

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

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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 methods” (DQMC, CI):

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
- **A better treatment of electron correlations is guaranteed**

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Nice to keep some advantages of KS-DFT:

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

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TD-DFT for correlation + Exact exchange

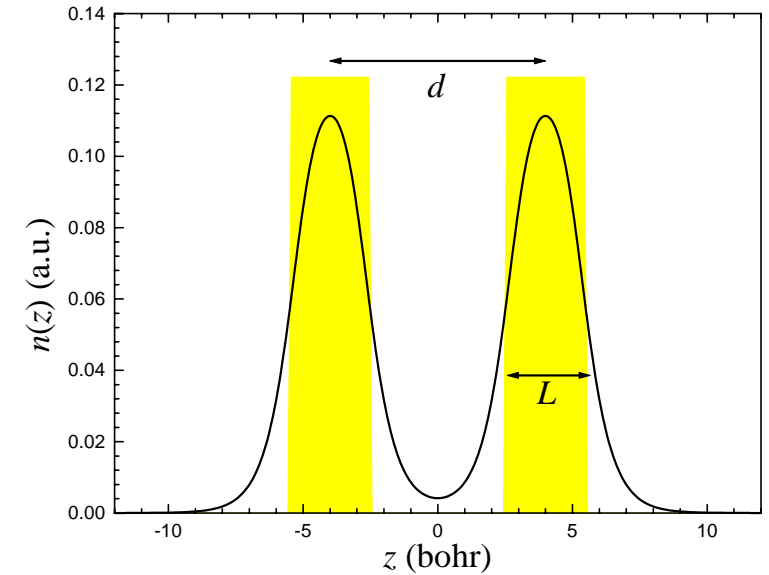
– *use a fully microscopic theory to build “advanced” $E_{XC}[n]$ –*

- Step towards “chemical accuracy”
- May solve situations where 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 $r_s = 1.25$)

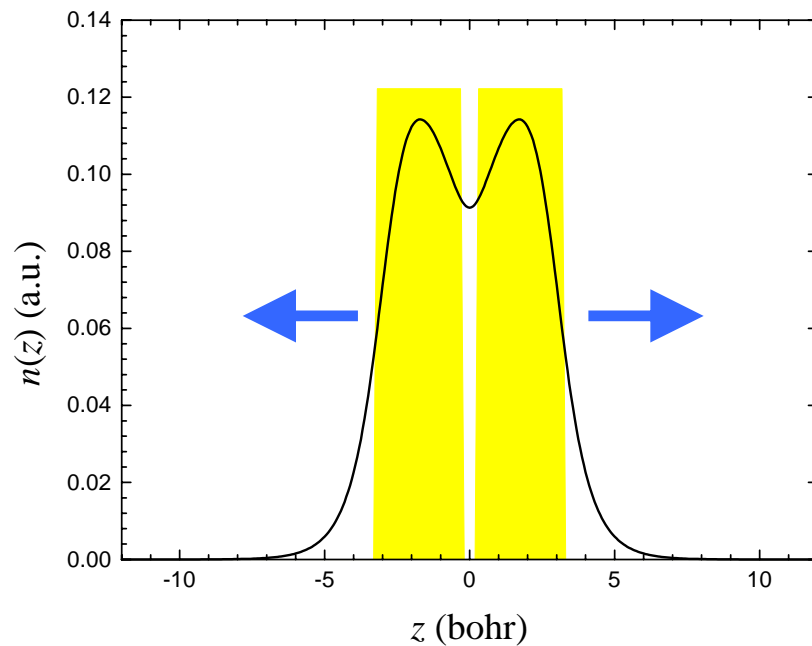
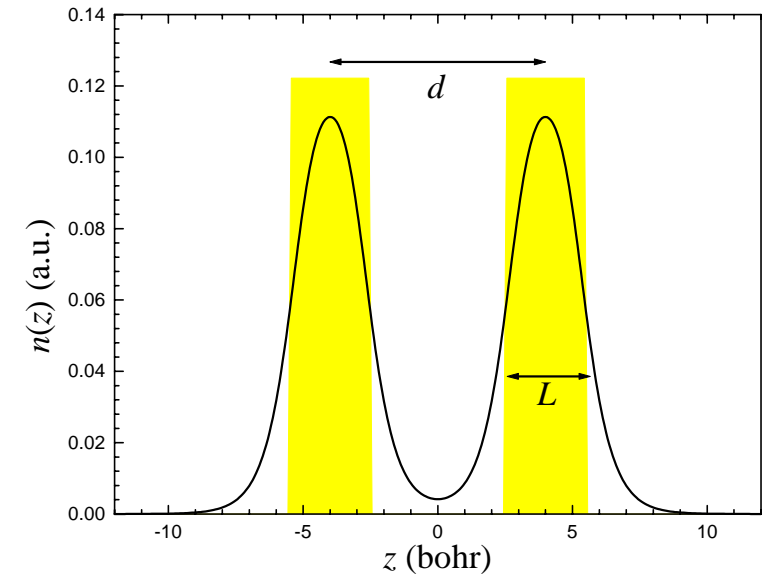


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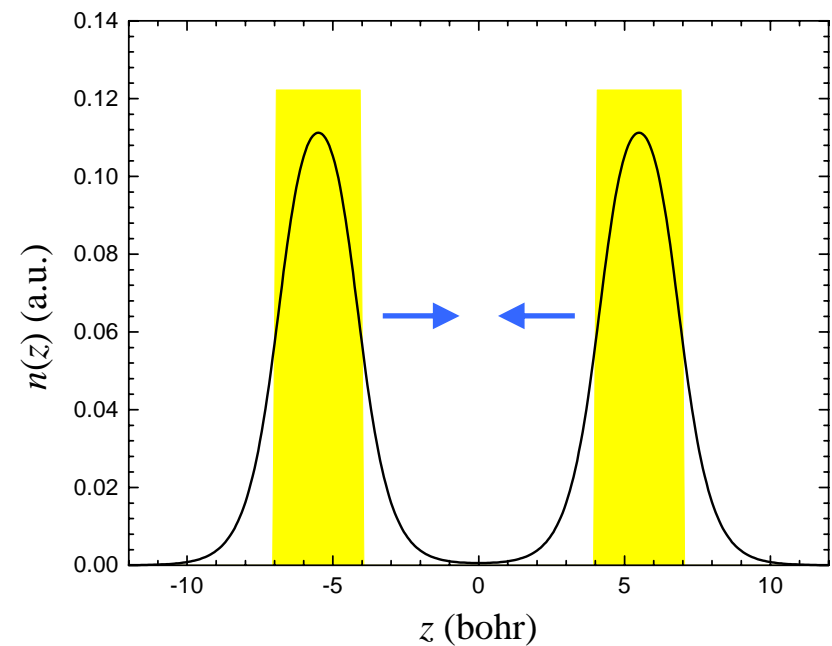
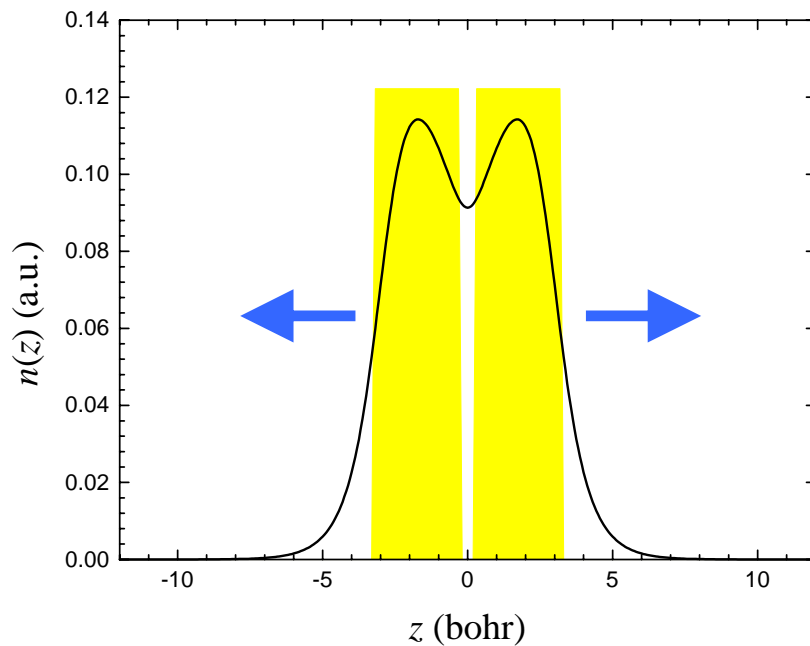
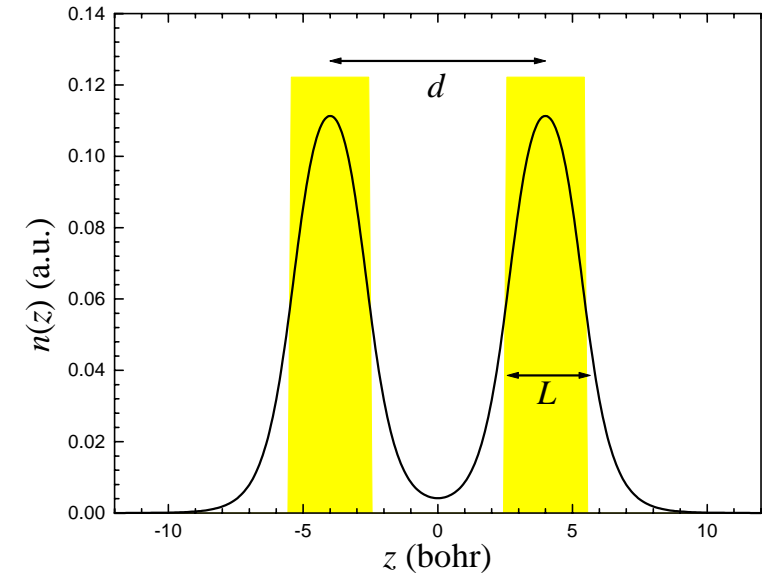
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If $d \approx 3$ bohr : There is a *strong repulsive* force

If $d \gg 0$: 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:

$$d_0 = 6.38 \text{ bohr} ; D = 0.53 \text{ mHa/e}$$

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

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

Note that LDA/GGA cannot describe vdW forces

A brief theoretical background

Exact exchange:

$$E_X[n] = -\frac{1}{2} \sum_{\sigma} \int d\mathbf{r} d\mathbf{r}' \frac{1}{|\mathbf{r} - \mathbf{r}'|} \left| \sum_n^{\text{occ}} \phi_{n,\sigma}^*(\mathbf{r}) \phi_{n,\sigma}(\mathbf{r}') \right|^2$$

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} : $\delta a(\omega) = \chi_a(\omega) \delta f_{\text{ext}}(\omega)$

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

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

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

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Exact correlation: fluctuation-dissipation theorem + adiabatic connection

$$\begin{aligned} E_{XC}[n] &= -W_H[n] + \int_0^1 d\lambda \langle \Phi_{\lambda} | \hat{W} | \Phi_{\lambda} \rangle \\ &= -\frac{1}{2} \int_0^1 d\lambda \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{1}{r_{12}} \left[\delta(\mathbf{r}_1 - \mathbf{r}_2) n(\mathbf{r}_1) - \frac{1}{\pi} \int_0^{+\infty} d\omega \Im[\chi_{\lambda}(\mathbf{r}_1, \mathbf{r}_2; \omega)] \right] \end{aligned}$$

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Exact exchange:

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Exact correlation: fluctuation-dissipation theorem + adiabatic connection

Subtracting $E_X[n]$

$$E_C[n] = -\frac{1}{2} \int_0^1 d\lambda \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{1}{r_{12}} \left[\frac{1}{\pi} \int_0^{+\infty} d\omega [\chi_{\lambda}(\mathbf{r}_1, \mathbf{r}_2; i\omega) - \chi_0(\mathbf{r}_1, \mathbf{r}_2; i\omega)] \right]$$

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.

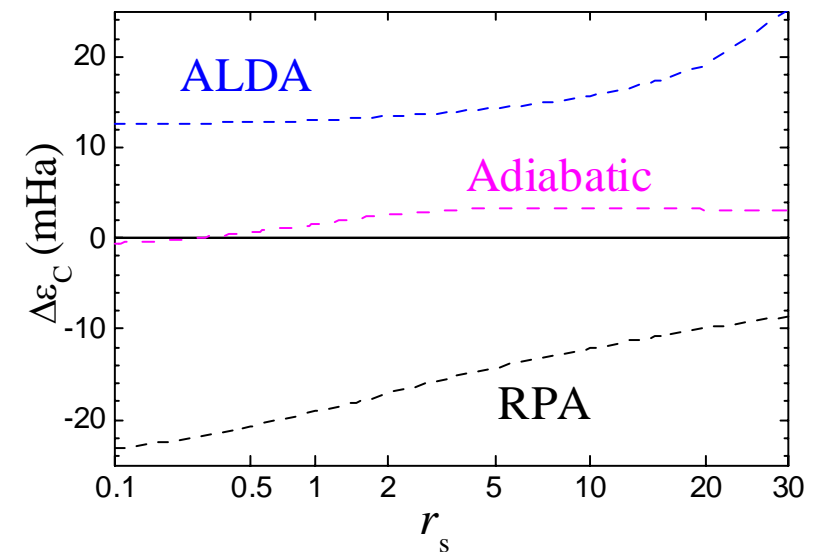
HEG results of some [simple] choices

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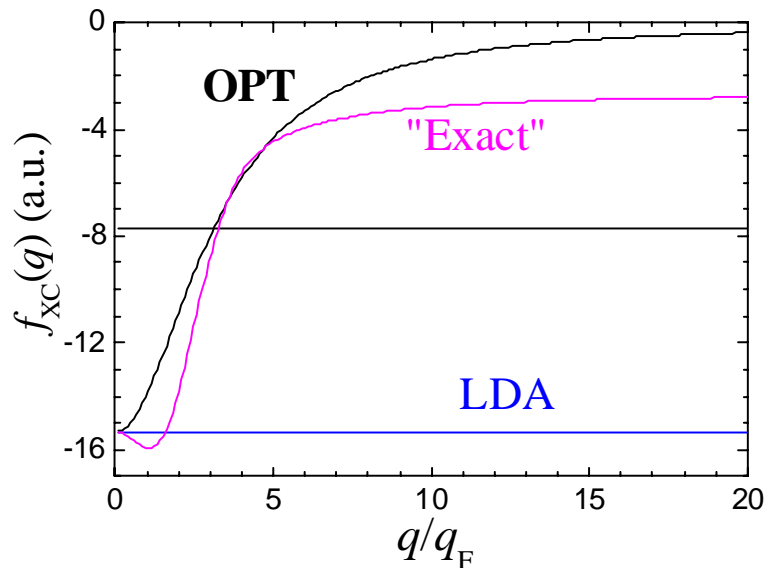
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The OPT kernel will be **static**, **nonlocal**, and simple:



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

For an arbitrary inhomogeneous system we rescale the kernel:

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

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/cm²)
 (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 |

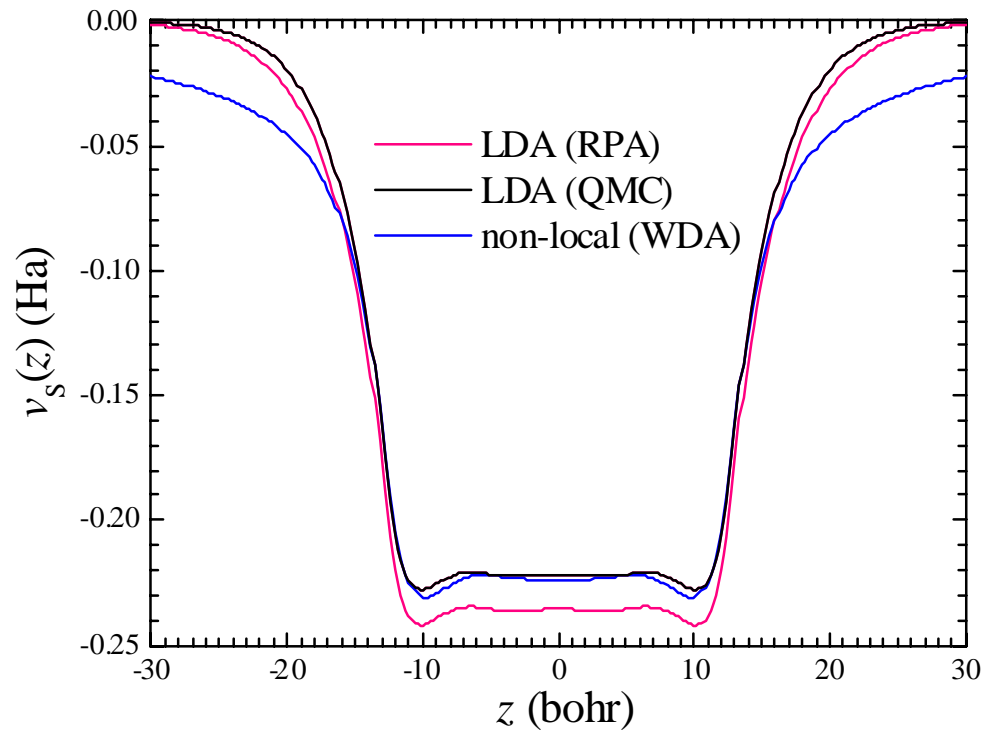
NOTE: Numerical uncertainties of ACFDT results: 0.1 – 0.5 %

Some notes about self-consistency:

KS-TDF is **variational**:

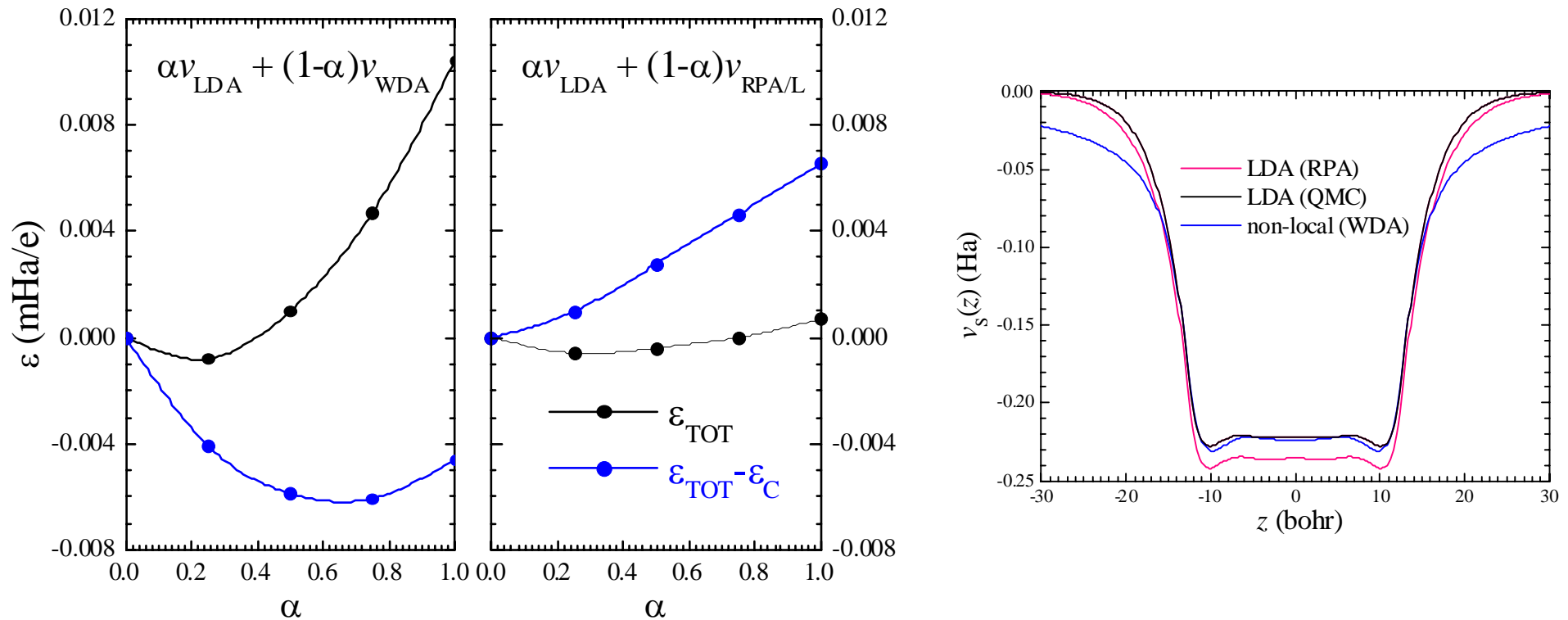
Linear deviations from the potential (or the density) that minimises $E[n]$ induces **quadratic** deviations on the energy.

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



$$r_s = 4; L = 25.6 \text{ bohr}$$

Some notes about self-consistency (OPT)



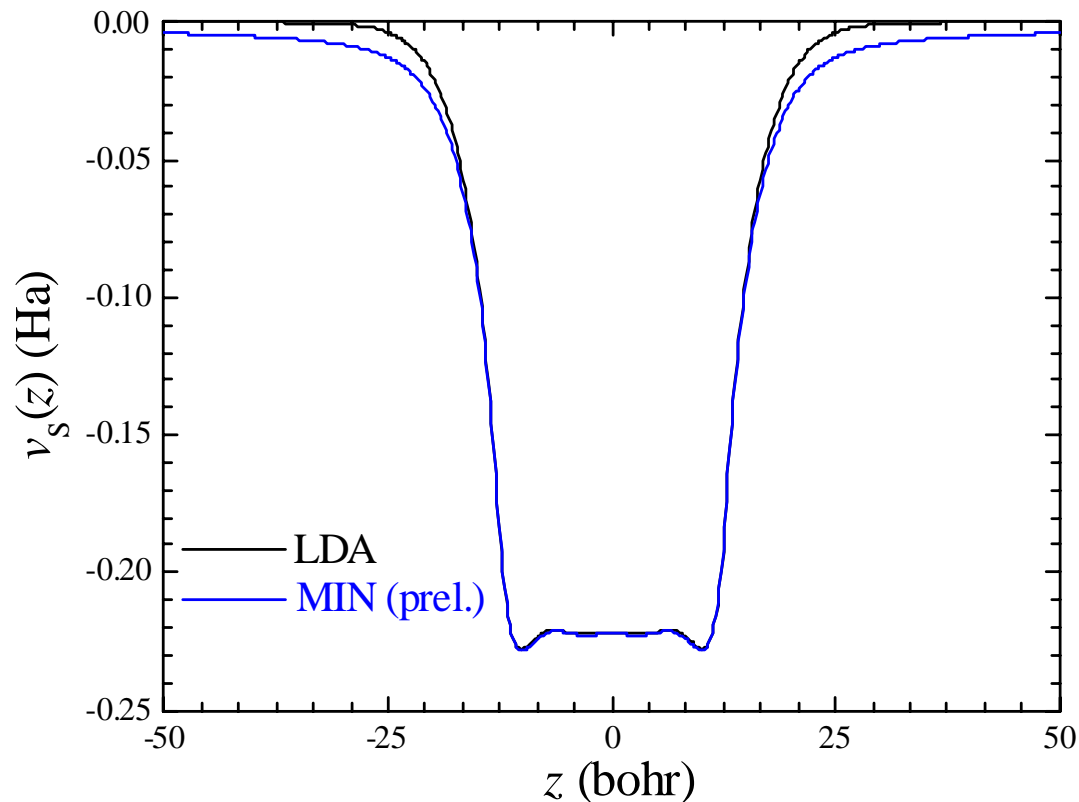
The variation on the total energy per electron is ~ 0.01 mHa (0.015%)

Some notes about self-consistency (OPT)

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

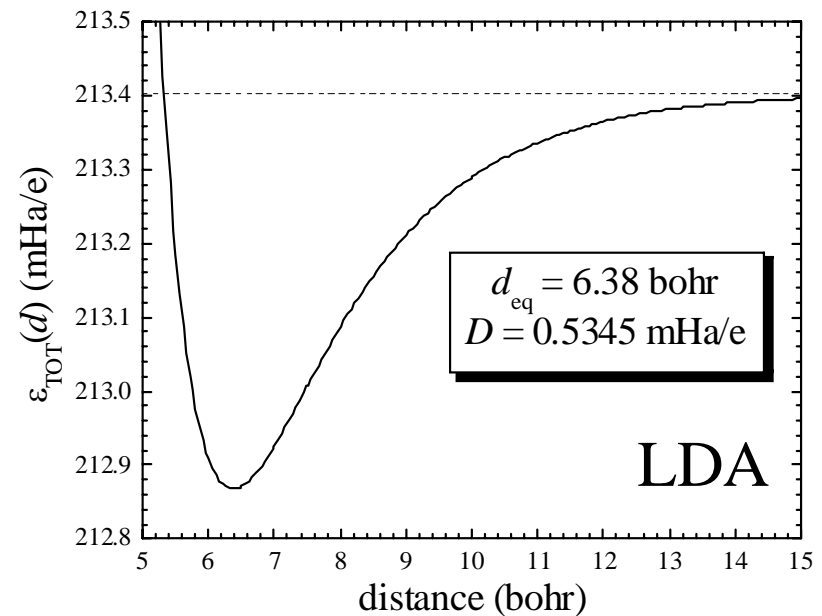
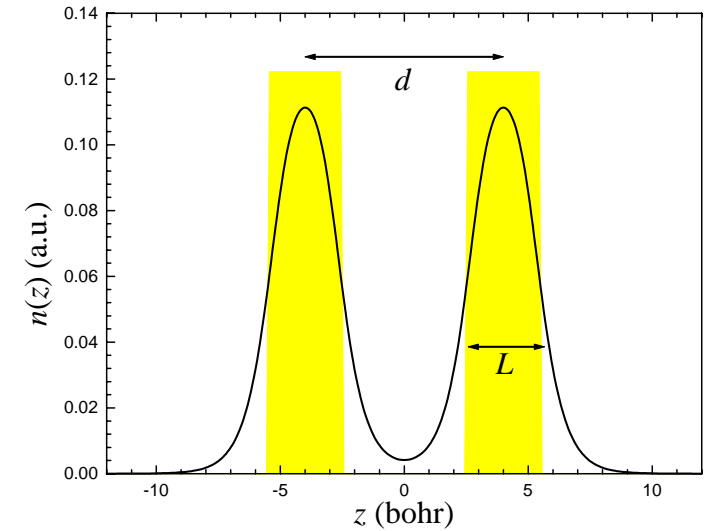
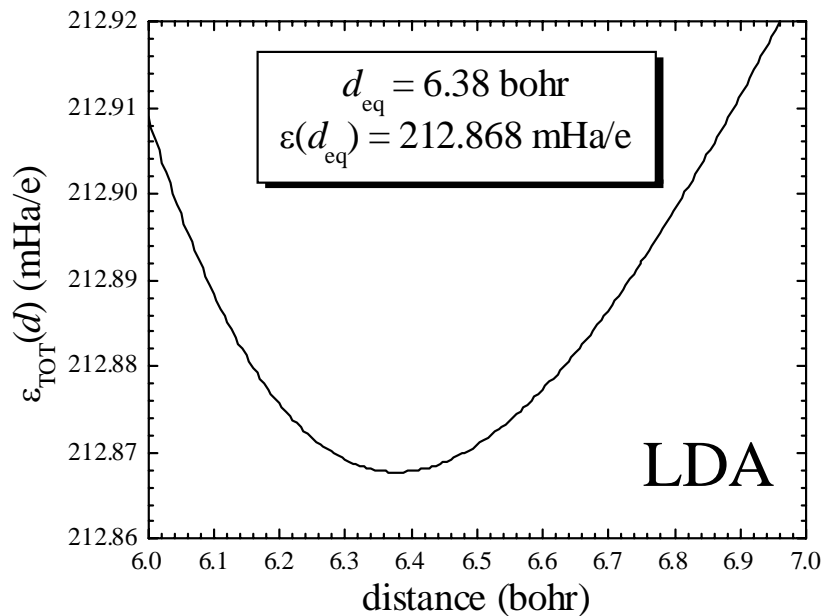
$$E[n_{SC}] - E[n_{LDA}] = - (9 \pm 1) \times 10^{-4} \text{ mHa/e}$$

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



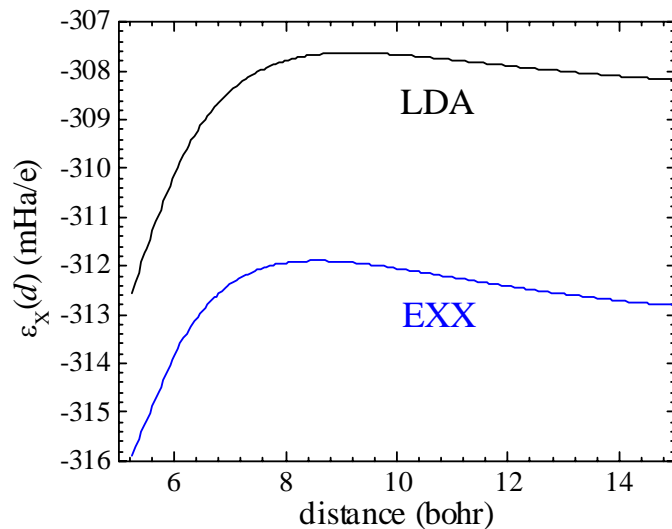
4. A MODEL LAYERED MATERIAL

Structural properties of the "jellycule" (LDA)

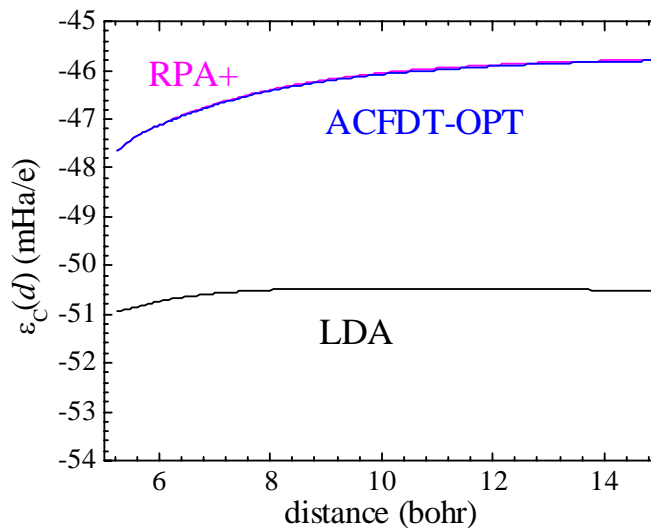


Fully microscopic corrections to LDA:

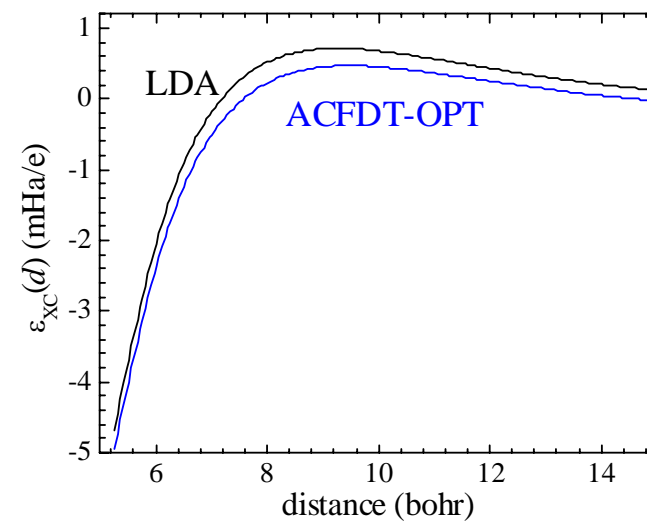
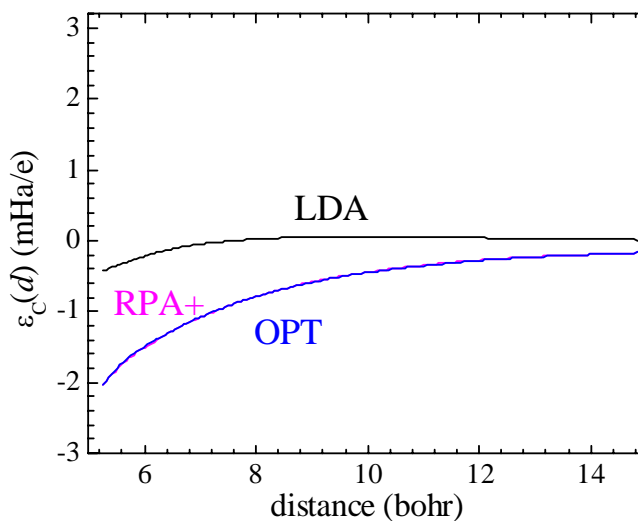
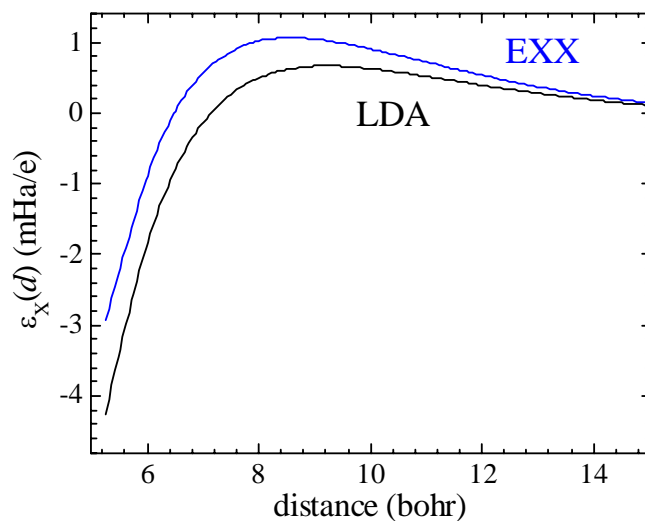
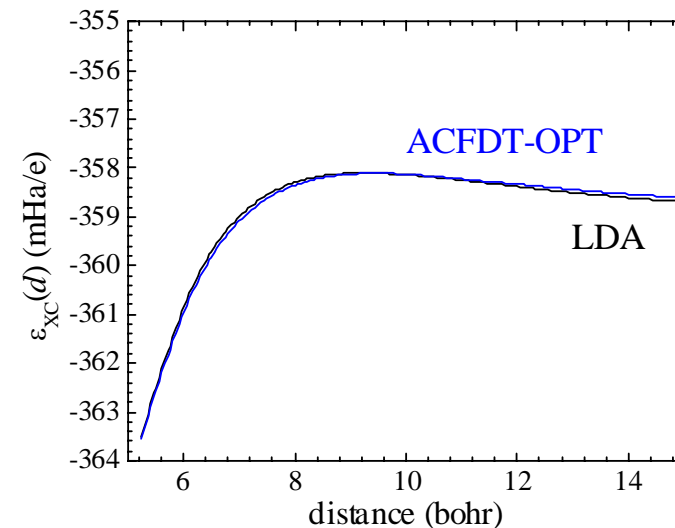
EXCHANGE



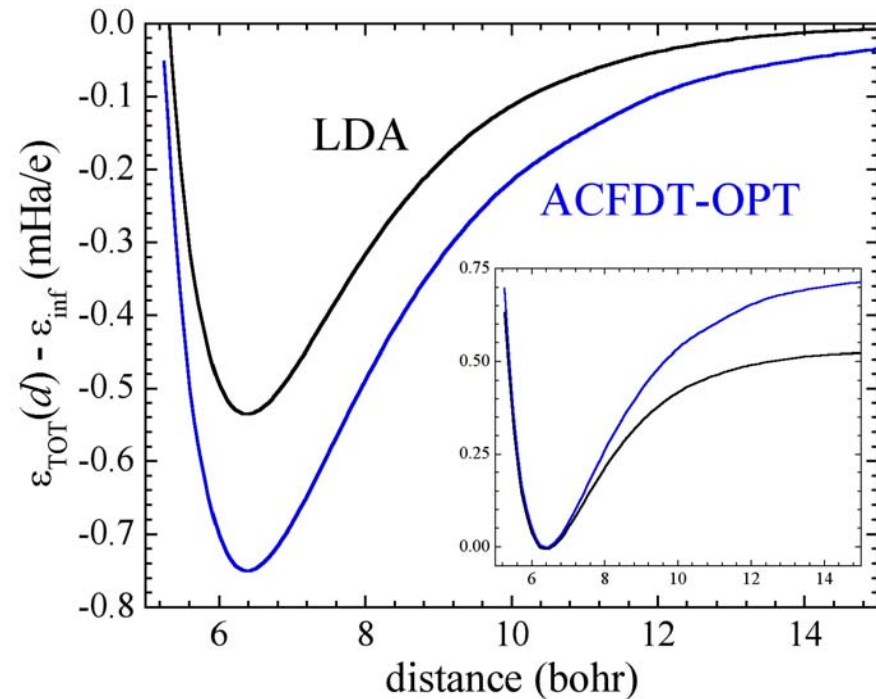
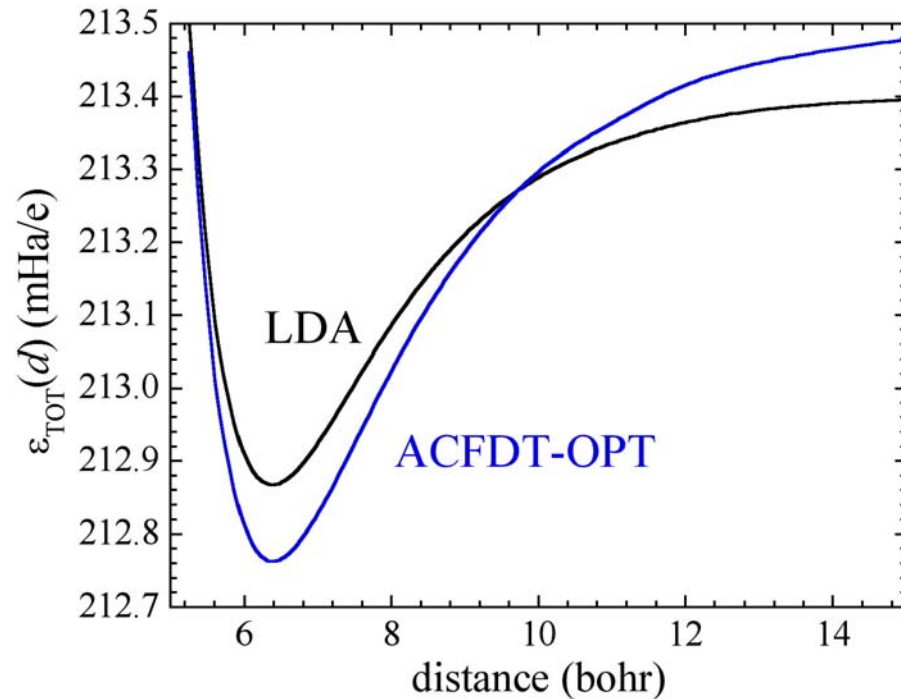
CORRELATION



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

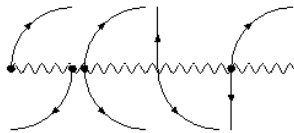
Some remarks:

- 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

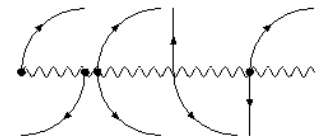
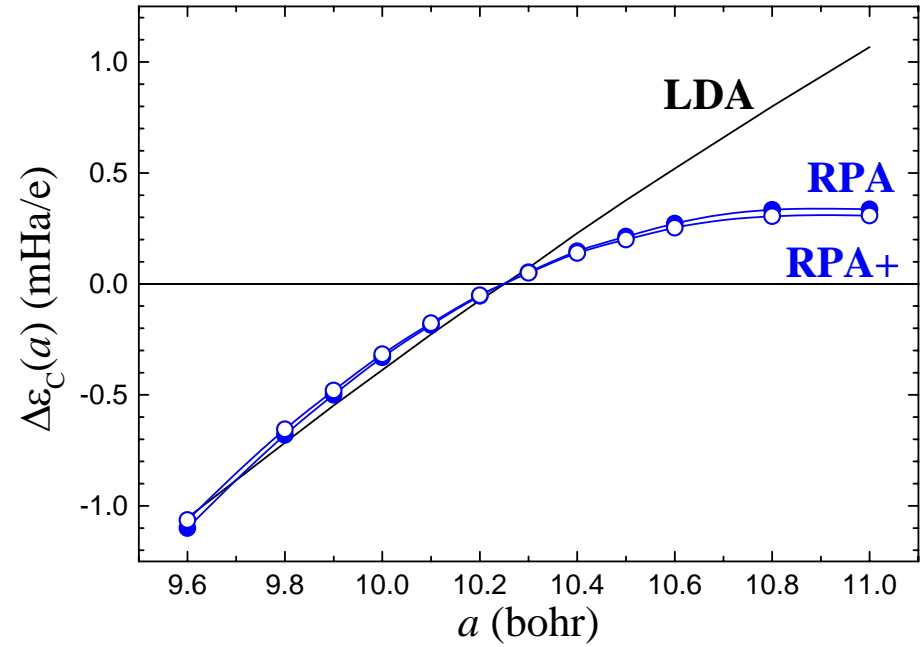
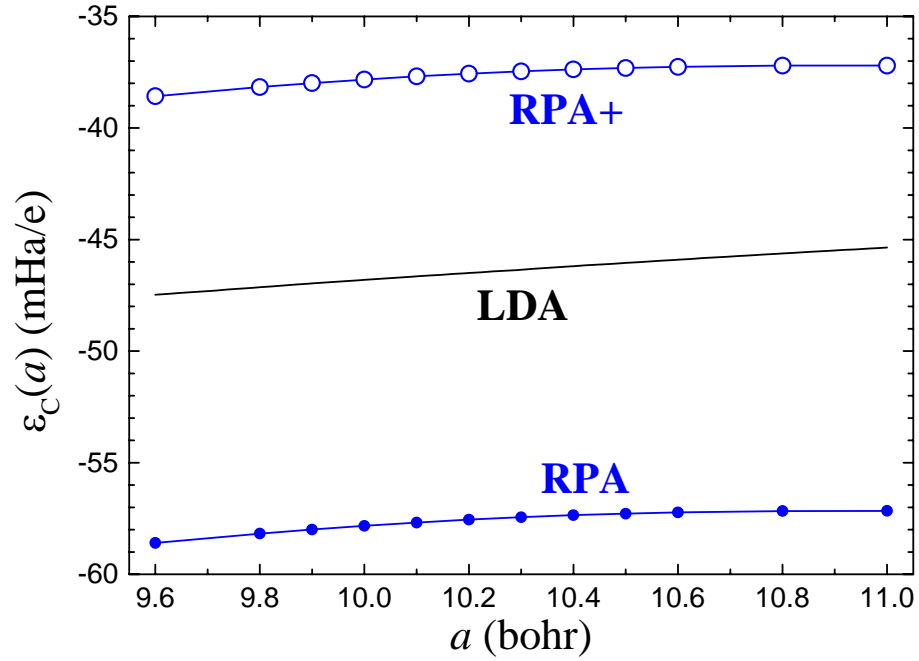
Bethe-Salpeter equation

Ab-initio $f_{xc}(\mathbf{r}, \mathbf{r}', \omega)$ kernel

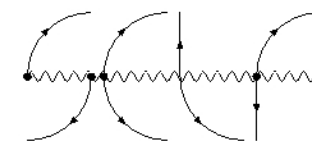
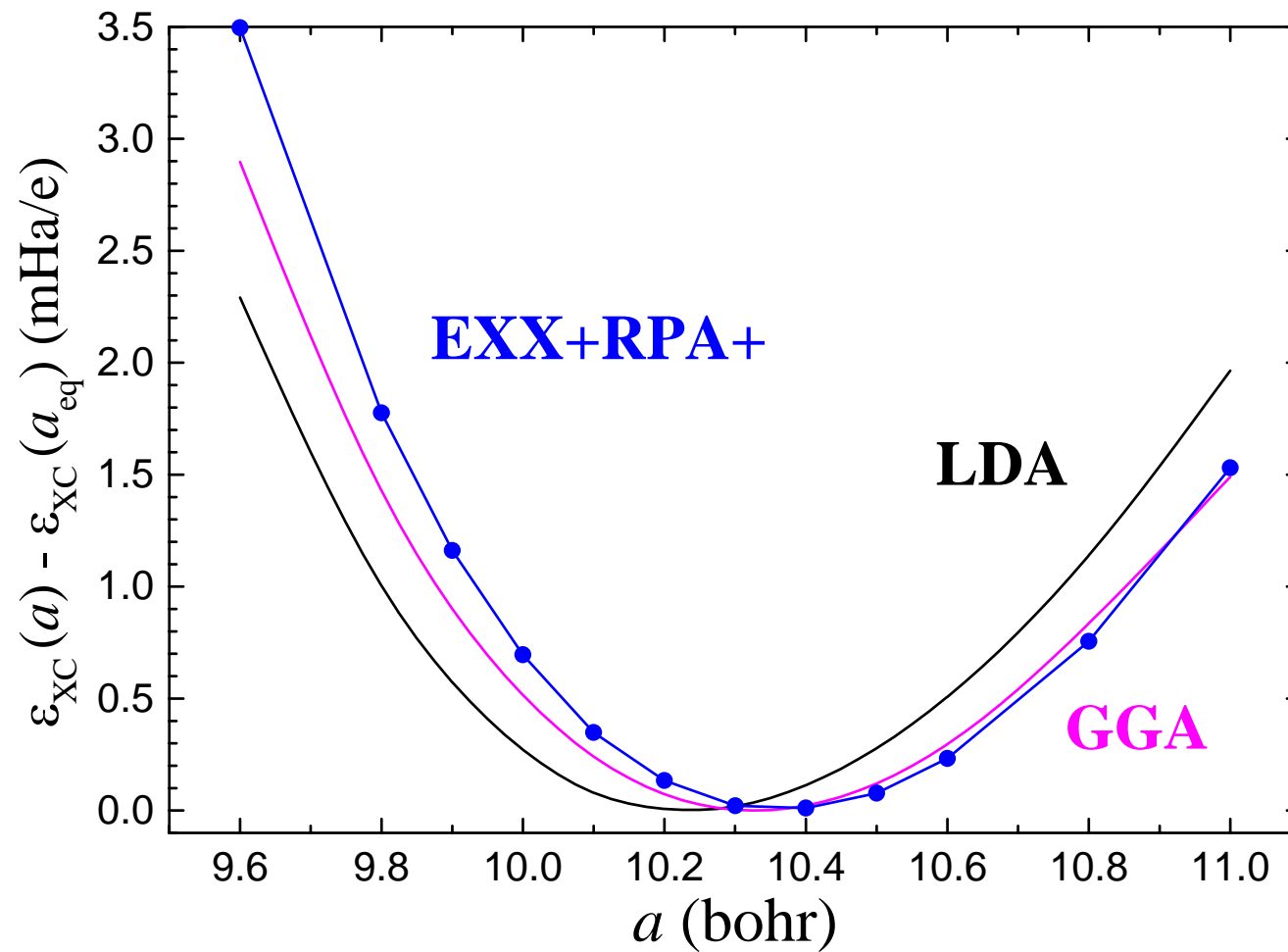
Quasiparticle properties (GW and GW Γ)

EXX-ACFDT XC energies

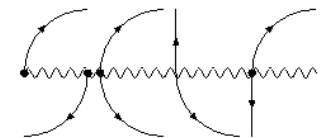
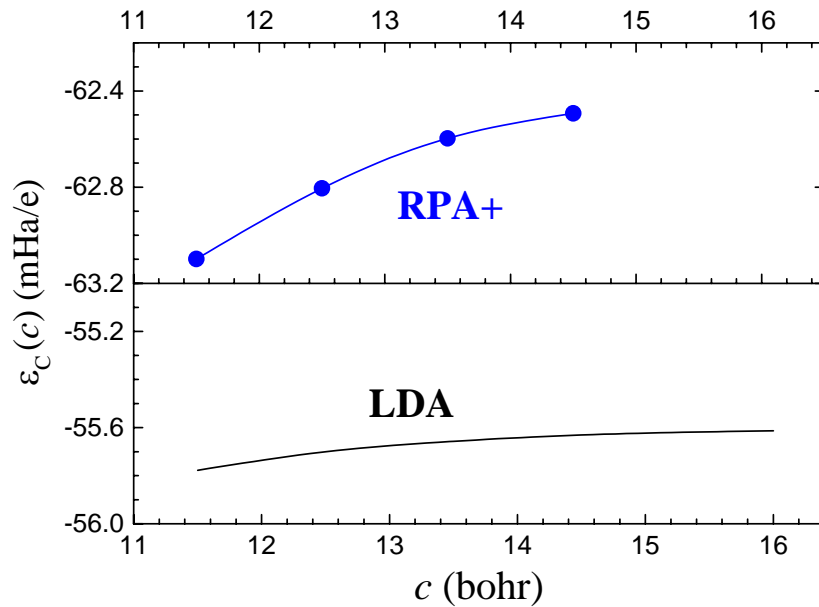
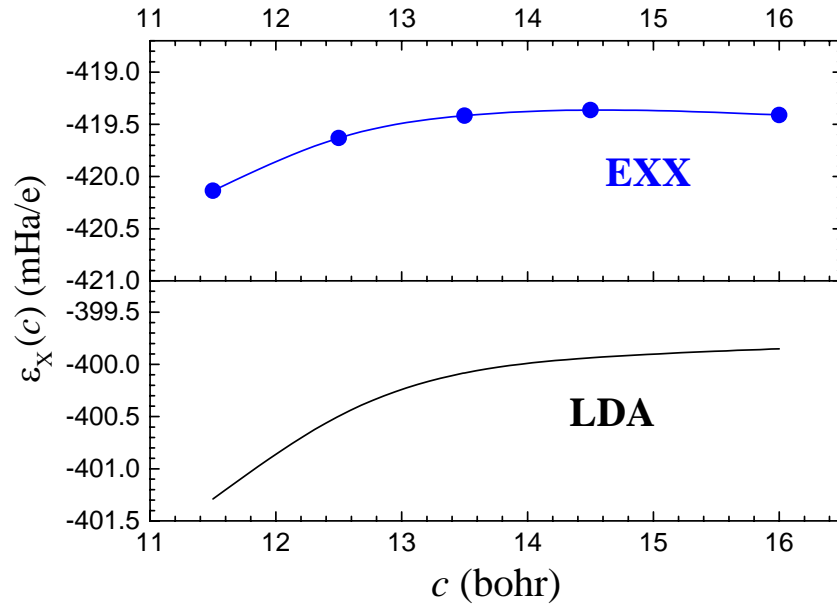
Silicon:



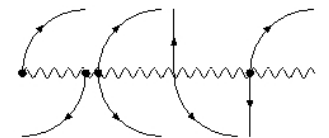
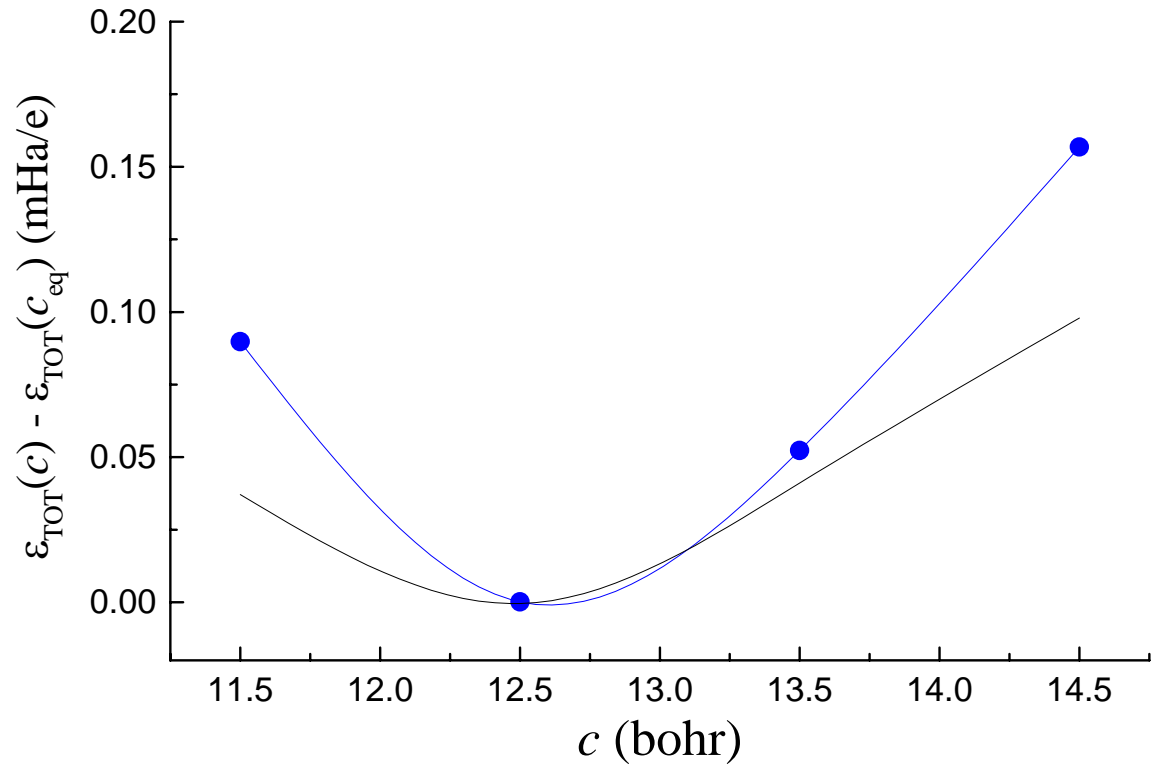
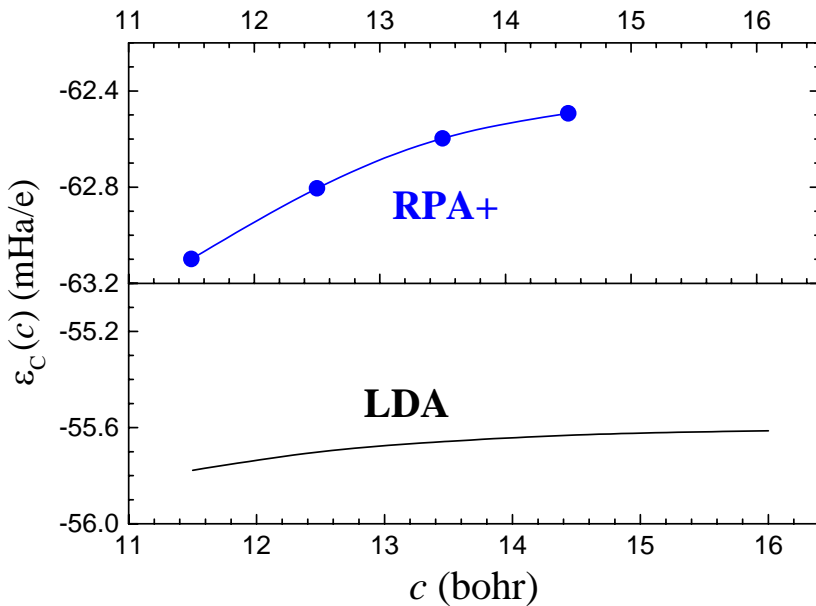
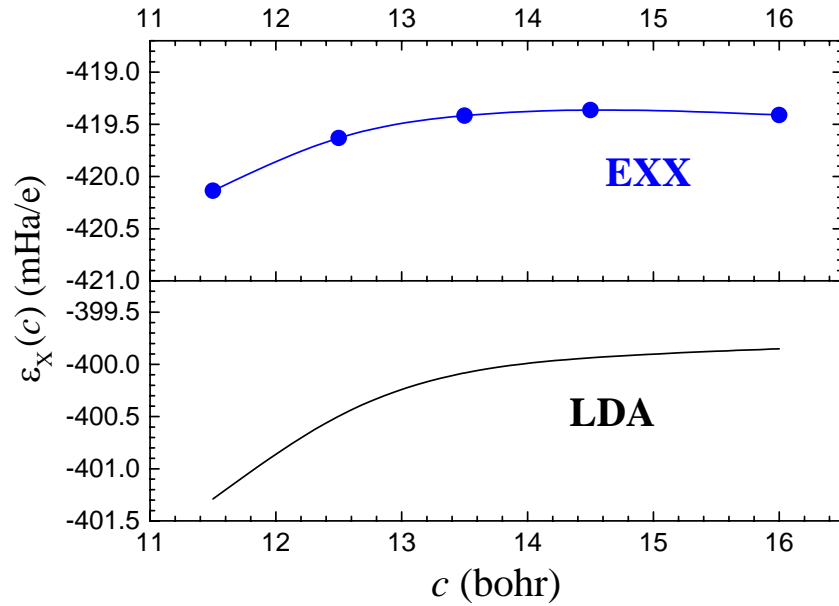
Silicon:



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 