TD-DFT: A USEFUL TOOL TO CALCULATE ACCURATE CORRELATION ENERGIES?

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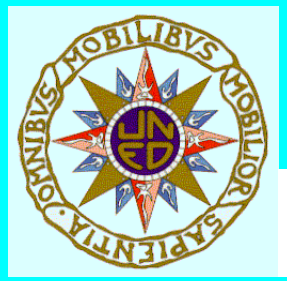

Universidad Nacional de Educación a Distancia

1. INTRODUCTION

Kohn-Sham DFT (KS-DFT):

Exact theory

Interacting system → Fictitious KS system

Approximation to $E_{XC}[n]$ are needed

Simple mean-field approaches work

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Exact (up to numerical convergence)

Very expensive

Delicate convergence issues

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A compromise: "Fully microscopic approaches":

Exact theory

Approximations required

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“Fully microscopic approaches”:

- Exact “Many-body-theory” expressions
- Further approximations are needed for practical use
- Approaches are made at a deeper level than in standard LDA/GGA
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Nice to keep some advantages of KS-DFT:

- Interacting system $\rightarrow$ Fictitious KS system
- Variational character: *self-consistency* $\equiv$ *minimisation of total energy*
- The variational parameter is the density $n(\mathrm{r})$ – or the KS potential $v_S(\mathrm{r})$ –

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TD-DFT for correlation + Exact exchange

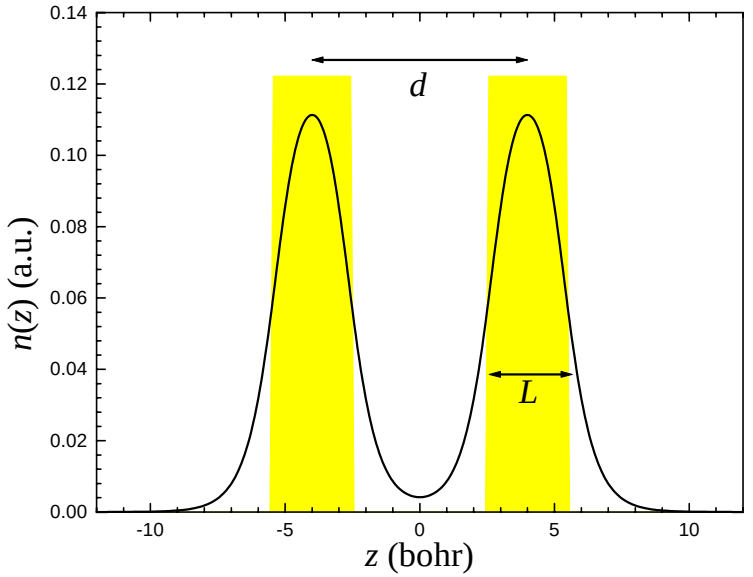
– use a fully microscopic theory to build "advanced" $E_{XC}[n]$ –

- Step towards "chemical accuracy"
- May solve situations were standard KS lacks predictive accuracy
- X and C treated in the same fashion

A very simple example (a “toy system”):

Two “jellium” slabs

(width: L = 3 bohr; mean density r_S = 1.25)



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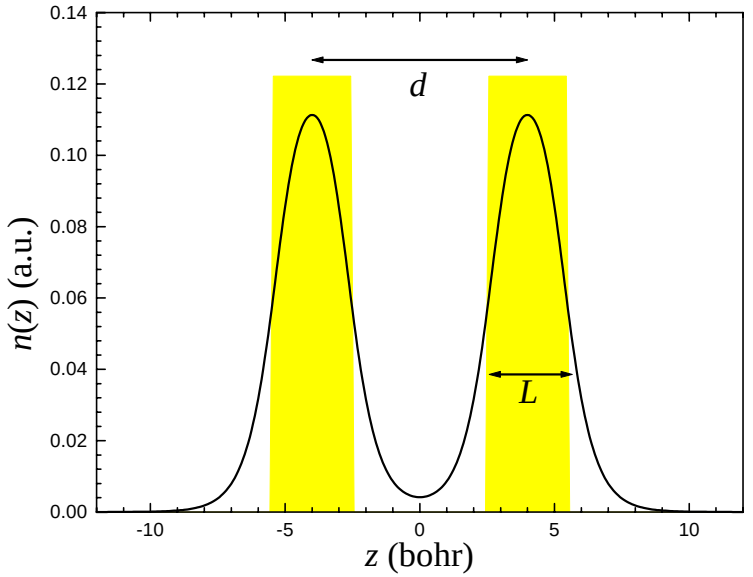

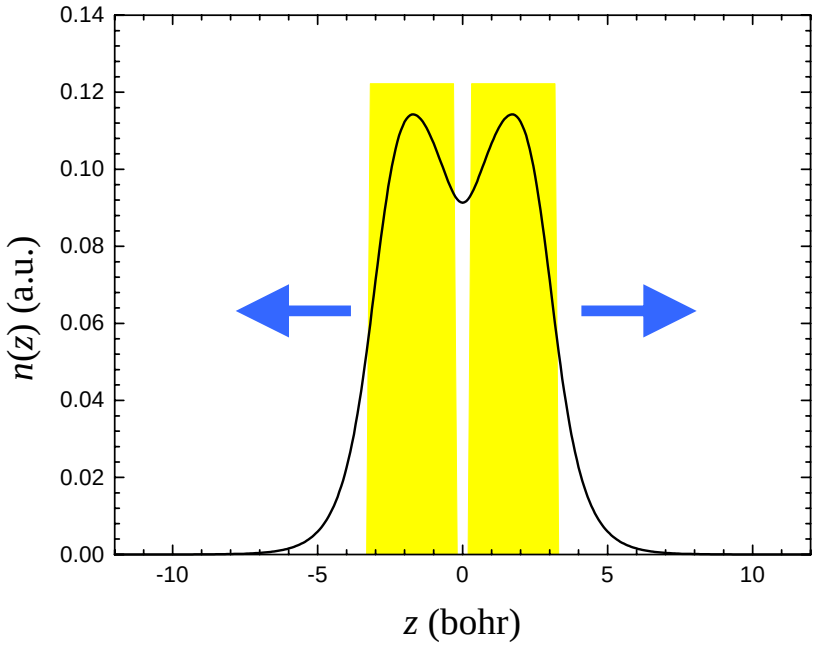

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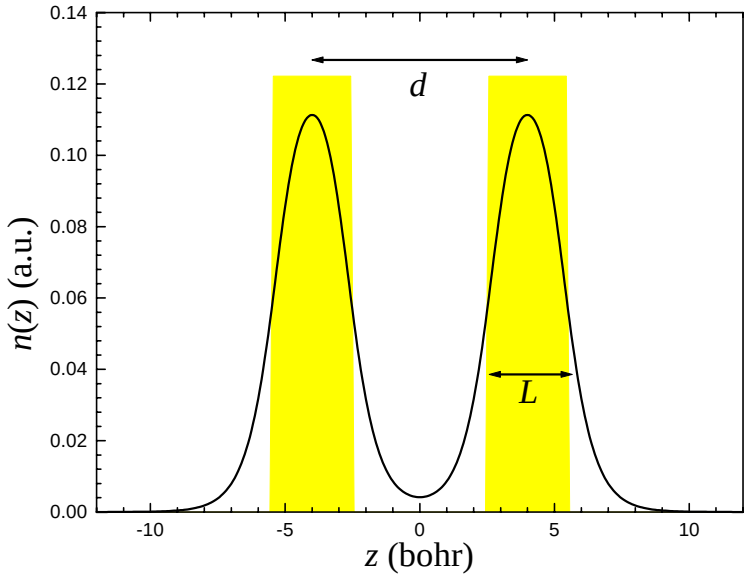
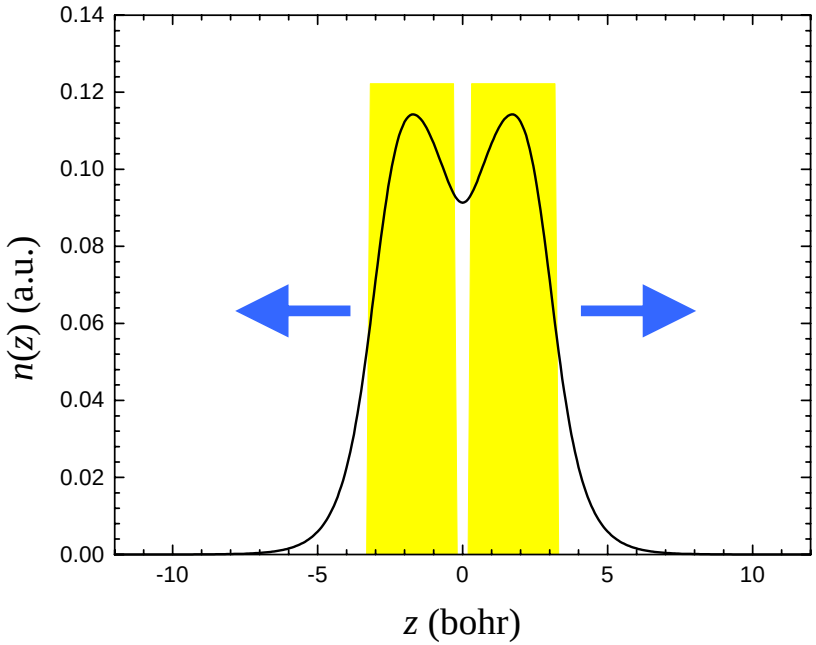
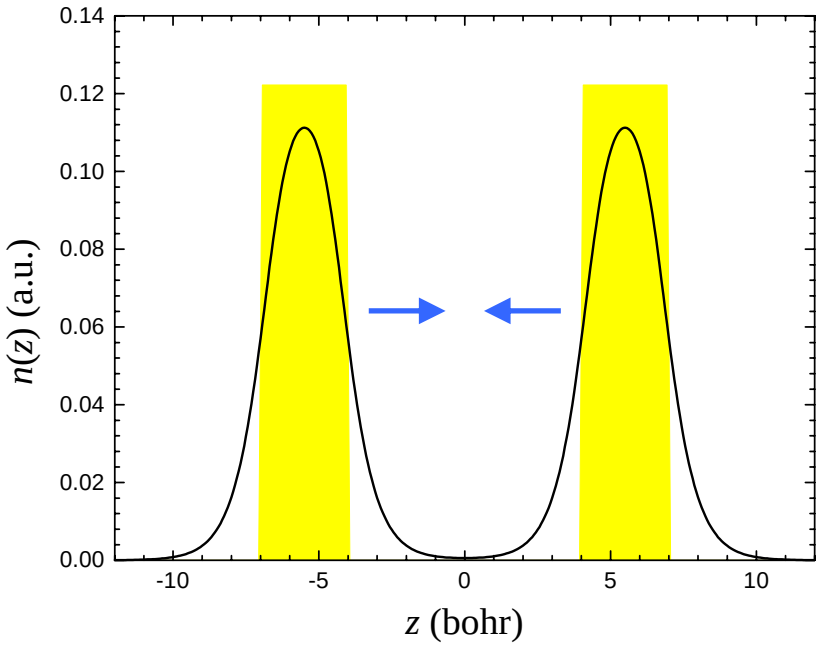


If $d \approx 3$ bohr : There is a *strong repulsive* force

If $d >> 0$: There is a *weak van der Waals attractive* force $\propto - d^{-7/2}$





It reaches *mechanical equilibrium* at a distance d_0 (a “jellycule”)

A brief summary of some KS results:

a) The LDA predicts a weak bond between the films:

d_0 = 6.38 bohr ; D = 0.53 mHa/e

b) The EXX (+local C) does not bind the films

c) The GGA binds very weakly the films at $d_0 >> 0$

Note that LDA/GGA cannot describe vdW forces

A brief theoretical background

Exact exchange:

$$E_{\mathrm{X}}[n] = -\frac{1}{2}\sum_{\sigma}\int d\mathbf{r}\,d\mathbf{r}'\,\frac{1}{|\mathbf{r}-\mathbf{r}'|}\left|\sum_{n}^{\mathrm{occ}}\phi^{*}_{n,\sigma}(\mathbf{r})\phi_{n,\sigma}(\mathbf{r}')\right|^{2}$$

Exact correlation: fluctuation-dissipation theorem + adiabatic connection

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Exact correlation: fluctuation-dissipation theorem + adiabatic connection

$\chi_a(\omega)$ is the linear response associated to an observable $\hat{a}$: $\delta a(\omega) = \chi_a(\omega)\delta f_{\mathrm{ext}}(\omega)$

$$(\Delta a)_{\mathrm{gs}} = -\frac{1}{\pi}\int_0^{+\infty} \mathrm{d}\omega\,\Im[\chi_a(\omega)] \quad \text{and} \quad \mathrm{w}(\omega) = -2\delta f^{*}_{\mathrm{ext}}(\omega)\Im[\chi_a(\omega)]f_{\mathrm{ext}}(\omega)$$

$a \to n(\mathbf{r})$:

$$\langle\hat{W}\rangle_{\mathrm{gs}} = W_{\mathrm{H}}[n_{\mathrm{gs}}] - \frac{1}{2}\int \mathrm{d}\mathbf{r}_1\,\mathrm{d}\mathbf{r}_2\,\frac{1}{r_{12}}\left[\delta(\mathbf{r}_1-\mathbf{r}_2)n_{\mathrm{gs}}(\mathbf{r}_1) - \frac{1}{\pi}\int_0^{+\infty}\mathrm{d}\omega\,\Im[\chi(\mathbf{r}_1,\mathbf{r}_2;\omega)]\right]$$

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Exact correlation: fluctuation-dissipation theorem + adiabatic connection

$$E_{\mathrm{XC}}[n] = -W_{\mathrm{H}}[n] + \int_0^1 \mathrm{d}\lambda \left\langle \Phi_\lambda \middle| \hat{W} \middle| \Phi_\lambda \right\rangle$$

$$= -\frac{1}{2}\int_0^1 \mathrm{d}\lambda \int \mathrm{d}\mathbf{r}_1\,\mathrm{d}\mathbf{r}_2\,\frac{1}{r_{12}}\left[\delta(\mathbf{r}_1-\mathbf{r}_2)n(\mathbf{r}_1) - \frac{1}{\pi}\int_0^{+\infty}\mathrm{d}\omega\,\Im[\chi_\lambda(\mathbf{r}_1,\mathbf{r}_2;\omega)]\right]$$

A brief theoretical background

Exact exchange:

$$E_{\mathrm{X}}[n] = -\frac{1}{2}\sum_{\sigma}\int d\mathbf{r}\,d\mathbf{r}'\,\frac{1}{|\mathbf{r}-\mathbf{r}'|}\left|\sum_{n}^{\mathrm{occ}}\phi^{*}_{n,\sigma}(\mathbf{r})\phi_{n,\sigma}(\mathbf{r}')\right|^{2}$$

Exact correlation: fluctuation-dissipation theorem + adiabatic connection

Substracting $E_{\mathrm{X}}[n]$

$$E_{C}[n] = -\frac{1}{2}\int_{0}^{1}\mathrm{d}\lambda\int \mathrm{d}\mathbf{r}_1\,\mathrm{d}\mathbf{r}_2\,\frac{1}{r_{12}}\left[\frac{1}{\pi}\int_{0}^{+\infty}\mathrm{d}\omega\left[\chi_{\lambda}(\mathbf{r}_1,\mathbf{r}_2;\mathrm{i}\omega)-\chi_{0}(\mathbf{r}_1,\mathbf{r}_2;\mathrm{i}\omega)\right]\right]$$

2. ENERGY-OPTIMIZED KERNELS

We need to evaluate the λ-interacting density response:

$$\chi_\lambda(\mathbf{r},\mathbf{r}';i\omega) = \chi_0(\mathbf{r},\mathbf{r}';i\omega) + \int d\mathbf{r}_1 d\mathbf{r}_2 \chi_0(\mathbf{r},\mathbf{r}_1;i\omega)\left[\frac{\lambda}{r_{12}} + f_{XC,\lambda}(\mathbf{r}_1,\mathbf{r}_2;i\omega)\right]\chi_\lambda(\mathbf{r}_2,\mathbf{r}';i\omega)$$

$f_{XC,\lambda}$ is the XC kernel of the fictitious λ-system.

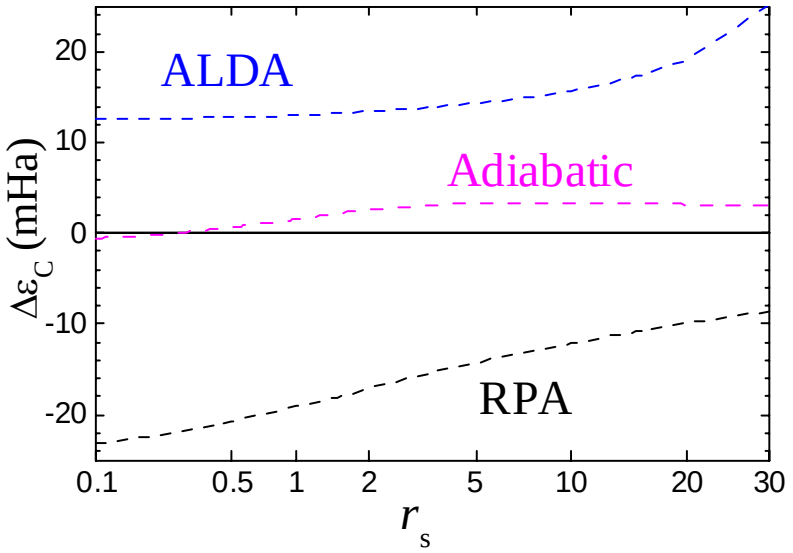
HEG results of some [simple] choices

RPA $f_{XC,\lambda} = 0$

ALDA $f_{XC,\lambda}(\mathbf{r},\mathbf{r}';\omega) = \lambda^{-1}\kappa_{XC}(\lambda^{-3}n(\mathbf{r}))\delta(\mathbf{r}_{12})$

Parametrisation of the static HEG kernel (COR)

[from M. Lein *et al*, PRB 61, 13431 (2000)]



We want to reproduce the exact C energy of the HEG:

a) Design an "energy-optimised" kernel **(OPT)**
[Dobson & Wang, PRB **62**, 10038 (2000)]

b) Add a LDA (or GGA) term to the RPA-ACFDT **(RPA+)**
[Kurth & Perdew, PRB **59**, 10461 (1999)]

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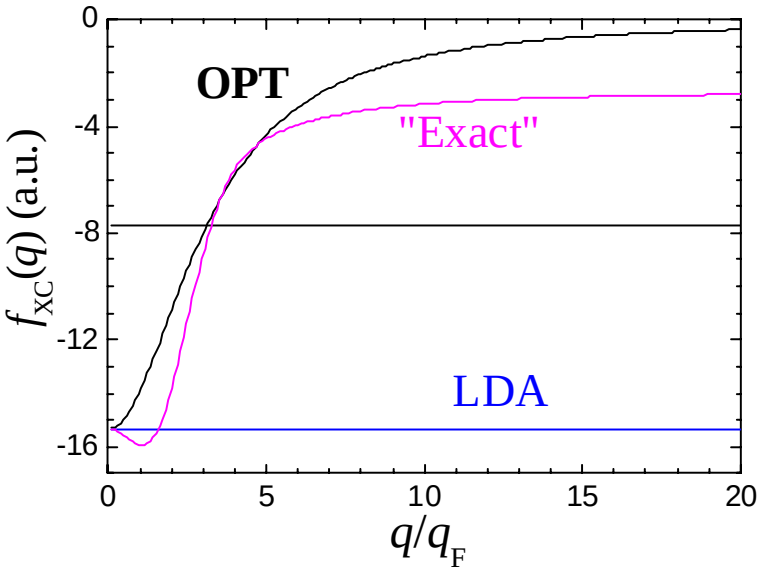
The OPT kernel will be **static**, **nonlocal,** and simple:



$$f_{\mathrm{XC}}^{\mathrm{heg}}(n;\mathbf{q};\mathrm{i}\omega) \approx f_{\mathrm{opt}}^{\mathrm{heg}}(n;\mathbf{q}) = \frac{\kappa_{\mathrm{XC}}(n)}{1+\beta(n)q^2}$$

For an arbitrary inhomogeneous system we rescale the kernel:

$$f_{\mathrm{XC},\lambda}(\mathbf{r}_1,\mathbf{r}_2;\mathrm{i}\omega) \approx \frac{1}{\lambda} f_{\mathrm{opt}}^{\mathrm{heg}}\left(\frac{n(\mathbf{r}_1)+n(\mathbf{r}_2)}{2\lambda^3}, \lambda|\mathbf{r}_1-\mathbf{r}_2|\right)$$

3. APPLICATION: JELLIUM SLABS

A toy system (again). **Our aim:**

a) A first analysis of the XC results

b) Assess the robustness of the energy-optimisation procedure

c) Analyse the importance of self-consistency

We will focus on a single slab: $r_s = 4$; $L = 25.6$ bohr

Energy (mHa/e)

(using LDA wave-functions to evaluate EXX and ACFDT)

T_S	E_{el}	E_X		E_C					
		LDA	**EXX**	**LDA**	**RPA**	**RPA+**	**OPT**	**OPT(*L*)**	**Cor**
67.13	0.55	- 111.54	- 112.44	- 31.34	- 45.16	- 30.25	- 30.28	- 30.4	- 27.1

T_S	E_{el}	E_X		E_{XC}					
		LDA	**EXX**	**LDA**	**RPA**	**RPA+**	**OPT**	**OPT(*L*)**	**Cor**
67.13	0.55	- 111.54	- 112.44	- 142.88	- 157.60	- 142.69	- 142.72	- 142.8	- 139.5

a) LDA: slight compensation between exchange and correlation

b) The optimisation procedure is **very robust.**

"Splitting" energy (mHa/e)

ΔT_S	ΔE_{el}	ΔE_X		ΔE_C					
		LDA	**EXX**	**LDA**	**RPA**	**RPA+**	**OPT**	**OPT(*L*)**	**Cor**
- 1.90	+ 0.48	+ 2.88	+ 1.83	+ 0.51	+ 1.72	+ 1.64	+ 1.64	+ 1.65	+ 1.65

ΔT_S	ΔE_{el}	ΔE_X		ΔE_{XC}					
		LDA	**EXX**	**LDA**	**RPA**	**RPA+**	**OPT**	**OPT(*L*)**	**Cor**
- 1.90	+ 0.48	+ 2.88	+ 1.83	+ 3.39	+ 3.55	+ 3.47	+ 3.47	+ 3.48	+ 3.48

a) LDA: strong compensation between exchange and correlation

b) Any well-motivated inclusion of local-field effects **gives the same results**, reducing the RPA correction.

Limit of infinite width: "splitting" energy (per surface unit) is twice
the “jellium” surface energy

Long-standing problem:
a strong deviation between DQMC and LDA results

Very likely [J.M. Pitarke, PRB in press]: wrong DQMC surface energies due to a failure in the extrapolation to the infinite width limit.

The finite width results suggest:
actual jellium surface energies lies between LDA and RPA

XC contribution to the surface energy (erg/cm^2)

(EXX+ACFDT values from LDA wave-functions)

r_S	**KS-LDA**	**RPA**	**OPT**	**RPA+**
2.0	3355.	3470	3422	3419
2.3	2019.	2099	2066	2063
3.0	764.1	803	788	785
4.0	261.5	279.0	273.0	270.5
5.0	111.1	119.5	116.5	115.0
dev. (%)	**-2.0 – -4.6**	**+1.4 – +2.6**	–	**-0.1 – -1.3**

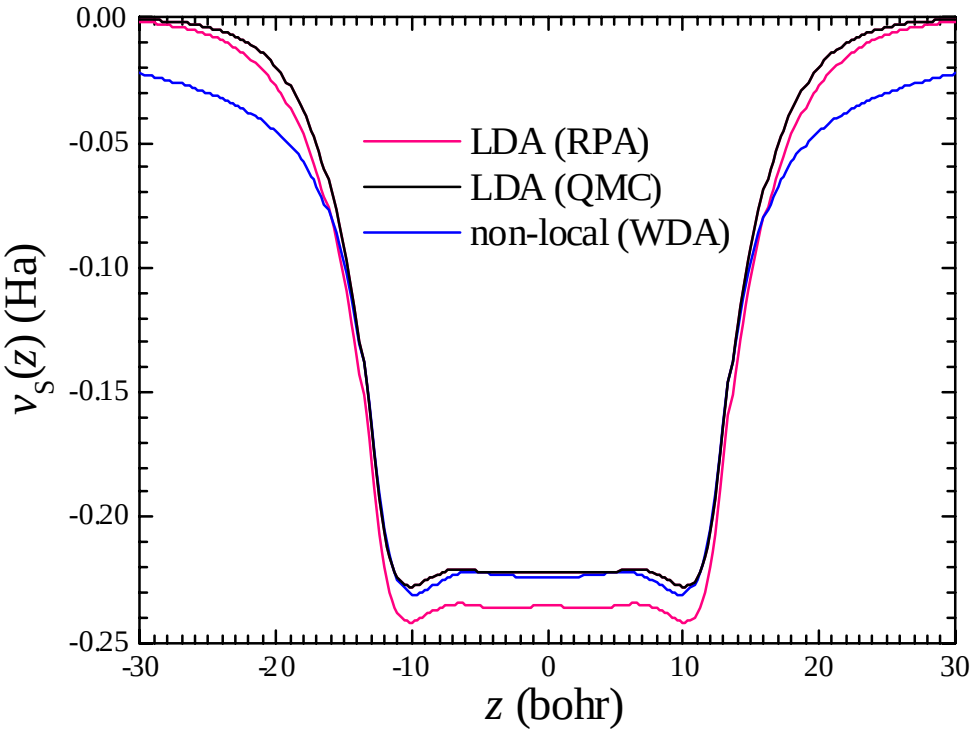
NOTE: Numerical uncertainties of ACFDT results: 0.1 – 0.5 %

Some notes about self-consistency:

KS-TDF is **variational**:

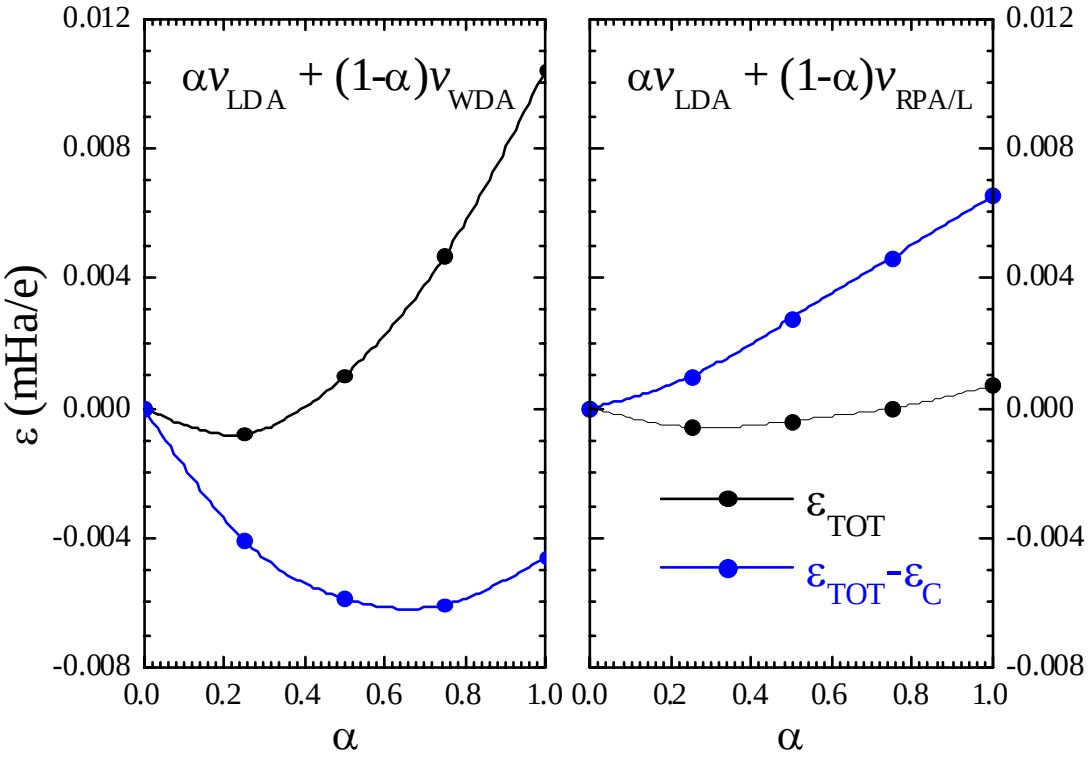
Linear deviations from the potential (or the density) that minimises $E[n]$ induces quadratic deviations on the energy.

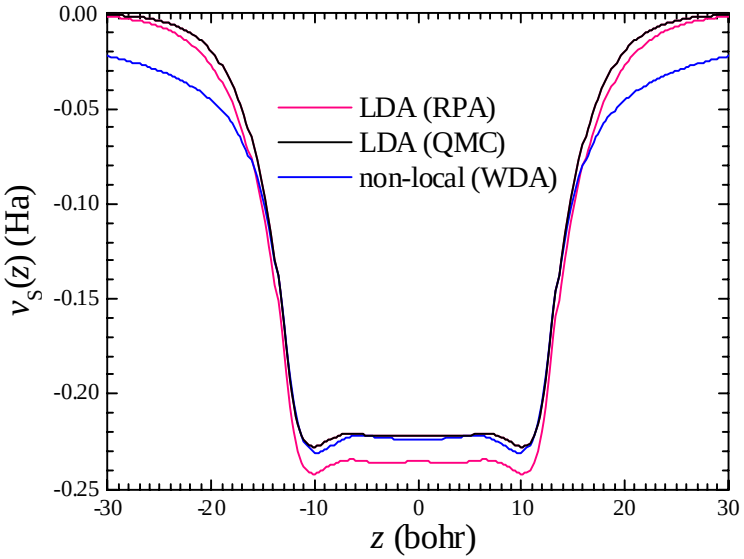
1st test: linear mixing of v_S's from different XC functionals:



$r_s = 4$; $L = 25.6$ bohr

Some notes about self-consistency (OPT)





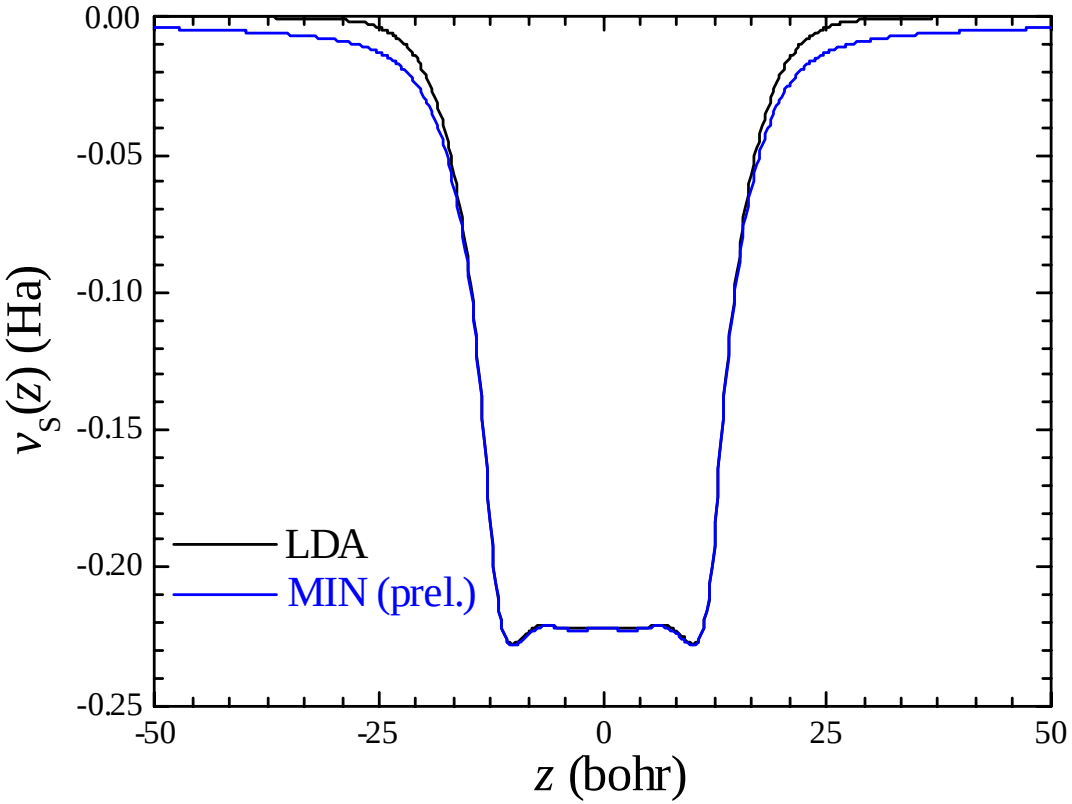
The variation on the total energy per electron is ~0.01 mHa (0.015%)

Some notes about self-consistency (OPT)

An estimation of the actual self-consistent gs energy:
minimisation over a parametrised v_S potential

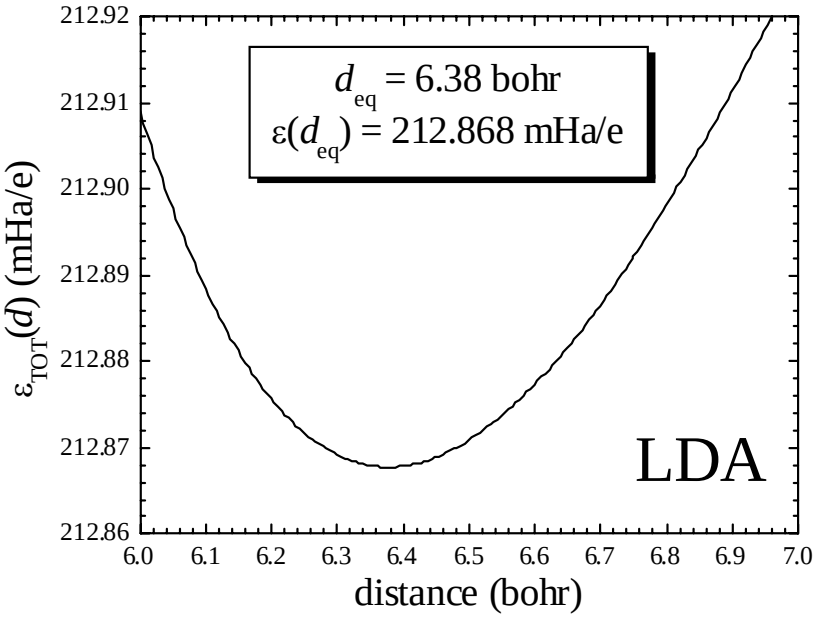
$$E[n_{SC}] - E[n_{LDA}] = -(9 \pm 1) \times 10^{-4} \text{ mHa/e}$$

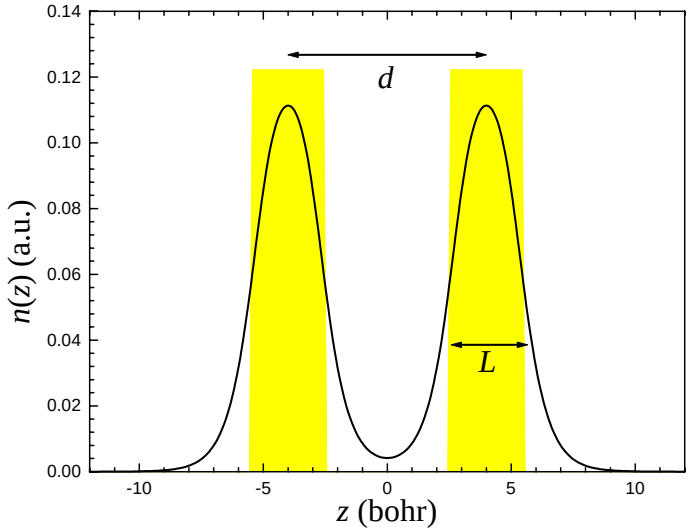
(the ACFDT-OPM total energy from LDA wavefunctions is **75.044 mHa/e**)

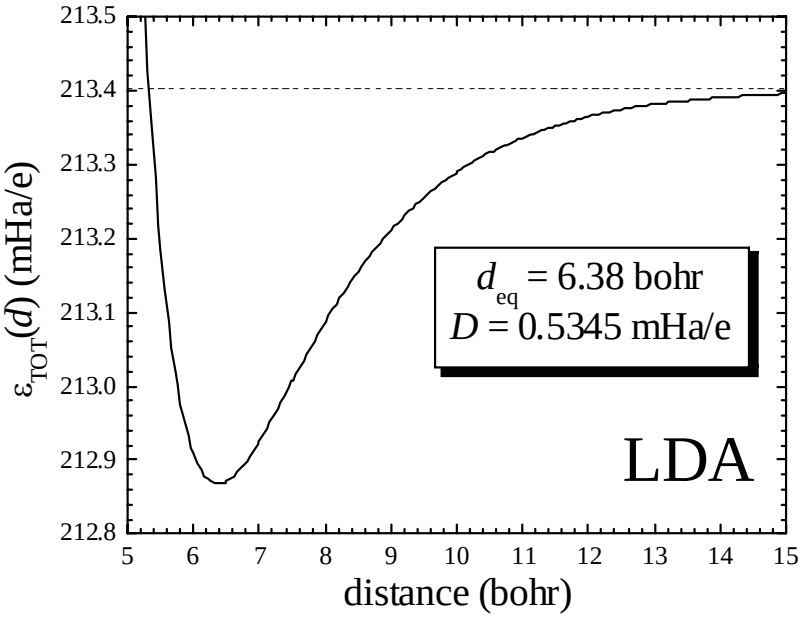


4. A MODEL LAYERED MATERIAL

Structural properties of the "jellycule" (LDA)

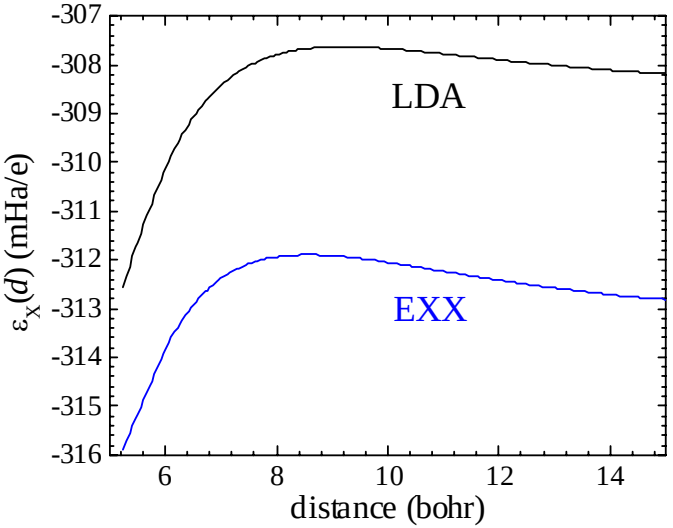


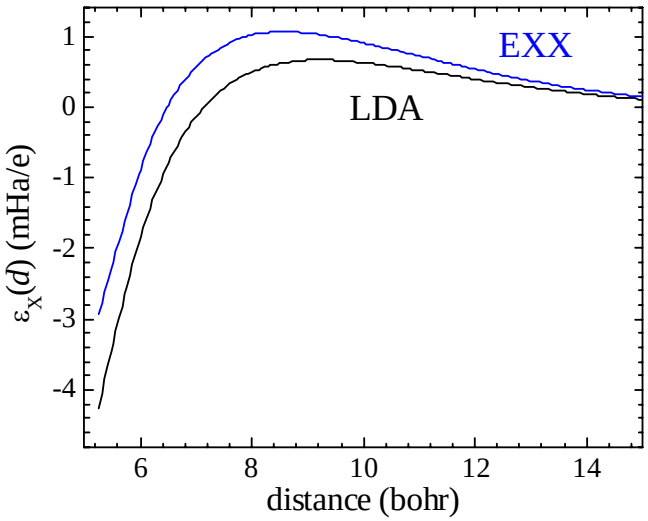




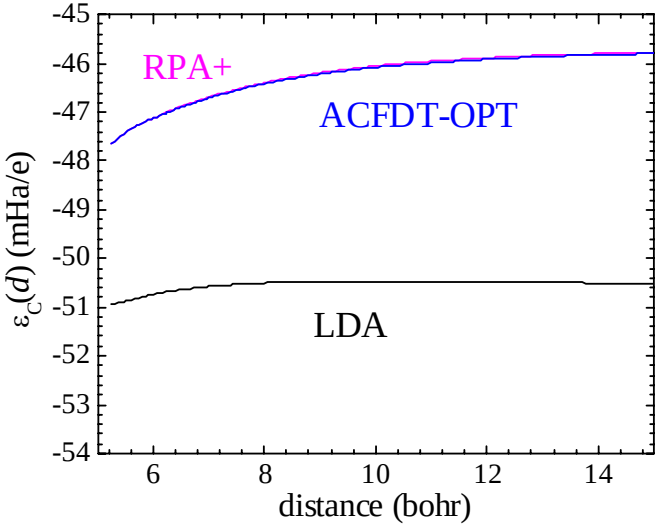
Fully microscopic corrections to LDA:

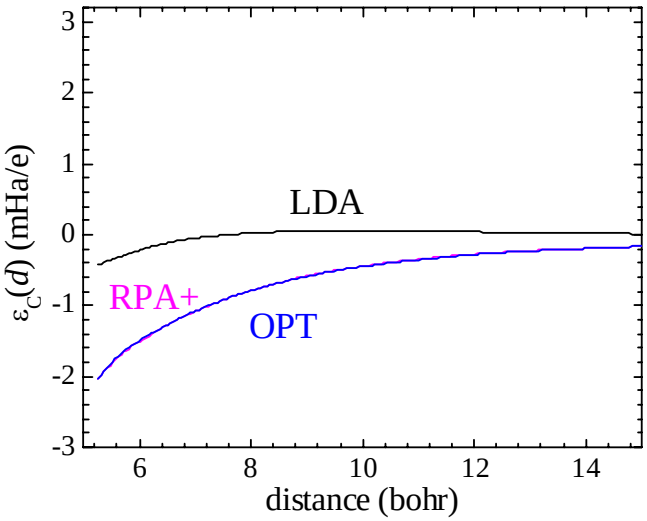
EXCHANGE



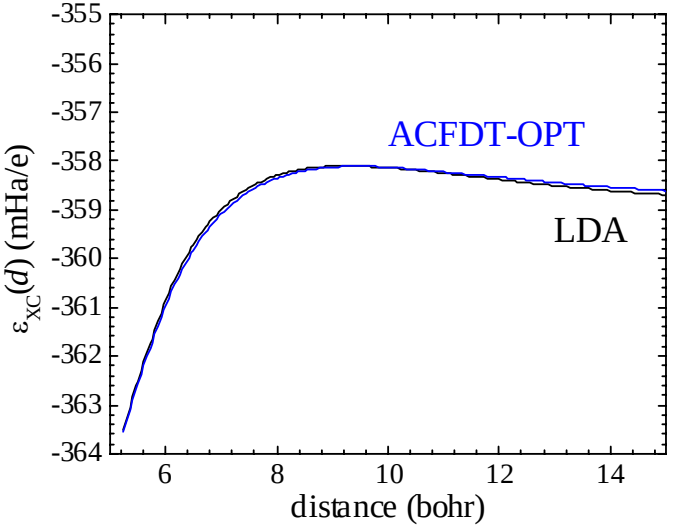


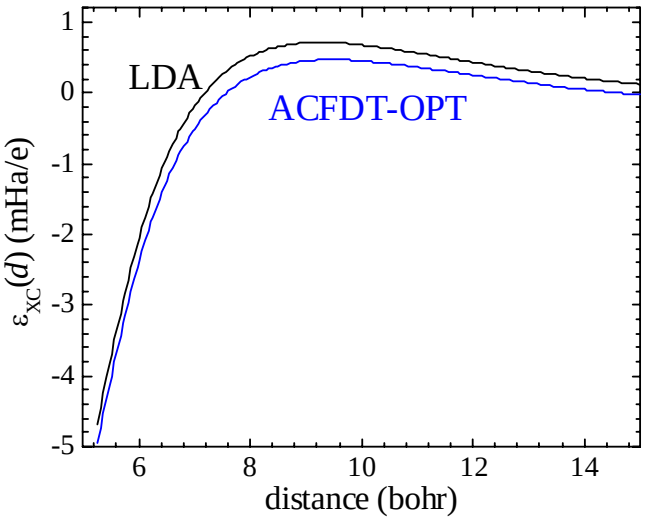
CORRELATION



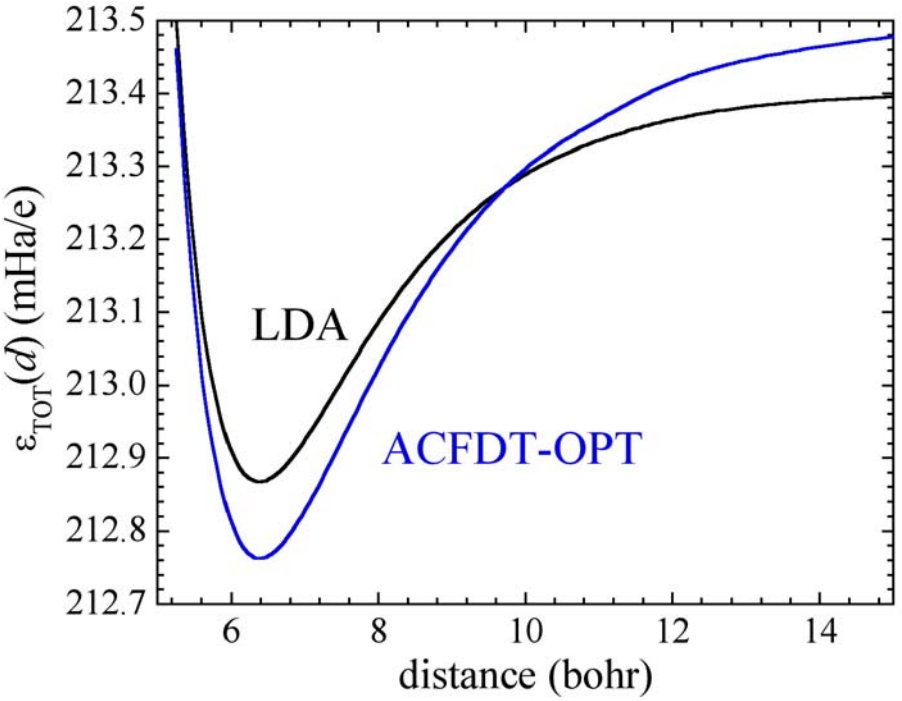


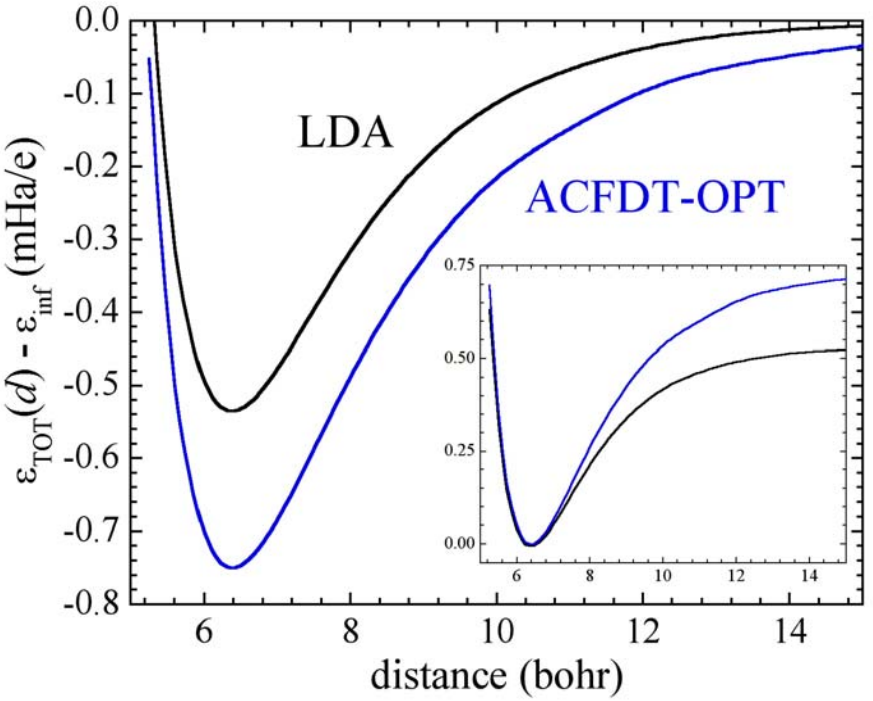
EXCHANGE/CORR.





Final result





The ACFDT-OPT equilibrium layer–layer distance is practically the same

The LDA *underbinds* a 30% the layers

In the RPA, the equilibrium distance is slightly smaller and the binding energy slightly greater than OPT

5. "REAL" SYSTEMS

Some remarks:

a) We work under the pseudopotential approximation

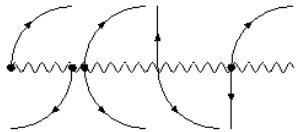
b) We use a plane-wave representation

c) Note that, in this case the correlation energy per volume unit is

$$\frac{E_C[n]}{V} = -\int_0^1 d\lambda \int_0^{+\infty} \frac{d\omega}{2\pi} \int_0^{+\infty} \frac{d\mathbf{k}}{(2\pi)^3} \sum_{\mathbf{G}} \frac{4\pi}{|\mathbf{k}+\mathbf{G}|^2} \Delta\chi_\lambda(\mathbf{k},\mathbf{G},\mathbf{G};i\omega)$$

d) The "critical" convergence parameters are the number of bands to build χ_0 and the sampling of the BZ.

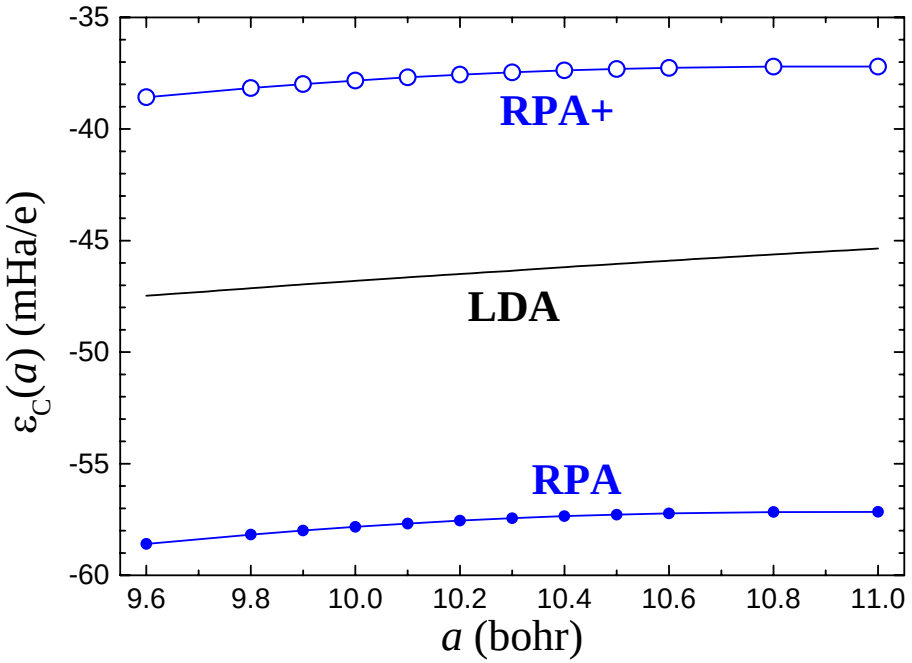
e) We use **Andrea Marini's**

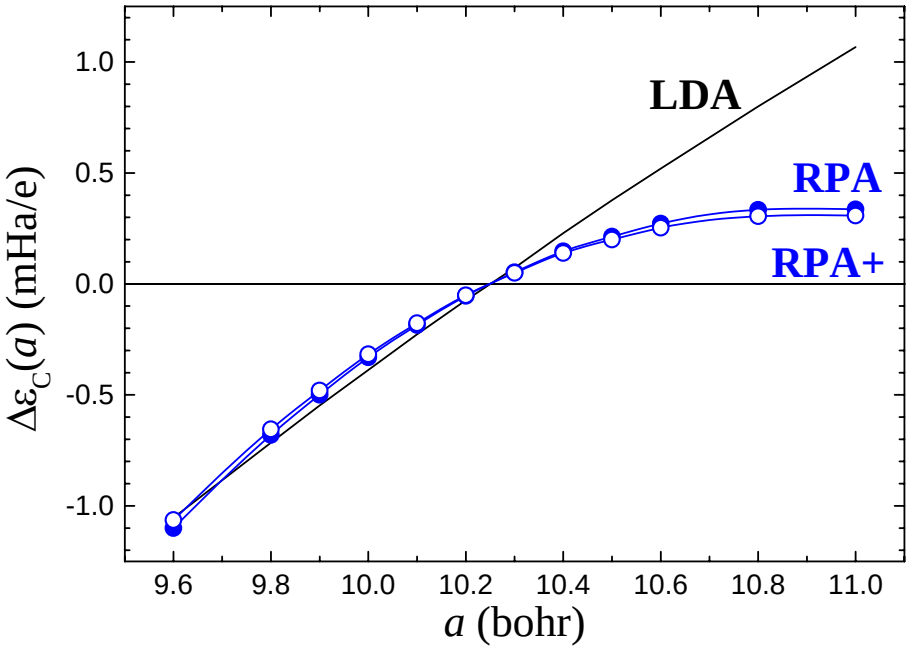


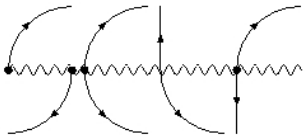
A shiny pot of fun and happiness

TD-DFT
Bethe-Salpeter equation
Ab-initio f_{xc} (**r**,**r'**,ω) kernel
Quasiparticle properties (*GW* and *GW*Γ)
EXX-ACFDT XC energies

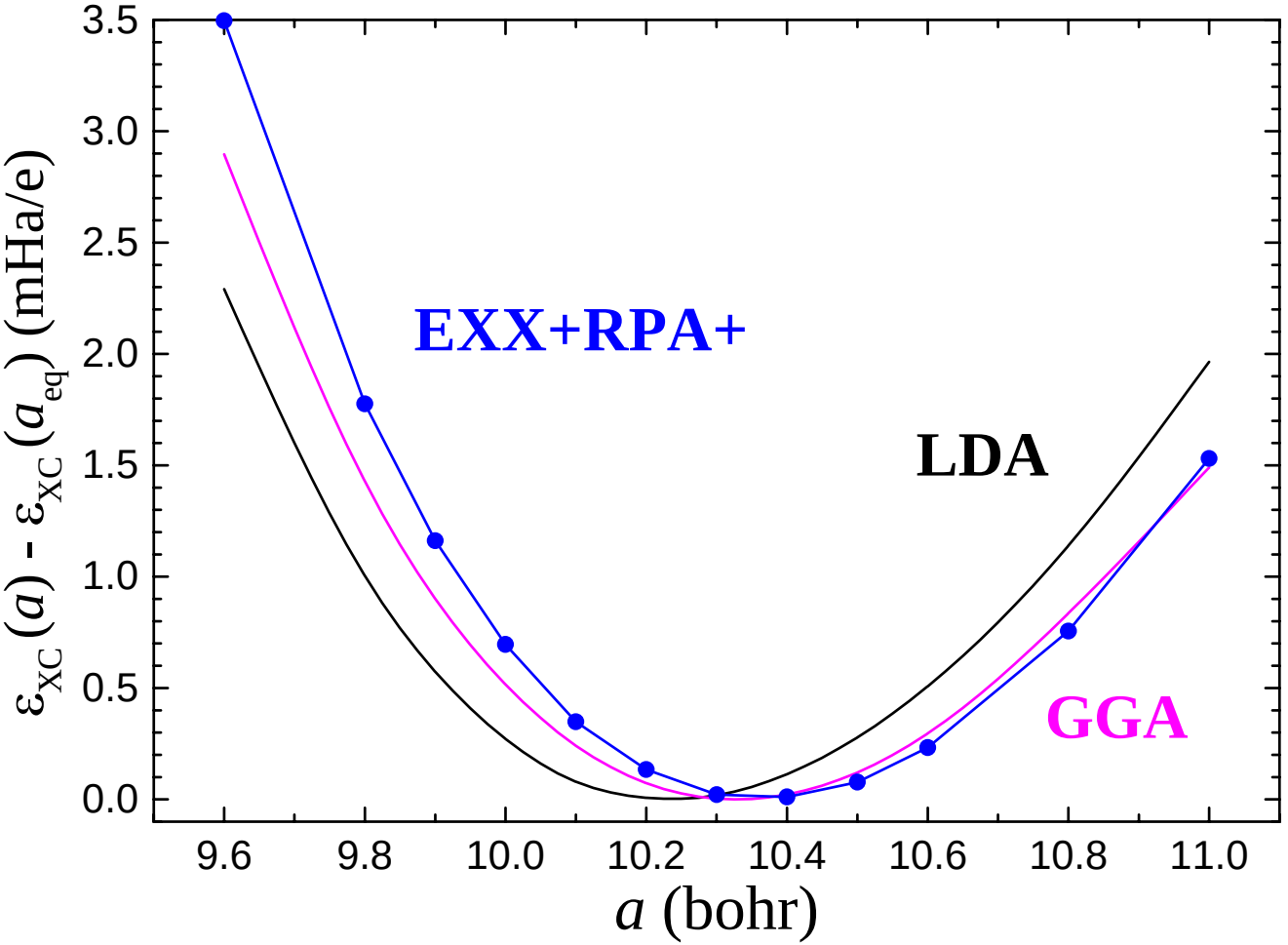
Silicon:

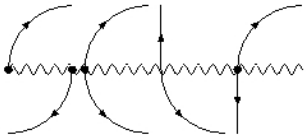

-35
-40
-45
-50
-55
-60
RPA+
LDA
RPA
9.6
9.8
10.0
10.2
10.4
10.6
10.8
11.0
$\varepsilon_C(a)$ (mHa/e)
a (bohr)


1.0
0.5
0.0
-0.5
-1.0
LDA
RPA
RPA+
9.6
9.8
10.0
10.2
10.4
10.6
10.8
11.0
$\Delta\varepsilon_C(a)$ (mHa/e)
a (bohr)

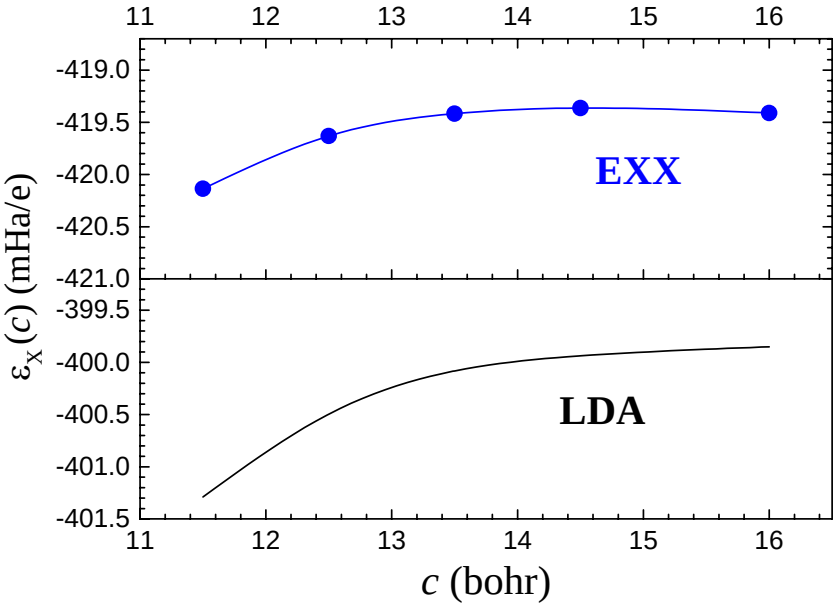


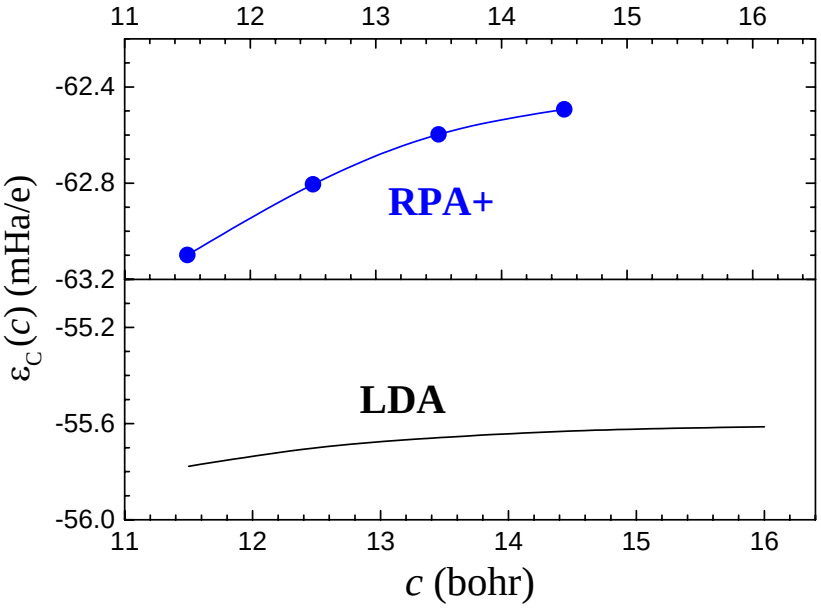
Silicon:

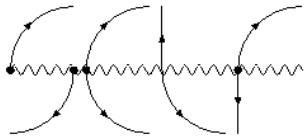

3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
9.6
9.8
10.0
10.2
10.4
10.6
10.8
11.0
$\varepsilon_{XC}(a) - \varepsilon_{XC}(a_{eq})$ (mHa/e)
a (bohr)
EXX+RPA+
LDA
GGA



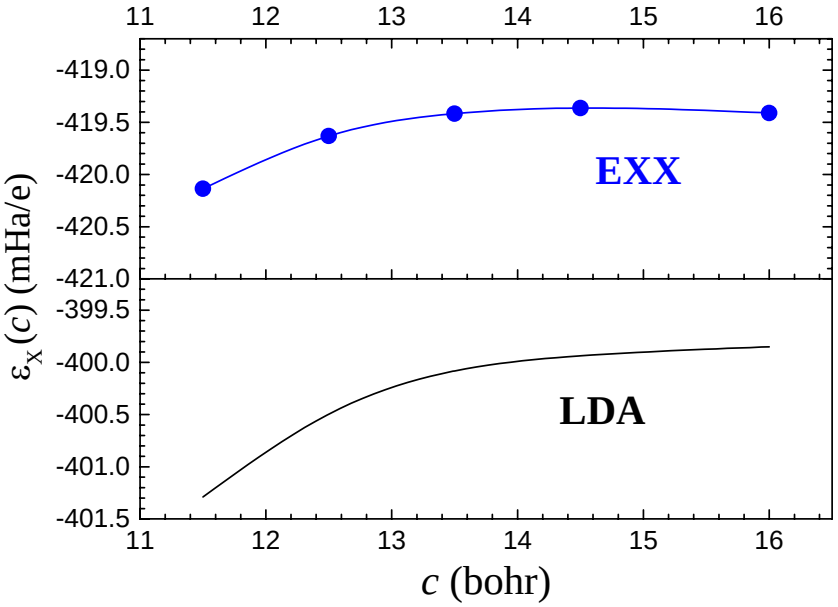
Boron nitride (preliminary results):

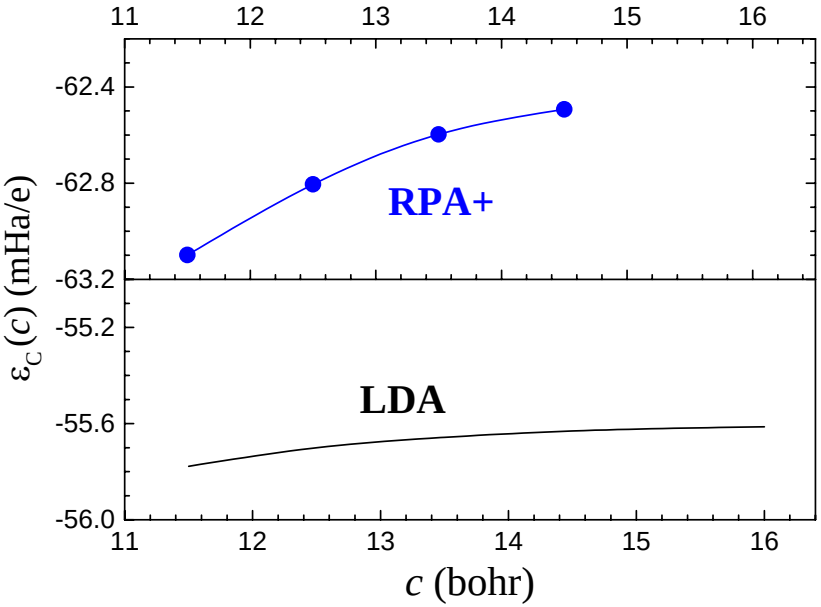


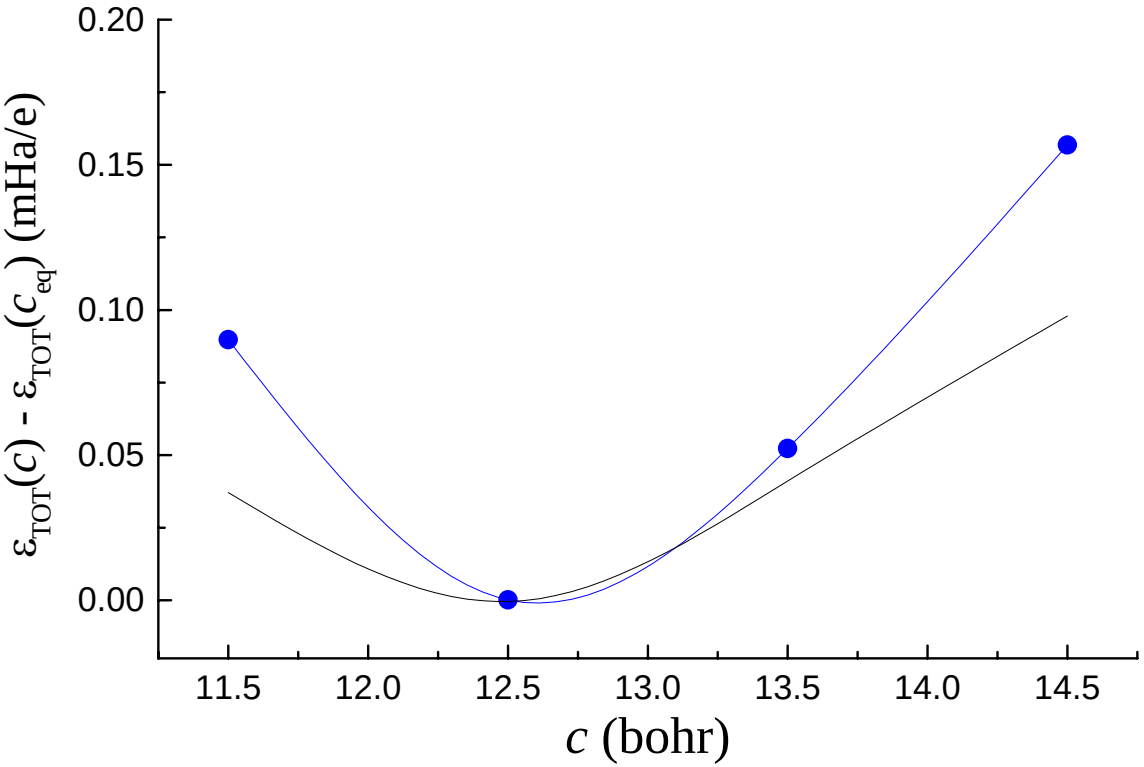


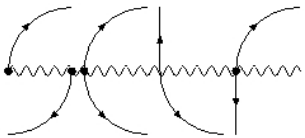


Boron nitride (preliminary results):









CONCLUSIONS

KS – EXX+ACFDT: a fully microscopic method
Local field corrections: an energy optimisation procedure **(very robust)**
Application to model and real systems: evident improvement upon LDA/GGA

PERSPECTIVES

Better kernels (SIC)
A deeper study of self-consistency
Other materials and comparison with other microscopic methods (MBPT)
Technical improvements of the implementation in