R}^3), \quad \langle\Psi_m|\Psi_n\rangle = \delta_{mn}, \quad 0 \leq p_n \leq 1, \quad \sum_{n=1}^{+\infty} p_n = 1$$

The first order reduced density operator associated with Γ is

$$\gamma_\Gamma = \sum_{n=1}^{+\infty} p_n \gamma_{\Psi_n}. \quad \text{Note that } \rho_\Gamma(\mathbf{r}) = \gamma_\Gamma(\mathbf{r}, \mathbf{r})$$

It holds

$$\gamma_\Gamma^* = \gamma_\Gamma, \quad 0 \leq \gamma_\Gamma \leq 1, \quad \mathbf{Tr}(\gamma_\Gamma) = N, \quad \mathbf{Tr}(H_N^0 \Gamma) = \mathbf{Tr}\left(-\frac{1}{2}\Delta\gamma_\Gamma\right)$$

Ensemble N -representability of first-order reduced density matrices

$$\begin{aligned} \mathcal{C}_N &= \{\gamma \mid \exists \Gamma \in \mathcal{D}_N \text{ s.t. } \gamma_\Gamma = \gamma\} \\ &= \{\gamma \in \mathcal{S}(L^2(\mathbb{R}^3)) \mid 0 \leq \gamma \leq 1, \mathbf{Tr}(\gamma) = N, \mathbf{Tr}(-\Delta\gamma) < \infty\} \end{aligned}$$

 Lieb approach (Janak functional)

$$\begin{aligned}
 T_J(\rho) &= \inf \left\{ \mathbf{Tr}(H_N^0 \Gamma), \Gamma \in \mathcal{D}_N \text{ s.t. } \rho_\Gamma = \rho \right\} \\
 &= \inf \left\{ \mathbf{Tr} \left(-\frac{1}{2} \Delta \gamma_\Gamma \right), \Gamma \in \mathcal{D}_N \text{ s.t. } \rho_\Gamma = \rho \right\} \\
 &= \inf \left\{ \mathbf{Tr} \left(-\frac{1}{2} \Delta \gamma \right), \gamma \in \mathcal{C}_N \text{ s.t. } \rho_\gamma = \rho \right\} \quad \text{where } \rho_\gamma(\mathbf{r}) = \gamma(\mathbf{r}, \mathbf{r}) \\
 &= \inf \left\{ \sum_{i=1}^{+\infty} \frac{1}{2} n_i \int_{\mathbb{R}^3} |\nabla \phi_i|^2, \phi_i \in H^1(\mathbb{R}^3), \int_{\mathbb{R}^3} \phi_i \phi_j = \delta_{ij}, \right. \\
 &\quad \left. 0 \leq n_i \leq 1, \sum_{i=1}^{+\infty} n_i |\phi_i|^2 = \rho \right\}
 \end{aligned}$$

3 - Kohn-Sham and extended Kohn-Sham models

Kohn-Sham model

1. For N *non interacting* electrons, the density functional is (approximately) given by

$$T_{\text{KS}}(\rho) = \left\{ \sum_{i=1}^N \frac{1}{2} \int_{\mathbb{R}^3} |\nabla \phi_i|^2, \quad \phi_i \in H^1(\mathbb{R}^3) \quad \int_{\mathbb{R}^3} \phi_i \phi_j = \delta_{ij} \quad \sum_{i=1}^N |\phi_i|^2 = \rho \right\}$$

2. For a classical charge distribution of density ρ , the Coulomb interaction reads

$$J(\rho) \stackrel{\text{def}}{=} \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\rho(x) \rho(y)}{|x - y|} dx dy$$

3. Kohn and Sham proposed the following decomposition of F_{LL}

$$F_{\text{LL}}(\rho) = T_{\text{KS}}(\rho) + J(\rho) + E_{\text{xc}}(\rho) \quad \text{where} \quad E_{\text{xc}}(\rho) \stackrel{\text{def}}{=} F_{\text{LL}}(\rho) - T_{\text{KS}}(\rho) - J(\rho)$$

E_{xc} is called the **exchange-correlation functional**

Exchange-correlation functional

$$|E_{\text{xc}}(\rho)| \ll J(\rho) \text{ and } T_{\text{KS}}(\rho)$$

A possible approximation of $E_{\text{xc}}(\rho)$ is

$$E_{\text{xc}}^{\text{LDA}}(\rho) = \int_{\mathbb{R}^3} e_{\text{xc}}(\rho(x)) dx$$

where $e_{\text{xc}}(\bar{\rho})$ is the exchange-correlation energy density in a homogeneous electron gas of density $\bar{\rho}$

→ **Local Density Approximation (LDA)**

The function $e_{\text{xc}} : \mathbb{R}_+ \rightarrow \mathbb{R}$ is obtained by interpolation of asymptotic expansions and benchmark Quantum Monte Carlo calculations on the homogeneous electron gas

Rewriting the minimization problem in terms of $\Phi = (\phi_1, \dots, \phi_N)$, one obtains

$$E^0 \simeq \inf \left\{ E^{\text{KS}}(\Phi), \quad \Phi = (\phi_1, \dots, \phi_N) \in (H^1(\mathbb{R}^3))^N, \quad \int_{\mathbb{R}^3} \phi_i \phi_j = \delta_{ij} \right\}$$

$$\begin{aligned} E^{\text{KS}}(\Phi) &= \frac{1}{2} \sum_{i=1}^N \int_{\mathbb{R}^3} |\nabla \phi_i|^2 + \int_{\mathbb{R}^3} \rho_{\Phi} V \\ &+ \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\rho_{\Phi}(\mathbf{r}) \rho_{\Phi}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + \int_{\mathbb{R}^3} e_{\text{xc}}(\rho_{\Phi}(\mathbf{r})) d\mathbf{r} \end{aligned}$$

with

$$V(\mathbf{r}) = - \sum_{k=1}^M \frac{z_k}{|\mathbf{r} - \mathbf{R}_k|} \quad \rho_{\Phi}(\mathbf{r}) = \sum_{i=1}^N |\phi_i(\mathbf{r})|^2$$

Existence of solutions for neutral and positively charged systems:
Le Bris (1993)

Although obtained by totally different approaches, Hartree-Fock and Kohn-Sham LDA models have similar mathematical structures

Hartree-Fock

Kohn-Sham LDA

$$E^0 \underset{\approx}{\lesssim} \inf \{ E^{\text{HF}}(\Phi), \quad \Phi \in \mathcal{S}_N \}$$

$$E^0 \simeq \inf \{ E^{\text{KS}}(\Phi), \quad \Phi \in \mathcal{S}_N \}$$

$$E^{\text{HF}}(\Phi) = \frac{1}{2} \sum_{i=1}^N \int_{\mathbb{R}^3} |\nabla \phi_i|^2 + \int_{\mathbb{R}^3} \rho_{\Phi} V + J(\rho_{\Phi}) - \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{|\gamma_{\Phi}(\mathbf{r}, \mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'$$

$$E^{\text{KS}}(\Phi) = \frac{1}{2} \sum_{i=1}^N \int_{\mathbb{R}^3} |\nabla \phi_i|^2 + \int_{\mathbb{R}^3} \rho_{\Phi} V + J(\rho_{\Phi}) + \int_{\mathbb{R}^3} e_{\text{xc}}(\rho_{\Phi}(\mathbf{r})) d\mathbf{r}$$

$$\mathcal{S}_N = \left\{ \Phi = (\phi_1, \dots, \phi_N) \in (H^1(\mathbb{R}^3))^N, \quad \int_{\mathbb{R}^3} \phi_i \phi_j = \delta_{ij} \right\}$$

Euler-Lagrange equations (Euler-Lagrange + invariance + loc. min.)

$$\begin{cases} -\frac{1}{2}\Delta\phi_i + \mathcal{W}_\Phi\phi_i = \varepsilon_i\phi_i & 1 \leq i \leq N \\ \int_{\mathbb{R}^3} \phi_i\phi_j = \delta_{ij} & 1 \leq i, j \leq N \end{cases}$$

- In the Hartree-Fock model, the potential \mathcal{W}_Φ is nonlocal

$$\mathcal{W}_\Phi^{\text{HF}}\phi = \left(V + \rho_\Phi \star \frac{1}{|\mathbf{r}|} \right) \phi - \int_{\mathbb{R}^3} \frac{\gamma_\Phi(\cdot, \mathbf{r}')}{|\cdot - \mathbf{r}'|} \phi(\mathbf{r}') d\mathbf{r}'$$

while it is local in the Kohn-Sham LDA model

$$\mathcal{W}_\Phi^{\text{KS-LDA}}\phi = \left(V + \rho_\Phi \star \frac{1}{|\mathbf{r}|} + \frac{de_{\text{xc}}}{d\rho}(\rho_\Phi) \right) \phi$$

- In the Hartree-Fock model, $\varepsilon_1 \leq \varepsilon_2 \leq \dots \leq \varepsilon_N$ are the lowest N eigenvalues of $-\frac{1}{2}\Delta + \mathcal{W}_\Phi$, while it is not known whether this property holds true for the Kohn-Sham LDA model

Improvements of the LDA: Jacob's ladder (Perdew)

| Heaven | Exact exchange–correlation functional |
|--------|--|
| Rung 5 | explicit functionals of the Kohn-Sham occupied and unoccupied orbitals SAOP, ... |
| Rung 4 | explicit functionals of the density matrix (ex: hybrid functionals) 1/2 & 1/2, B3P, B3LYP, PBE0, O3LYP, X3LYP, mPW1PW91, BMK, PWB6K, B1B95, PW6B95, TPSSh, M05, |
| Rung 3 | meta-GGA (explicit in $\rho(\mathbf{r})$, $\nabla\rho(\mathbf{r})$, $\Delta\rho(\mathbf{r})$ and $\tau(\mathbf{r}) = \sum_{i=1}^N \nabla\phi_i(\mathbf{r}) ^2$) BR89, tauPBE, VSXC, BB95, TPSS, PBS00, LAP, ... |
| Rung 2 | GGA (explicit in $\rho(\mathbf{r})$ and $\nabla\rho(\mathbf{r})$) SIC, PW91, BLYP, mPWPW91, PBE, revPBE, G96LYP, HCTH, OPTX, EDF1, ... |
| Rung 1 | LDA (explicit in $\rho(\mathbf{r})$) |
| Earth | |

An example of variational problem of GGA type
(spin-unpolarized electron pair)

$$\inf \left\{ E(\phi), \phi \in H^1(\mathbb{R}^3), \int_{\mathbb{R}^3} |\phi|^2 = 1 \right\}$$

$$E(\phi) = \int_{\mathbb{R}^3} |\nabla \phi|^2 + \int_{\mathbb{R}^3} \rho_\phi V + J(\rho_\phi) + \int_{\mathbb{R}^3} h(\rho_\phi, |\nabla \phi|^2) \quad \text{with } \rho_\phi(\mathbf{r}) = 2\phi^2(\mathbf{r})$$

Euler-Lagrange equation

$$-\frac{1}{2} \operatorname{div} \left(\left(1 + \frac{\partial h}{\partial \kappa}(\rho_\phi, |\nabla \phi|^2) \right) \nabla \phi \right) + \left(V + \rho_\phi \star |\mathbf{r}|^{-1} + \frac{\partial h}{\partial \rho}(\rho_\phi, |\nabla \phi|^2) \right) \phi = \varepsilon \phi$$

cf. Anantharaman and E.C. 2008, submitted

Extended Kohn-Sham LDA model

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

$$\mathcal{E}(\gamma) = \mathbf{Tr} \left(-\frac{1}{2} \Delta \gamma \right) + \int_{\mathbb{R}^3} \rho_\gamma V + J(\rho_\gamma) + \int_{\mathbb{R}^3} e_{\text{xc}}(\rho_\gamma), \quad \rho_\gamma(\mathbf{r}) = \gamma(\mathbf{r}, \mathbf{r})$$

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

$$\gamma = \sum_{i=1}^{+\infty} n_i |\phi_i\rangle \langle \phi_i|$$

$$\int_{\mathbb{R}^3} \phi_i \phi_j = \delta_{ij}, \quad 0 \leq n_i \leq 1, \quad \sum_{i=1}^{+\infty} n_i = N, \quad \phi_i \in H^1(\mathbb{R}^3)$$

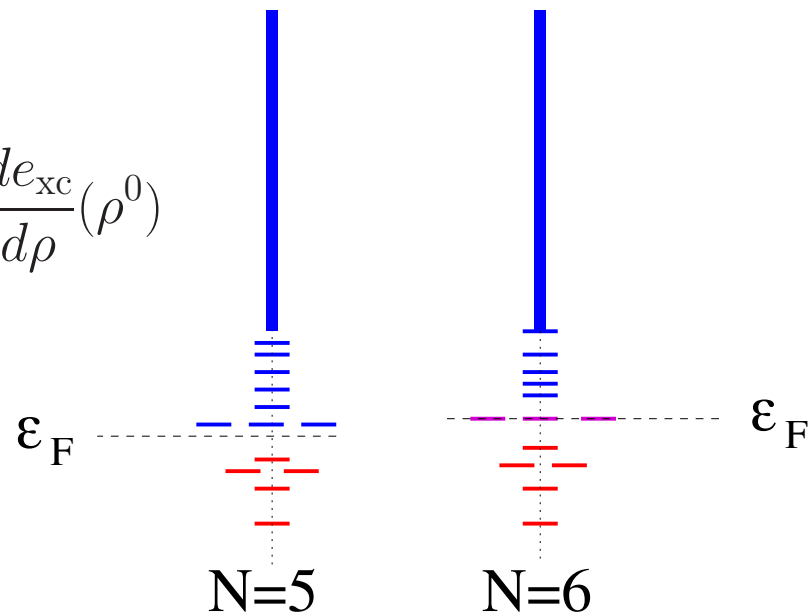
Extended Kohn-Sham LDA equations

$$\gamma^0 = \sum_i n_i |\phi_i\rangle \langle \phi_i|$$

$$\rho^0(\mathbf{r}) = \sum_i n_i |\phi_i(\mathbf{r})|^2$$

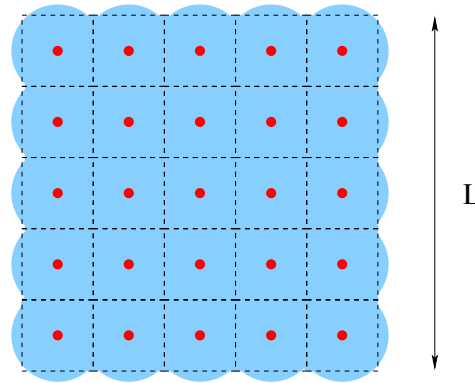
$$\left\{ \begin{array}{l} H_{\rho^0} \phi_i = \varepsilon_i \phi_i \\ \int_{\mathbb{R}^3} \phi_i \phi_j = \delta_{ij} \end{array} \right. \quad \text{and} \quad \left\{ \begin{array}{l} n_i = 1 \text{ if } \varepsilon_i < \varepsilon_F, \\ 0 \leq n_i \leq 1 \text{ if } \varepsilon_i = \varepsilon_F, \\ n_i = 0 \text{ if } \varepsilon_i > \varepsilon_F, \end{array} \right. \quad \sum_i n_i = N$$

$$H_{\rho^0} = -\frac{1}{2}\Delta + V + \rho^0 \star |\mathbf{r}|^{-1} + \frac{de_{xc}}{d\rho}(\rho^0)$$



4 - Bulk (thermodynamic) limits

Bulk limit for the perfect crystal (reduced HF model)



$$\left\{ \begin{array}{l} \rho_L^{\text{nuc}} = \sum_{\mathbf{R} \in \mathcal{R} \cap \Lambda_L} z \delta(\cdot - \mathbf{R}) \\ zL^3 \text{ electrons} \end{array} \right. \longrightarrow \left\{ \begin{array}{l} E_L^0 \quad \text{ground state energy} \\ \rho_L^0 \quad \text{ground state density} \\ \gamma_L^0 \quad \text{ground state density matrix} \end{array} \right.$$

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

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

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

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

What is going on when the crystal contains local defects?

→ talk by M. Lewin