Density functionals beyond standard local and semi-local density approximations

Nicola Colonna

Trieste 17/01/2017

THEOS

THEORY AND SIMULATION
OF MATERIALS

EPFL

ÉCOLE POLYTECHNIQUE
FÉDÉRALE DE LAUSANNE

Outline

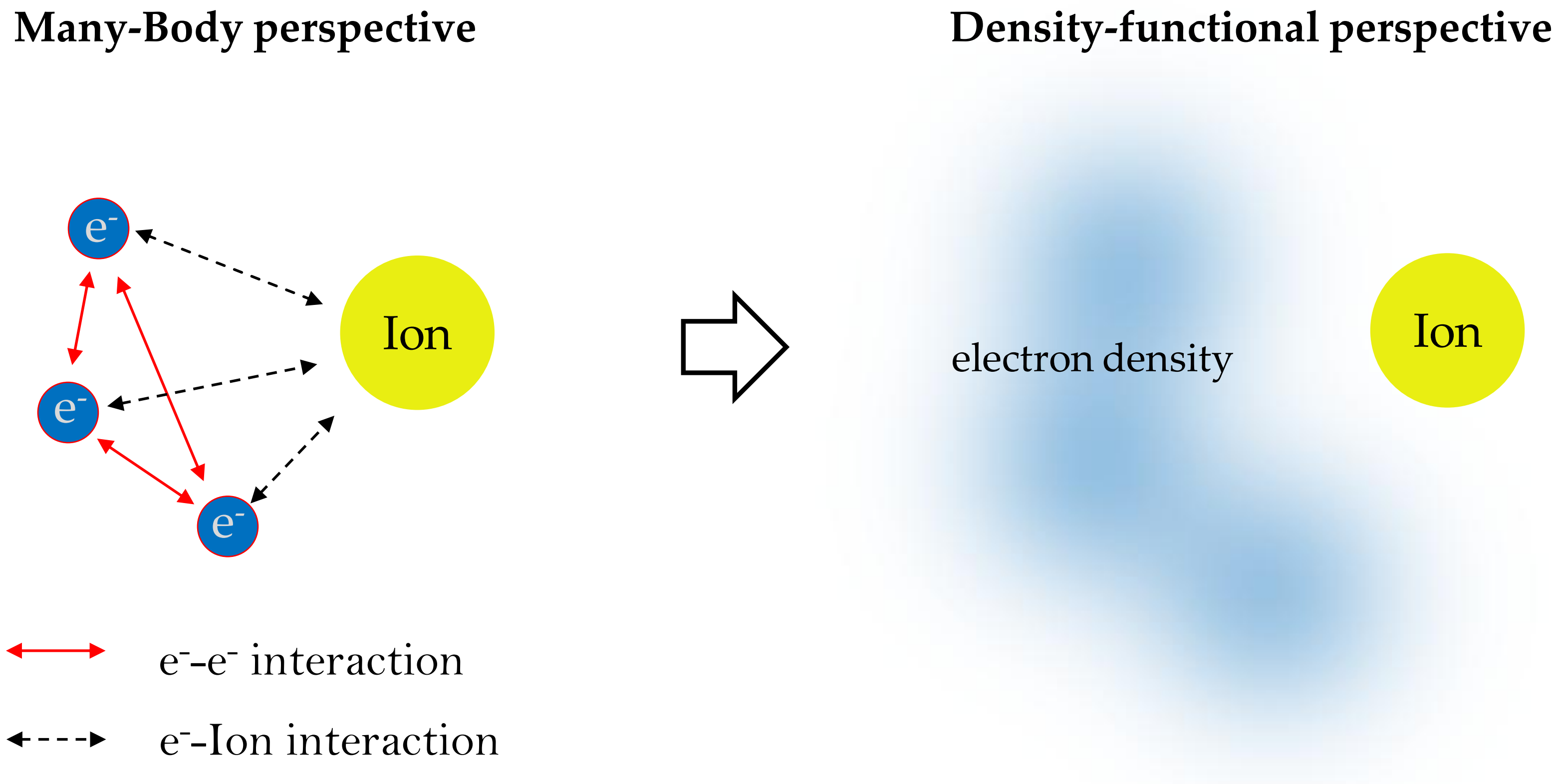
- Introduction
- Adiabatic Connection Formula
  - Exact expression for the xc Energy
- Hybrid Functionals
  - Exact Exchange Energy, Range separation
- Van der Waals interaction in DFT
  - Simple corrections
  - Truly non-local density functionals
- RPA and beyond

Some remarks on DFT

- DFT is a **formally exact** theory for the Many-Body problem:

$$E = \min_{n} \left\{ F[n] + \int d\mathbf{r}\, V_{ext}(\mathbf{r}) n(\mathbf{r}) \right\}$$

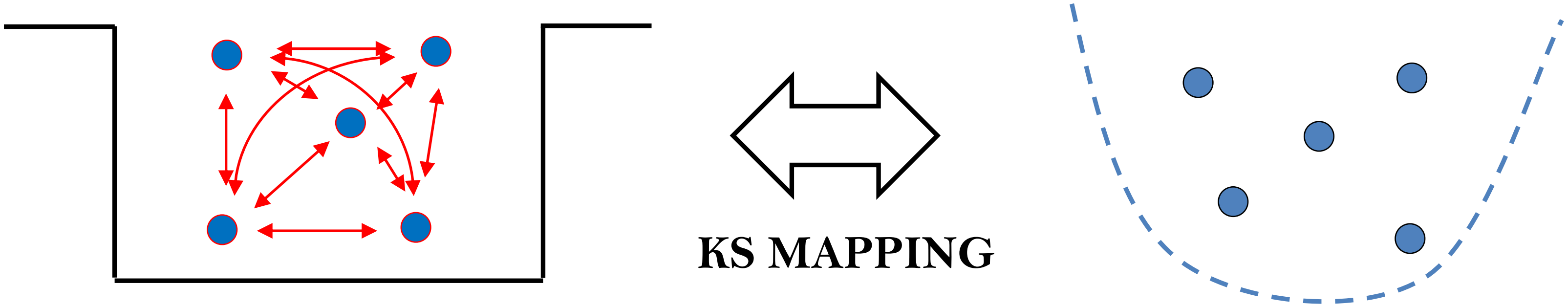
- It changes perspective from many-body wave-function to **ground state density**



Hoenberg and Kohn (1964)

Kohn-Sham Density Functional Theory

$$E[n] = T_s[n] + E_H[n] + E_{xc}[n] + \int d\mathbf{r}\, V_{ext}(\mathbf{r}) n(\mathbf{r})$$



KS MAPPING

● electrons

↔ interaction

— external potential $v_{ext}(\mathbf{r})$

● Kohn-Sham particles
(non-interacting)

- - - effective potential $v_{KS}(\mathbf{r})$

$$\left[-\frac{\hbar^2}{2m_e}\nabla^2 + v_{KS}[n](\mathbf{r})\right]\phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r}) \qquad n(\mathbf{r}) = \sum_{i=1}^{N} |\phi_i(\mathbf{r})|^2$$

$$v_{KS}[n](\mathbf{r}) = V_{ext}(\mathbf{r}) + e^2 \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})}$$

Kohn and Sham (1965)

The exchange-correlation functional

- The central quantity in KS-DFT is the XC energy

$$v_{KS}[n](\mathbf{r}) = V_{ext}(\mathbf{r}) + e^2 \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})}$$

- In most of the situation the XC energy can be reasonably approximated by simple local or semi-local functionals:

Local or semi-local approximations: LDA/GGAs

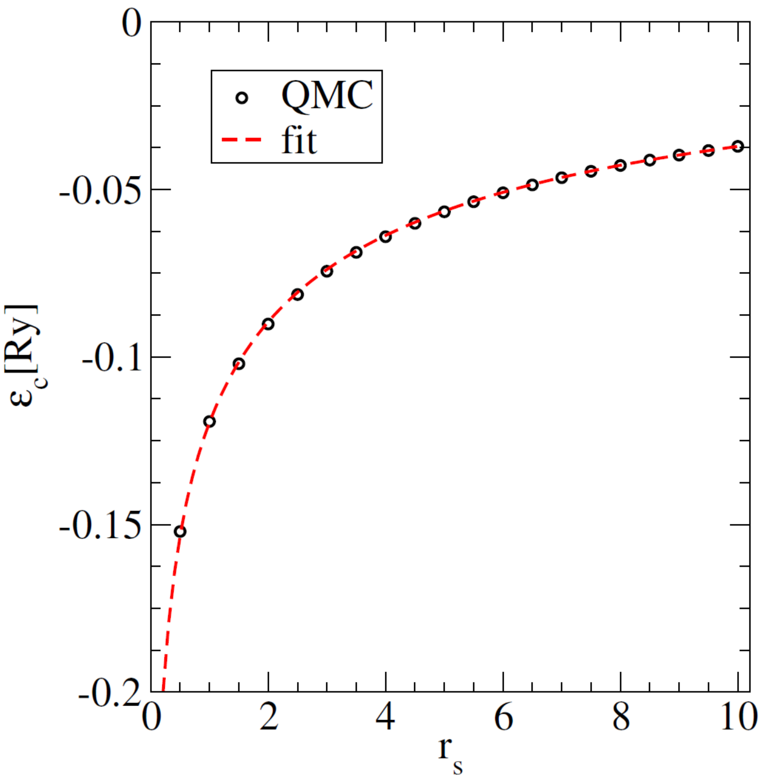
$$E_{xc}^{LDA} = \int d\mathbf{r}\ \varepsilon_{xc}^{LDA}[n(\mathbf{r})]n(\mathbf{r})$$

$$E_{xc}^{GGA} = \int d\mathbf{r}\ \varepsilon_{xc}^{GGA}[n(\mathbf{r}), \nabla n(\mathbf{r})]n(\mathbf{r})$$

- Within LDA GGAs the KS method becomes very similar to Hartree approach, making KS-DFT **very attractive from a computational point of view**.

The Local Density Approximation

The xc energy density of the inhomogeneous system in **r** is locally approximated with that of a homogeneous electron gas with density n(**r**)



$$E_{\mathbf{xc}}^{\mathrm{LDA}} = \int d\mathbf{r}\, n(\mathbf{r}) \varepsilon_{\mathbf{xc}}^{\mathrm{HEG}}(n(\mathbf{r}))$$

- The exchange energy has an analytic expression:

$$\varepsilon_{\mathbf{x}}^{\mathrm{HEG}} = -\frac{0.916}{r_s} \qquad \frac{4}{3}\pi r_s^3 = \frac{1}{n}$$

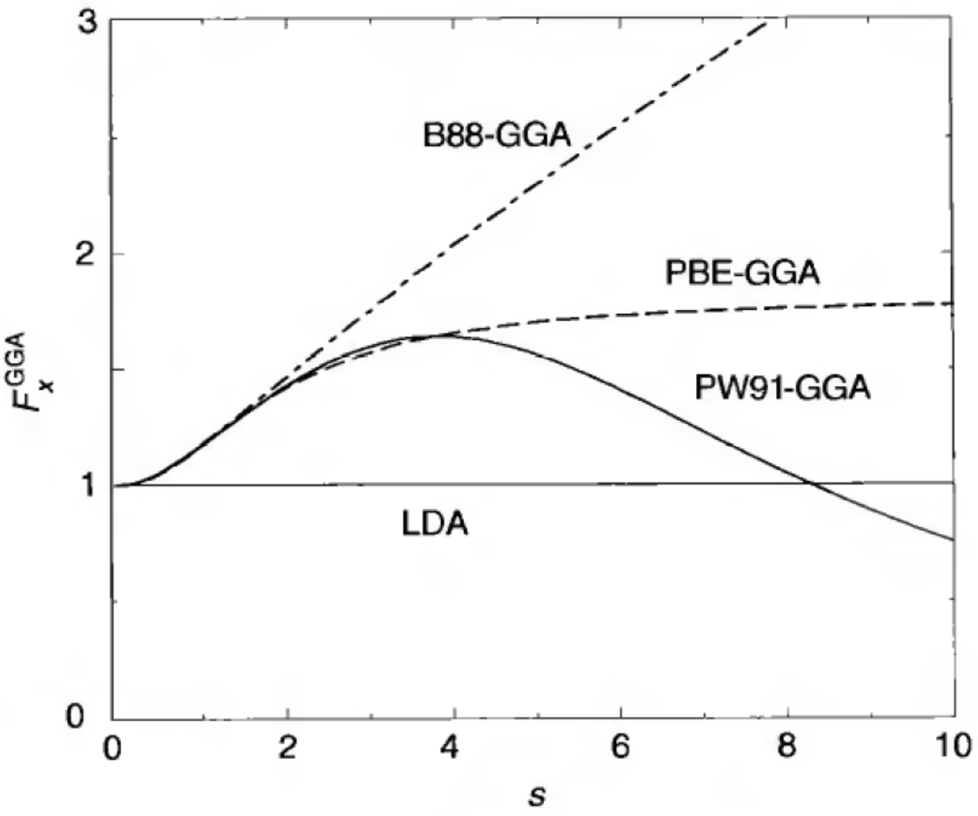
- The correlation part
  - know analytically for r_s -> 0
  - fitted on accurate QMC data for r_s<100 Ceperley and Alder PRL **45**, 56 (1980) :

$$\begin{aligned}\varepsilon_{\mathbf{c}}^{\mathrm{HEG}} &= -0.2846/(1 + 1.0529\sqrt{r_s} + 0.3334 r_s) && r_s \geq 1 \\ &= -0.0960 + 0.0622 \ln r_s - 0.0232 r_s + 0.0040 r_s \ln r_s && r_s < 1\end{aligned}$$

The Generalized Gradient Approximation

First step beyond LDA: include the dependence on the **gradient of the density**

$$E_{\mathbf{xc}}^{\mathrm{GGA}} = \int d\mathbf{r}\, n(\mathbf{r})\varepsilon_{\mathrm{xc}}(n(\mathbf{r}), \nabla n(\mathbf{r})) = \int d\mathbf{r}\, n(\mathbf{r})\varepsilon_{\mathrm{x}}^{\mathrm{HEG}}(n(\mathbf{r}))F_{\mathrm{xc}}\,(n(\mathbf{r}), \nabla n(\mathbf{r}))$$



- F_{xc} dimensionless enhancement factor over the HEG exchange. Function of the density and reduced density gradient s:

$$s = \left.\frac{|\nabla n|}{2k_F n}\right|_{n(\mathbf{r})}$$

- Not a unique recipe for F_{xc}

B88	Becke (1988)
PW91	Perdew & Wang (1991)
PBE	Perdew et al. (1996)
…	

R. Martin, *Electronic Structure. Basic theory and Practical Methods*

LDA and GGA performace

Binding energy (in eV) of Small Molecules

	Exp	LDA	Δ	PBE	Δ
H2	4.75	4.91	+0.16	4.54	-0.21
Be2	0.11	0.56	+0.45	0.42	+0.31
B2	3.08	3.85	+0.77	3.34	+0.26
O2	5.23	7.62	+2.39	6.30	+1.07
Na2	0.8	0.88	+0.08	0.77	-0.03
Si2	3.1	4.01	+0.91	3.52	+0.42
Cu2	2.03	2.62	+0.59	2.12	+0.09

	Exp	LDA	Δ	PBE	Δ
HF	6.12	7.04	+0.92	6.18	+0.06
CO	11.23	12.94	+1.69	11.65	+0.42
BF	7.97	9.12	+1.15	8.09	+0.12
LiF	6.07	6.75	+0.68	6.01	-0.06
LiH	2.64	2.64	+0.00	2.32	+0.32
H_2O	10.17	11.63	+0.46	10.26	+0.09
CO_2	17.08	20.57	+3.49	18.16	+1.08

Mean Absolute error on the G2-1 set:

LDA = 1.5 eV PBE = 0.4 eV

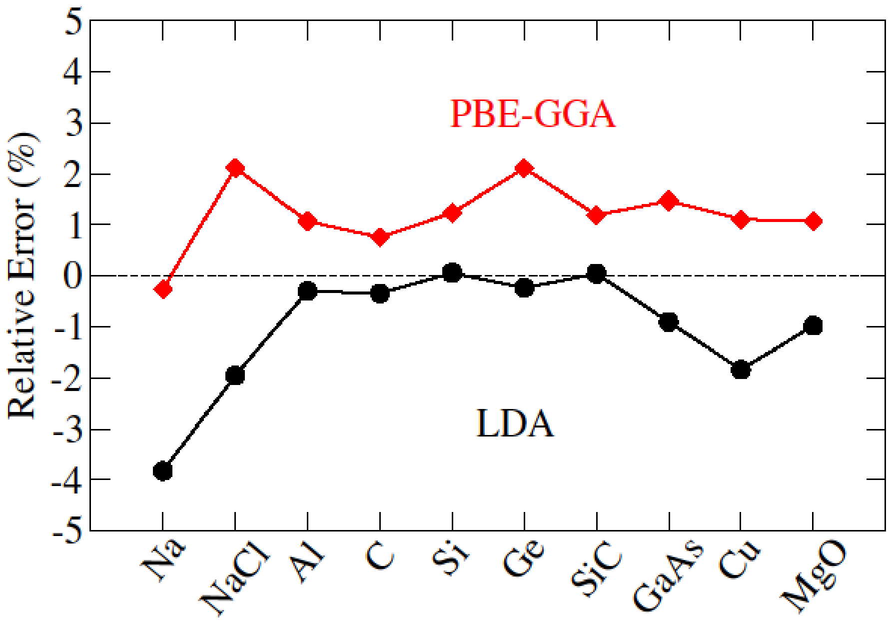
LDA binding energies too high. GGA corrects the LDA overbinding but is still far from the chemical accuracy (1 Kcal/mol ≈ 0.05 eV)

Curtiss *et al.* JCP **106**, 1063 (1997); Paier *et al.* JCP **122**, 234102 (2005)

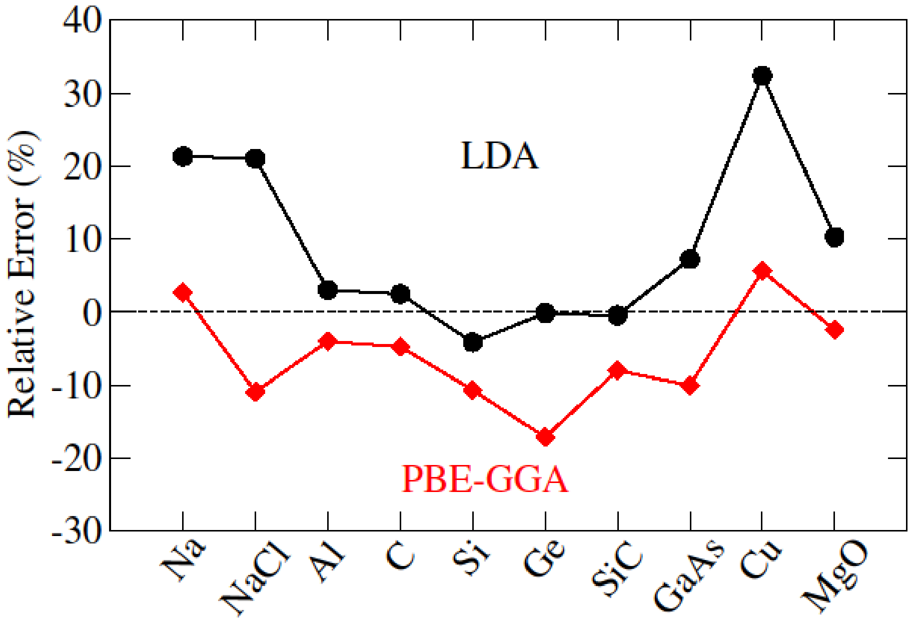
LDA and GGA performace

Structural properties of bulk systems

Equilibrium lattice constant



Bulk modulus



LDA tends to "**overbinds**".
GGA to "**underbinds**" even though the error is more variable.

LDA tends to be too **stiff**.
GGA too **soft**.

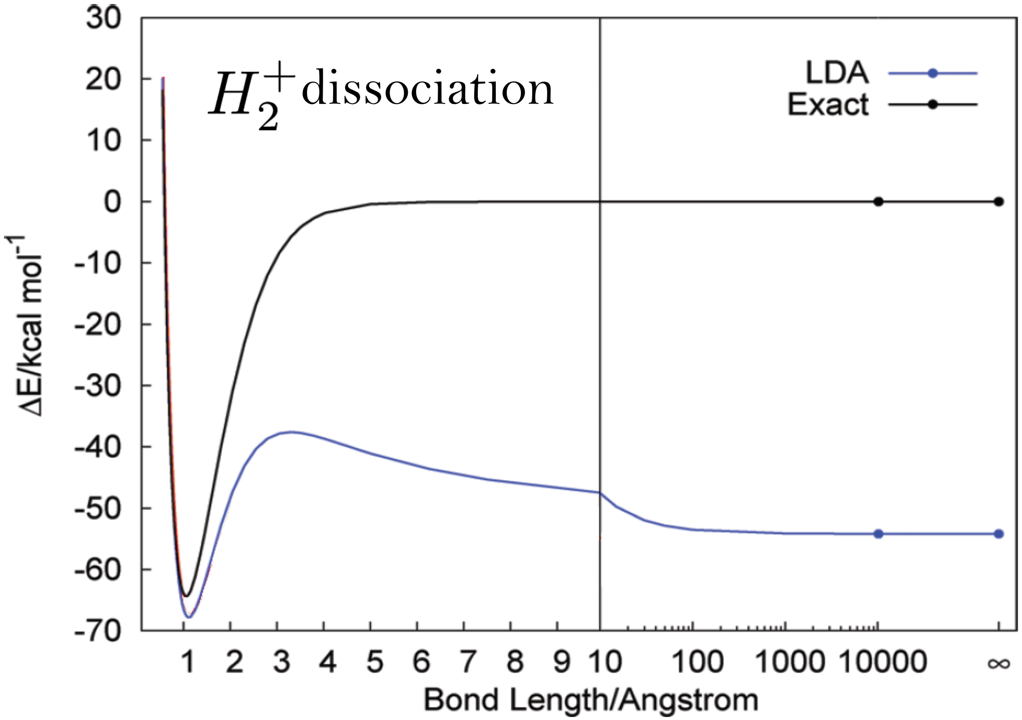
For comparison of LDA and GGA in bulk systems see PRB 69, 075102 (2004)

Kohn-Sham Density Functional Theory

$$\left[-\frac{\hbar^2}{2m_e}\nabla^2 + v_{KS}[n](\mathbf{r})\right]\phi_i(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r}) \qquad n(\mathbf{r}) = \sum_{i=1}^{N}|\phi_i(\mathbf{r})|^2$$

$$E[n] = T_s[n] + E_H[n] + E_{xc}[n] + \int d\mathbf{r}\, V_{ext}(\mathbf{r})n(\mathbf{r})$$

Exact in principle but within LDA/GGAs xc functionals



Self-interaction error

For one electron systems the interaction term should be zero:

$$E_H[\rho_1] + E_{xc}[\rho_1] = 0$$

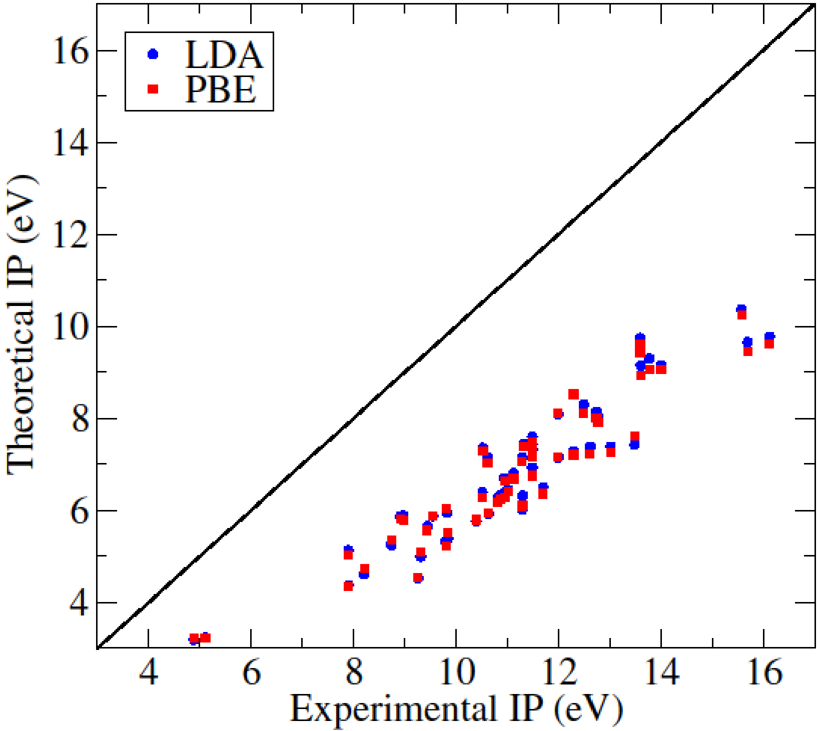
Within LDA/GGAs the cancellation is NOT always perfect

Kohn-Sham Density Functional Theory

$$n(\mathbf{r}) \overset{|\mathbf{r}|\to\infty}{\sim} exp[-2\sqrt{2IP}|\mathbf{r}|] \qquad n(\mathbf{r}) \overset{|\mathbf{r}|\to\infty}{\sim} exp[-2\sqrt{2[-\varepsilon_{ho}]}|\mathbf{r}|]$$

$$IP = E(N-1) - E(N) = -\varepsilon_{ho}$$

Exact in principle but within LDA/GGAs xc functionals



Self-interaction error

Self-interaction error leads to **incorrect asymptotic behavior of the KS potential.**

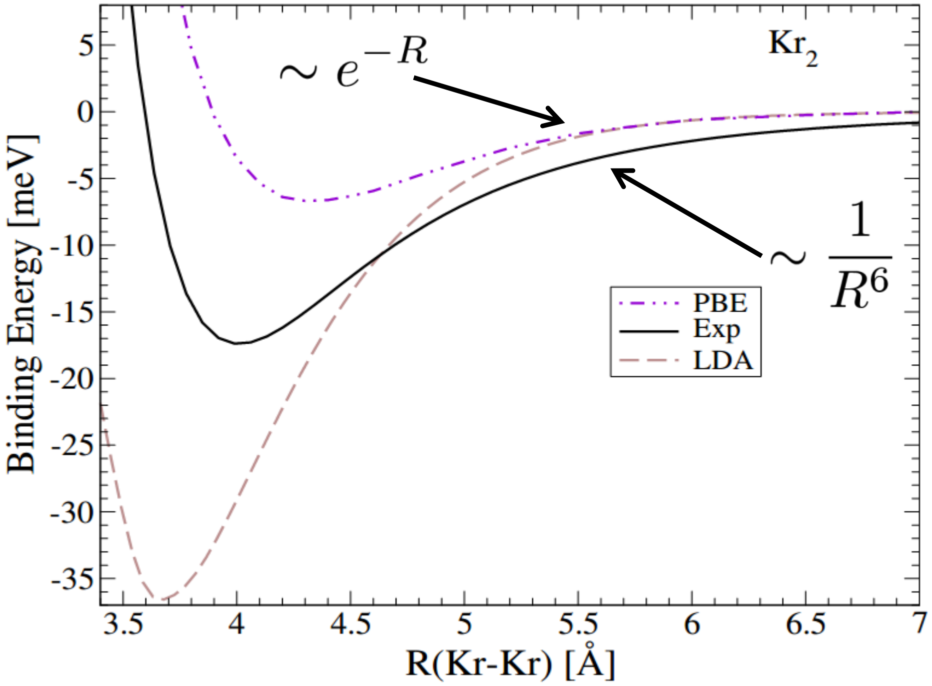
	LDA/GGAs	Exact
$v_{xc}(r)$	$-e^{-\alpha r}$	$-1/r$

Kohn-Sham Density Functional Theory

$$\left[-\frac{\hbar^2}{2m_e}\nabla^2 + v_{KS}[n](\mathbf{r})\right]\phi_i(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r}) \qquad n(\mathbf{r}) = \sum_{i=1}^{N}|\phi_i(\mathbf{r})|^2$$

$$E[n] = T_s[n] + E_H[n] + E_{xc}[n] + \int d\mathbf{r}\, V_{ext}(\mathbf{r})n(\mathbf{r})$$

Exact in principle but within LDA/GGAs xc functionals



Weakly bound systems

LDA and GGAs give binding or repulsion only when there is charge density overlap

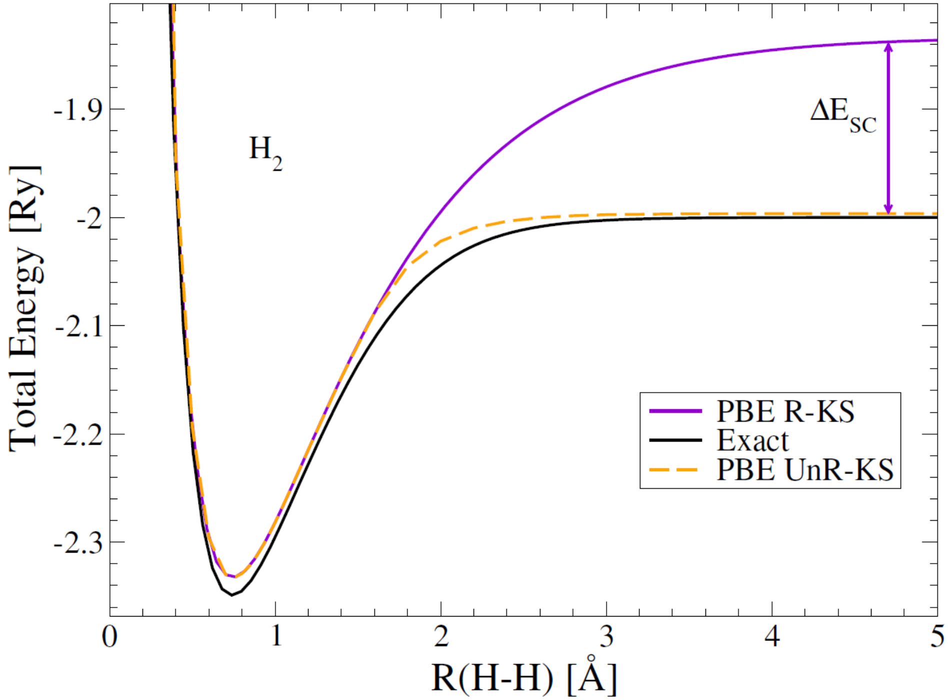
WRONG exponential decay of the interaction energy between separate fragments

Kohn-Sham Density Functional Theory

$$\left[-\frac{\hbar^2}{2m_e}\nabla^2 + v_{KS}[n](\mathbf{r})\right]\phi_i(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r}) \qquad n(\mathbf{r}) = \sum_{i=1}^{N}|\phi_i(\mathbf{r})|^2$$

$$E[n] = T_s[n] + E_H[n] + E_{xc}[n] + \int d\mathbf{r}\, V_{ext}(\mathbf{r})n(\mathbf{r})$$

Exact in principle but within LDA/GGAs xc functionals



Dissociation in open shell fragments (Strong correlation)

Static (left-right) correlation is missing. Can be mimicked breaking the spin symmetry.

Symmetry dilemma

	Sym	Ene
R-KS	✓	✗
UnR-KS	✗	✓

Local and semilocal functionals: summary

- LDA overbinds. Lattice constant too small, bulk moduli too big
- GGA (over)correct LDA overbinding. Softens the bond increasing lattice constant decreasing bulk moduli
- In general structural, elastic and vibrational properties often good enough
- For most elements LDA/GGA predict the correct structure for a material
- LDA/GGA are far from the chemical accuracy
- LDA/GGA are not self-interaction free
- Van der Waals (dispersion) forces are not included
- Qualitative failure in strongly correlated system

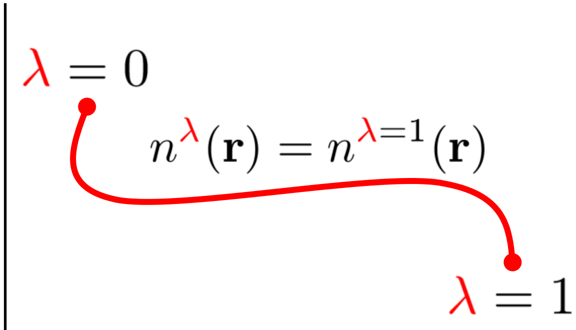
Better functional approximations needed!

Outline

- Introduction
- Adiabatic Connection Formula
  - Exact expression for the xc Energy
- Hybrid Functionals
  - Exact Exchange Energy, Range separation
- Van der Waals interaction in DFT
  - Simple corrections
  - Truly non-local density functionals
- RPA and beyond

The Adiabatic Connection Formula

Adiabatic coupling



$\lambda = 0$

$n^{\lambda}(\mathbf{r}) = n^{\lambda=1}(\mathbf{r})$

$\lambda = 1$

$$\hat{H}^{\lambda} = \hat{T} + \lambda\hat{W} + \hat{v}^{\lambda}$$

$$\hat{v}^{\lambda=0} = \hat{v}_{KS}$$

$$\hat{v}^{\lambda=1} = \hat{v}_{ext}$$

D.C.Langreth and J. P. Perdew,
- Solid State Comm. **17**, 1425 (1975)
- Phys. Rev. B **15**, 2884 (1977)

The Adiabatic Connection Formula

- According to the **Hellmann-Feynman** theorem

$$\frac{dE^\lambda}{d\lambda} = \langle\Psi^\lambda|\frac{dH^\lambda}{d\lambda}|\Psi^\lambda\rangle = \langle\Psi^\lambda|W|\Psi^\lambda\rangle + \int d\mathbf{r}\, n(\mathbf{r})\frac{dv^\lambda}{d\lambda}$$

- Integrating over λ between 0 and 1

$$E = E_0 + \int_0^1 d\lambda\langle\Psi^\lambda|W|\Psi^\lambda\rangle + \int d\mathbf{r}\,[v_{ext}(\mathbf{r}) - v_{KS}(\mathbf{r})]\, n(\mathbf{r})$$

- With the usual decomposition for the total energy

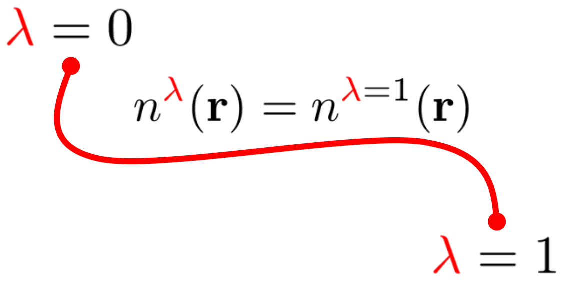
$$E = T_s + E_H + E_{xc} + \int d\mathbf{r}\, n(\mathbf{r})v_{ext}(\mathbf{r})$$

$$E_0 = T_s + \int d\mathbf{r}\, n(\mathbf{r})v_{KS}(\mathbf{r})$$

- We obtain an **exact expression** for the interaction Energy

$$\boxed{E_{Hxc} = \int_0^1 d\lambda\langle\Psi^\lambda|W|\Psi^\lambda\rangle}$$

Adiabatic coupling



$\lambda = 0$

$n^\lambda(\mathbf{r}) = n^{\lambda=1}(\mathbf{r})$

$\lambda = 1$

$$\hat{H}^\lambda = \hat{T} + \lambda\hat{W} + \hat{v}^\lambda$$

$$\hat{v}^{\lambda=0} = \hat{v}_{KS}$$

$$\hat{v}^{\lambda=1} = \hat{v}_{ext}$$

D.C.Langreth and J. P. Perdew,
- Solid State Comm. **17**, 1425 (1975)
- Phys. Rev. B **15**, 2884 (1977)

The exchange-correlation hole

$$E_{xc} = \int_0^1 d\lambda \langle \Psi^\lambda | W | \Psi^\lambda \rangle - \frac{e^2}{2} \int d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

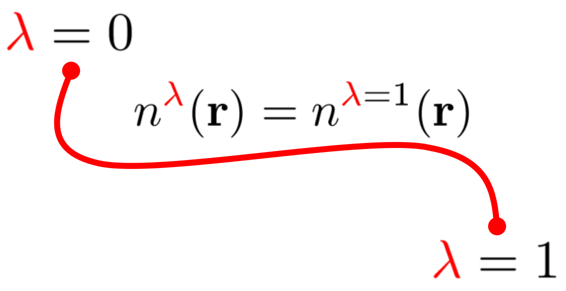
$$\langle \Psi^\lambda | W | \Psi^\lambda \rangle = \frac{e^2}{2} \int d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \boxed{g_\lambda(\mathbf{r}, \mathbf{r}')}$$

Pair correlation function: probability to find a particle in **r'** given a particle in **r**

$$g_\lambda(\mathbf{r}, \mathbf{r}') = 1 + \frac{\langle \delta\hat{n}(\mathbf{r}) \delta\hat{n}(\mathbf{r}') \rangle_\lambda}{n(\mathbf{r}) n(\mathbf{r}')} - \frac{\delta(\mathbf{r} - \mathbf{r}')}{n(\mathbf{r})}$$

$$\tilde{g}(\mathbf{r}, \mathbf{r}') = \int_0^1 d\lambda \, g_\lambda(\mathbf{r}, \mathbf{r}')$$ Coupling constant average

Adiabatic coupling



$\lambda = 0$

$n^\lambda(\mathbf{r}) = n^{\lambda=1}(\mathbf{r})$

$\lambda = 1$

$$\hat{H}^\lambda = \hat{T} + \lambda \hat{W} + \hat{v}^\lambda$$

$$\hat{v}^{\lambda=0} = \hat{v}_{KS}$$

$$\hat{v}^{\lambda=1} = \hat{v}_{ext}$$

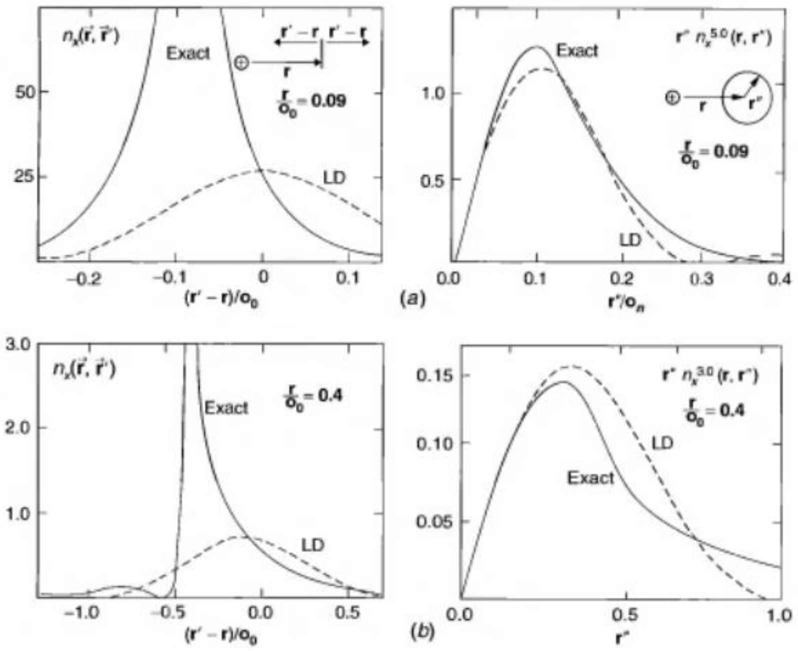
$$\boxed{E_{\mathrm{xc}} = \frac{e^2}{2} \int d\mathbf{r} d\mathbf{r}' n(\mathbf{r}) \frac{1}{|\mathbf{r} - \mathbf{r}'|} n_{\mathrm{xc}}(\mathbf{r}, \mathbf{r}') \qquad n_{\mathrm{xc}}(\mathbf{r}, \mathbf{r}') = [\tilde{g}(\mathbf{r}, \mathbf{r}') - 1] \, n(\mathbf{r}')}$$

The electron density n(**r**) interacts with the electron density of the XC hole n_{xc}(**r**)

The exchange-correlation hole

The electron density n(**r**) interacts with the electron density of the XC hole $n_{xc}(\mathbf{r})$

$$E_{\text{xc}} = \frac{e^2}{2}\int d\mathbf{r}d\mathbf{r}'n(\mathbf{r})\frac{1}{|\mathbf{r}-\mathbf{r}'|}n_{\text{xc}}(\mathbf{r},\mathbf{r}') \qquad n_{\text{xc}}(\mathbf{r},\mathbf{r}') = [\tilde{g}(\mathbf{r},\mathbf{r}')-1]\,n(\mathbf{r}')$$



Exchange hole (left) and its spherical average (right) for Ne atom. Solid line exact, dashed line LDA

Gunnarson *et al.* PRB **13**, 4274 (1979)

- **Only the spherical average** of the xc-hole is **needed** for the xc-energy

$$E_{\text{xc}} = \frac{4\pi e^2}{2}\int d\mathbf{r}n(\mathbf{r})\int_0^\infty du\,\frac{n_{\text{xc}}^{\text{sph}}(\mathbf{r},u)}{u}u^2$$

$$u = |\mathbf{r}-\mathbf{r}'|$$

- Spherical average are reasonably well reproduced within the LDA
- The LDA n_{xc} satisfies important sum rules → systematic cancellation of errors

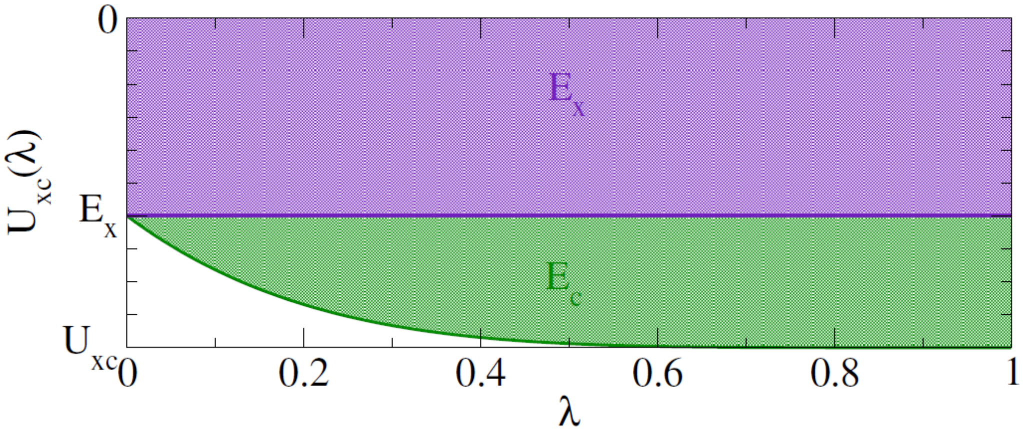
Explain the unexpected success of LDA also for non-homogeneous systems

Outline

- Introduction
- Adiabatic Connection Formula
  - Exact expression for the xc Energy
- Hybrid Functionals
  - Exact Exchange Energy, Range separation
- Van der Waals interaction in DFT
  - Simple corrections
  - True non-local density functionals
- RPA and beyond

Approximations from the AC Formula

$$E_{\mathbf{xc}} = \int_0^1 d\lambda \, \langle \Psi^\lambda | W | \Psi^\lambda \rangle - E_H = \int_0^1 d\lambda \, U_{\mathbf{xc}}(\lambda)$$



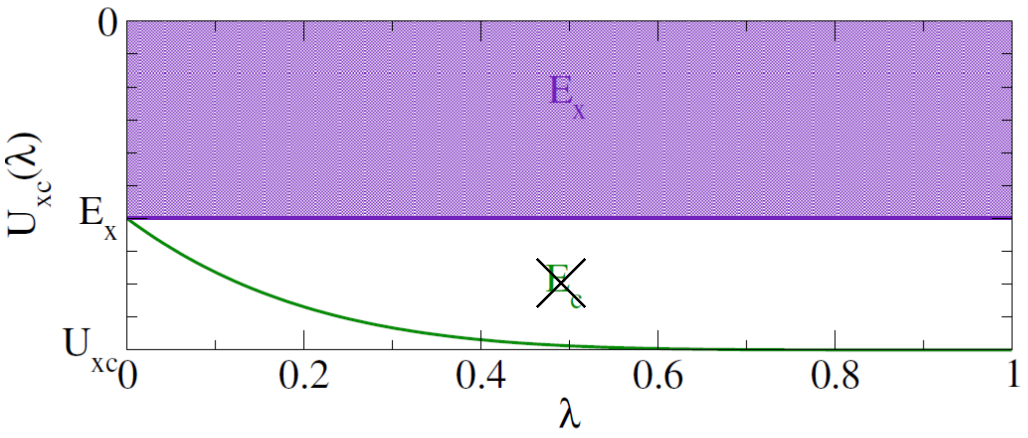
At λ=0: U_{xc} (λ=0) = E_x Exchange only

$$E_x = -\frac{e^2}{2} \int d\mathbf{r} d\mathbf{r}' \frac{\left|\sum_i^{occ} \phi_i^*(\mathbf{r})\phi_i(\mathbf{r}')\right|^2}{|\mathbf{r} - \mathbf{r}'|}$$

✓ Hartree-Fock is the exact solution for non interacting systems.
Exactly cancel the self-interaction

Approximations from the AC Formula

$$E_{\mathrm{xc}} = \int_0^1 d\lambda \, \langle \Psi^\lambda | W | \Psi^\lambda \rangle - E_H = \int_0^1 d\lambda \, U_{\mathrm{xc}}(\lambda)$$



At λ=0: $U_{\mathrm{xc}}(\lambda=0) = E_x$ Exchange only

$$E_x = -\frac{e^2}{2} \int d\mathbf{r} d\mathbf{r}' \frac{\left|\sum_i^{occ} \phi_i^*(\mathbf{r}) \phi_i(\mathbf{r}')\right|^2}{|\mathbf{r} - \mathbf{r}'|}$$

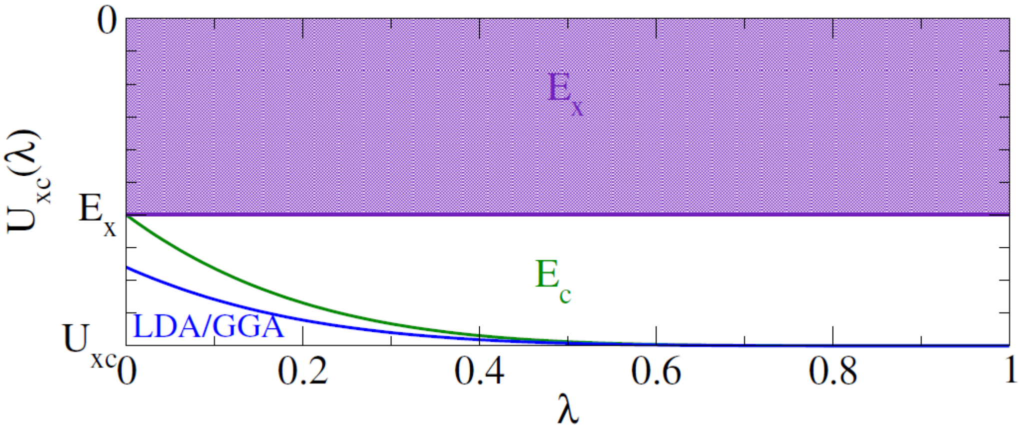
✓ Hartree-Fock is the exact solution for non interacting systems. **Exactly cancel the self-interaction**

1) Just take the value at λ=0: $E_{xc} = E_x$

- Very drastic approximation for the xc-energy (NO correlation at all)

Approximations from the AC Formula

$$E_{\mathbf{xc}} = \int_0^1 d\lambda \, \langle \Psi^\lambda | W | \Psi^\lambda \rangle - E_H = \int_0^1 d\lambda \, U_{\mathbf{xc}}(\lambda)$$



At λ=0: $U_{xc}(\lambda=0) = E_x$ Exchange only

$$E_x = -\frac{e^2}{2} \int d\mathbf{r} d\mathbf{r}' \frac{\left| \sum_i^{occ} \phi_i^*(\mathbf{r}) \phi_i(\mathbf{r}') \right|^2}{|\mathbf{r} - \mathbf{r}'|}$$

✓ Hartree-Fock is the exact solution for non interacting systems. **Exactly cancel the self-interaction**

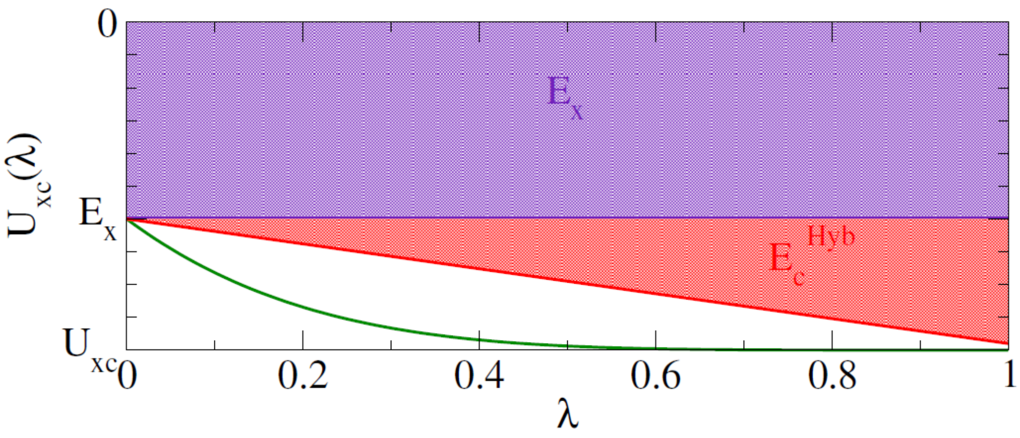
1) Just take the value at λ=0: $E_{xc} = E_x$
   - Very drastic approximation for the xc-energy (NO correlation at all)

Observations:

- LDA/GGA too negative close to $\lambda = 0$
- HF exact at $\lambda = 0$
- DFT usually improves for large λ

Approximations from the AC Formula

$$E_{\mathrm{xc}} = \int_0^1 d\lambda \, \langle \Psi^\lambda | W | \Psi^\lambda \rangle - E_H = \int_0^1 d\lambda \, U_{\mathrm{xc}}(\lambda)$$



At λ=0: $U_{xc}(\lambda=0) = E_x$ Exchange only

$$E_x = -\frac{e^2}{2} \int d\mathbf{r} d\mathbf{r}' \frac{\left|\sum_i^{occ} \phi_i^*(\mathbf{r}) \phi_i(\mathbf{r}')\right|^2}{|\mathbf{r} - \mathbf{r}'|}$$

✓ Hartree-Fock is the exact solution for non interacting systems. **Exactly cancel the self-interaction**

1) Just take the value at λ=0: $E_{xc} = E_x$
   - Very drastic approximation for the xc-energy (NO correlation at all)

2) Simple linear interpolation: $U_{xc}(\lambda) \approx U_{xc}(\lambda=0) + \lambda[U_{xc}(\lambda=1) - U_{xc}(\lambda=0)]$
   - DFT improves for large λ $\quad U_{\mathrm{xc}}(\lambda = 1) \simeq U_{\mathrm{xc}}^{LDA} = \int d\mathbf{r} \, u_{\mathrm{xc}}^{HEG}[n(\mathbf{r})] n(\mathbf{r})$

$$E_{\mathrm{xc}} = \frac{1}{2} E_x + \frac{1}{2} U_{\mathrm{xc}}^{LDA}$$

First Hybrid scheme (Half-Half):
Becke JCP **98**, 1372 (1993)

Hybrid Functionals

Basic Idea: Interpolate between non local Hartree-Fock (λ=0) and local DFT (λ=1)

3-parameter: combination of x-HF, x-B88(xGGA), c-LYP(cGGA) and xc-LDA

$$E_{\mathrm{xc}}^{\mathrm{B3}} = E_{\mathrm{xc}}^{\mathrm{LDA}} + a_0(E_{\mathrm{x}}^{\mathrm{HF}} - E_{\mathrm{x}}^{\mathrm{LDA}}) + a_x(E_{\mathrm{x}}^{\mathrm{B88}} - E_{\mathrm{x}}^{\mathrm{LDA}}) + a_c(E_{\mathrm{c}}^{\mathrm{LYP}} - E_{\mathrm{c}}^{\mathrm{LDA}})$$

- Fitted on thermochemical data: $a_0 = 0.20$, $a_x=0.72$, $a_c=0.81$ ➔ **B3LYP**
  [Becke et *al*. JCP **98**, 5648 (1993)]

Simplification: $a_x=(1-a_0)$, $a_c=1$. Only 1 mixing parameter
[Becke et *al*. JCP **104**, 1040 (1996)]

$$E_{\mathrm{xc}}^{\mathrm{hyb}} = E_{\mathrm{xc}}^{\mathrm{DFT}} + a_0\left(E_{\mathrm{x}}^{\mathrm{HF}} - E_{\mathrm{x}}^{\mathrm{DFT}}\right)$$

- Fitted on thermochemical data: $a_0 = 0.16$ or 0.28 (depending on which GGA)
- Comparison with 4° order perturbation theory: $a_0 = 1/4$ ➔ **PBE0**
  [Perdew et *al*. JCP **105**, 9982 (1996)]

$$E_{\mathrm{xc}}^{\mathrm{PBE0}} = E_{\mathrm{xc}}^{\mathrm{PBE}} + \frac{1}{4}\left(E_{\mathrm{x}}^{\mathrm{HF}} - E_{\mathrm{x}}^{\mathrm{PBE}}\right)$$

Exchange Energy Functional

$$E^{\mathrm{HF}} = -\frac{1}{2}\sum_{\mathbf{k},v}\sum_{\mathbf{q},v'}\int d\mathbf{r}d\mathbf{r}'\,\frac{\psi^*_{\mathbf{k},v}(\mathbf{r})\psi_{\mathbf{k}-\mathbf{q},v'}(\mathbf{r})\psi_{\mathbf{k},v}(\mathbf{r}')\psi^*_{\mathbf{k}-\mathbf{q},v'}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

- **Implicit functional of the density**: can be brought back to the realm of DFT using an Optimized Effective Potential scheme (OEP):

$$v_{\mathrm{x}}(\mathbf{r}) = \frac{\delta E^{\mathrm{HF}}}{\delta n(\mathbf{r})} = \int d\mathbf{r}' \int d\mathbf{r}'' \sum_{\mathbf{k},v} \frac{\delta E^{\mathrm{HF}}}{\delta \psi^*_{\mathbf{k},v}(\mathbf{r}')}\,\frac{\delta \psi^*_{\mathbf{k},v}(\mathbf{r}')}{\delta v_{KS}(\mathbf{r}'')}\,\frac{\delta v_{KS}(\mathbf{r}'')}{\delta n(\mathbf{r})} + \mathrm{c.c.}$$

$$\frac{\delta E^{\mathrm{HF}}}{\delta \psi^*_{\mathbf{k},v}} = V^{\mathrm{HF}}|\psi_{\mathbf{k},v}\rangle$$

Non-local HF potential

$$\frac{\delta v_{\mathrm{KS}}(\mathbf{r}'')}{\delta n(\mathbf{r})} = \chi_0^{-1}(\mathbf{r}'',\mathbf{r})$$

KS response function

$$\frac{\delta \psi^*_{\mathrm{KS}}(\mathbf{r}')}{\delta v_{\mathrm{KS}}(\mathbf{r}'')} = {\sum_{\mathbf{k}',v'}}' \psi^*_{\mathbf{k}',v'}\,\frac{\psi_{\mathbf{k}',v'}\psi^*_{\mathbf{k},v}}{\varepsilon_{\mathbf{k},v}-\varepsilon_{\mathbf{k}',v'}}$$

First order Perturbation Theory

Rigorous but involved and computationally expensive

Exchange Energy Functional

$$E^{\mathrm{HF}} = -\frac{1}{2}\sum_{\mathbf{k},v}\sum_{\mathbf{q},v'}\int d\mathbf{r}d\mathbf{r}'\,\frac{\psi^*_{\mathbf{k},v}(\mathbf{r})\psi_{\mathbf{k}-\mathbf{q},v'}(\mathbf{r})\psi_{\mathbf{k},v}(\mathbf{r}')\psi^*_{\mathbf{k}-\mathbf{q},v'}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

- **Implicit functional of the density**: can be brought back to the realm of DFT using an Optimized Effective Potential scheme (OEP):

$$v_{\mathrm{x}}(\mathbf{r}) = \frac{\delta E^{\mathrm{HF}}}{\delta n(\mathbf{r})} = \int d\mathbf{r}' \int d\mathbf{r}'' \sum_{\mathbf{k},v} \frac{\delta E^{\mathrm{HF}}}{\delta \psi^*_{\mathbf{k},v}(\mathbf{r}')}\,\frac{\delta \psi^*_{\mathbf{k},v}(\mathbf{r}')}{\delta v_{KS}(\mathbf{r}'')}\,\frac{\delta v_{KS}(\mathbf{r}'')}{\delta n(\mathbf{r})} + \mathrm{c.c.}$$

$$\frac{\delta E^{\mathrm{HF}}}{\delta \psi^*_{\mathbf{k},v}} = V^{\mathrm{HF}}|\psi_{\mathbf{k},v}\rangle$$

Non-local HF potential

$$\frac{\delta v_{\mathrm{KS}}(\mathbf{r}'')}{\delta n(\mathbf{r})} = \chi_0^{-1}(\mathbf{r}'',\mathbf{r})$$

KS response function

$$\frac{\delta \psi^*_{\mathrm{KS}}(\mathbf{r}')}{\delta v_{\mathrm{KS}}(\mathbf{r}'')} = {\sum_{\mathbf{k}',v'}}' \psi^*_{\mathbf{k}',v'}\,\frac{\psi_{\mathbf{k}',v'}\psi^*_{\mathbf{k},v}}{\varepsilon_{\mathbf{k},v}-\varepsilon_{\mathbf{k}',v'}}$$

First order Perturbation Theory

Direct minimization wrt the wfcs instead

Non local HF potential using PWs

$$V^{\mathrm{HF}}\psi_{\mathbf{k},v}(\mathbf{r}) = -\sum_{\mathbf{q},v'}\int d\mathbf{r}d\mathbf{r}'\frac{\psi^*_{\mathbf{k}-\mathbf{q},v'}(\mathbf{r}')\psi_{\mathbf{k},v}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\psi_{\mathbf{k}-\mathbf{q},v'}(\mathbf{r})$$

- FFT pseudo wfc to real space

$$\psi_{\mathbf{k},v}(\mathbf{k}+\mathbf{G}) \quad \xrightarrow{\text{FFT}} \quad \psi_{\mathbf{k},v}(\mathbf{r})$$

- For each **q** point and occupied band v′ build the “charge density”

$$\rho^{v,v'}_{\mathbf{q}}(\mathbf{r}') = \psi^*_{\mathbf{k}-\mathbf{q},v'}(\mathbf{r}')\psi_{\mathbf{k},v}(\mathbf{r}')$$

- FFT “charge density” to G space and solve Poisson eq.

$$\rho^{v,v'}_{\mathbf{q}}(\mathbf{r}') \quad \xrightarrow{\text{FFT}} \quad \rho^{v,v'}_{\mathbf{q}}(\mathbf{q}+\mathbf{G}) \quad \Longrightarrow \quad V^{v,v'}_{\mathbf{q}}(\mathbf{q}+\mathbf{G}) = \frac{4\pi}{|\mathbf{q}+\mathbf{G}|^2}\rho^{v,v'}_{\mathbf{q}}(\mathbf{q}+\mathbf{G})$$

- FFT back to real space, multiply by wfc and accumulate over **q** and v′

$$V^{v,v'}_{\mathbf{q}}(\mathbf{q}+\mathbf{G}) \quad \xrightarrow{\text{FFT}} \quad V^{v,v'}_{\mathbf{q}}(\mathbf{r}) \quad \Longrightarrow \quad V^{\mathrm{HF}}\psi_{\mathbf{k},v}(\mathbf{r}) = V^{\mathrm{HF}}\psi_{\mathbf{k},v}(\mathbf{r}) + V^{v,v'}_{\mathbf{q}}(\mathbf{r})\psi_{\mathbf{k}-\mathbf{q},v'}(\mathbf{r})$$

Hybrid functional using PWs: q+G=0 divergence

$$E^{\mathrm{HF}} = -\frac{1}{2}\sum_{\mathbf{k},v}\sum_{\mathbf{q},v'}\int d\mathbf{r}d\mathbf{r}'\,\frac{\psi^*_{\mathbf{k},v}(\mathbf{r})\psi_{\mathbf{k}-\mathbf{q},v'}(\mathbf{r})\psi_{\mathbf{k},v}(\mathbf{r}')\psi^*_{\mathbf{k}-\mathbf{q},v'}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

… in reciprocal space …

$$E^{\mathrm{HF}} = -\frac{4\pi}{2\Omega}\frac{\Omega}{(2\pi)^3}\int_{BZ} d\mathbf{q}\sum_{G}\frac{A(\mathbf{q}+\mathbf{G})}{|\mathbf{q}+\mathbf{G}|^2} \qquad A(\mathbf{q}+\mathbf{G}) = \frac{\Omega}{(2\pi)^3}\int_{BZ} d\mathbf{k}|\rho^{\mathbf{k}-\mathbf{q},v'}_{\mathbf{k},v}(\mathbf{q}+\mathbf{G})|^2$$

BZ integration problematic due to an **integrable divergence** for **q+G**→ 0

- Add and subtract an easily integrable term displaying the same divergence [Gygi and Baldereschi PRB 334, 4405 (1986)]
- PW input flag: `exxdiv_treatment='gygi-baldereschi'`

$$E^{\mathrm{HF}} = -\frac{4\pi}{2\Omega}\left\{\frac{\Omega}{(2\pi)^3}\boxed{\int_{BZ} d\mathbf{q}\sum_{G}\frac{A(\mathbf{q}+\mathbf{G})-A(0)e^{-\alpha|\mathbf{q}+\mathbf{G}|^2}}{|\mathbf{q}+\mathbf{G}|^2}} + \frac{\Omega}{(2\pi)^3}\boxed{\int_{BZ} d\mathbf{q}\sum_{G}\frac{A(0)e^{-\alpha|\mathbf{q}+\mathbf{G}|^2}}{|\mathbf{q}+\mathbf{G}|^2}}\right\}$$

Smooth function: standard q-point sampling OK

Easy function: analytic integration

Hybrid functional using PWs: q+G=0 divergence

$$E^{\mathrm{HF}} = -\frac{4\pi}{2\Omega}\left\{ \boxed{\frac{\Omega}{(2\pi)^3}\int_{BZ} d\mathbf{q} \sum_{G} \frac{A(\mathbf{q}+\mathbf{G}) - A(0)e^{-\alpha|\mathbf{q}+\mathbf{G}|^2}}{|\mathbf{q}+\mathbf{G}|^2}} + \boxed{\frac{\Omega}{(2\pi)^3}\int_{BZ} d\mathbf{q} \sum_{G} \frac{A(0)e^{-\alpha|\mathbf{q}+\mathbf{G}|^2}}{|\mathbf{q}+\mathbf{G}|^2}} \right\}$$

$$\boxed{} = \frac{\Omega}{(2\pi)^3}\sqrt{\frac{\pi}{\alpha}}A(0)$$

Analytic integration

$$\boxed{} \simeq \frac{1}{N_q}\sum_{G,q}{}' \frac{A(\mathbf{q}+\mathbf{G})}{|\mathbf{q}+\mathbf{G}|^2} - \frac{1}{N_q}\sum_{G,q}{}' \frac{A(0)e^{-\alpha|\mathbf{q}+\mathbf{G}|^2}}{|\mathbf{q}+\mathbf{G}|^2} + \frac{1}{N_q}\lim_{\mathbf{q}\to 0} \frac{A(\mathbf{q}) - A(0)\exp^{-\alpha|\mathbf{q}|^2}}{|\mathbf{q}|^2}$$

$$= \frac{1}{N_q}\sum_{G,q}{}' \frac{A(\mathbf{q}+\mathbf{G})}{|\mathbf{q}+\mathbf{G}|^2} - \frac{1}{N_q}\sum_{G,q}{}' \frac{A(0)e^{-\alpha|\mathbf{q}+\mathbf{G}|^2}}{|\mathbf{q}+\mathbf{G}|^2} + \frac{1}{N_q}\lim_{\mathbf{q}\to 0} \frac{A(\mathbf{q}) - A(0)}{|\mathbf{q}|^2} + \frac{1}{N_q}\alpha A(0)$$

NO divergence anymore, still the explicit **treatment of the q→0 term is necessary**

$$E^{\mathrm{HF}} = -\frac{4\pi}{2\Omega}\left\{ \frac{\Omega}{(2\pi)^3}\frac{1}{N_q}\left[\sum_{q,G}{}' \frac{A(\mathbf{q}+\mathbf{G})}{|\mathbf{q}+\mathbf{G}|^2} + \lim_{\mathbf{q}\to 0}\frac{A(\mathbf{q}) - A(0)}{|\mathbf{q}|^2}\right] + D\ A(0) \right\}$$

$$D = \frac{1}{N_q}\left[-\sum_{q,G}{}' \frac{\exp^{-\alpha|\mathbf{q}+\mathbf{G}|^2}}{|\mathbf{q}+\mathbf{G}|^2} + \alpha\right] + \frac{\Omega}{(2\pi)^3}\sqrt{\frac{\pi}{\alpha}}$$

- **Calculated once at the beginning of the run**
- **Independent of α**

V. Nguyen and S. de Gironcoli PRB **79**, 205114 (2008) Broqvist et *al*. PRB **80** 085114 (2009)

Hybrid functional using PWs: q+G=0 divergence

$$E^{\mathrm{HF}} = -\frac{4\pi}{2\Omega}\left\{\frac{\Omega}{(2\pi)^3}\frac{1}{N_q}\left[\sum_{q,G}{}' \frac{A(\mathbf{q}+\mathbf{G})}{|\mathbf{q}+\mathbf{G}|^2} + \boxed{\lim_{\mathbf{q}\to 0}\frac{A(\mathbf{q})-A(0)}{|\mathbf{q}|^2}}\right] + D\,A(0)\right\}$$

□ : Evaluated with an extrapolation procedure

$$E_d^{\mathrm{HF}} = \omega_d\left\{f(0) + \sum_{qG}^{\mathrm{d}}{}' f(\mathbf{q}+\mathbf{G})\right\}$$

$$E_c^{\mathrm{HF}} = \omega_c\left\{f(0) + \sum_{qG}^{\mathrm{c}}{}' f(\mathbf{q}+\mathbf{G})\right\}$$

Coarse grid includes only every second point in each direction ω_d=1/8 ω_c

$$E_d^{\mathrm{HF}} = \frac{1}{8}\omega_c\left\{f(0) + \sum_{qG}^{\mathrm{d}}{}' f(\mathbf{q}+\mathbf{G})\right\}$$

$$E_c^{\mathrm{HF}} = \omega_c\left\{f(0) + \sum_{qG}^{\mathrm{c}}{}' f(\mathbf{q}+\mathbf{G})\right\}$$

Assuming the integrals are converged (E_c=E_d)

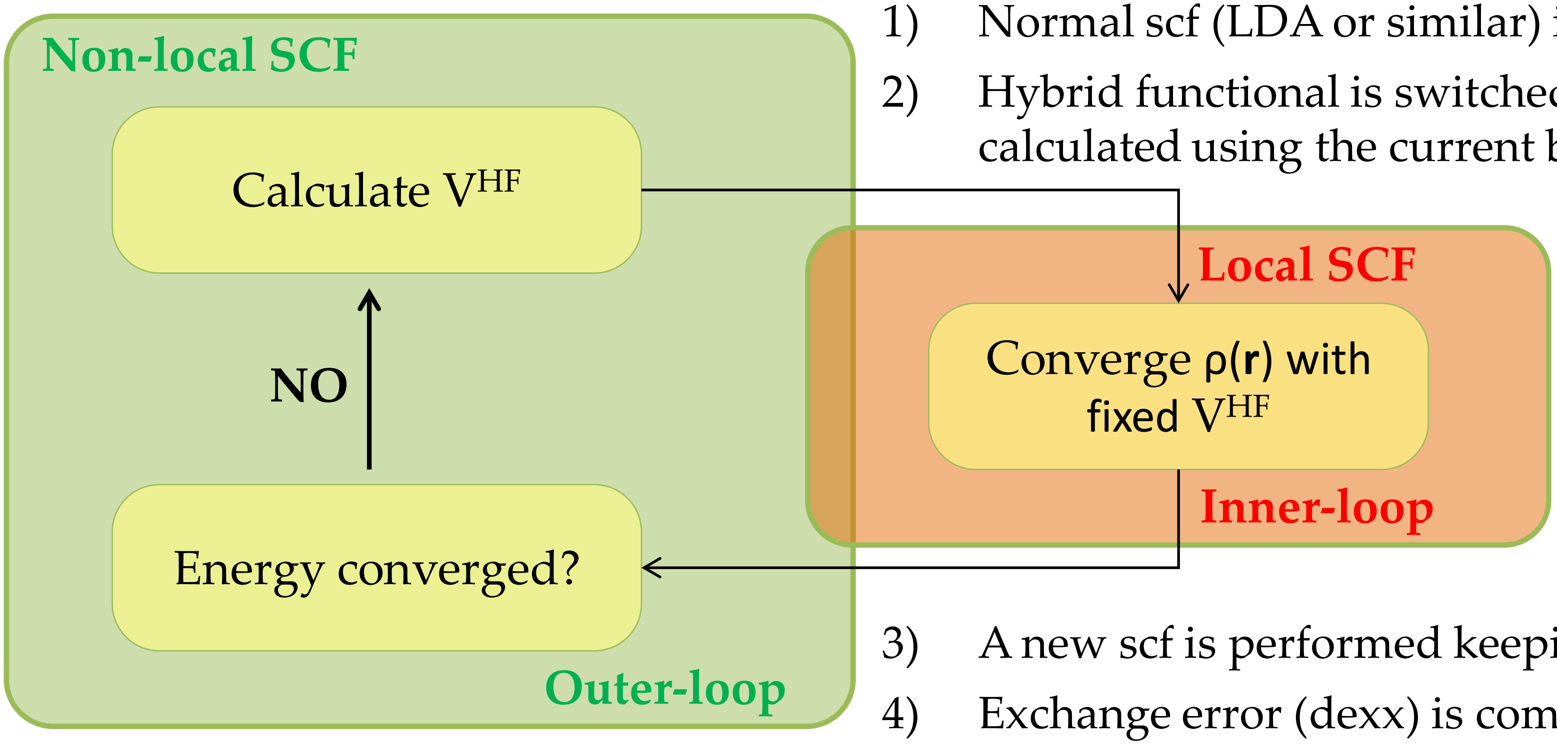
$$\lim_{\mathbf{q}\to 0}\frac{A(\mathbf{q})-A(0)}{|\mathbf{q}|^2} = \frac{1}{7}\sum_{Gq}^{d}{}' \frac{A(\mathbf{q}+\mathbf{G})}{|\mathbf{q}+\mathbf{G}|^2} - \frac{8}{7}\sum_{Gq}^{c}{}' \frac{A(\mathbf{q}+\mathbf{G})}{|\mathbf{q}+\mathbf{G}|^2}$$

PW input flag: `x_gamma_extrapolation (T/F)`

V. Nguyen and S. de Gironcoli PRB **79**, 205114 (2008)

Hybrid functional : nested self-consistency

- Non-local HF potential and energy calculation are more expensive than standard LDA/GGA (see next slide)
- **Idea:** Converge local and non-local quantities in **separated loops**



Non-local SCF

Calculate V^{HF}

NO

Energy converged?

Outer-loop

Local SCF

Converge $\rho(\mathbf{r})$ with fixed V^{HF}

Inner-loop

1) Normal scf (LDA or similar) is performed
2) Hybrid functional is switched. V^{HF} is calculated using the current best wfcs
3) A new scf is performed keeping V^{HF} fixed
4) Exchange error (dexx) is computed
5) If dexx > thr the procedure is repeated

Hybrid Functionals: scaling

- **Kinetic operator + local potential:** NPW + 2FFT + NRXX
- **Non-local (KB) pseudopotential:** N_{KB} x 2NPW (with $N_{KB} \sim N_{bnd}$)
- **Non-local HF operator:** ~ N_q x N_{bnd} x (2FFT+ …)

From 10 to 100 times slower than standard case!

How to save computational time:

- Reduce the mesh of q points (at the price of loosing some accuracy): input variable nqx1, nqx2, nqx3 (in QE they are equal to the k-point mesh by default).
- **Adaptive compressed exchange (ACE) algorithm** (in QE need to add a compilation flag -D__EXX_ACE) [Lin JCTC **12**, 2242 (2016)].
- Neglect the long-range exchange: **range-separated hybrids** (see next slide). Less points for the BZ sampling.

Range separated Hybrid Functionals

Basic Idea: Split the electron-electron interaction in short and long range

$$\frac{1}{r} = \underbrace{\frac{\mathrm{erfc}(\omega \mathrm{r})}{r}}_{\mathrm{sr}} + \underbrace{\frac{\mathrm{erf}(\omega \mathrm{r})}{r}}_{\mathrm{lr}}$$

ω **tunes the range separation**

Key observation: **Non-local (HF) and local (DFT) long-range exchange are small** and **tends to cancel** each other (especially in metallic systems) [Heyd et *al*. JCP **118**, 8207 (2003)]

$$E_{\mathrm{xc}}^{\omega\mathrm{PBEh}} = aE_{\mathrm{x}}^{\mathrm{HF,sr}}(\omega) + (1-a)E_{\mathrm{x}}^{\mathrm{PBE,sr}}(\omega) + E_{\mathrm{x}}^{\mathrm{PBE,lr}}(\omega) + E_{c}^{\mathrm{PBE}}$$

ω=0.106 bohr^{-1} optimized to experimental data set; **a_0=1/4** from PBE0 idea ➔ **HSE06**
[Krukau et *al*. JCP **125**, 224106 (2006)]

- Treat **only short range** part with nonlocal **HF** ➔ reduction in computational effort
- Reduce to PBE0 for ω=0 and to PBE for ω=∞
- Finite ω = interpolation between PBE0 and PBE

Hybrid Functionals: how do they performe

Atomization energy of Small Molecules

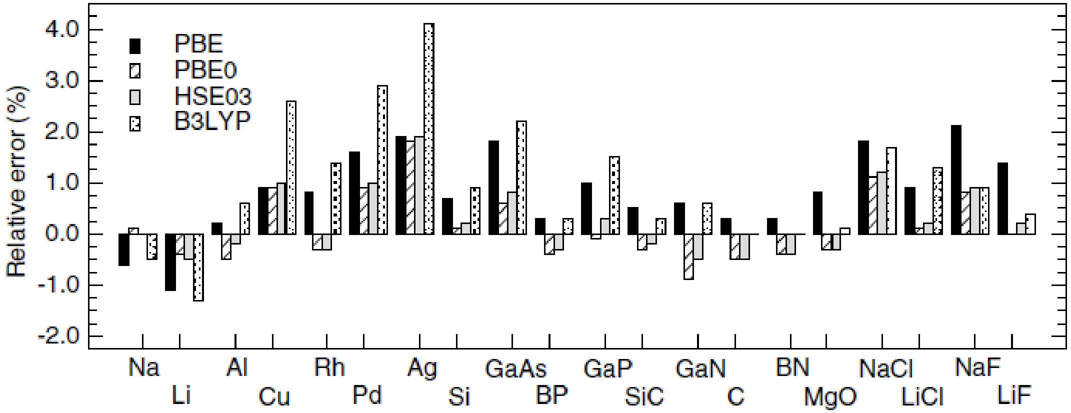
	MAE(G2)	MAE (G2-1)	Max AE (G2)	Max AE (G2-1)
LDA	83.7	36.4	216	84
PBE	17.1	8.6	52	26
BLYP	7.1	4.7	28	15
B3LYP	**3.1**	**2.4**	**20**	**10**
PBE0	**4.8**	**3.5**	**24**	**10**

Mean Absolute Error (MAE) in Kcal/mol for the G2 (148 molecules) and G2-1((55 molecules) sets.

Curtiss et *al*. JCP **106**, 1063 (1997); Scuseria *et al*. JCP **110**, 5029 (1999)

Hybrid Functionals: how do they performe

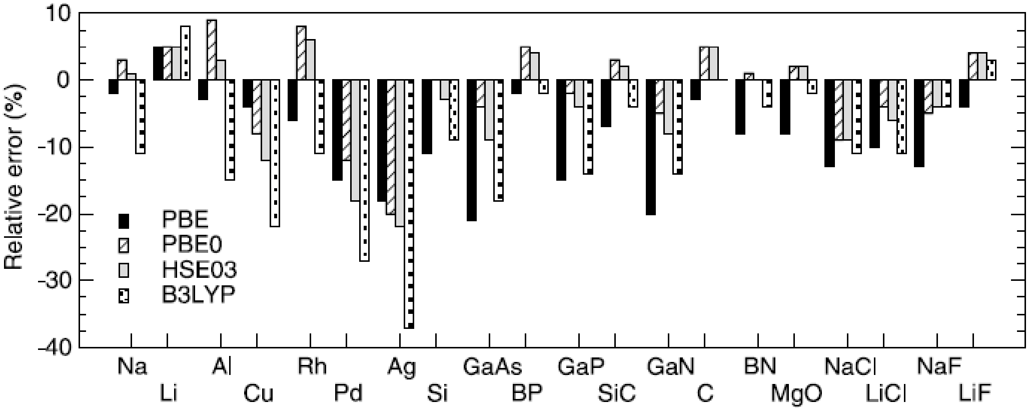
Lattice constants of selected solids



	PBE	PBE0	HSE	B3LYP
MRE	0.8	0.1	0.2	1.0
MARE	1.0	0.5	0.5	1.2
No Metals (Si-LiF)				
MRE	1.0	0.0	0.1	0.8
MARE	1.0	0.4	0.5	0.8

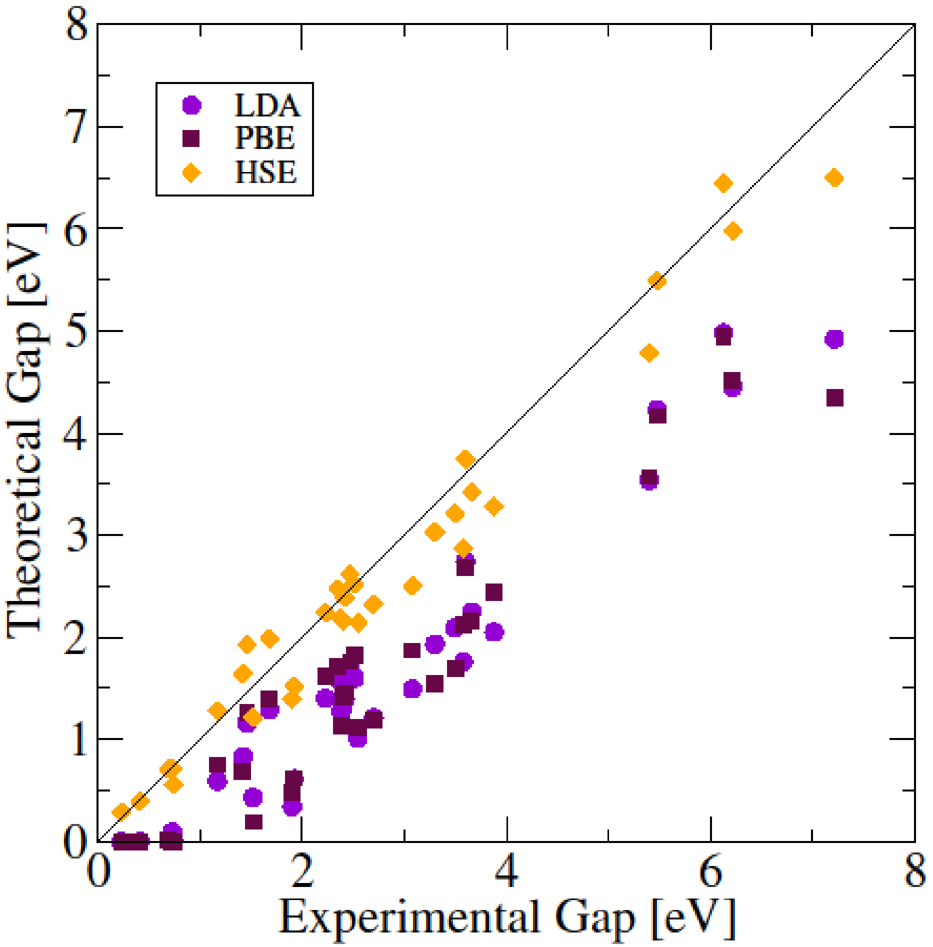
Bulk moduli of selected solids

	PBE	PBE0	HSE	B3LYP
MRE	-9.8	-1.2	-3.1	-10.2
MARE	9.4	5.7	6.4	11.4
No Metals (Si-LiF)				
MRE	-10.4	-0.7	-1.8	-6.8
MARE	10.4	3.8	4.6	7.4



Marsman *et al.* J. Phys: Condens. Matter **20**, 064201 (2008)

Hybrid Functionals: how do they performe



- Improved band gaps for semiconducting system

- HSE correctly predict semiconducting behavior in systems where LDA/GGA predicts a metal

Error (in eV) for 40 simple and binary semiconductors and insulators

	LDA	PBE	HSE
ME	-1.14	-1.13	**-0.17**
MAE	1.14	1.13	**0.26**
Max (+)	--	--	**0.32**
Min(-)	-2.30	-2.88	**-0.72**

Caveat: band gap is a more fundamental issue than Local vs Hybrids !

Heyd *et al*. JCP **123**, 174101 (2005)

Hybrid functional: summary

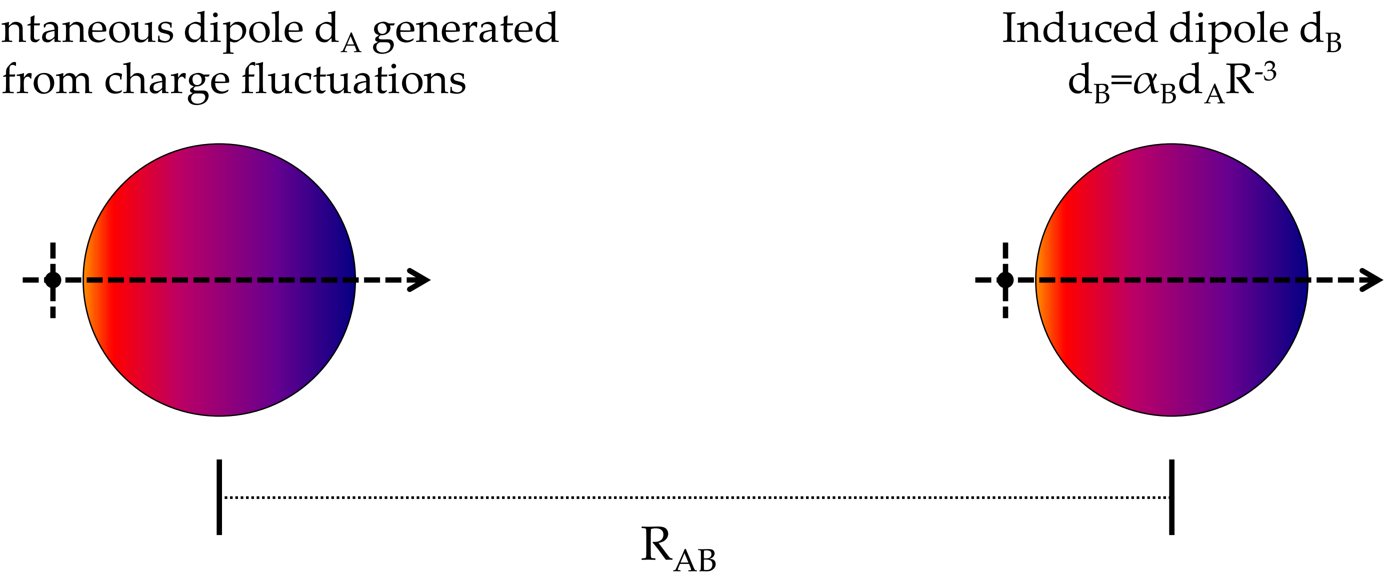
- Address the self-interaction and the delocalization error of LDA/GGA
- Leads to a systematic improvement over LDA and GGA
- On average better energetic and structural properties (especially for molecules and insulator, less for metals)
- Band gaps greatly improves
- Computationally order of magnitude more expensive than LDA/GGA (can be alleviated using smart algorithms or range-separation)
- Mixing parameter a_0 is in principle system dependent

Outline

- Introduction
- Adiabatic Connection Formula
  - Exact expression for the xc Energy
- Hybrid Functionals
  - Exact Exchange Energy, Range separation
- Van der Waals interaction in DFT
  - Simple corrections
  - True non-local density functionals
- RPA and beyond

Van der Waals interactions

- Crucial for biomolecules, sparse matter, adsorption on surfaces …
- Dispersion forces arise from the interaction of transient electric multipoles
- Instantaneous dipole – induced dipole is the leading term



Instantaneous dipole d_A generated from charge fluctuations

Induced dipole d_B
$d_B=\alpha_B d_A R^{-3}$

R_{AB}

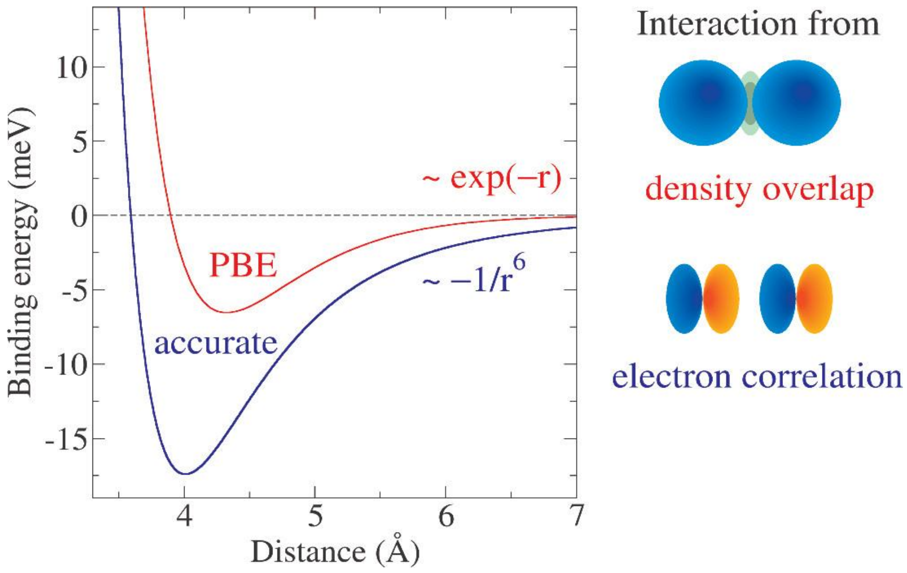
Two neutral atom separated by R_{AB} much larger than the atomic size, so that the corresponding wavefunctions do dot overlap

$$E = -C_6^{AB} R^{-6} \qquad C_6 \propto \alpha_A \alpha_B \qquad \alpha = \text{dipolar polarizability}$$

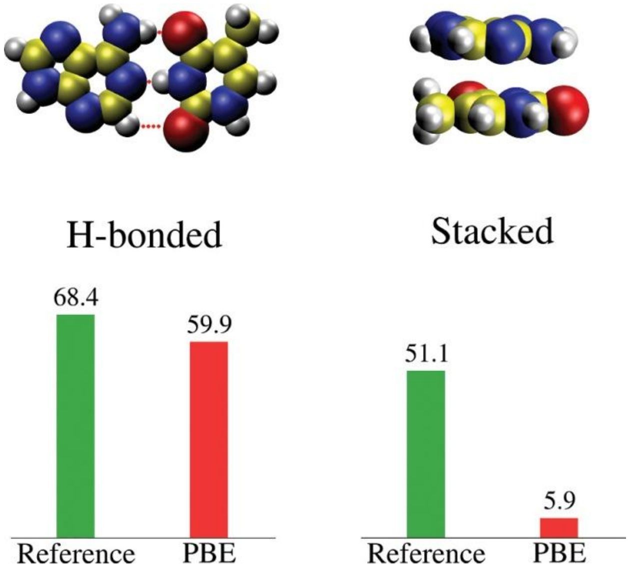
Van der Waals interactions

- It is a **pure (non-local) correlation effect** (not present at the HF level)
- Because of their intrinsic local nature LDA/GGA cannot describe vdW interaction
- LDA/GGAs give binding or repulsion only when there is charge density overlap
- WRONG exponential decay of the interaction energy between separate fragments

Binding curve for Kr dimer



Two binding configuration of DNA base pair adenine thymine



Klimeš and Michaelides JCP **137**, 120901 (2012)

How to deal with vdW interactions?

- Neglect it
  - or use functionals fitted to a vdW database
- Use a simple C_6R^{-6} correction (DFT-D)
  - Grimme, Tkatchenko-Scheffler, Becke-Johnson
- Develop a truly non-local functional
  - vdW-DF, vdW-DF2, vv10
- RPA and beyond RPA

How to deal with vdW interactions?

- Use a simple C_6R^{-6} correction (DFT-D2)

  [S. Grimme, J. Comp. Chem **27**, 1787 (2006)]

$$E_{\mathrm{DFT-D}} = E_{\mathrm{DFT}} + E_{\mathrm{Disp}} \qquad E_{\mathrm{Disp}} = -s_6 \sum_{i=1}^{N_{at}-1} \sum_{j=i+1}^{N_{at}} \frac{C_6^{ij}}{R_{ij}^6} f_{dmp}(R_{ij})$$

- Pair-wise additive
- s_6 global scaling factor that depends on the DF used
- C_6^{ij} dispersion coefficient for every atom pair ij

$$C_6^{ij} = \sqrt{C_6^i C_6^j} \qquad C_6^i \propto I_i \alpha_i$$

I_i: Ionization potential
α_i: dipole polarizability

- f_{dmp} damping function to avoid singularities for small R_{ij}

$$f_{\mathrm{dmp}}(R_{ij}) = \frac{1}{1 + e^{-d(R_{ij}/R_{ij}^0 - 1)}}$$

- I_i , a_i and R^0_i tabulated for each isolated atom and **insensitive from the chemical environment**

How to deal with vdW interactions?

- Use a simple C_6R^{-6} correction + environment dependent C_6

  [S. Grimme et *al*. JCP **132**, 1154104 (2010)] **DFT-D3**
  [A. Tkatchenko and M. Scheffler, PRL **102**, 073005 (2009)] **vdW(TS)**
  [A. Becke and E. Johnson JCP **122**, 154104 (2005)] **XDM**

- **DFT-D3**: precalculated C_6 coefficients in different hybridization states. They are interpolated during the calculation to get the appropriate dispersion coefficient

- **DFT-TS**: Only needs free atom references. They are scaled during the calculation according to the effective volume of the atom in the system:

$$C_6^i = \left(\frac{V^i[n(\mathbf{r})]}{V^i_{\text{free}}[n(\mathbf{r})]}\right)^2 C_6^{i,\text{free}}$$

$$\alpha_i = \left(\frac{V^i[n(\mathbf{r})]}{V^i_{\text{free}}[n(\mathbf{r})]}\right) \alpha_i^{\text{free}}$$

$$\Longrightarrow \qquad C_6^{ij} = \frac{\alpha_i \alpha_j C_6^i C_6^j}{\alpha_j C_6^i + \alpha_i C_6^j}$$

How to deal with vdW interactions?

- Truly non-local functionals

$$E_c^{\mathrm{nl}} = \frac{\hbar}{2}\int d\mathbf{r}\int d\mathbf{r}' n(\mathbf{r})\Phi(\mathbf{r},\mathbf{r}')n(\mathbf{r}')$$

vdW-DF: Dion et *al*. PRL **92**, 246401 (2006)]
vdW-DF2: Lee et al. , PRB **82**, 081101 (2010)]
VV09: Vydrov and van Voorhis, PRL 103, 063004 (2009)]
VV10: Vydrov and van Voorhis, JCP **133**, 244203 (2010)]

- RPA functional and beyond

[Ren et *al*. J. of Material Science **47**, 7447 (2012)] Review on the RPA

Both are based on the **Adiabatic Connection Fluctuation Dissipation Theorem (ACFDT)**

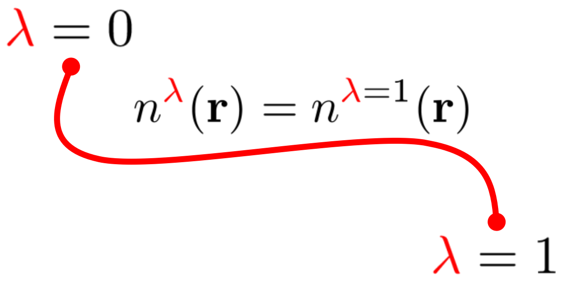
The ACFDT theorem

$$E_{Hxc} = \int_0^1 d\lambda \langle \Psi^\lambda | W | \Psi^\lambda \rangle$$

$$\langle \Psi^\lambda | W | \Psi^\lambda \rangle = \frac{e^2}{2} \int d\mathbf{r} d\mathbf{r}' \frac{n^{(2)}_\lambda(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

$$n^{(2)}_\lambda(\mathbf{r},\mathbf{r}') = \boxed{\langle \delta\hat{n}(\mathbf{r}) \delta\hat{n}(\mathbf{r}') \rangle_\lambda} + \underset{\text{Hartree}}{\boxed{n(\mathbf{r})n(\mathbf{r}')}} - \delta(\mathbf{r}-\mathbf{r}')n(\mathbf{r})$$

Adiabatic coupling


$\lambda = 0$

$n^\lambda(\mathbf{r}) = n^{\lambda=1}(\mathbf{r})$

$\lambda = 1$

$$\hat{H}^\lambda = \hat{T} + \lambda \hat{W} + \hat{v}^\lambda$$

$$\hat{v}^{\lambda=0} = \hat{v}_{KS}$$

$$\hat{v}^{\lambda=1} = \hat{v}_{ext}$$

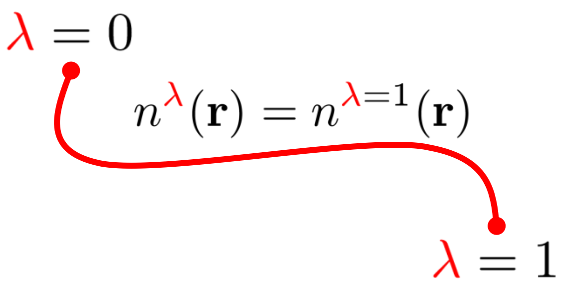
The ACFDT theorem

$$E_{Hxc} = \int_0^1 d\lambda \langle \Psi^\lambda | W | \Psi^\lambda \rangle$$

$$\langle \Psi^\lambda | W | \Psi^\lambda \rangle = \frac{e^2}{2} \int d\mathbf{r} d\mathbf{r}' \frac{n_\lambda^{(2)}(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

$$n_\lambda^{(2)}(\mathbf{r},\mathbf{r}') = \boxed{\langle \delta\hat{n}(\mathbf{r}) \delta\hat{n}(\mathbf{r}') \rangle_\lambda} + \underset{\text{Hartree}}{\boxed{n(\mathbf{r}) n(\mathbf{r}')}} - \delta(\mathbf{r}-\mathbf{r}') n(\mathbf{r})$$

Adiabatic coupling



$\lambda = 0$

$n^\lambda(\mathbf{r}) = n^{\lambda=1}(\mathbf{r})$

$\lambda = 1$

$$\hat{H}^\lambda = \hat{T} + \lambda \hat{W} + \hat{v}^\lambda$$

$$\hat{v}^{\lambda=0} = \hat{v}_{KS}$$

$$\hat{v}^{\lambda=1} = \hat{v}_{ext}$$

Fluctuation Dissipation Theorem

Density Fluctuation → Energy Dissipation , i.e. Im[χ]

$$\langle \delta\hat{n}(\mathbf{r}) \delta\hat{n}(\mathbf{r}') \rangle_\lambda = -\frac{\hbar}{\pi} \int_0^\infty du\, \chi^\lambda(\mathbf{r},\mathbf{r}';iu)$$

Exchange-correlation Energy from the ACFDT

$$\boxed{E_{xc} = -\frac{1}{2} \int_0^1 d\lambda \int d\mathbf{r} d\mathbf{r}' \frac{e^2}{|\mathbf{r}-\mathbf{r}'|} \left\{ \frac{\hbar}{\pi} \int_0^\infty du \chi^\lambda(\mathbf{r},\mathbf{r}';iu) + \delta(\mathbf{r}-\mathbf{r}') n(\mathbf{r}) \right\}}$$

The ACFDT theorem

$$E_{xc} = -\frac{1}{2}\int_0^1 d\lambda \int d\mathbf{r}d\mathbf{r}'\,\frac{e^2}{|\mathbf{r}-\mathbf{r}'|}\left\{\frac{\hbar}{\pi}\int_0^\infty du\chi^\lambda(\mathbf{r},\mathbf{r}';iu)+\delta(\mathbf{r}-\mathbf{r}')n(\mathbf{r})\right\}$$

- Replacing χ^λ with χ^0, the KS **exact-exchange Energy** is obtained:

$$E_x = -\frac{e^2}{2}\int d\mathbf{r}d\mathbf{r}'\,\frac{\left|\sum_i^{occ}\phi_i(\mathbf{r})\phi_i(\mathbf{r}')\right|^2}{|\mathbf{r}-\mathbf{r}'|}$$

Cancels out the spurious self-interaction error present in Hartree energy

- The **Correlation Energy** can be thus separated:

$$\boxed{E_c = -\frac{\hbar}{2\pi}\int_0^1 d\lambda\int_0^\infty du\;\mathrm{Tr}\left\{v_c\left[\chi^\lambda(iu)-\chi^0(iu)\right]\right\}}$$

Perfectly combine with E_x: NO ambiguity

The problem is reduced to **find** suitable **approximations for the response function**

Used as a starting point for further semplification: non-local vdW

$$E_c^{\mathrm{nl}} = \frac{\hbar}{2}\int d\mathbf{r}\int d\mathbf{r}'n(\mathbf{r})\Phi(\mathbf{r},\mathbf{r}')n(\mathbf{r}')$$

Dyson-like equation from **TDDFT**:

$$\chi_\lambda = \chi_0 + \chi_0\left[\lambda v_c + f_{xc}^\lambda\right]\chi_\lambda$$

Needs approximate f_{xc}: RPA, RPAx,…

Long range asymptote of dispersion interaction

$$E_c = -\frac{\hbar}{2\pi}\int_0^1 d\lambda \int_0^\infty du \ \mathrm{Tr}\left\{v_c\left[\chi^\lambda(iu) - \chi^0(iu)\right]\right\}$$

1) Assume an **RPA like** response function: $\chi^\lambda = \tilde{\chi} + \lambda\tilde{\chi}v_c\chi^\lambda$ Analytic λ integration

2) Assume **well separated fragmen**ts A and B: $\chi = \chi_{AA} + \chi_{BB} + \delta\chi$

3) **Expand to second order** in the inter-fragment coulomb interaction

$$E^{(2)}_{\mathrm{AB}} = -\frac{\hbar}{2\pi}\int d\mathbf{r}_A \int d\mathbf{r}'_A \int d\mathbf{r}_B \int d\mathbf{r}'_B \ \frac{e^2}{|\mathbf{r}_A - \mathbf{r}_B|}\frac{e^2}{|\mathbf{r}'_A - \mathbf{r}'_B|}\int_0^\infty du \ \chi_{AA}(\mathbf{r}_A, \mathbf{r}'_A, iu)\chi_{BB}(\mathbf{r}_B, \mathbf{r}'_B, iu)$$

4) Introduce the dynamical polarizability tensor: $\chi(\mathbf{r}, \mathbf{r}', iu) = e^{-2}\partial_{r_i}\partial_{r'_j}\alpha_{ij}(\mathbf{r}, \mathbf{r}', iu)$

5) **Local** and **isotropic** approximation: $\alpha_{ij}(\mathbf{r}, \mathbf{r}', iu) = \delta_{ij}\alpha(\mathbf{r}, iu)\delta(\mathbf{r}, \mathbf{r}')$

$$E^{(2)} = -\frac{3\hbar}{\pi}\int_0^\infty du \int_A d\mathbf{r} \int_B d\mathbf{r}' \ \frac{\alpha(\mathbf{r}, iu)\alpha(\mathbf{r}', iu)}{|\mathbf{r} - \mathbf{r}'|^6} \quad \longrightarrow \quad -\frac{C_6^{\mathrm{AB}}}{R^6}$$

Lu et al., JCP **133**, 1554110 (2010)
Dobson, *Lecture Notes in Physics, Berlin Springer Verlag*, vol. 837 p. 417 (2012)
Vydrov and van Voorhis, *Lecture Notes in Physics, Berlin Springer Verlag*, vol 837 p. 443 (2012)

Long range asymptote of dispersion interaction

Second order **interaction** energy **between two** finite **non overlapping fragments** within a **local and isotropic** approximation for the **polarizability** tensor:

$$E^{(2)} = -\frac{3\hbar}{\pi}\int_0^\infty du \int_A d\mathbf{r} \int_B d\mathbf{r}' \, \frac{\alpha(\mathbf{r}, iu)\alpha(\mathbf{r}', iu)}{|\mathbf{r}-\mathbf{r}'|^6}$$

Average dynamic polarizability

$$\bar{\alpha}(iu) = \int d\mathbf{r}\ \alpha(\mathbf{r}, iu)$$

f-sum rule

$$\lim_{u\to\infty} \bar{\alpha}(iu) = Ne^2/mu^2$$

Local polarizability model

$$\alpha(\mathbf{r}, iu) = \frac{e^2}{m}\frac{n(\mathbf{r})}{\omega_0^2(\mathbf{r}) + u^2}$$

$$\boxed{E^{(2)} = -\frac{3e^4\hbar}{2m^2}\int_A d\mathbf{r}\int_B d\mathbf{r}' \, \frac{n(\mathbf{r})n(\mathbf{r}')}{\omega_0(\mathbf{r})\omega_0(\mathbf{r}')[\omega_0(\mathbf{r}) + \omega_0(\mathbf{r}')]|\mathbf{r}-\mathbf{r}'|^6}}$$

Vydrov and van Voorhis, *Lecture Notes in Physics, Berlin Springer Verlag*, vol 837 p. 443 (2012)

Truly non-local functionals for general geometries

$$E_c = E_c^0 + E_c^{\mathrm{nl}} \qquad E_c^{\mathrm{nl}} = \frac{\hbar}{2}\int d\mathbf{r}\int d\mathbf{r}' n(\mathbf{r})\Phi(\mathbf{r},\mathbf{r}')n(\mathbf{r}')$$

1) Applicable to **general geometries** with appropriate choice of Φ from a simplified ACFDT formula [Dion et al. PRL **92**, 246401 (2006)]

2) $E_c^0[n]$ Local Density Approximation

3) $\Phi(\mathbf{r},\mathbf{r}') = \Phi(n(\mathbf{r}), \nabla n(\mathbf{r}), n(\mathbf{r}'), \nabla n(\mathbf{r}'), |\mathbf{r}-\mathbf{r}'|)$

4) Local model for the polarizability plus a single-pole approximation

5) $\Phi(\mathbf{r},\mathbf{r}') \longrightarrow -\dfrac{3e^4}{2m^2}\dfrac{1}{\omega_0(\mathbf{r})\omega_0(\mathbf{r}')[\omega_0(\mathbf{r})+\omega_0(\mathbf{r}')]|\mathbf{r}-\mathbf{r}'|^6}$

6) Characteristic frequency ω_0 determined locally from HEG properties

7) $\omega_0(\mathbf{r})$ depends only on the density and its gradient in **r**

Truly non-local functionals for general geometries

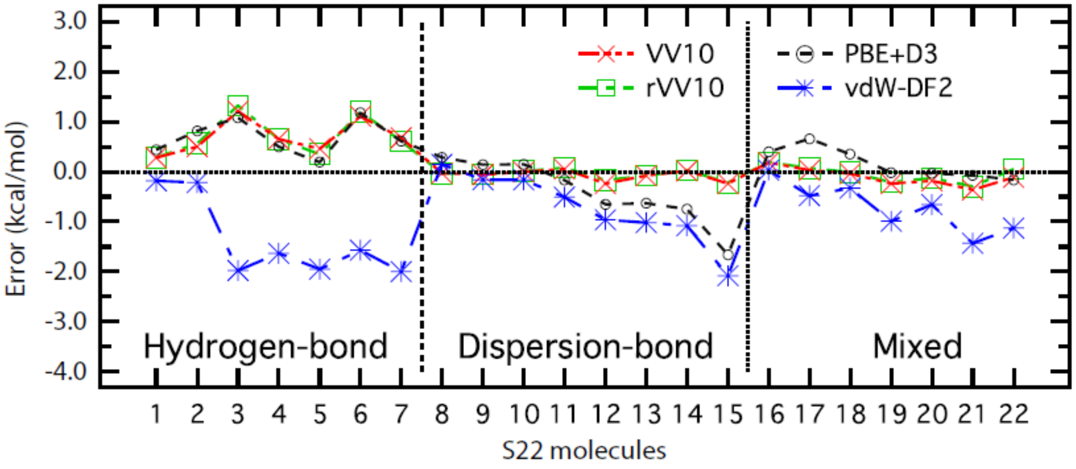
$$E_c = E_c^0 + E_c^{\mathrm{nl}} \qquad E_c^{\mathrm{nl}} = \frac{\hbar}{2}\int d\mathbf{r}\int d\mathbf{r}'\, n(\mathbf{r})\Phi(\mathbf{r},\mathbf{r}')n(\mathbf{r}')$$

Different Local Polarizability models differ by the definition of ω_0

	$\omega_0[n(\mathbf{r}), \nabla n(\mathbf{r})]$ in E_c^{nl}		$E_{\mathbf{xc}}^{\mathrm{LDA/GGA}}$	C_6 error
vdW-DF	$\frac{9\hbar}{8\pi m}\left[k_{\mathrm{F}}(1-\mu s^2) - \frac{4\pi}{3e^2}\varepsilon_c^{\mathrm{LDA}}\right]^2$	with $\mu = 0.09434$	**SLA+PW+RPBE**	**18.5%**
vdW-DF2	$\frac{9\hbar}{8\pi m}\left[k_{\mathrm{F}}(1-\mu s^2) - \frac{4\pi}{3e^2}\varepsilon_c^{\mathrm{LDA}}\right]^2$	with $\mu = 0.20963$	**SLA+PW+RPW86**	**60.9%**
vv09	$\frac{\hbar}{3m}\left[k_{\mathrm{F}}(1-\mu s^2)\right]^2$	with $\mu = 0.22$	**SLA+PW+RPBE**	**10.4%**
vv10	$\sqrt{\frac{\omega_p^2}{3} + C\frac{\hbar^2}{m^2}\left\lvert\frac{\nabla n}{n}\right\rvert^4}$	with $C = 0.0089$	**SLA+PBE+RPW86**	**10.7%**

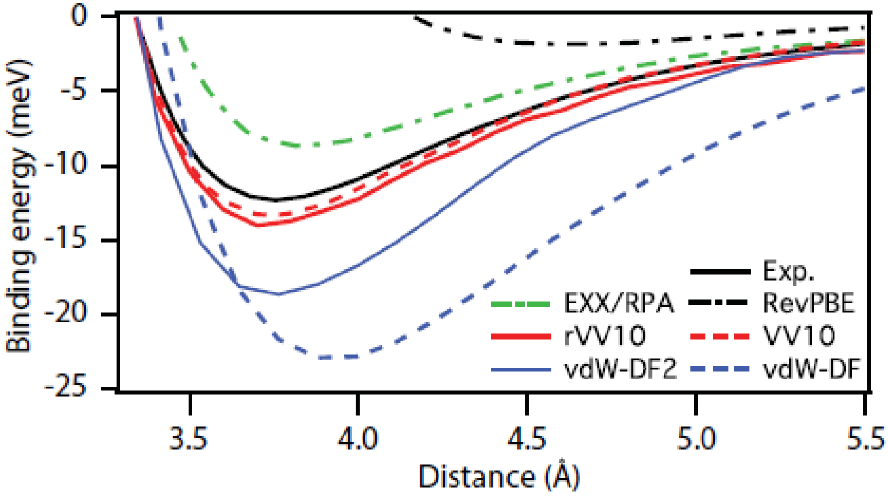
Vydrov and van Voorhis, *Lecture Notes in Physics, Berlin Springer Verlag*, vol 837 p. 443 (2012)

Performance of vdW functionals



Binding energy differences (in kcal/mol) for the molecules in the s22 set (non-covalent bonding) wrt CCSD(T)

Potential energy curve of the Ar dimer

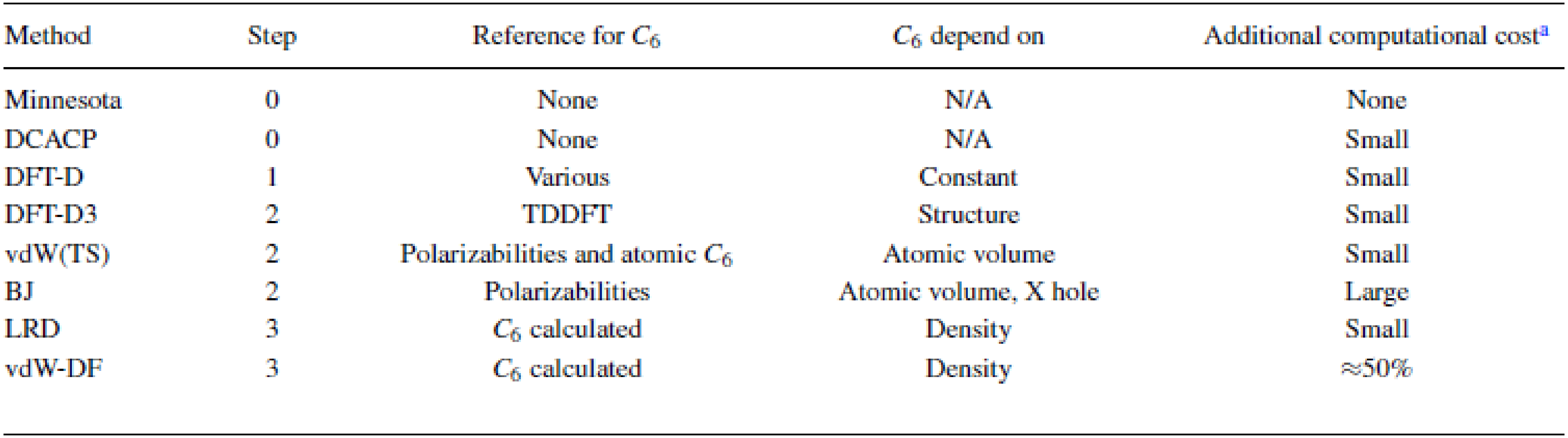


Lattice constant and bulk moduli of selected solids

Complex	vdW-DF2	rVV10	PBE	Ref.
Lattice constants (Å)				
Cu	3.76	3.68	3.65	3.60
Al	4.08	4.02	4.04	4.02
Si	5.52	5.48	5.46	5.42
C (diamond)	3.61	3.58	3.57	3.54
NaCl	5.69	5.59	5.70	5.57
Bulk moduli (GPa)				
Cu	97.0	124.6	139	142.0
Al	60.1	79.0	78.6	79.4
Si	79.6	86.5	88.3	99.2
C (diamond)	395.0	424.4	429	443.0
NaCl	26.0	27.9	22.8	26.6

Sabatini *et al.* PRB **87**, 041108(R) (2013)

vdW functionals: Summary



Method	Step	Reference for C_6	C_6 depend on	Additional computational cost[a]
Minnesota	0	None	N/A	None
DCACP	0	None	N/A	Small
DFT-D	1	Various	Constant	Small
DFT-D3	2	TDDFT	Structure	Small
vdW(TS)	2	Polarizabilities and atomic C_6	Atomic volume	Small
BJ	2	Polarizabilities	Atomic volume, X hole	Large
LRD	3	C_6 calculated	Density	Small
vdW-DF	3	C_6 calculated	Density	≈50%

Klimeš and Michaelides JCP **137**, 120901 (2012)

- ✓ Computationally no more expensive than LDA/GGA
- ✓ Satisfactory results in most of the cases: C6 coefficients, binding energies, equilibrium geometries in good agreement with experiments
- × Only pair-wise additive
- × All DFT-D have a certain degree of empiricism (input reference C6, damping function …)
- × For vdW-DF not clear which exchange functional to use. Local approximation of the polarizability

Outline

- Introduction
- Adiabatic Connection Formula
  - Exact expression for the xc Energy
- Hybrid Functionals
  - Exact Exchange Energy, Range separation
- Van der Waals interaction in DFT
  - Simple corrections
  - True non-local density functionals
- RPA and beyond

The RPA and RPAx functionals

$$E_c = -\frac{\hbar}{2\pi}\int_0^1 d\lambda \int_0^\infty du \; \mathrm{Tr}\left\{v_c\left[\chi^\lambda(iu) - \chi^0(iu)\right]\right\}$$

Direct evaluation of the ACFDT formula is possible when χ is given

$$\chi_0(\mathbf{r},\mathbf{r}',iu) = \sum_{ij}(f_i - f_j)\frac{\phi_i^*(\mathbf{r})\phi_j(\mathbf{r})\phi_j^*(\mathbf{r}')\phi_i(\mathbf{r}')}{\varepsilon_i - \varepsilon_j + iu}$$

KS non-interacting response function

$$\chi^\lambda(iu) = \chi^0(iu) + \chi^0(iu)[\lambda v_c + f_{xc}^\lambda(iu)]\chi^\lambda(iu)$$

Dyson-like equation from TDDFT

- **RPA:** $f_{\mathrm{xc}}^\lambda = 0 \quad \Rightarrow \quad \chi^\lambda = \chi_0 + \lambda\chi_0 v_c \chi^\lambda$

$$E_c^{\mathrm{RPA}} = \frac{\hbar}{2\pi}\int_0^\infty du \; \mathrm{Tr}\{\ln[I - v_c\chi_0(iu)] + v_c\chi_0(iu)\}$$

- **RPAx:** $f_{\mathrm{xc}}^\lambda = \lambda f_x \quad \Rightarrow \quad \chi^\lambda = \chi_0 + \lambda\chi_0[v_c + f_x]\chi^\lambda$

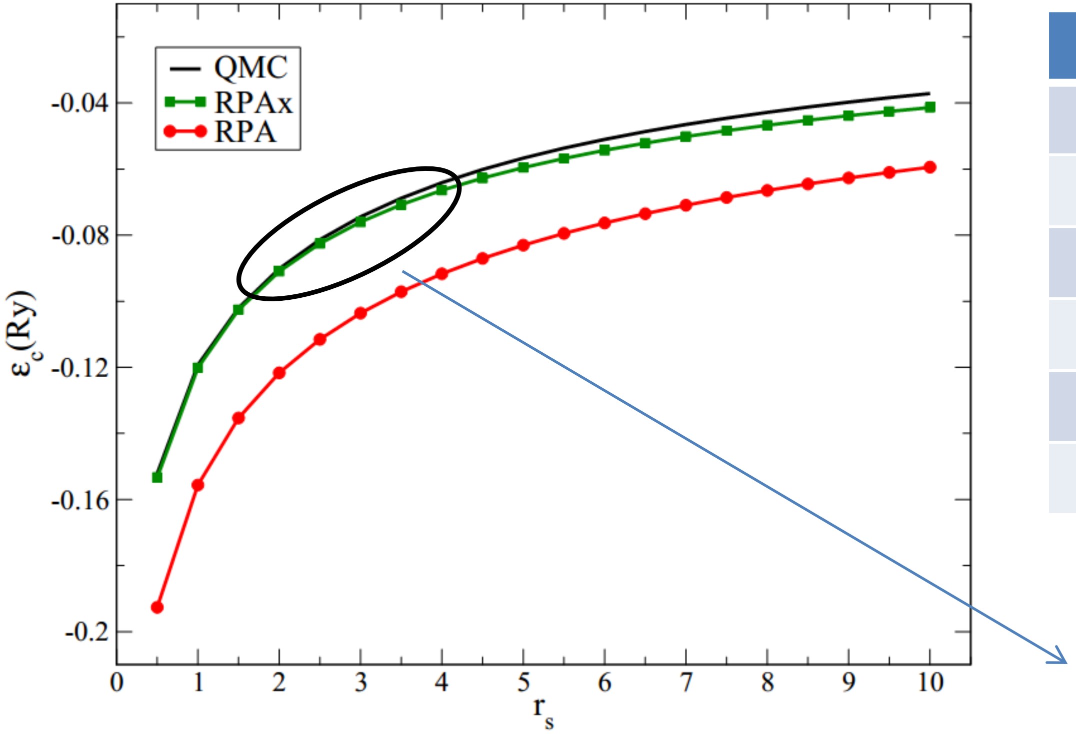
$$E_c^{\mathrm{RPAx}} = \frac{\hbar}{2\pi}\int_0^\infty du \; \mathrm{Tr}\left\{\frac{v_c}{v_c + f_x}\ln[I - (v_c + f_x)\chi_0(iu)] + v_c\chi_0(iu)\right\}$$

RPA and RPAx: Homogeneous electron gas

1. Testing system
2. Local Density Approximation for the Correlation Energy beyond RPA(x):

$$E_c = E_c^{(2)} + \Delta E_c$$

$$\Delta E_c \simeq \Delta E_c^{LDA} = \int d\mathbf{r}\; n(\mathbf{r}) \left\{ \varepsilon_c[n(\mathbf{r})] - \varepsilon_c^{(2)}[n(\mathbf{r})] \right\}$$



r_s	RPA	RPAx	QMC
0.5	-0.194	-0.154	-0.153
1.0	-0.157	-0.121	-0.119
3.0	-0.105	-0.077	-0.074
5.0	-0.084	-0.060	-0.056
8.0	-0.068	-0.047	-0.043
10.0	-0.061	-0.042	-0.037

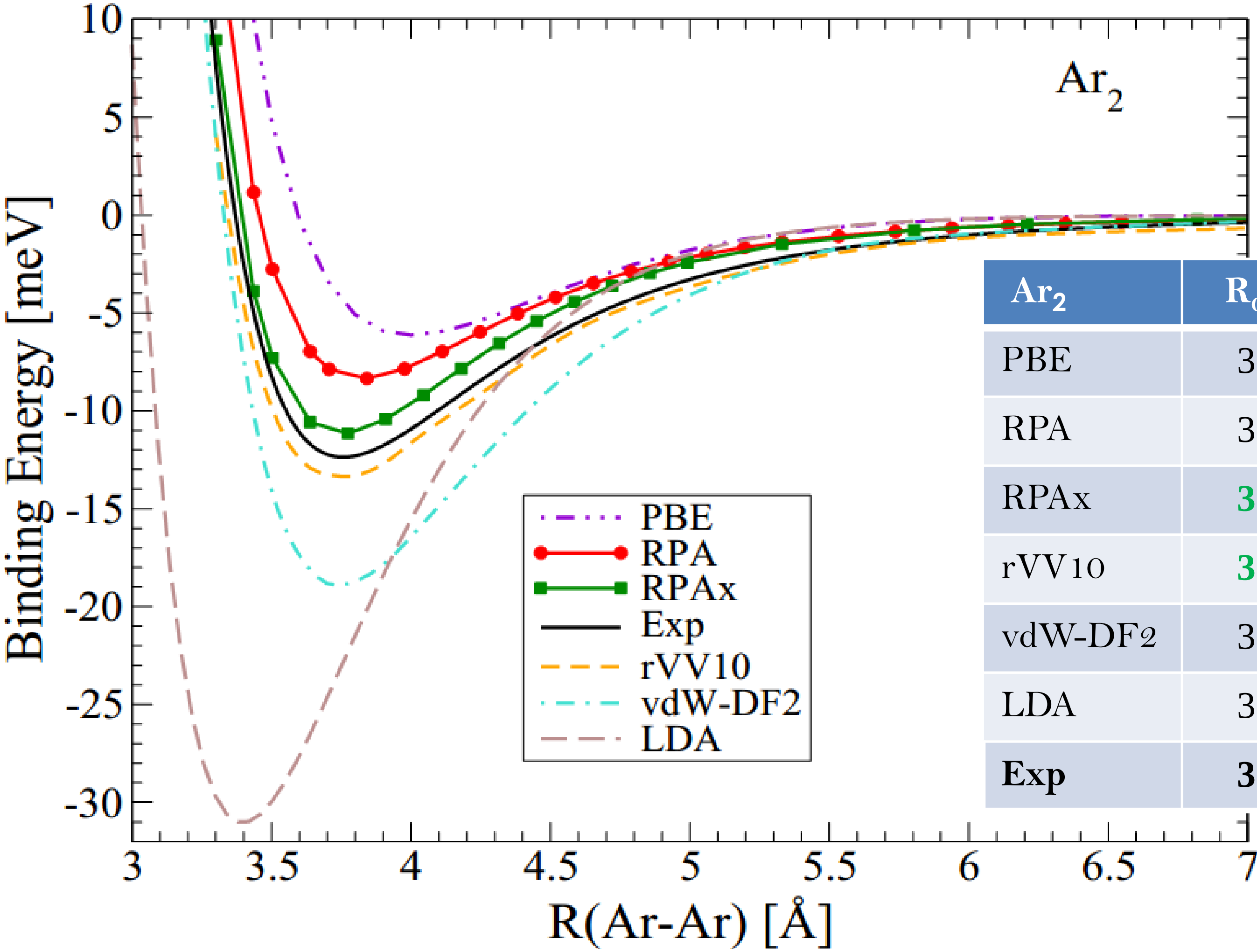
RPAx **much better** than RPA

$2 < r_s < 5$ typical metal densities

Colonna *et al*. PRB **90**, 125150 (2014)

RPA and RPAx: vdW dimers

Good description of van der Waals interactions without any empiricism/fitting parameter

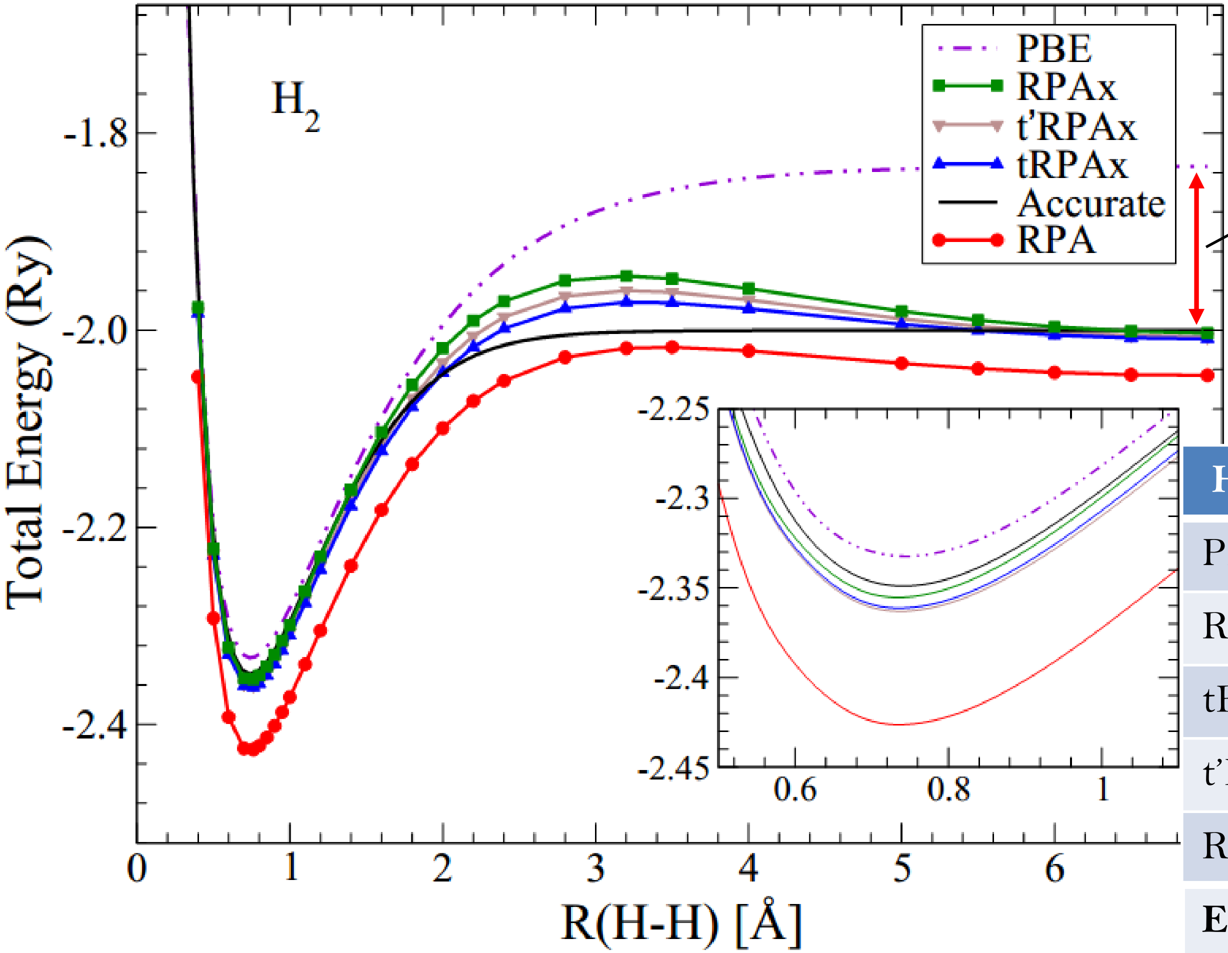


Ar_2	R_0(Å)	BE(meV)	ω(cm^{-1})
PBE	3.99	6.1	23.4
RPA	3.84	8.3	26.8
RPAx	3.75	11.1	30.8
rVV10	3.75	13.4	32.3
vdW-DF2	3.74	18.6	38.6
LDA	3.39	31.0	58.3
Exp	**3.76**	**12.4**	**31.2**

Colonna *et al.* PRB **93**, 195108 (2016)

RPA and RPAx: covalent bond

Improved **dissociation limit** without artificially breaking the spin symmetry



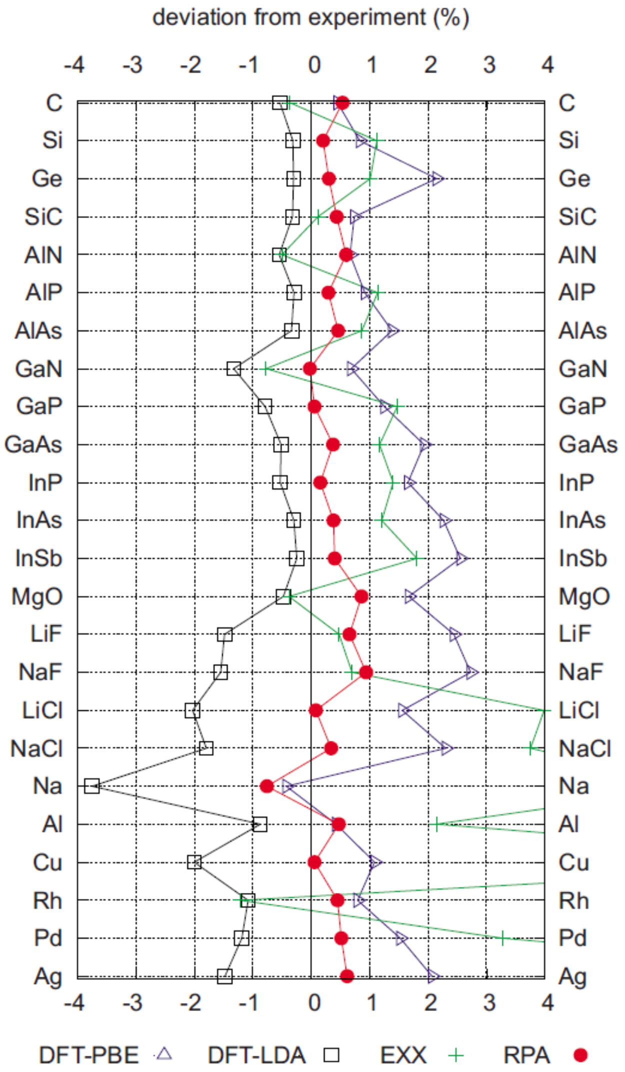
Static correlation error !

H_2	R_0(Å)	BE(eV)	ω(cm^{-1})
PBE	0.755	6.78	4219
RPAx	0.738	4.41	4530
tRPAx	0.742	4.48	4506
t'RPAx	0.738	4.45	4406
RPA	0.740	4.85	4520
Exp	**0.741**	**4.75**	**4529**

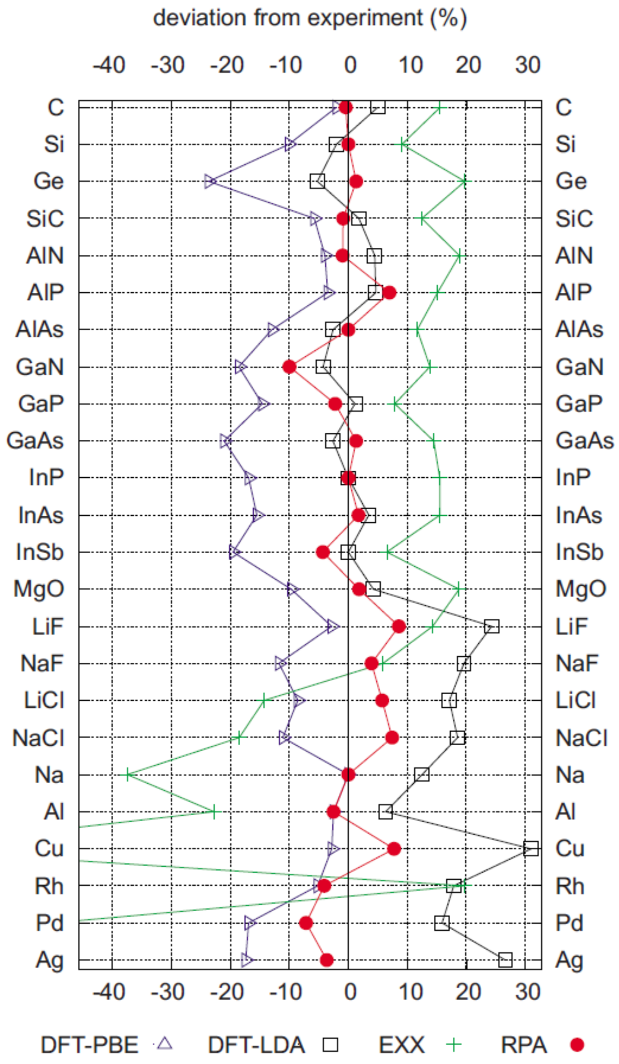
Colonna *et al*. PRB **90**, 125150 (2014)

RPA: solids

Lattice Constant



Bulk Moduli



	Insulator	Metal
LDA	0.8%	1.7%
PBE	1.6%	1.1%
EXX	1.2%	5.8%
RPA	**0.4%**	**0.5%**

	Insulator	Metal
LDA	7%	14%
PBE	12%	8%
EXX	14%	46%
RPA	**3%**	**5%**

Harl *et al.* PRB **81**, 115126 (2010)

RPA functionals: summary

- Consistently derived from the ACFD formula
- Functional of occupied and empty states
- Perfectly combine with Exact Exchange (HF) energy. No ambiguity in the choice of the exchange
- Address the static correlation problem
- Computationally way more expansive than LDA/GGA
- Almost always computed non-selfconsistently as a post LDA/GGA

Summary

- LDA: Simple and well defined. Good geometry, overbinding
- GGA: Improved energetics, good geometries
- Hybrid Functionals: Address the self-interaction error
- Van der Waals functionals: Good compromise of accuracy and computational cost
- RPA and beyond: Promising for further functional improvement, very expensive.

THE END

Thank you for the attention!

Exercise 1 (afternoon session)

1. Verify the importance of the Exx divergence treatment
   - For each one of the following cases, run few PBE0 scf calculations for the N_2 molecule increasing the dimension of the simulation box:
     a) Neglect the **q**+**G**=**0** term (**exxdiv_treatment='none'**)
     b) Use the Gygi-Baldereschi scheme without gamma extrapolation (**exxdiv_treatment='g-b', x_gamma_extrapolation=.FALSE.**)
     c) Use Gygi-Baldereschi scheme with gamma extrapolation (**exxdiv_treatment='g-b', x_gamma_extrapolation='.TRUE.**
   - Plot the Exchange energy as a function of the simulation box for all the analyzed cases a) b) c)

PW input and bash script

PW input

```
&SYSTEM
  ibrav = 1
  celldm(1) = …
  input_dft = “PBE0”
  exxdiv_treatment = “none”
  x_gamma_extrapolation = .FALSE.
/
```

cubic lattice
size of the supercell
Force the functional from input
which div treatment?
gamma extrapolation?

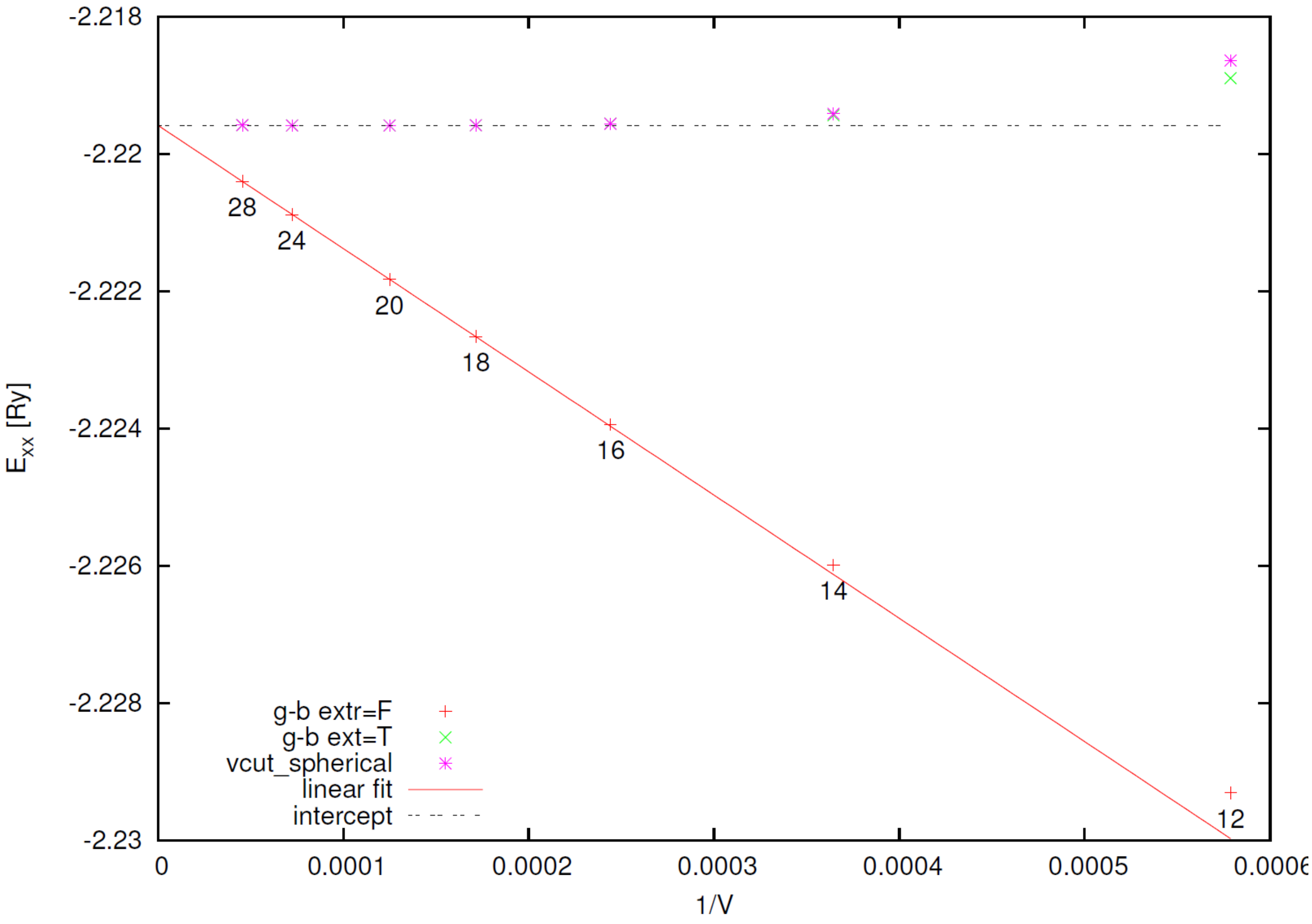
Change the celldm(1) parameter with a simple **bash script**

```
for alat in 12 14 16 18 20 24 28; do
cat > pbe0.in << EOF
…
&SYSTEM
 celldm(1) = $alat
…
EOF
pw.x < pbe0.in > pbe0_alat${alat}.out
done
```

Loop over alat
Write pbe0.in file until EOF
set the parameter
End of file
Execute pw
End of the loop

Convergence of the Exx energy

1. Verify the importance of the Exx divergence treatment



Exercise 2: Atomization energy

2. Calculate the atomization energy of the N_2 molecule

$$\Delta E = E^{\mathrm{mol}} - \sum_i E_i^{\mathrm{atom}}$$

- Choose the simulation box size according to the tests done in the exercise1
- Calculate ΔE using PBE, PBE0 (and HSE) funtional
- Compare with the experimetal value: 226 Kcal/mol

Exercise 3: graphite layer binding energy

3) Estimate the graphite out-of-plane lattice parameter c and the interlayer binding energy:

$$\Delta E = E(c_{\text{eq.}}) - E(c = \infty)$$

- Run few PBE scf calculations changing the c lattice parameter. The graphite has a hexagonal lattice (ibrav=4). The `celldm(3)` parameter define the c/a ratio. Change it according to the suggestion in the README.txt file.
- Plot the BE using the energy of the structure with the bigget value of c as a reference.
- Repeat the calulation using the DFT-D2 and vdw-df2 methods: `vdw_corr='DFT-D'` `input_dft='vdw-df2'`
- Compare the results with RPA and Exp equilibrium lattice constant and interlayer binding energy (in the files RPA.dat Exp.dat)

Exercise 3: graphite layer binding energy

3) Estimate the graphite out-of-plane lattice parameter c and the interlayer binding energy