

Density-functionals from linear response theory: Implementation in ABINIT and results for H₂ and Be₂

Martin Fuchs^{1,2} and Xavier Gonze¹

¹ *Unité PCPM, Université Catholique de Louvain, Louvain-la-Neuve, Belgium*

² *Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany*

Thanks to

Yann-Michel Niquet *PCPM / UCL*

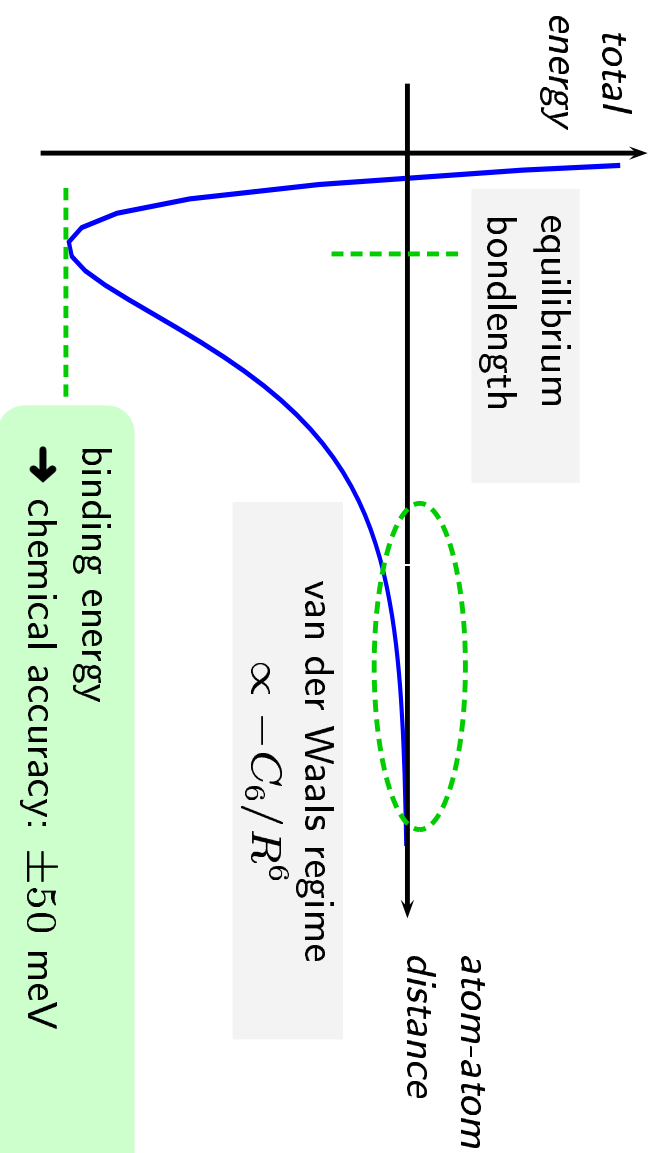
Kieron Burke *Dept. Chemistry & Chem. Biology / Rutgers Univ.*

Introduction

Task:

- Standard DFT within local-density (LDA) or generalized gradient approximations (GGA) computationally simple & often successful, but has well known shortcomings
- molecular binding energies not in general given within **chemical accuracy**
 - **activation energy barriers** in chemical reactions often underestimated
 - **van der Waals interactions** are described improperly

Schematic potential energy curve for a dimer



Typical error in binding energies	
LSDA	-1.5 eV
PBE GGA(-)	0.4 eV
B3LYP (-)	0.1 eV

This work

Study of (fully nonlocal, orbital dependent) XC functionals based on the **adiabatic-connection fluctuation-dissipation theorem**.

Theory: Adiabatic-Connection Fluctuation-Dissipation Theorem

- Adiabatic connection: KS system $\lambda e^2 = 0 \longrightarrow$ physical system $\lambda e^2 = 1$

$$E_{xc}[n] = \int_0^1 \langle \Psi_\lambda[n] | \hat{W} | \Psi_\lambda[n] \rangle - U[n] d\lambda \quad W = 1/r \text{ is e-e Coulomb interaction}$$

- Fluctuation-dissipation theorem:

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

... using dynamical density response

real & smooth in u fct.

- From noninteracting Kohn-Sham to interacting response by TD-DFT

$$\chi_0(iu, \mathbf{r}, \mathbf{r}') = \sum_{i,j} \frac{f_j - f_i}{i\hbar u - (\epsilon_j - \epsilon_i)} \frac{\varphi_i^*(\mathbf{r}) \varphi_j(\mathbf{r}) \varphi_j^*(\mathbf{r}') \varphi_i(\mathbf{r}')}{\epsilon_i[n]} \dots \text{KS eigenvalues}$$

$\varphi_i([n], \mathbf{r}) \dots$ KS orbitals

$$\chi_\lambda(iu) = \chi_0(iu) + \chi_0(iu) \cdot K_\lambda^{hxc}(iu) \cdot \chi_\lambda(iu)$$

"Dyson-like equation"
6d(space) \otimes 2d(spin)

... using Coulomb and XC kernel

In principle ACFDT formula gives exact XC functional
In practice starting point for fully nonlocal approximations

DC Langreth, JP Perdew, Sol State Commun 17, 1425 (1975); O Gunnarsson, BI Lundqvist, PRB 13, 4275 (1976)

ACFDT XC functionals in this work - approximations

✚ density & XC potential (Kohn-Sham system) in LDA, GGA or xOEP

✚ XC kernel

- RPA Coulomb kernel only: $K_{\lambda}^{hxc}(iu) = \frac{\lambda e^2}{r}$. . . no XCI
- RPA+ short-range correlations (expected too strong in RPA) corrected by a local-density approximation [1]

$$E^{XC,RPA+}[n] = E^{XC,RPA}[n] + E^{C,LDA}[n] - E^{C,RPA-LDA}[n]$$

. . . exact for homogeneous electron gas!

- PGG exchange kernel $K_{\lambda}^{X}(\mathbf{r}, \mathbf{r}', iu)$ in approximation by Petersilka et al. [2]
. . . cancels RPA's self-correlation in 1e systems!

✚ pseudopotential plane-wave method <http://www.abinit.org>

[1] S Kurth, JP Perdew, *Phys Rev B* 59, 10461 (1999); Z Yan, JP Perdew, S Kurth, *Phys Rev B* 61, 16430 (2000)

[2] M Petersilka, UJ Gossmann, EKV Gross, *Phys Rev Lett* 76, 1212 (1996).

This work: ACDFEFT XC for molecules with ABINIT

Implementation in pseudopotential plane-wave supercell framework

- Need frequency dependent density response, KS & interacting, $z = iu!$
Work in reciprocal space **Γ -point & spin-averaged**

$$\chi_{0GG'}(q = 0; iu) = \sum_i^{occ} \sum_j^{unocc} \Phi_{ij}^* d_{ij}(iu) \Phi_{ijG'}$$

cpu time	memory
$N_{occ} N_{unocc} N_{pw}^2$	N_{pw}^2

$$\sum_{G''G'''} (1 - K_{\lambda G G''}^{hxc}) \chi_{\lambda G''G'''} = \chi_{0GG'}$$

N_{pw}^3	$2 N_{pw}^2$
------------	--------------

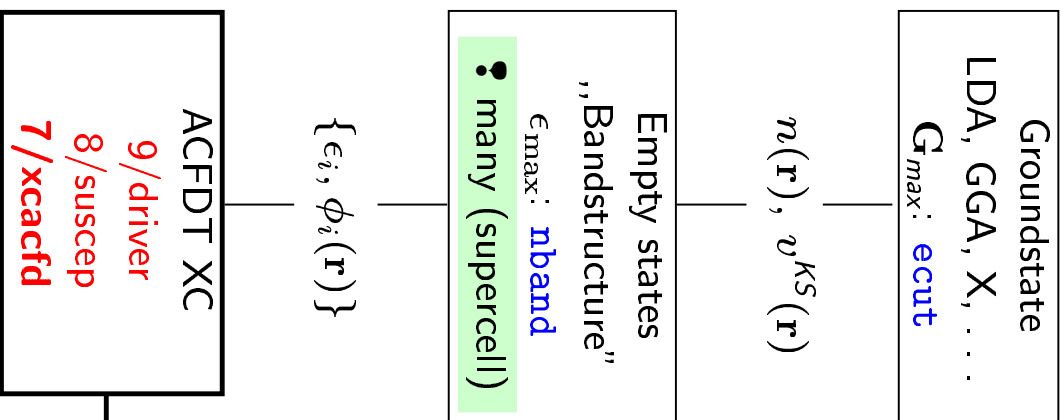
RPA, PGG, TDLDA kernels (static)

- Convergence control
 - Number of unoccupied states: $\chi_0 = \chi_0 \Big|_{\epsilon \leq \epsilon_{max}} + \chi_0 \Big|_{\epsilon > \epsilon_{max}}$ \leftarrow closure technique
 - $\int du$: Gauss-rational quadrature 10 . . . 50pt. \leftarrow HOMO-LUMO gap, ϵ_{min}^{max}
 - $\int d\lambda$: Gauss-Legendre 4 . . . 12pt. \leftarrow dynamic vs. static correlation
 - plane-wave basis set \leftarrow cutoff $\approx 1/2$ of groundstate calc.
supercell \leftarrow XC seems less sensitive than X and C
- Pseudopotentials from LDA, GGA, xOEP

Computation of XC energy in RPA, RPA+, PGG for He, H₂, Be₂.

Resources for Be₂: 30 . . . 160 cpuh on 4Gbyte/ 4 proc Alpha EV67/667 MHz (Compaq ES40)

ABINIT implementation - present status



xcacfld

$$E_X = -\frac{1}{2} \text{tr} \left\{ \frac{1}{r} \gamma^* \gamma \right\}_G \quad \gamma = \text{KS density matrix}$$

8/suscep_dyn $G_{max}: \text{diecut}$

Frequency loop for correlation energy

$$E_C = \sum_p w_p \epsilon_C(iu_p) \quad C = \text{RPA, PGG, TDLLDA: ikhxc}$$

7/getfreqsus $p:\text{nfreqsus}, u_{min}:\text{freqsus}[lo, hi]$

$$\chi_{GG'}^{KS}(iu_p) \quad G:\text{diecut cutoff}, \epsilon > \epsilon_{max}:\text{dielam, diegap}$$

8/suscep_dyn $\chi^{KS} = \chi_{<}^{KS} + \chi_{>}^{KS}$, symmetrization

8/susk[mm]_dyn $\chi_{<}^{KS} = \sum_{ij} \Phi_{ij}^* d_{ij} \Phi_{ijG'}$

Coupling strength integration

control: **useri**

$$\epsilon_C(iu_p) = -\frac{1}{2\pi} \sum_{\lambda q} w_q \text{tr} \left\{ \frac{1}{r} [\chi_{\lambda q} - \chi^{KS}] \right\}_G \Big|_{u_p}$$

7/dielcell[7,8,9] kernels RPA[7], PGG[8], TDLLDA[9]

Interacting response **recursively**

$$(1 - [K_{\lambda q} - K_{\lambda q-1}][\chi_{\lambda q-1}]) \chi_{\lambda q} = \chi_{\lambda q-1}$$

7/dyson_ls

linear system solver

or: **dyson_gi**

2nd order, e^4 correlation

$$\frac{d}{d\lambda} \chi_{\lambda} = \chi_{\lambda} \left(\frac{d}{d\lambda} K_{\lambda} \right) \chi_{\lambda}$$

dyson_sc

$$\text{SCF approach } \chi_{\lambda, G'} = \frac{\Delta n(G)}{\Delta v(G')} \Big|_{\lambda}$$

• ram N^2
cpu N^4
serial

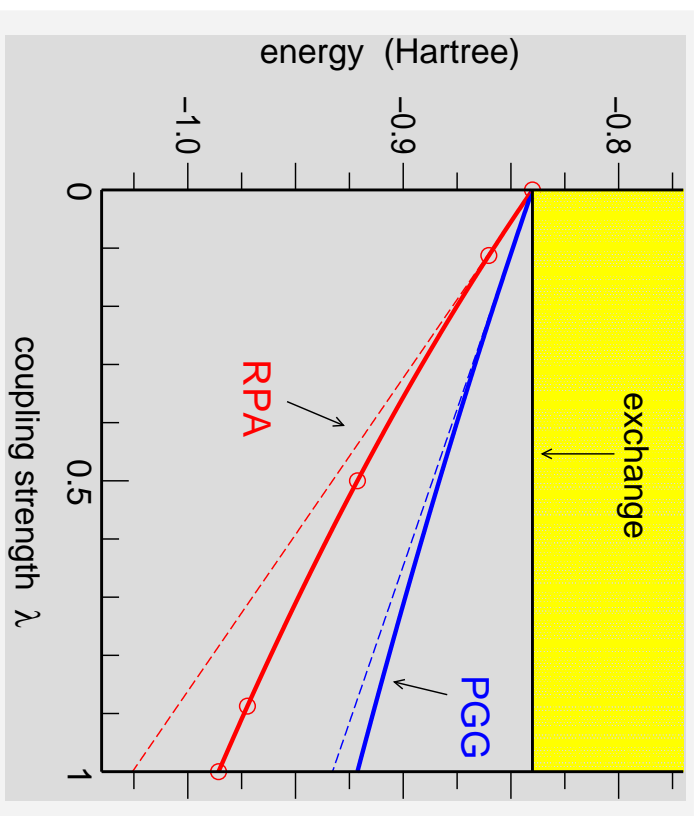
blas2

• ram $2N^2$
cpu N^3

• blas3
parallel
OpenMP

Results: He atom . . . a first illustration

Adiabatic connection $U_{\lambda}^{XC}[n]$



Correlation energy (mHartree)

potential	pseudo	$-2/r$
RPA	-78	-93
RPA+	-43	-96*
PBG	-44	-47
exact	-43	-48*
LDA		-112
PBE GGA		-42

post xOEP calculation

- ❗ Absolute XC energy too negative in RPA . . .
- here: self-correlation error, in general: spin $\uparrow\uparrow$ electrons get too close
- ♥ . . . but accurate with local correction (RPA+) or exchange kernel (PBG)

Results: “simple” H₂ & “tricky” Be₂ bond

Binding energies & bond lengths

H₂

	E_b (eV)	R_0 (bohr)
LSDA	-4.92	1.44
PBE GGA	-4.54	1.41
xOEP	-3.64	1.38
RPA	-4.72	1.39
RPA+	-4.75	1.40
PGG	-4.85	1.40
expt.	-4.75	1.40

- post xOEP calculation

Be₂

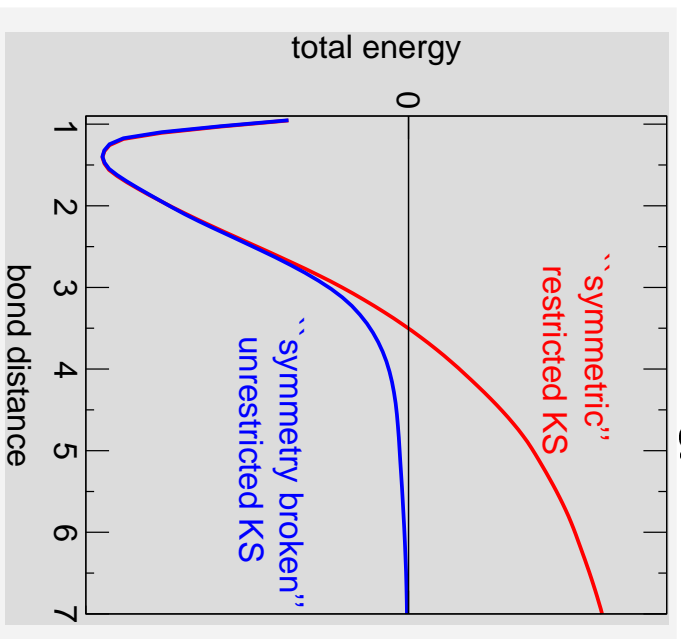
	E_b (eV)	R_0 (bohr)
LDA	-0.56	4.52
PBE GGA	-0.43	4.57
xOEP	+0.45 (+0.41)*	-
RPA	-0.08 (-0.13)*	4.55
RPA+	-0.06 (-0.10)*	4.59
PGG	-0.07 (-0.12)*	4.61
CI	-0.11	4.63
expt.	-0.10 . . . -0.13	4.63

- post LDA & exchange pseudopotential
* post LDA & LDA pseudopotential

- ♥ RPA and RPA+ both accurate, errors in total energy differences cancel
- ❗ PGG slightly overbinds H₂ → correlation kernel needed?

Molecular dissociation & the symmetry dilemma

H₂ Potential Energy Curve



- ✓ KS groundstate is single determinant

$$\text{MO's: } \sigma_g(\mathbf{r}) \longrightarrow \frac{1}{\sqrt{2}} \{s_a(\mathbf{r}) + s_b(\mathbf{r})\} = \sqrt{\frac{n(\mathbf{r})}{2}}$$

- ✓ Heitler-London picture for dissociation

$$\Psi_\infty \longrightarrow \{H^\bullet + H^\bullet\} = \frac{1}{2} \{s_a(\mathbf{r}_1)s_b(\mathbf{r}_2) + s_b(\mathbf{r}_1)s_a(\mathbf{r}_2)\}$$

- ✗ spin restricted HF, LDA, GGA:

dissociation incorrect!

$$\Psi_\infty^{KS} \longrightarrow H^\bullet + \frac{1}{2} (H^- + H^+)$$

- ... not enough left-right (static) correlation
- ... local correlation hole cannot „localize“ delocalized exchange hole

- ✗ Use spin unrestricted UHF, LSDA, GGA:

inversion **symmetry broken**,

$$n_\uparrow(\mathbf{r}) \neq n_\downarrow(\mathbf{r}), \langle S^2 \rangle > 0$$

Proper dissociation **without** symmetry breaking . . . demonstrated within DFT

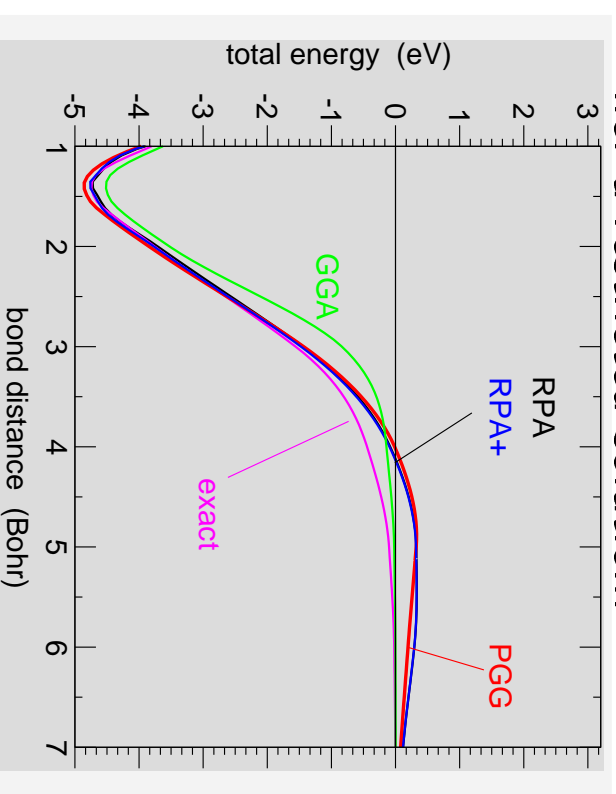
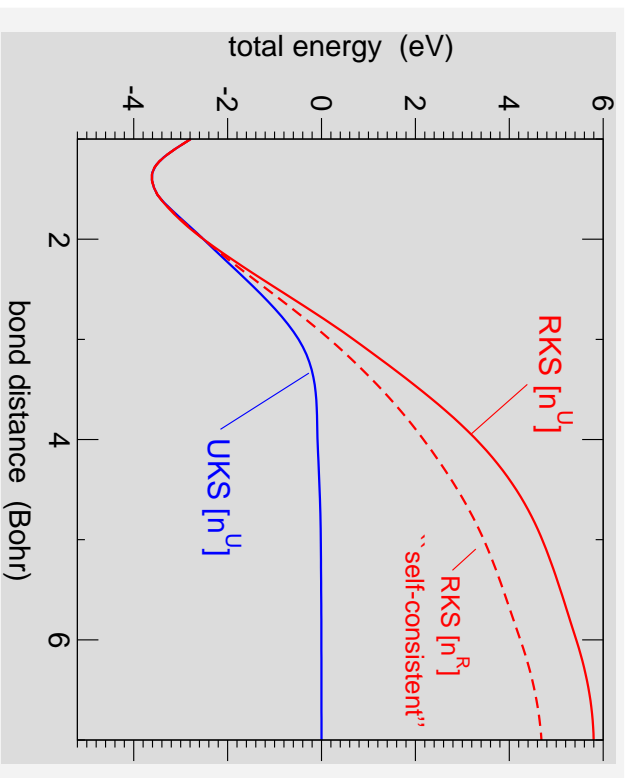
H₂ potential energy curve from ACFD approach

Exchange-only total energy . . .

. . . + correlation energy in RPA

Use total n^U of unrestricted scheme

i.e. a restricted solution!



GGA spin-polarized!

- ♥ RPA also gets the dissociation limit right . . . (errors < 0.5 eV)
- ♥ RPA+ and PGG (exchange kernel) perform similarly to RPA
- ! Spurious repulsion at $R \simeq 5$ bohr

M Fuchs, K Burke, Y-M Niquet, X Gonze, submitted to PRL (2002):

Exact CI data from W Kolos, L Wolniewicz, *J Chem Phys* 43, 2429 (1965)

Perspective

ACFDT XC functionals within RPA & PGG . . .

- ✓ can now be computed for **real systems**, using ABINIT
- ✓ RPA, RPA+, PGG nearly **chemically accurate** for binding energies, here: H₂ dimer and the weakly bound Be₂ dimer
- ✓ can yield accurate **potential energy** curve
 - . . . near equilibrium & in dissociation limit
 - . . . **van der Waals interactions** included
 - . . . overcome **energy vs. symmetry dilemma** of LDA, GGA & Co.
- ❖ are not perfect: false repulsion at intermediate separations
 - . . . seen in Be₂ and N₂ too
- ❖ can be refined: further work / implementation needed regarding
 - . . . **correlation kernel** requires attention, likely beyond TDLLDA
 - . . . need **accurate KS density / potential** to begin with
 - self-consistency (v_{xc}^{RPA} . . .)
 - . . . spin-polarized case, $\chi_{GG'}(\mathbf{q} \neq 0)$ & $\sum_{\mathbf{q}}^{IBZ}$
 - . . . computational efficiency (serial ↔ parallel balance, memory)

Future!