Mathematical foundations of DFT

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1 - Electronic hamiltonians

2 - Constrained search

3 - Kohn-Sham and extended Kohn-Sham models

4 - Thermodynamic limits

1 - Electronic hamiltonians

$$\widehat{H}_N = -\sum_{i=1}^{N} \frac{1}{2}\nabla^2_{\mathbf{r}_i} - \sum_{i=1}^{N}\sum_{k=1}^{M} \frac{z_k}{|\mathbf{r}_i - \mathbf{R}_k|} + \sum_{1\leq i<j\leq N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} = \widehat{T} + \widehat{V}_{\text{ne}} + \widehat{V}_{\text{ee}}$$

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

N : **number of electrons**
M : **number of nuclei**
$z_k \in \mathbb{N}$: **charge of the** k^{th} **nucleus**
$\mathbf{R}_k \in \mathbb{R}^3$: **position of the** k^{th} **nucleus**

$\mathbf{r}_i$: **position of the** i^{th} **electrons**

N-electron wavefunctions and density matrices

- $\mathcal{H}_N : N$-**electron state space**

$$\boxed{\mathcal{H}_N = \bigwedge^N \mathcal{H}_1} \qquad \mathcal{H}_1 = L^2(\mathbb{R}^3, \mathbb{C}^2)$$

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$$\Psi \in \mathcal{H}_N \quad \Leftrightarrow \quad \begin{cases} \Psi(\cdots, \mathbf{r}_j, \cdots, \mathbf{r}_i, \cdots) = -\Psi(\cdots, \mathbf{r}_i, \cdots, \mathbf{r}_j, \cdots) \in \mathbb{C} \\ \langle \Psi | \Psi \rangle := \displaystyle\int_{(\mathbb{R}^3)^N} |\Psi(\mathbf{r}_1, \cdots, \mathbf{r}_N)|^2 \, d\mathbf{r}_1 \cdots d\mathbf{r}_N < \infty \end{cases}$$

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- $\mathcal{W}_N$: **set of normalized wavefunctions with finite energy (pure states)**

$$\mathcal{W}_N = \left\{ \Psi \in \mathcal{H}_N \mid \langle \Psi | \Psi \rangle = 1, \ \langle \Psi | \widehat{T} | \Psi \rangle < \infty \right\}, \qquad \widehat{T} = -\sum_{i=1}^{N} \frac{1}{2} \nabla_{\mathbf{r}_i}^2$$

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- $\mathcal{D}_N$: **set of density operators with finite energy $\mathcal{D}_N$ (mixed states)**

$$\mathcal{D}_N := \left\{ \widehat{\Gamma} \textbf{ linear op. on } \mathcal{H}_N \mid \widehat{\Gamma}^\dagger = \widehat{\Gamma}, \ 0 \leq \widehat{\Gamma} \leq 1, \ \textbf{Tr}(\widehat{\Gamma}) = 1, \ \textbf{Tr}(\widehat{T}\widehat{\Gamma}) < \infty \right\}$$

The electronic problem for a fixed nuclear configuration $\{z_k, \mathrm{R}_k\}_{1\leq k\leq M}$

$$\widehat{H}_N = -\sum_{i=1}^{N} \frac{1}{2}\nabla^2_{\mathbf{r}_i} - \sum_{i=1}^{N}\sum_{k=1}^{M} \frac{z_k}{|\mathbf{r}_i - \mathbf{R}_k|} + \sum_{1\leq i<j\leq N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \qquad \textbf{self-adjoint op. on } \mathcal{H}_N$$

Theorem (Zhislin '61): **if** $N \leq \sum_{k=1}^{M} z_k$ **(neutral or positively charged system), then**

$$\sigma(\widehat{H}_N) = \{E_0 \leq E_1 \leq E_2 \cdots\} \cup [\Sigma, +\infty).$$

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self-adjoint op. on $\mathcal{H}_N$

The bound states are obtained by solving the Schrödinger equation

$$\boxed{\widehat{H}_N\Psi = E\Psi, \quad \Psi \in \mathcal{W}_N}$$

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The ground state is obtained by solving the minimization problem

$$\boxed{E_0 = \min_{\Psi\in\mathcal{W}_N} \langle\Psi|\widehat{H}_N|\Psi\rangle}$$

(pure-state formulation)

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$$\boxed{E_0 = \min_{\Psi\in\mathcal{W}_N}\langle\Psi|\widehat{H}_N|\Psi\rangle} \qquad \textbf{(pure-state formulation)}$$

or, equivalently, the minimization problem

$$\boxed{E_0 = \min_{\widehat{\Gamma}\in\mathcal{D}_N}\mathbf{Tr}(\widehat{H}_N\widehat{\Gamma})} \qquad \textbf{(mixed-state formulation)}$$

2 - Constrained search

Electronic densities

- **Electronic density associated to a wavefunction** $\Psi \in \mathcal{W}_N$

$$\Psi \quad \mapsto \quad n_\Psi(\mathbf{r}) = N \int_{(\mathbb{R}^3)^{N-1}} \left|\Psi(\mathbf{r}, \mathbf{r}_2, \cdots, \mathbf{r}_N)\right|^2 d\mathbf{r}_2 \cdots d\mathbf{r}_N$$

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- **Electronic density associated to an** N**-body density operator** $\widehat{\Gamma} \in \mathcal{D}_N$

$$\widehat{\Gamma} = \sum_{l=1}^{+\infty} f_l |\Psi_l\rangle\langle\Psi_l| \quad \overset{\textbf{linear}}{\mapsto} \quad n_{\widehat{\Gamma}}(\mathbf{r}) = \sum_{l=1}^{+\infty} f_l \, n_{\Psi_l}(\mathbf{r})$$

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Theorem (N**-representability of densities).**

We have

$$\{n \mid \exists \Psi \in \mathcal{W}_N \textbf{ s.t. } n_\Psi = n\} = \left\{n \mid \exists \widehat{\Gamma} \in \mathcal{D}_N \textbf{ s.t. } n_{\widehat{\Gamma}} = n\right\} = \mathcal{R}_N,$$

where

$$\mathcal{R}_N := \left\{ n \geq 0, \ \int_{\mathbb{R}^3} n(\mathbf{r}) \, d\mathbf{r} = N, \ \int_{\mathbb{R}^3} |\nabla \sqrt{n}(\mathbf{r})|^2 \, d\mathbf{r} < \infty \right\}.$$

Usual splitting the electronic hamiltonian

$$\widehat{H}_N = -\sum_{i=1}^{N} \frac{1}{2}\nabla^2_{\mathbf{r}_i} - \sum_{i=1}^{N}\sum_{k=1}^{M} \frac{z_k}{|\mathbf{r}_i - \mathbf{R}_k|} + \sum_{1\leq i<j\leq N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} = \underbrace{\widehat{T} + \widehat{V}_{\rm ne}}_{\textbf{1-body}} + \underbrace{\widehat{V}_{\rm ee}}_{\textbf{2-body}}.$$

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Hohenberg-Kohn splitting of the electronic hamiltonian

$$\widehat{H}_N = \underbrace{\widehat{T} + \widehat{V}_{\text{ee}}}_{\text{generic}} + \underbrace{\widehat{V}_{\text{ne}}}_{\text{specific (to the molecular system considered)}}$$

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$$\widehat{H}_N = \underbrace{\widehat{T} + \widehat{V}_{\rm ee}}_{\text{generic}} + \underbrace{\widehat{V}_{\rm ne}}_{\text{specific (to the molecular system considered)}}$$

$$\boxed{\langle \Psi | \widehat{H}_N | \Psi \rangle = \langle \Psi | \widehat{T} + \widehat{V}_{\rm ee} | \Psi \rangle + \langle \Psi | \widehat{V}_{\rm ne} | \Psi \rangle = \langle \Psi | \widehat{T} + \widehat{V}_{\rm ee} | \Psi \rangle + \int_{\mathbb{R}^3} n_\Psi V}$$

$$V(\mathbf{r}) = -\sum_{k=1}^{M} \frac{z_k}{|\mathbf{r} - \mathbf{R}_k|}$$

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$$\widehat{H}_N = -\sum_{i=1}^{N} \frac{1}{2}\nabla^2_{\mathbf{r}_i} - \sum_{i=1}^{N}\sum_{k=1}^{M} \frac{z_k}{|\mathbf{r}_i - \mathbf{R}_k|} + \sum_{1\leq i<j\leq N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} = \underbrace{\widehat{T} + \widehat{V}_{\rm ne}}_{\textbf{1-body}} + \underbrace{\widehat{V}_{\rm ee}}_{\textbf{2-body}}.$$

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$$V(\mathbf{r}) = -\sum_{k=1}^{M} \frac{z_k}{|\mathbf{r} - \mathbf{R}_k|}$$

$$\boxed{\textbf{Tr}\left(\widehat{H}_N\widehat{\Gamma}\right) = \textbf{Tr}\left(\left(\widehat{T} + \widehat{V}_{\rm ee}\right)\widehat{\Gamma}\right) + \textbf{Tr}\left(\widehat{V}_{\rm ne}\widehat{\Gamma}\right) = \textbf{Tr}\left(\left(\widehat{T} + \widehat{V}_{\rm ee}\right)\widehat{\Gamma}\right) + \int_{\mathbb{R}^3} n_{\widehat{\Gamma}} V}$$

Constrained search I: pure state formulation (Levy '79, Lieb '83)

$$E_0 = \inf_{\Psi \in \mathcal{W}_N} \langle \Psi | \widehat{H}_N | \Psi \rangle$$

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\begin{aligned}
E_0 &= \inf_{\Psi \in \mathcal{W}_N} \langle \Psi | \widehat{H}_N | \Psi \rangle \\
&= \inf_{n \in \mathcal{R}_N} \left(\inf_{\Psi \in \mathcal{W}_N \,|\, n_\Psi = n} \langle \Psi | \widehat{H}_N | \Psi \rangle \right)
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&= \inf_{n\in\mathcal{R}_N} \left(\left(\inf_{\Psi\in\mathcal{W}_N\,|\,n_\Psi=n} \langle\Psi|\widehat{T}+\widehat{V}_{\mathrm{ee}}|\Psi\rangle \right) + \int_{\mathbb{R}^3} nV \right).
\end{aligned}
$$

Let

$$
\boxed{F_{\mathrm{LL}}[n] = \inf_{\Psi\in\mathcal{W}_N\,|\,n_\Psi=n} \langle\Psi|\widehat{T}+\widehat{V}_{\mathrm{ee}}|\Psi\rangle}
$$

Levy-Lieb functional.

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We have

$$
\boxed{E_0 = \inf_{n \in \mathcal{R}_N} \left(F_{\rm LL}[n] + \int_{\mathbb{R}^3} n V \right).}
$$

Constrained search II: mixed state formulation (Valone '80, Lieb '83)

$$
\begin{aligned}
E_0 &= \inf_{\widehat{\Gamma}\in\mathcal{D}_N} \mathbf{Tr}(\widehat{H}_N\widehat{\Gamma}) \\
&= \inf_{n\in\mathcal{R}_N} \left(\inf_{\widehat{\Gamma}\in\mathcal{D}_N \,|\, n_{\widehat{\Gamma}}=n} \mathbf{Tr}(\widehat{H}_N\widehat{\Gamma}) \right) \\
&= \inf_{n\in\mathcal{R}_N} \left(\inf_{\widehat{\Gamma}\in\mathcal{D}_N \,|\, n_{\widehat{\Gamma}}=n} \left(\mathbf{Tr}\left((\widehat{T}+\widehat{V}_{\mathrm{ee}})\widehat{\Gamma} \right) + \int_{\mathbb{R}^3} n_{\widehat{\Gamma}} V \right) \right) \\
&= \inf_{n\in\mathcal{R}_N} \left(\left(\inf_{\widehat{\Gamma}\in\mathcal{D}_N \,|\, n_{\widehat{\Gamma}}=n} \left(\mathbf{Tr}\left((\widehat{T}+\widehat{V}_{\mathrm{ee}})\widehat{\Gamma} \right) \right) \right) + \int_{\mathbb{R}^3} nV \right).
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$$

Let

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\boxed{F_{\mathrm{L}}[n] = \inf_{\widehat{\Gamma}\in\mathcal{D}_N \,|\, n_{\widehat{\Gamma}}=n} \mathbf{Tr}\left((\widehat{T}+\widehat{V}_{\mathrm{ee}})\widehat{\Gamma} \right)}
$$

Lieb functional.

We have

$$
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$$

$F_{\rm L}[n_0] = F_{\rm LL}[n_0]$ **if** n_0 **is pure-state** V**-representable, that is if** n_0 **is the density associated with a ground state wavefunction for some external potential** V**.**

$F_{\rm L}$ **is the convex hull of** $F_{\rm LL}$**.**

No explicit expressions of the functionals $F_{\rm L}$ **and** $F_{\rm LL}$ **are available.**

Approximations are needed for numerical simulations!

3 - Kohn-Sham and extended Kohn-Sham models

Density functional theory for non-interacting electrons

	Hamiltonian	Levy-Lieb	Valone-Lieb
Interacting e$^-$	$\widehat{H}_N = (\widehat{T} + \widehat{V}_{\rm ee}) + \widehat{V}_{\rm ne}$	$F_{\rm LL}[n]$	$F_{\rm L}[n]$
Non-interacting e$^-$	$\widehat{H}^0_N = \widehat{T} + \widehat{V}_{\rm ne}$	$T_{\rm LL}[n]$	$T_{\rm J}[n]$

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Can $T_{\rm LL}[n]$ be "easily" computed? **No.**

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Can $T_{\rm J}[n]$ be "easily" computed? **Yes! $\rightarrow$ (extended) Kohn-Sham model**

One-body reduced density matrix (1-RDM)

- **1-RDM associated to a wavefunction** $\Psi \in \mathcal{W}_N$

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

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- **1-RDM associated to an** N**-body density operator** $\widehat{\Gamma} \in \mathcal{D}_N$

$$\widehat{\Gamma} = \sum_{l=1}^{+\infty} f_l |\Psi_l\rangle\langle\Psi_l| \quad \overset{\textbf{linear}}{\mapsto} \quad \gamma_{\widehat{\Gamma}}(\mathbf{r},\mathbf{r}') = \sum_{l=1}^{+\infty} f_l\,\gamma_{\Psi_l}(\mathbf{r},\mathbf{r}')$$

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Relation between the 1-RDM and the density

$$n_\Psi(\mathbf{r}) = \gamma_\Psi(\mathbf{r},\mathbf{r}), \qquad n_{\widehat{\Gamma}}(\mathbf{r}) = \gamma_{\widehat{\Gamma}}(\mathbf{r},\mathbf{r}) \qquad \textbf{(in some weak sense)}.$$

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$$\widehat{\Gamma} = \sum_{l=1}^{+\infty} f_l |\Psi_l\rangle\langle\Psi_l| \quad \overset{\textbf{linear}}{\mapsto} \quad \gamma_{\widehat{\Gamma}}(\mathbf{r},\mathbf{r}') = \sum_{l=1}^{+\infty} f_l\, \gamma_{\Psi_l}(\mathbf{r},\mathbf{r}')$$

Relation between the 1-RDM and the density

$$n_\Psi(\mathbf{r}) = \gamma_\Psi(\mathbf{r},\mathbf{r}), \qquad n_{\widehat{\Gamma}}(\mathbf{r}) = \gamma_{\widehat{\Gamma}}(\mathbf{r},\mathbf{r}) \qquad \textbf{(in some weak sense)}.$$

Expressions of the kinetic energy as a function of the 1-RDM

$$\langle\Psi|\widehat{T}|\Psi\rangle = \frac{1}{2}\int_{\mathbb{R}^3} \left(-\nabla^2_{\mathbf{r}}\gamma_\Psi(\mathbf{r},\mathbf{r}')|_{\mathbf{r}'=\mathbf{r}}\right)\,d\mathbf{r}$$

$$\mathbf{Tr}\left(\widehat{T}\widehat{\Gamma}\right) = \frac{1}{2}\int_{\mathbb{R}^3} \left(-\nabla^2_{\mathbf{r}}\gamma_{\widehat{\Gamma}}(\mathbf{r},\mathbf{r}')|_{\mathbf{r}'=\mathbf{r}}\right)\,d\mathbf{r}$$

Janak functional

$$T_{\mathrm{J}}[n] = \inf_{\widehat{\Gamma}\in\mathcal{D}_N \,|\, n_{\widehat{\Gamma}}=n} \mathbf{Tr}\left(\widehat{T}\widehat{\Gamma}\right) = \inf_{\gamma \,|\, \exists \widehat{\Gamma}\in\mathcal{D}_N \text{ s.t. } \gamma_{\widehat{\Gamma}}=\gamma,\, n_{\widehat{\Gamma}}=n} \frac{1}{2}\int_{\mathbb{R}^3} \left(-\nabla^2_{\mathbf{r}}\gamma(\mathbf{r},\mathbf{r}')|_{\mathbf{r}'=\mathbf{r}}\right)\, d\mathbf{r}$$

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Theorem (N-representability of mixed-state 1-RDM).

Let $\mathcal{G}_N := \left\{\gamma \mid \exists \widehat{\Gamma}\in\mathcal{D}_N \text{ s.t. } \gamma_{\widehat{\Gamma}}=\gamma\right\}$**. We have**

$$\mathcal{G}_N := \left\{\gamma(\mathbf{r},\mathbf{r}') = \sum_{i=1}^{+\infty}\nu_i\phi_i(\mathbf{r})\phi_i(\mathbf{r}')^* \;\middle|\; 0\le\nu_i\le 1,\ \sum_{i=1}^{+\infty}\nu_i = N,\ \int_{\mathbb{R}^3}\phi_i\phi_j^* = \delta_{i,j},\ \sum_{i=1}^{+\infty}\nu_i\int_{\mathbb{R}^3}|\nabla\phi_i|^2 < \infty\right\}.$$

Janak functional

$$T_{\mathrm{J}}[n] = \inf_{\widehat{\Gamma}\in\mathcal{D}_N \,|\, n_{\widehat{\Gamma}}=n} \mathbf{Tr}\left(\widehat{T}\widehat{\Gamma}\right) = \inf_{\gamma \,|\, \exists \widehat{\Gamma}\in\mathcal{D}_N \text{ s.t. } \gamma_{\widehat{\Gamma}}=\gamma,\, n_{\widehat{\Gamma}}=n} \frac{1}{2}\int_{\mathbb{R}^3} \left(-\nabla^2_{\mathbf{r}}\gamma(\mathbf{r},\mathbf{r}')|_{\mathbf{r}'=\mathbf{r}}\right)\, d\mathbf{r}$$

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$$\left.\int_{\mathbb{R}^3}\phi_i\phi_j^* = \delta_{i,j},\ \sum_{i=1}^{+\infty}\nu_i\int_{\mathbb{R}^3}|\nabla\phi_i|^2 < \infty\right\}.$$

"Explicit" expression of the Janak functional

$$T_{\mathrm{J}}[n] = \inf\left\{\frac{1}{2}\sum_{i=1}^{+\infty}\nu_i\int_{\mathbb{R}^3}|\nabla\phi_i|^2,\ 0\le\nu_i\le 1,\ \sum_{i=1}^{+\infty}\nu_i = N,\right.$$
$$\left.\int_{\mathbb{R}^3}\phi_i\phi_j^* = \delta_{i,j},\ \sum_{i=1}^{+\infty}\nu_i|\phi_i(\mathbf{r})|^2 = n(\mathbf{r})\right\}.$$

Exchange-correlation functional

$$F_{\mathrm{L}}[n] = \inf_{\widehat{\Gamma}\in\mathcal{D}_N \,|\, n_{\widehat{\Gamma}}=n} \mathbf{Tr}\left(\left(\widehat{T}+\widehat{V}_{\mathrm{ee}}\right)\widehat{\Gamma}\right) = T_{\mathrm{J}}[n] + E_{\mathrm{Hartree}}[n] + E_{\mathrm{xc}}[n]$$

where

- $T_{\mathrm{J}}[n]$**: Janak functional**
- $E_{\mathrm{Hartree}}[n] = \dfrac{1}{2}\displaystyle\int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}\,d\mathbf{r}'$**: classical Coulomb interaction**
- $E_{\mathrm{xc}}[n] := F_{\mathrm{L}}[n] - T[n] - E_{\mathrm{Hartree}}[n]$**: exchange-correlation functional.**

Local Density Approximation (LDA):

$$E_{\mathrm{xc}}^{\mathrm{LDA}}[n] = \int_{\mathbb{R}^3} e_{\mathrm{xc}}^{\mathrm{HEG}}(n(\mathbf{r}))\,d\mathbf{r}$$

$e_{\mathrm{xc}}^{\mathrm{HEG}}(\overline{n})$**: exchange-correlation energy density of a homogeneous electron gas of uniform density** $\overline{n}$**.**

Extended Kohn-Sham LDA model (orbital formulation)

$$E_0^{\mathrm{LDA}} = \inf \Bigg\{ E^{\mathrm{LDA}}(\{\phi_i, \nu_i\}),\ 0 \leq \nu_i \leq 1,\ \sum_{i=1}^{+\infty} \nu_i = N,$$
$$\int_{\mathbb{R}^3} \phi_i \phi_j^* = \delta_{i,j},\ \frac{1}{2} \sum_{i=1}^{+\infty} \nu_i \int_{\mathbb{R}^3} |\nabla \phi_i|^2 < \infty \Bigg\}.$$

ϕ_i**:** i^{th} **Kohn-Sham orbital**
ν_i**: occupation number of** ϕ_i

$$E^{\mathrm{LDA}}(\{\phi_i, \nu_i\}) = \frac{1}{2} \sum_{i=1}^{+\infty} \nu_i \int_{\mathbb{R}^3} |\nabla \phi_i|^2 + \int_{\mathbb{R}^3} n_{\{\phi_i,\nu_i\}} V + E_{\mathrm{Hartree}}[[n_{\{\phi_i,\nu_i\}}] + \int_{\mathbb{R}^3} e_{\mathrm{xc}}^{\mathrm{HEG}}(n_{\{\phi_i,\nu_i\}}(\mathbf{r}))\, d\mathbf{r}$$

$$n_{\{\phi_i,\nu_i\}}(\mathbf{r}) = \sum_{i=1}^{+\infty} \nu_i |\phi_i(\mathbf{r})|^2$$

Extended Kohn-Sham LDA model (density operator formulation)

density matrix $\gamma(\mathbf{r},\mathbf{r}') = \sum_{i=1}^{+\infty} \nu_i \phi_i(\mathbf{r})\phi_i(\mathbf{r}')^* \quad \leftrightarrow \quad \widehat{\gamma} = \sum_{i=1}^{+\infty} \nu_i |\phi_i\rangle\langle\phi_i|$ **density operator**

$$E_0^{\mathrm{LDA}} = \inf\left\{\mathcal{E}^{\mathrm{LDA}}(\widehat{\gamma}), \quad \widehat{\gamma} \in \mathcal{S}(L^2(\mathbb{R}^3)),\ 0 \le \widehat{\gamma} \le 1,\ \mathbf{Tr}(\widehat{\gamma}) = N,\ \mathbf{Tr}(-\Delta\widehat{\gamma}) < \infty\right\}$$

$$\mathcal{E}^{\mathrm{LDA}}(\widehat{\gamma}) = \mathbf{Tr}\left(-\frac{1}{2}\nabla^2\widehat{\gamma}\right) + \int_{\mathbb{R}^3} n_{\widehat{\gamma}}(\mathbf{r})V(\mathbf{r})\,d\mathbf{r} + E_{\mathrm{Hartree}}[n_{\widehat{\gamma}}] + \int_{\mathbb{R}^3} e_{\mathrm{xc}}^{\mathrm{HEG}}(n_{\widehat{\gamma}}(\mathbf{r}))\,d\mathbf{r},$$

$$n_{\widehat{\gamma}}(\mathbf{r}) = \gamma(\mathbf{r},\mathbf{r}) \qquad \textbf{in some weak sense.}$$

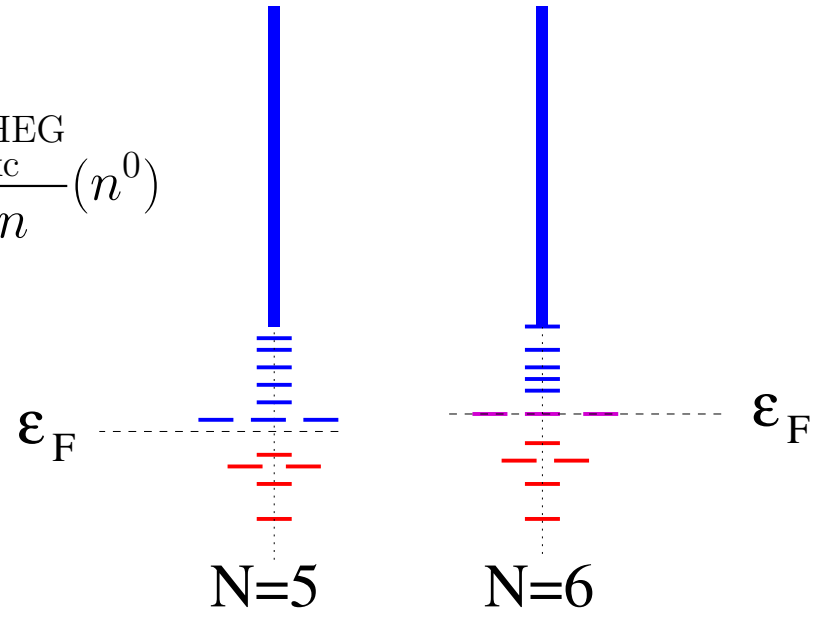
The minimization set $\left\{\widehat{\gamma} \in \mathcal{S}(L^2(\mathbb{R}^3)),\ 0 \le \widehat{\gamma} \le 1,\ \mathbf{Tr}(\widehat{\gamma}) = N,\ \mathbf{Tr}(-\Delta\widehat{\gamma}) < \infty\right\}$ **is convex and so are the first three terms of the LDA functional. On the other hand, the LDA exchange-correlation functional is concave.**

Extended Kohn-Sham LDA equations (first order optimality conditions)

$$\widehat{\gamma}^0 = \sum_i \nu_i |\phi_i\rangle\langle\phi_i|, \qquad \gamma^0(\mathbf{r},\mathbf{r}') = \sum_i \nu_i \phi_i(\mathbf{r})\phi_i(\mathbf{r}')^*, \qquad n^0(\mathbf{r}) = \gamma^0(\mathbf{r},\mathbf{r}) = \sum_i \nu_i |\phi_i(\mathbf{r})|^2$$

$$\begin{cases} H^{\mathrm{KS}}_{n^0}\,\phi_i = \varepsilon_i \phi_i \\ \displaystyle\int_{\mathbb{R}^3} \phi_i \phi_j^* = \delta_{ij} \end{cases} \quad \textbf{and} \quad \left| \begin{array}{l} \nu_i = 1 \textbf{ if } \varepsilon_i < \varepsilon_{\mathrm{F}}, \\ 0 \le \nu_i \le 1 \textbf{ if } \varepsilon_i = \varepsilon_{\mathrm{F}}, \\ \nu_i = 0 \textbf{ if } \varepsilon_i > \varepsilon_{\mathrm{F}}, \end{array} \right. \quad \sum_i \nu_i = N$$

$$H^{\mathrm{KS}}_{n^0} = -\frac{1}{2}\Delta + V + n^0 \star |\cdot|^{-1} + \frac{de^{\mathrm{HEG}}_{\mathrm{xc}}}{dn}(n^0)$$



Some comments

1. **For the exact exchange-correlation functional, the Kohn-Sham and extended Kohn-Sham models give the same ground state energy.**

2. **For approximate exchange-correlation functionals, the two models agree for "insulators", but may differ from "metals".**

3. **The extended Kohn-Sham is the one actually simulated when smearing techniques are used to fasten SCF convergence: it is the limit when T goes to zero of the finite-temperature Kohn-Sham model.**

4. **The density operator formulation of the (extended) Kohn-Sham model is very useful for the numerical simulation of very large systems (Kohn's "shortsightedness" principle = decay of $\gamma(\mathrm{r},\mathrm{r}')$ when $|\mathrm{r}-\mathrm{r}'| \to 0$).**

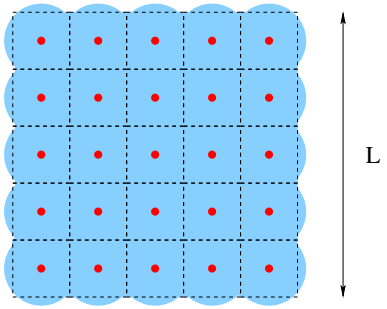
4 - Thermodynamic limits

DFT for crystals: some theoretical and practical issues

For each model (TFW, Hartree, LDA, GGA-PBE, B3LYP, ...),

1. Existence (and uniqueness) of the ground state density for molecules

2. Thermodynamic (bulk) limit for perfect crystals



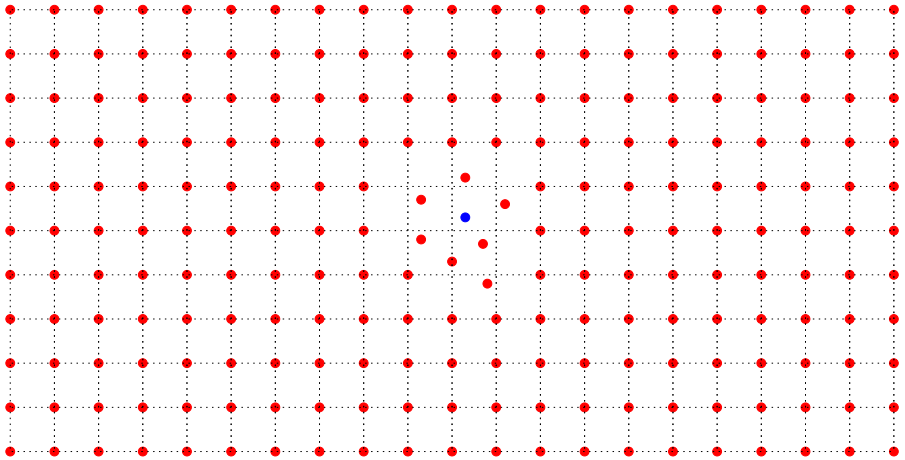
Neutral finite cluster ρ_L^{nuc}, ρ_L^0, $\widehat{\gamma}_L^0$

$$\int_{\mathbb{R}^3} \rho_L^{\mathrm{nuc}} = \int_{\mathbb{R}^3} \rho_L^0 = \mathbf{Tr}(\widehat{\gamma}_L^0) = NL^3$$

When $L \to \infty$, ρ_L^{nuc} **converges to some** $\mathcal{R}$**-periodic charge density** $\rho_{\mathrm{per}}^{\mathrm{nuc}}$**,**

- **does** ρ_L^0 **have a limit?**
- **is this limit some** $\mathcal{R}$**-periodic density** ρ_{per}^0**?**
- **can** ρ_{per}^0 **be characterized as a solution of some variational problem?**
- **can this problem be solved numerically?**
- **same questions for the limit** $\widehat{\gamma}_{\mathrm{per}}^0$ **of** $\widehat{\gamma}_L^0$**.**

3. Thermodynamic limits for crystals with local defects and screening effect



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

Formal definitions of the total charge of the defect

- $\displaystyle\int_{\mathbb{R}^3} m - \int_{\mathbb{R}^3} \rho^{m,\varepsilon_{\mathrm{F}}}$
- **and also for Kohn-Sham models,** $\displaystyle\int_{\mathbb{R}^3} m - \mathbf{Tr}(\widehat{Q}^{m,\varepsilon_{\mathrm{F}}})$

$$\mathbf{Tr}(\widehat{Q}^{m,\varepsilon_{\mathrm{F}}}) \neq \textstyle\int_{\mathbb{R}^3} \rho^{m,\varepsilon_{\mathrm{F}}} \qquad \longrightarrow \qquad \textbf{charge screening!}$$

State of the art of the mathematical analysis for 1, 2 and 3

	Molecules	Perfect crystals	Charge screening
TF	Lieb-Simon '77	Lieb-Simon '77	Lieb-Simon '77
TFW	Lieb '81	CLL '98	E.C.-Ehrlacher '11
DIOF	Blanc-E.C. '05	-	-
DDOF	?	?	?
Hartree	Solovej '91	CLL '01	E.C.-Lewin '10
LDA	Anantharaman-E.C. '09	non convex	non convex
GGA	??	??	??
B3LYP	??	??	??
Schrödinger	Zhislin '61	??? Fefferman '85 HLS '11	???

CLL: Catto-LeBris-Lions, HLS: Hainzl, Lewin, Solovej