

Introduction

The correlation energy of an electronic system can be expressed in terms the density response function through the adiabatic connection and fluctuation-dissipation theorem:

$$E_c[n] = - \int_0^1 d\lambda \int_0^\infty \frac{d\omega}{2\pi} \text{Tr}[v\chi^\lambda(i\omega) - v\chi^{KS}(i\omega)]$$

The λ -interacting response function can be approximated from time-dependent density functional theory through the Dyson equation:

$$\chi^\lambda = \chi^{KS} + \chi^{KS} f_{Hxc}^\lambda \chi^\lambda$$

with

$$f_{Hxc}^\lambda = \lambda v + f_{xc}^\lambda$$

Neglecting xc kernel leads to the well known Random Phase Approximation (RPA), which has proven very successful in describing dispersive interactions. However, RPA systematically underestimate atomization energies for molecules and solids [1,2] and severely underestimate total correlation energies (~ 0.4 eV per electron).

A simple approach to improve RPA is to include the Adiabatic Local Density Approximation (ALDA) for the xc kernel:

$$f_{xc}^{ALDA}[n](\mathbf{r}, \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}') f_{xc}^{ALDA}[n]$$

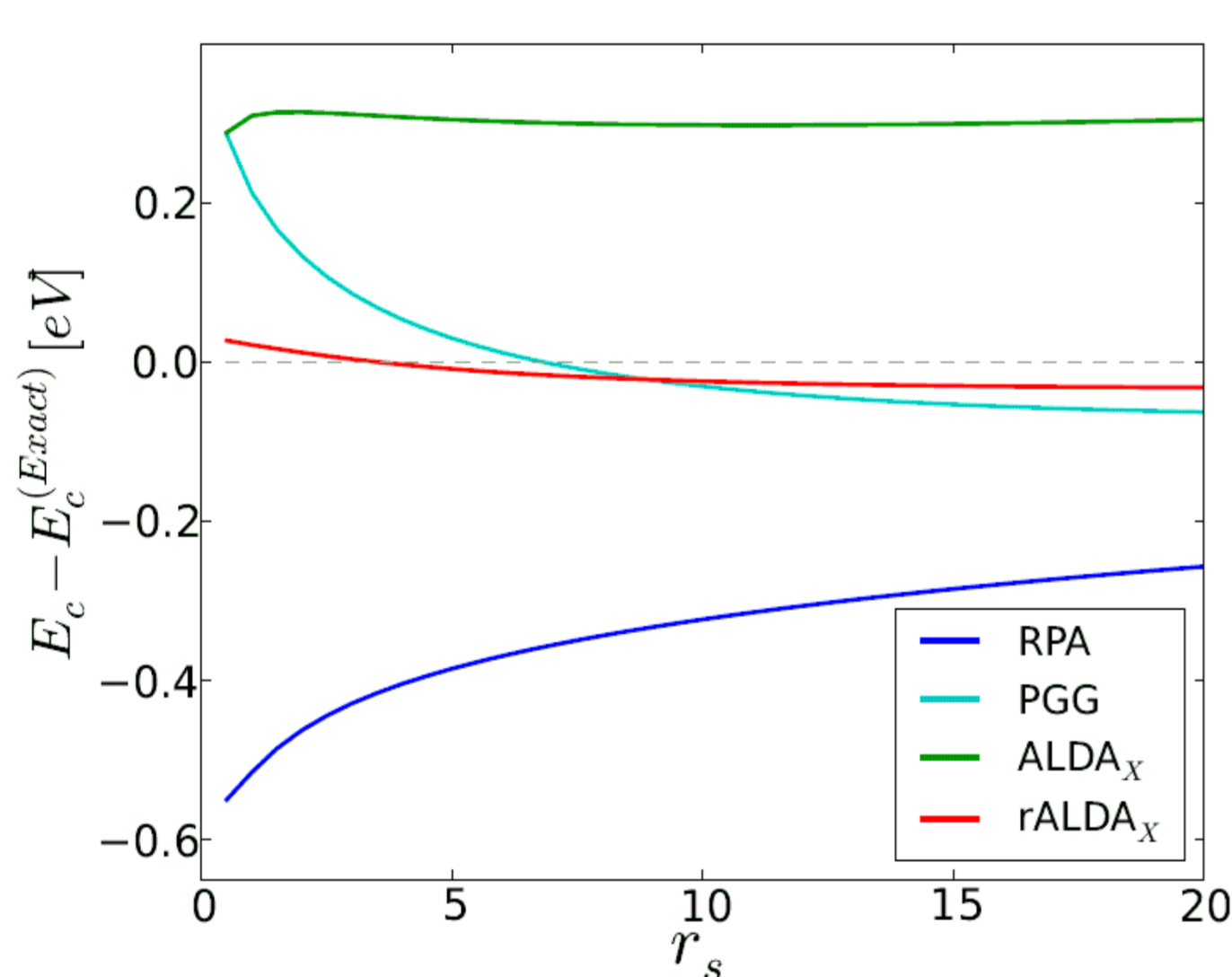
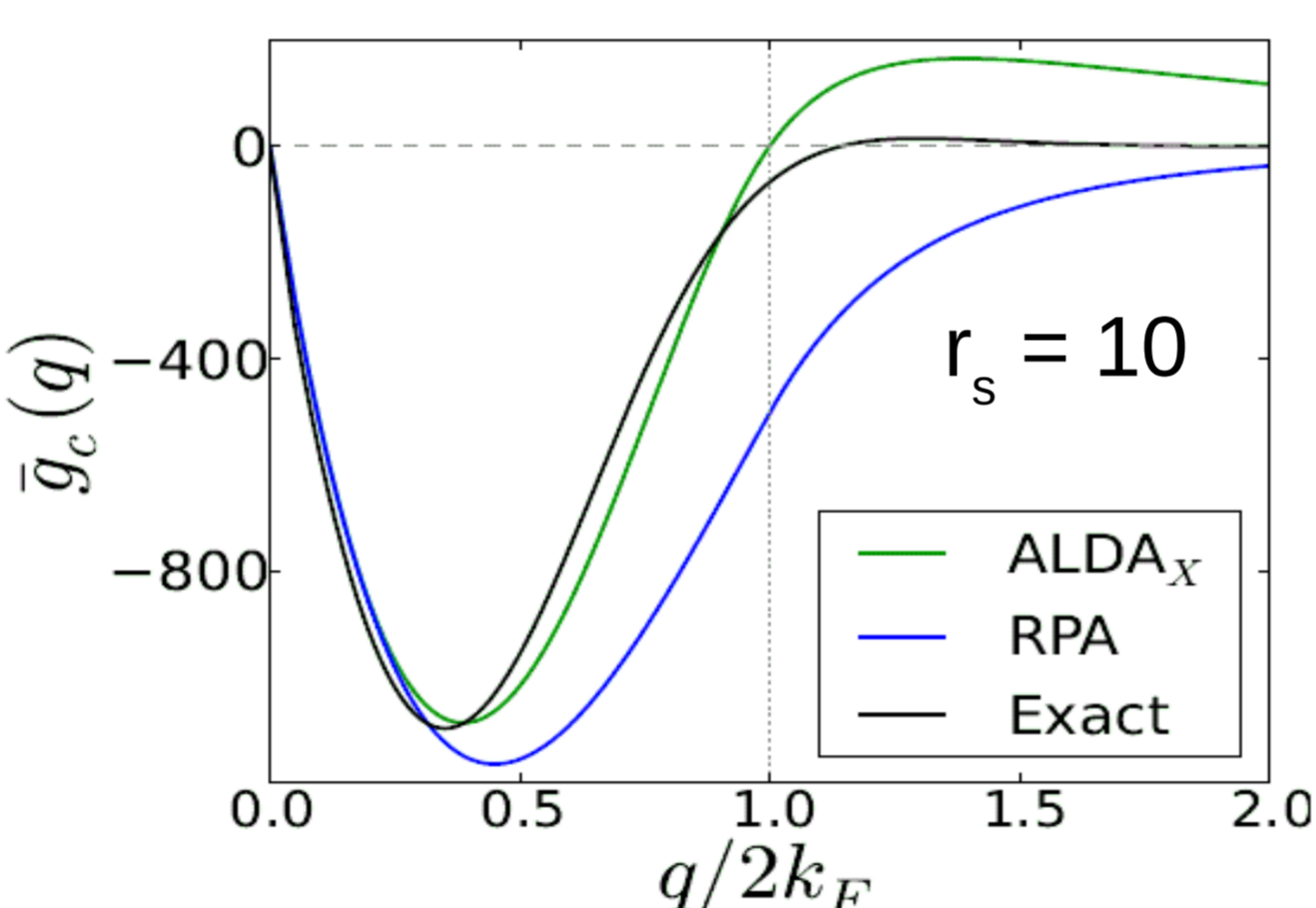
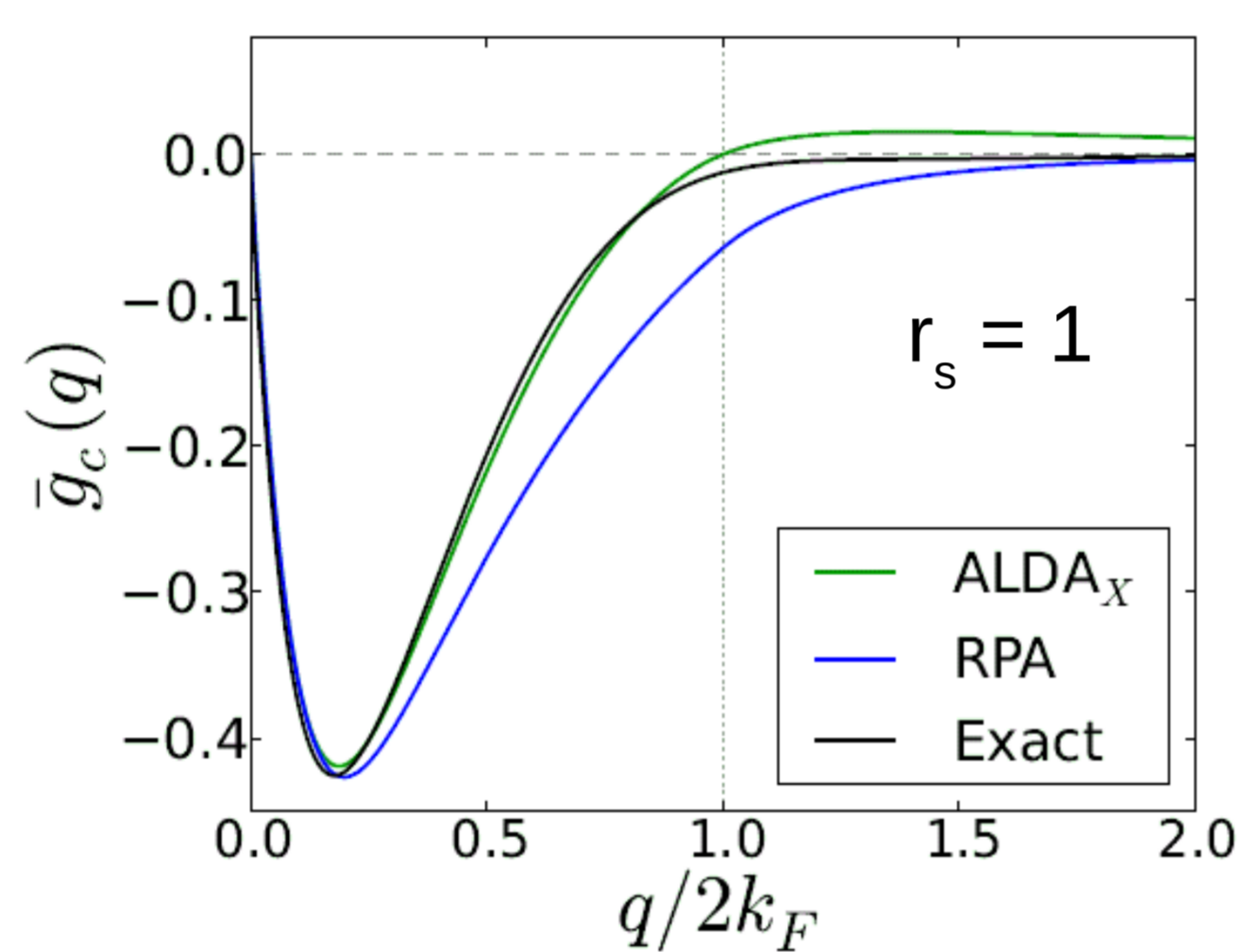
However, this kernel does not improve correlation energies and suffers from severe convergence problems [3].

The Homogeneous Electron Gas

The problem with ALDA can be analyzed in the Homogeneous electron Gas (HEG) [4]. The correlation energy is essentially obtained by integrating the coupling constant averaged correlation hole in q -space.

The correlation hole is well described by ALDA at low q , but has a slowly decaying positive tail, which renders the pair-distribution function divergent at the origin.

The correlation hole obtained from RPA is seen to result in much too small correlation energies.



Introducing a cutoff at $q=2k_F$ results in much better correlation energies for a wide range of densities.

The cutoff conserves the Norm of the correlation hole in real space which is given by the value at $q=0$.

Renormalized Kernel

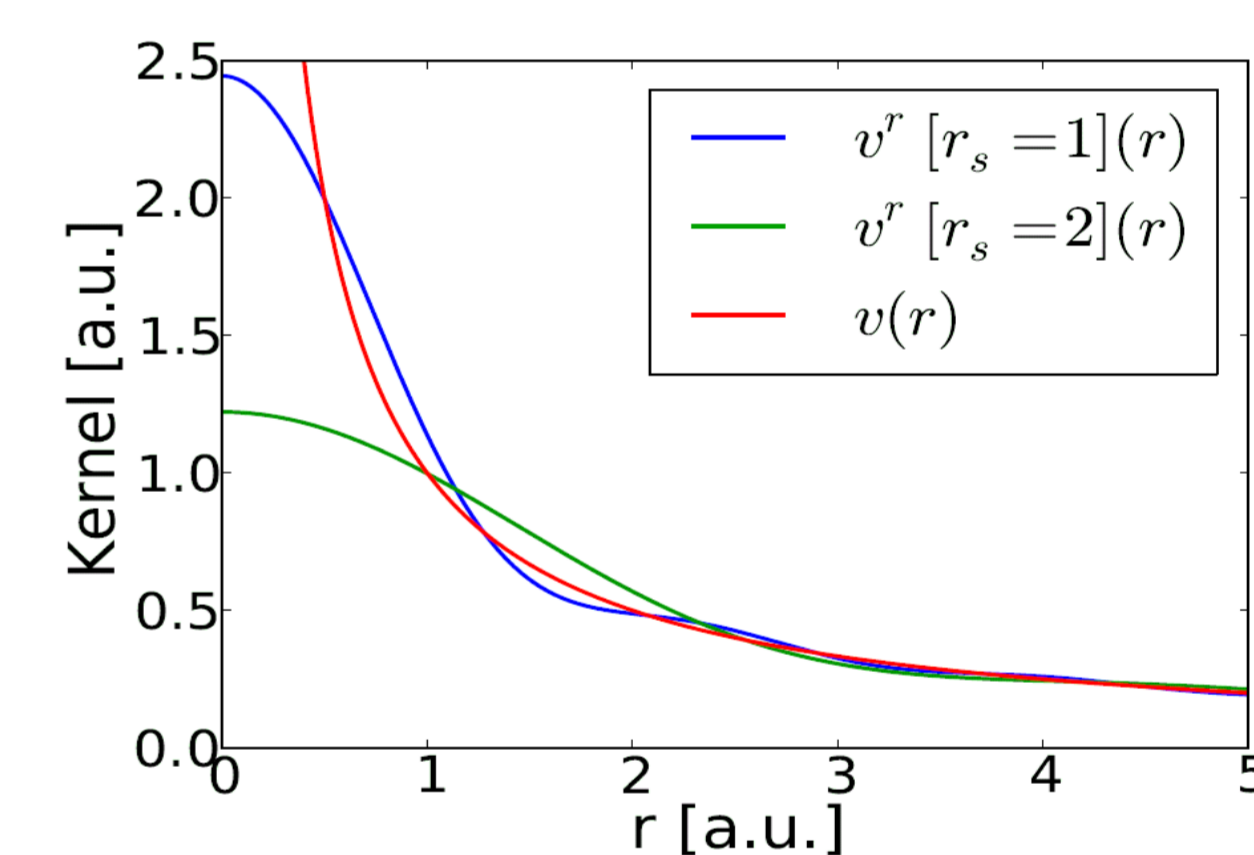
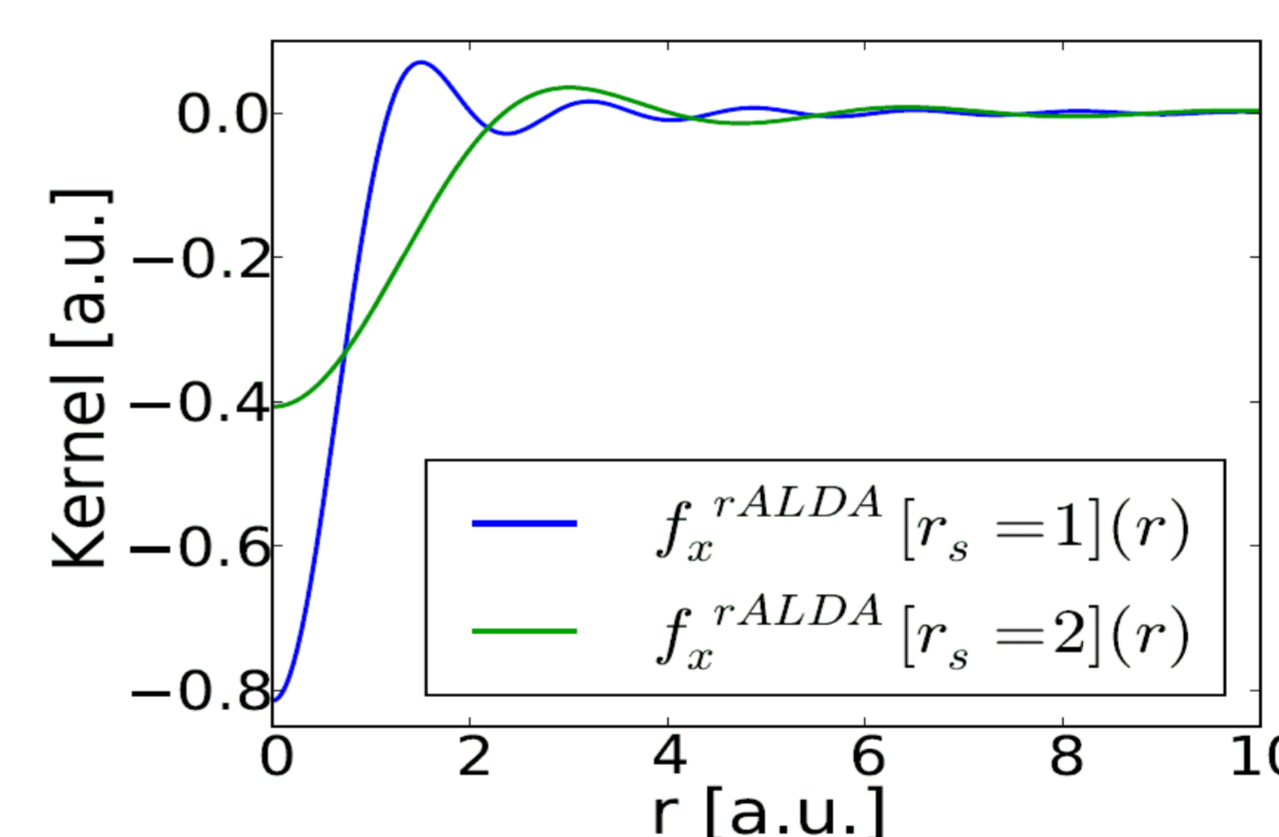
The cutoff is equivalent to applying the xc kernel

$$f_{Hxc}^{rALDA}[n](q) = \theta(2k_F - q) f_{Hxc}^{ALDA}[n]$$

Fourier transforming this gives

$$f_{Hxc}^{rALDA}[n](r) = f_x^{rALDA}[n](r) + v^r[n](r)$$

$$f_x^{rALDA}[n](r) = \frac{f_x^{ALDA}[n]}{2\pi^2 r^3} [\sin(2k_F r) - 2k_F r \cos(2k_F r)], \quad v^r[n](r) = \frac{1}{r} \frac{2}{\pi} \int_0^{2k_F r} \frac{\sin x}{x} dx$$



For large values of r , the kernel approaches the Hartree kernel and the method is expected to reproduce the accurate description of dispersive interactions of RPA.

It is straightforward to generalize this to inhomogeneous systems by taking

$$r \rightarrow |\mathbf{r} - \mathbf{r}'| \quad k_F \rightarrow (3\pi^2 \bar{n}(\mathbf{r}, \mathbf{r}'))^{1/3} \quad \bar{n}(\mathbf{r}, \mathbf{r}') = (n(\mathbf{r}) + n(\mathbf{r}'))/2$$

Atoms and Molecules

For simple atoms and molecules, the correlation energy from rALDA are much better described than within RPA or ALDA. The rALDA kernel also seems to perform better for molecular atomization energies [5].

	LDA	PBE	RPA	ALDA _x	rALDA	Exact
H	-14	-4	-13	6	-2	0
H ₂	-59	-27	-51	-16	-28	-26
He	-70	-26	-41	-19	-27	-26

Total correlation energies

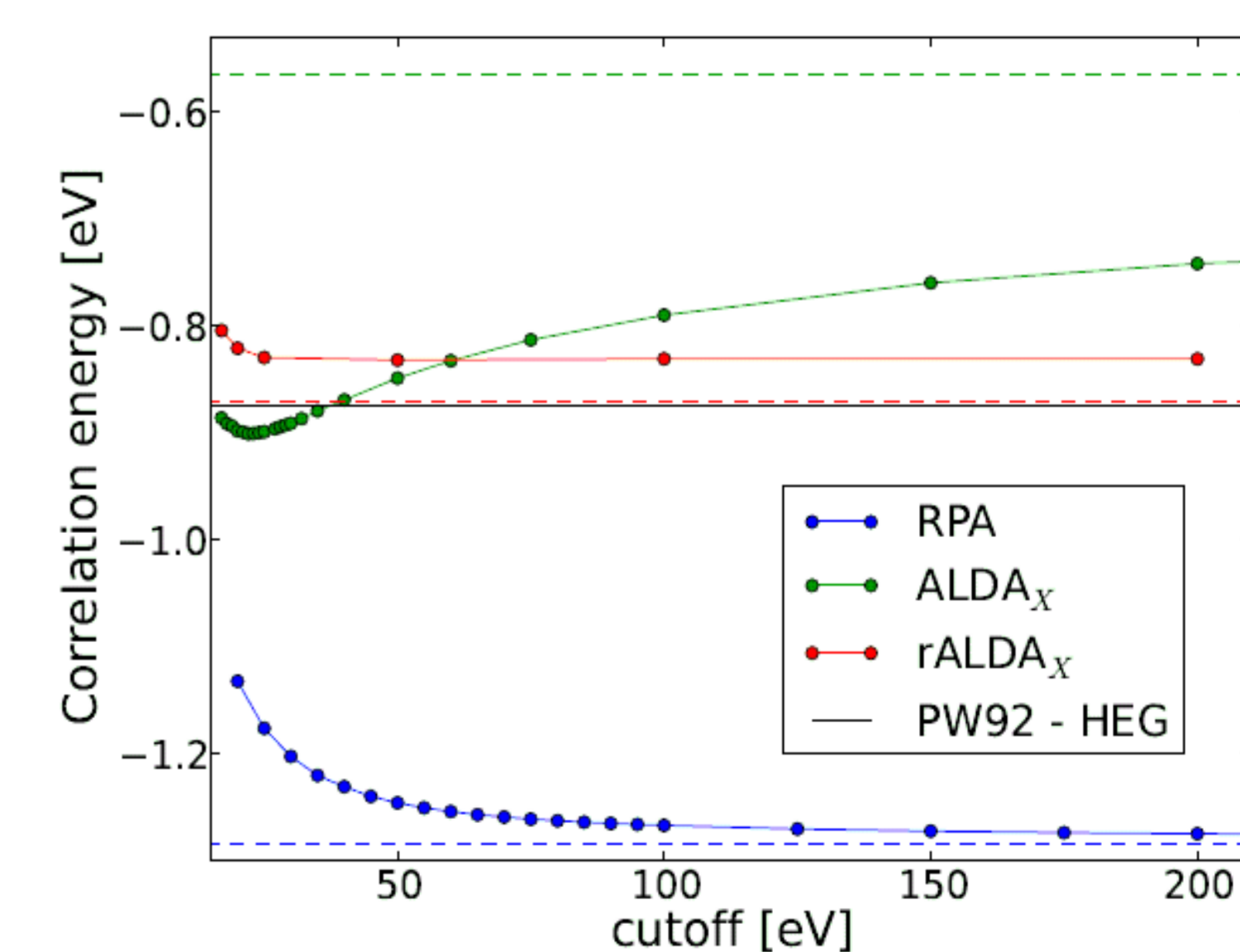
	LDA	PBE	RPA@LDA	RPA@PBE	ALDA	rALDA	Exp.
H ₂	-113	-105	-109	-109 (109)	-110	-107	-109
N ₂	-268	-244	-225	-224 (223)	-229	-226	-228
O ₂	-174	-144	-103	-112 (113)	-155	-118	-120
CO	-299	-269	-234	-242 (244)	-287	-253	-259
F ₂	-78	-53	-13	-30 (30)	-74	-39	-38
HF	-161	-142	-122	-130 (133)	-157	-136	-141
H ₂ O	-266	-234	-218	-222 (223)	-249	-225	-233
MAE	33	10.1	14.9	8.4	19	3.7	

Atomization energies

Bulk Sodium

As a first test for *ab initio* system we have applied the method to bulk Na. We compare with results for the HEG with the average valence density of Na.

The result from the renormalized kernel is in good agreement with the expected value for the HEG [5].



References:

- [1] F. Furche, Phys. Rev. B **64** 195120 (2001)
- [2] J. Harl et al., Phys. Rev. B **81** 115126 (2010)
- [3] F. Furche and T. V. Voorhis, J. Chem. Phys. B **122** 164106 (2005)
- [4] M. Lein et al., Phys. Rev. B **61** 13431 (2000)
- [5] T. Olsen and K. S. Thygesen, *Submitted*