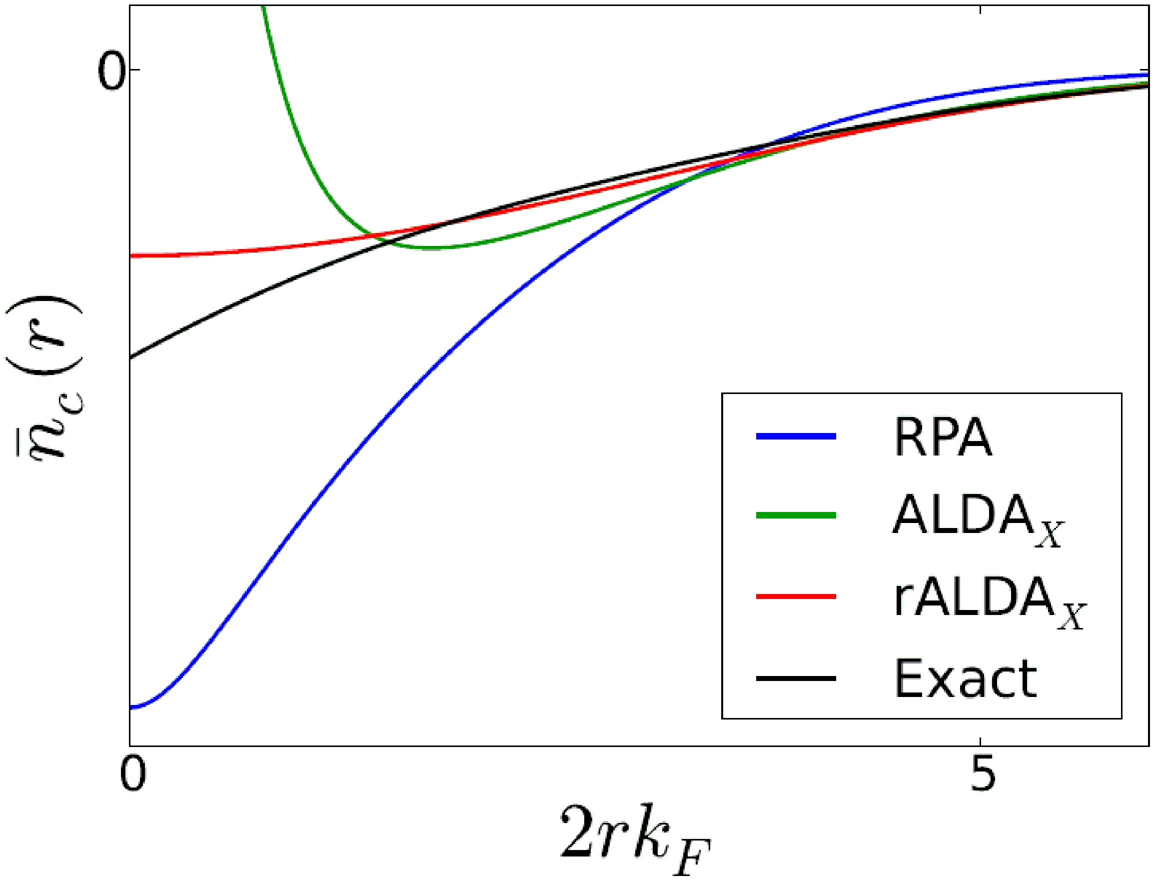
Beyond the Random Phase Approximation:

Approaching chemical accuracy with renormalized adiabatic local density approximations

Thomas Olsen and Kristian S. Thygesen



Outline

- Correlation energies from the adiabatic connection fluctuation-dissipation theorem
- Success and failures of RPA
- Extending RPA with an exchange-correlation kernel
  - The failure of local kernels
  - Introducing non-locality in adiabatic kernels
- Results with a renormalized adiabatic kernel

Correlation energy from ACDFT

The exact correlation energy in DFT can be written

$$E_c = \frac{-1}{2\pi}\int_0^1 d\lambda \int d\mathbf{r}\, d\mathbf{r}'\, \frac{e^2}{|\mathbf{r}-\mathbf{r}'|}\int_0^\infty d\omega \left[\chi^\lambda(\mathbf{r},\mathbf{r}';i\omega) - \chi^0(\mathbf{r},\mathbf{r}';i\omega)\right]$$

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The interacting response function can be obtained from TDDFT with a suitable approximation for the xc kernel:

$$\chi^\lambda(\omega) = \frac{\chi^0(\omega)}{1-[\lambda v + f_{xc}^\lambda(\omega)]\chi^0(\omega)}$$

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If f_{xc} is linear in λ, the coupling constant integration can be carried out:

$$E_c = \int_0^\infty \frac{d\omega}{2\pi} Tr\left[v(v+f_x)^{-1}\ln[1-\chi^0(i\omega)(v+f_x)] + v\chi^0(i\omega)\right]$$

RPA Correlation energy

Neglecting the exchange-correlation kernel gives the Random Phase Approximation (RPA)

$$E_c = \int_0^\infty \frac{d\omega}{2\pi} Tr\left[\ln[1-\chi^0(i\omega)v]+v\chi^0(i\omega)\right]$$

The expression is implemented in GPAW using a plane wave representation for the response function

Very easy to use...

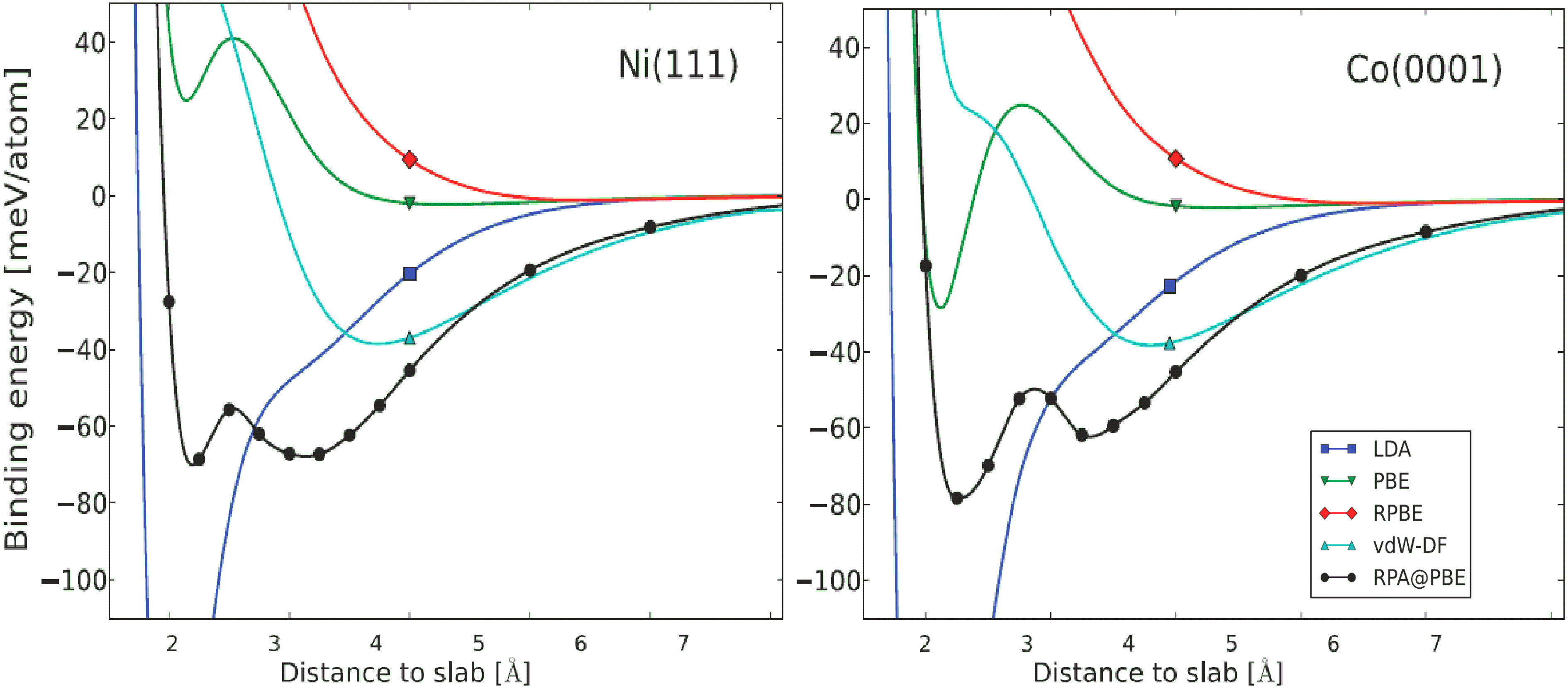
```
from gpaw.xc.rpa_correlation_energy import RPACorrelation
rpa = RPACorrelation(txt='rpa.txt')
E_c = rpa.get_rpa_correlation_energy(ecut=300)
```

… but significantly more time-consuming than standard KS calculations

RPA Correlation energy

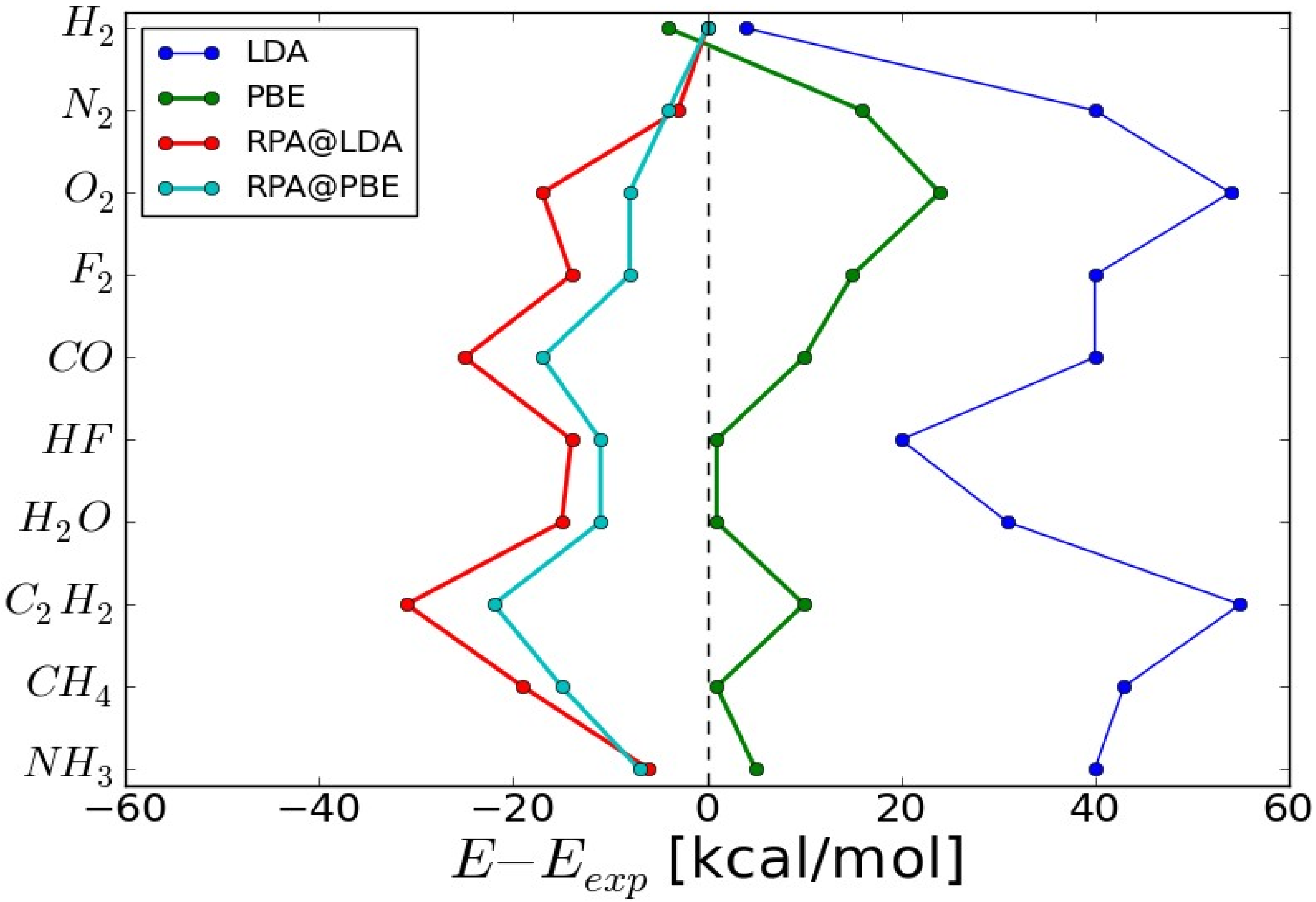
RPA gives an accurate description of van der Waals interactions

Graphene on metal surfaces



[T. Olsen and K. S. Thygesen, PRB **87** 075111 (2013)]

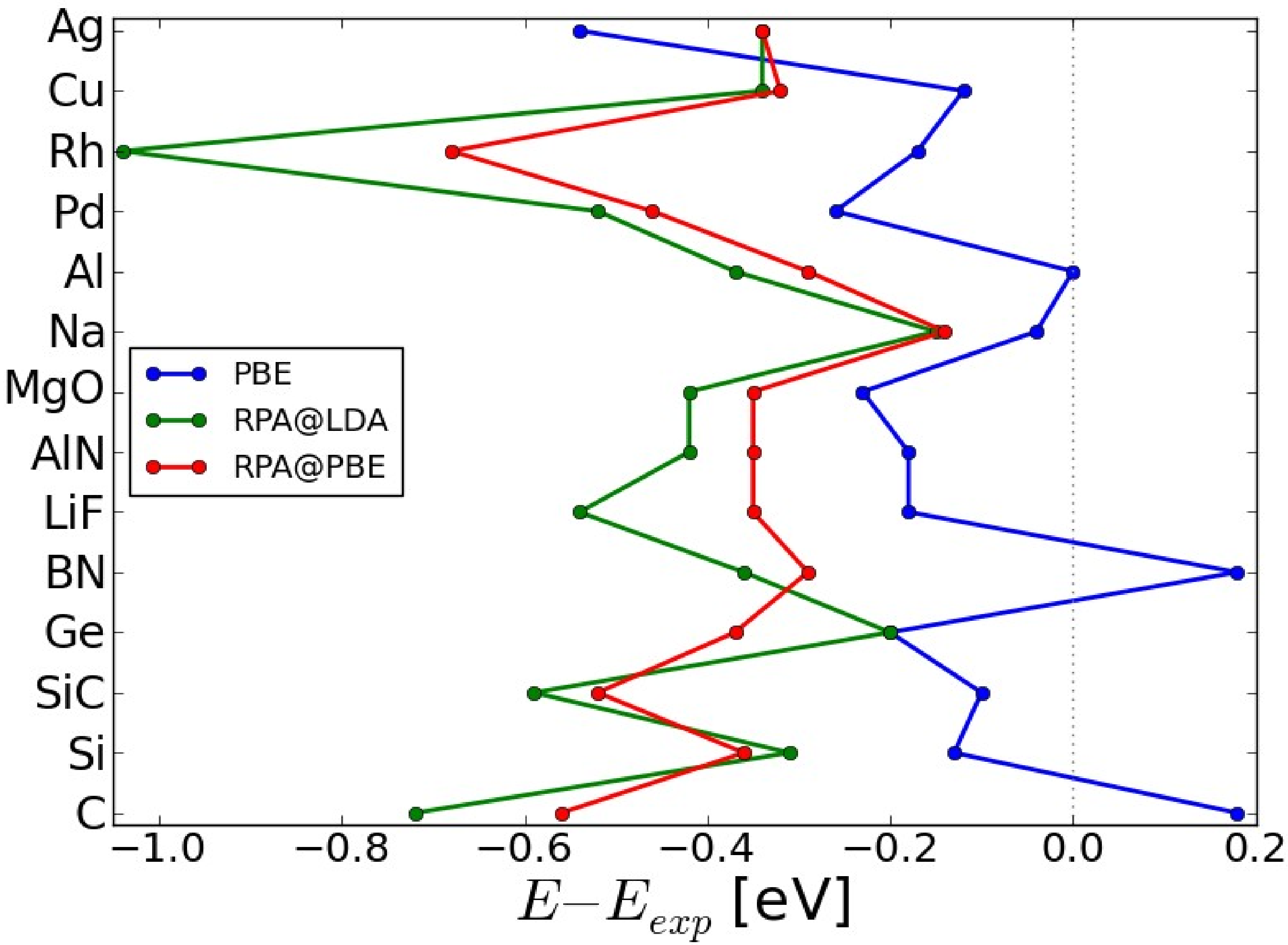
Atomization energies of small molecules



PBE: MEA – 9 kcal/mol = 0.39 ev

RPA@PBE: MEA – 10 kcal/mol = 0.43 ev

Cohesive energies of solids



PBE: MEA – 0.18 ev

RPA@PBE: MEA – 0.42 ev

Pros and cons in RPA

The RPA correlation is combined with exact exchange and the (first order) self-interaction error vanishes

Solves the CO puzzle. Correct order of adsorption energies on Pt(111)

Good description of strong static correlation

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Good description of strong static correlation

RPA suffers from large self-correlation errors - the correlation energy of a H atom is -0.6 eV

The atomization energies of small molecules are slightly worse than PBE – always underbinds

The cohesive energies of solids are worse than PBE

Beyond RPA

It should be possible to improve RPA by including a simple exchange-correlation kernel in the response function:

$$\chi^{\lambda} = \chi^{\mathrm{KS}} + \chi^{\mathrm{KS}} f^{\lambda}_{\mathrm{Hxc}} \chi^{\lambda}, \qquad f^{\lambda}_{\mathrm{Hxc}} = \lambda v + f^{\lambda}_{\mathrm{xc}}$$

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The simplest one can think of is the adiabatic LDA kernel

$$f^{\text{ALDA}}_{\text{xc}}[n](\mathbf{r},\mathbf{r}') = \delta(\mathbf{r}-\mathbf{r}') f^{\text{ALDA}}_{\text{xc}}[n], \qquad f^{\text{ALDA}}_{\text{xc}}[n] = \frac{d^2}{dn^2}(n e^{\text{HEG}}_{\text{xc}})|_{n=n(\mathbf{r})}$$

Furthermore, we only include exchange since $f_x^{\lambda} = \lambda f_x$

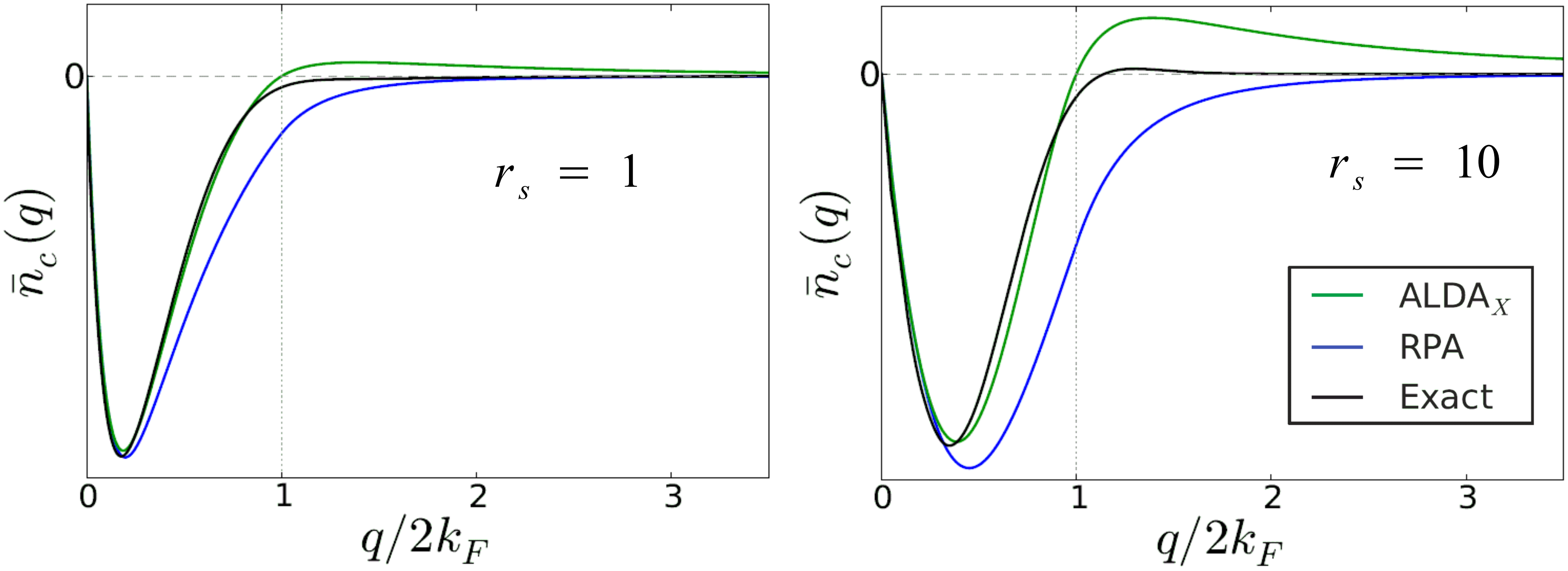
Such an approximation worsens results significantly!

[F. Furche and T. van Voorhis, JCP **122** 164106 (2005)

Homogeneous Electron Gas

To see why ALDA fails one can look at the Fourier transform of the correlation hole for the homogeneous electron gas

[M. Lein, E. K. U. Gross and J. P. Perdew, PRB **61** 13431 (2000)]



ALDA is not an exact approximation for the HEG!

The locality implies slow decay at large q = trouble

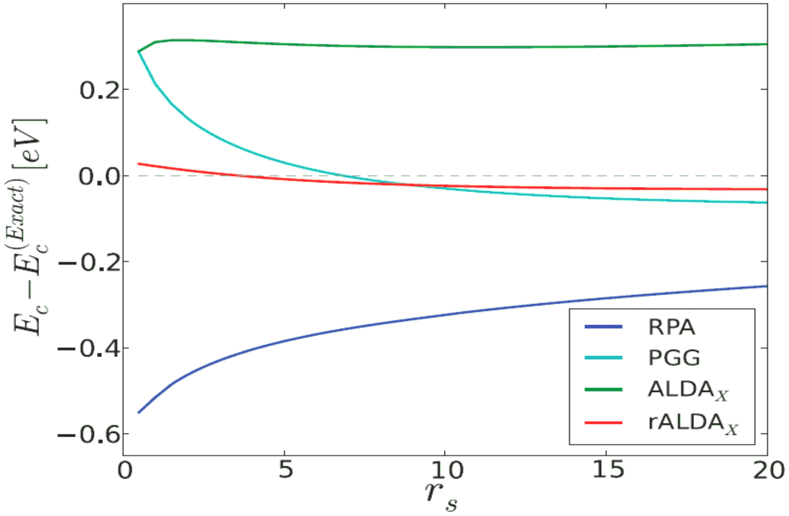
[F. Furche and T. van Voorhis, JCP **122** 164106 (2005)]

Homogeneous Electron Gas

If we make a cutoff at $q=2k_F$ equivalent to the truncated kernel

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

The correlation energy becomes accurate over a wide range of densities



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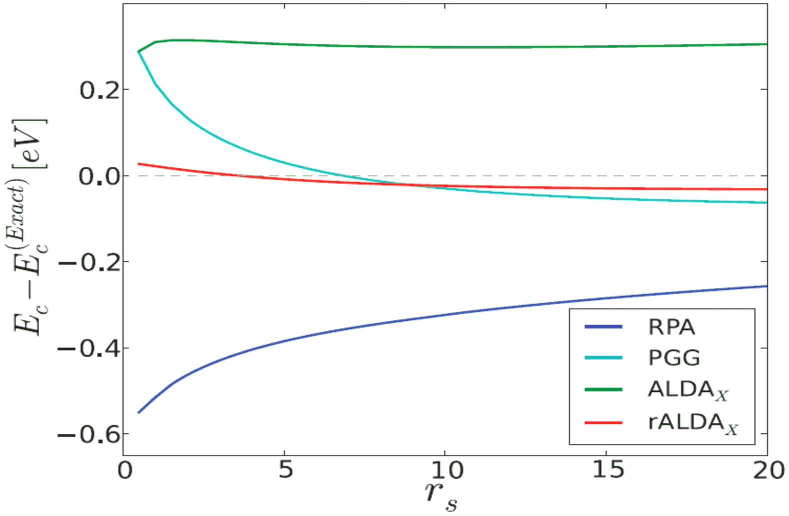

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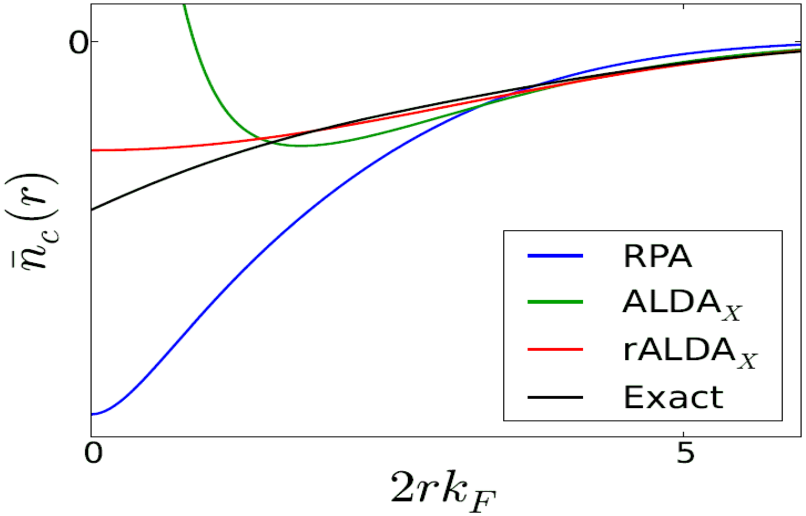

The real space correlation hole is also much better described than in both RPA and pure ALDA

[T. Olsen and K. S. Thygesen, PRB **86** 081103(R) (2012)]

rALDA

The procedure can be generalized to non-uniform systems by Fourier transforming to real space:

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

with

$$f_x^{\mathrm{rALDA}}[n](r) = \frac{f_x^{\mathrm{ALDA}}[n]}{2\pi^2 r^3}[\sin(2k_F r) - 2k_F r\cos(2k_F r)]$$

$$v^r[n](r) = \frac{1}{r}\frac{2}{\pi}\int_0^{2k_F r}\frac{\sin x}{x}dx.$$

We can then get the kernel for inhomogeneous systems by taking

$$r \to |\mathbf{r} - \mathbf{r}'| \qquad k_F \to [3\pi^2\tilde{n}(\mathbf{r},\mathbf{r}')]^{1/3}$$

$$\tilde{n}(\mathbf{r},\mathbf{r}') = (n(\mathbf{r}) + n(\mathbf{r}'))/2$$

[T. Olsen and K. S. Thygesen, PRB **86** 081103(R) (2012)]

Spin

There is not a unique way to generalize to spin-polarized systems

For a spinpaired system it is straightforward to show that

$$f_{Hxc} = \frac{1}{4} \sum_{\sigma\sigma'} f_{Hxc}^{\sigma\sigma'}$$

The ALDA Hartree-exchange kernel is

$$f_{Hx}^{ALDA} = \begin{bmatrix} V + 2\mathrm{f}_x^{ALDA}[2\mathrm{n}_\uparrow] & V \\ V & V + 2\mathrm{f}_x^{ALDA}[2\mathrm{n}_\downarrow] \end{bmatrix}$$

It is clear that we cannot simply introduce cutoff on the diagonal

Spin

Instead we take

$$f_{Hx}^{rALDA}=\begin{bmatrix} V^{r}[n_{\uparrow}+n_{\downarrow}]+2\mathrm{f}_{x}^{rALDA}[n_{\uparrow}+n_{\downarrow}] & V^{r}[n_{\uparrow}+n_{\downarrow}] \\ V^{r}[n_{\uparrow}+n_{\downarrow}] & V^{r}[n_{\uparrow}+n_{\downarrow}]+2\mathrm{f}_{x}^{rALDA}[n_{\uparrow}+n_{\downarrow}] \end{bmatrix}$$

This breaks spin-scaling for the kernel and it cannot be regarded as pure exchange

The choice is not unique!

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$$f_{Hx}^{rALDA} = \begin{bmatrix} V^r[n_\uparrow + n_\downarrow] + 2\mathrm{f}_x^{rALDA}[n_\uparrow + n_\downarrow] & V^r[n_\uparrow + n_\downarrow] \\ V^r[n_\uparrow + n_\downarrow] & V^r[n_\uparrow + n_\downarrow] + 2\mathrm{f}_x^{rALDA}[n_\uparrow + n_\downarrow] \end{bmatrix}$$

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The choice is not unique!

In contrast to RPA we need to represent the full spin-response function – Requires a lot of memory

rALDA

The rALDA kernel has been implemented in GPAW

There is no general framework for PAW corrections of two-point functions. The implementation uses all-electron density for kernel

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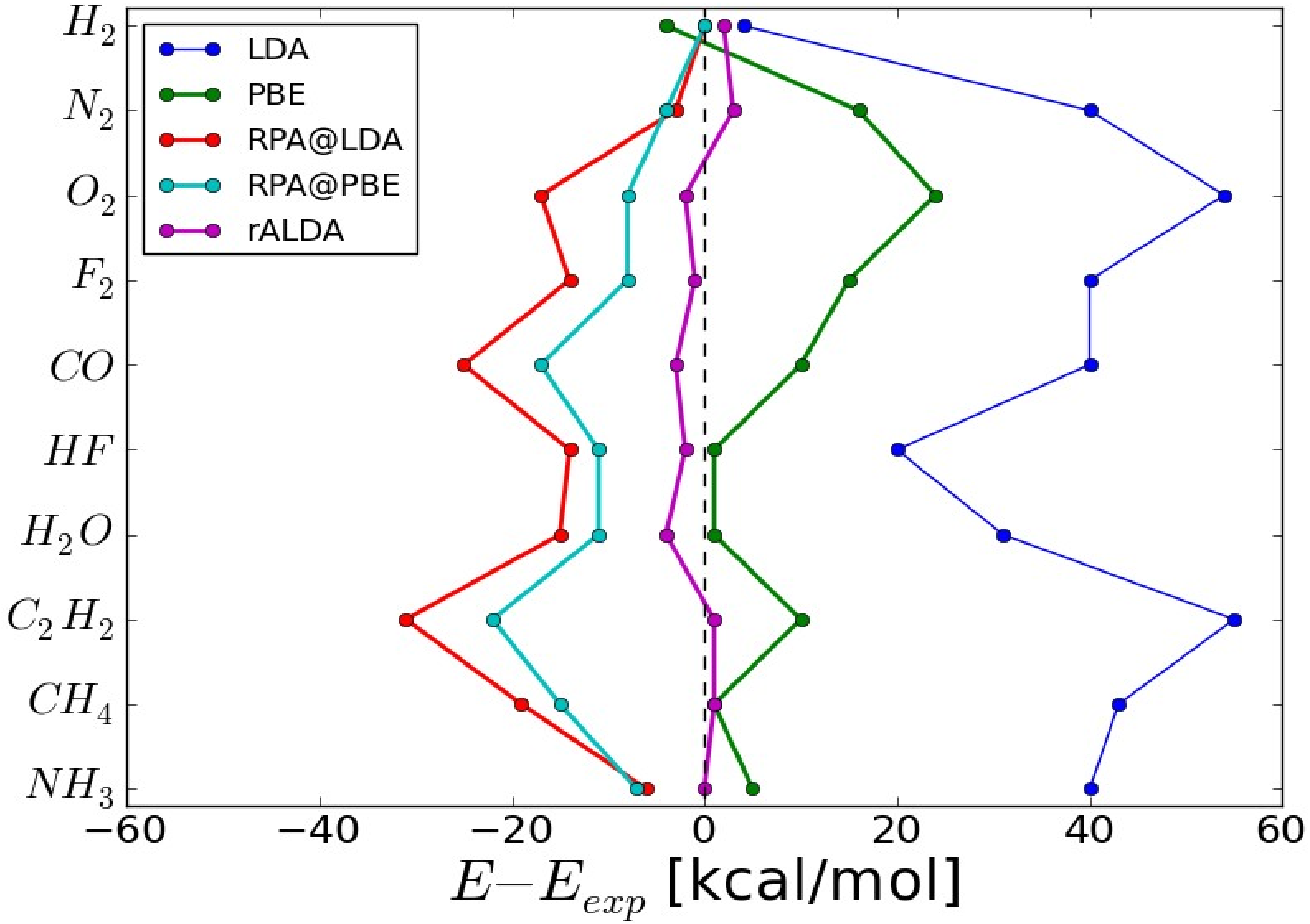
The method improves absolute correlation energies significantly compared to RPA

	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

Numbers are in kcal/mol = 43 meV

[T. Olsen and K. S. Thygesen, PRB **86** 081103(R) (2012)]

rALDA - molecules



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[T. Olsen and K. S. Thygesen, in preparation]

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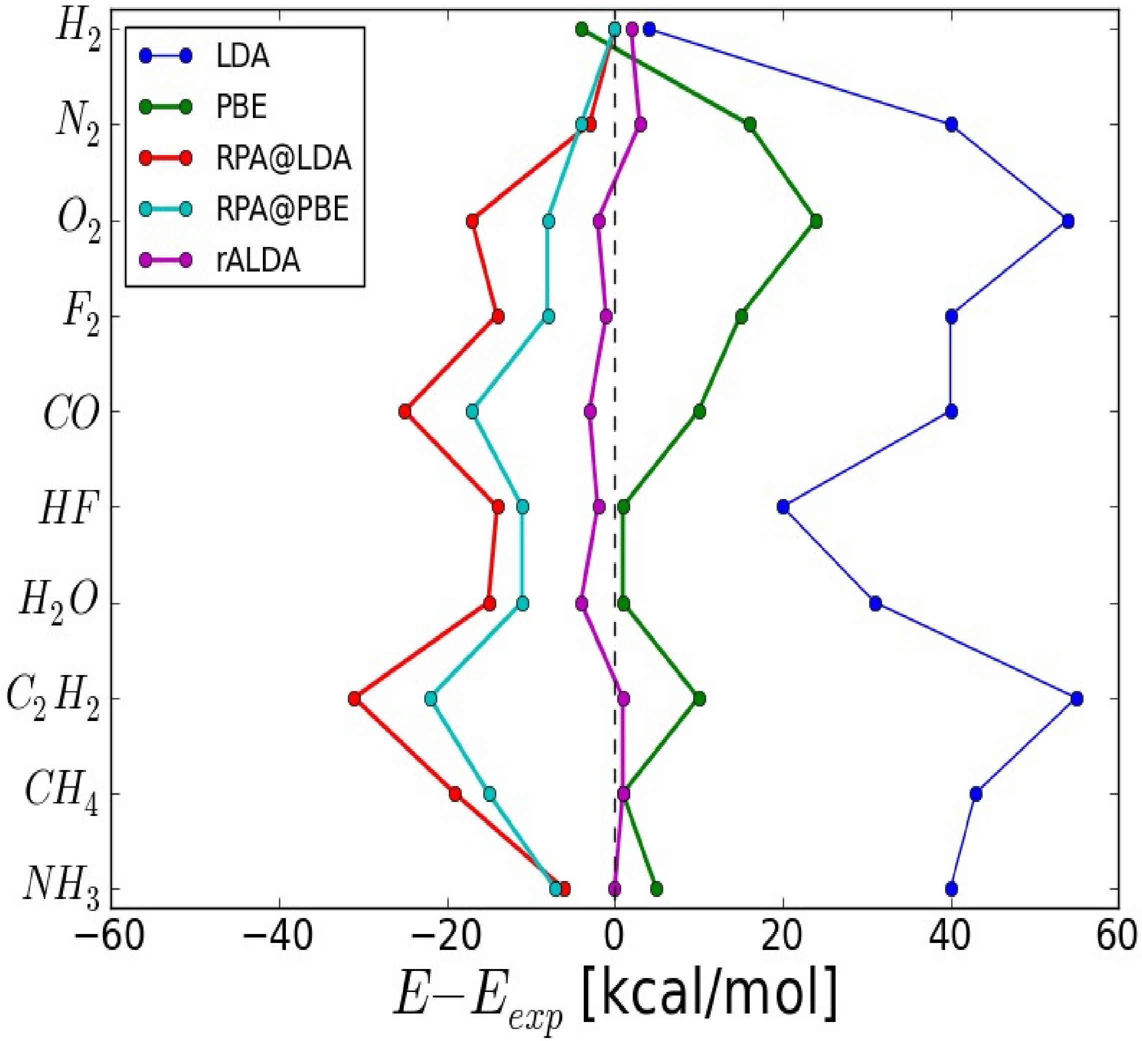


MEA (kcal/mol)

LDA:	37
RPA@LDA:	14
RPA@PBE:	10
PBE:	9
SOSEX:	5
rALDA:	2

Numbers are in kcal/mol = 43 meV

[T. Olsen and K. S. Thygesen, in preparation]

rALDA - solids

The two-point density makes the rALDA kernel non-periodic and one has two sample all unit cells (twice) in bulk systems:

$$f_{Hxc}^{rALDA}(\mathbf{G},\mathbf{G}',\mathbf{q}) = \frac{1}{V}\int_V d\mathbf{r}\int_V d\mathbf{r}' e^{-i\mathbf{G}\cdot\mathbf{r}}\tilde{f}(\mathbf{q};\mathbf{r},\mathbf{r}')e^{i\mathbf{G}'\cdot\mathbf{r}'}$$

with

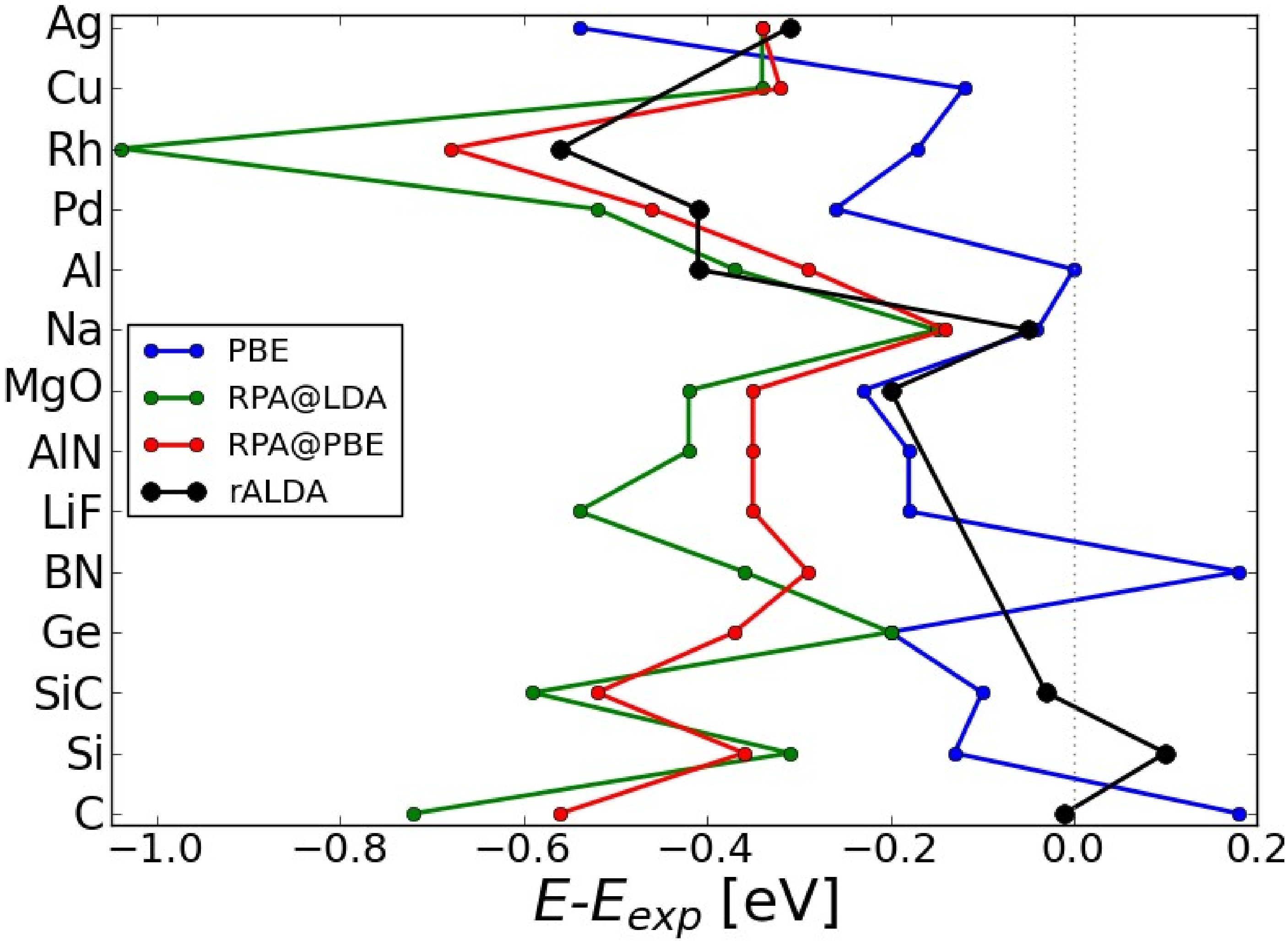
$$\tilde{f}(\mathbf{q};\mathbf{r},\mathbf{r}') = \frac{1}{N}\sum_{i,j} e^{i\mathbf{q}\cdot\mathbf{R}_{ij}} e^{-i\mathbf{q}\cdot(\mathbf{r}-\mathbf{r}')} f_{Hxc}^{rALDA}(\mathbf{r},\mathbf{r}'+\mathbf{R}_{ij})$$

The two-point density cannot be stored – Implementation involves loop over r' and double loop over all unit cells.

Very slow for solids!

[T. Olsen and K. S. Thygesen, in preparation]

rALDA - solids

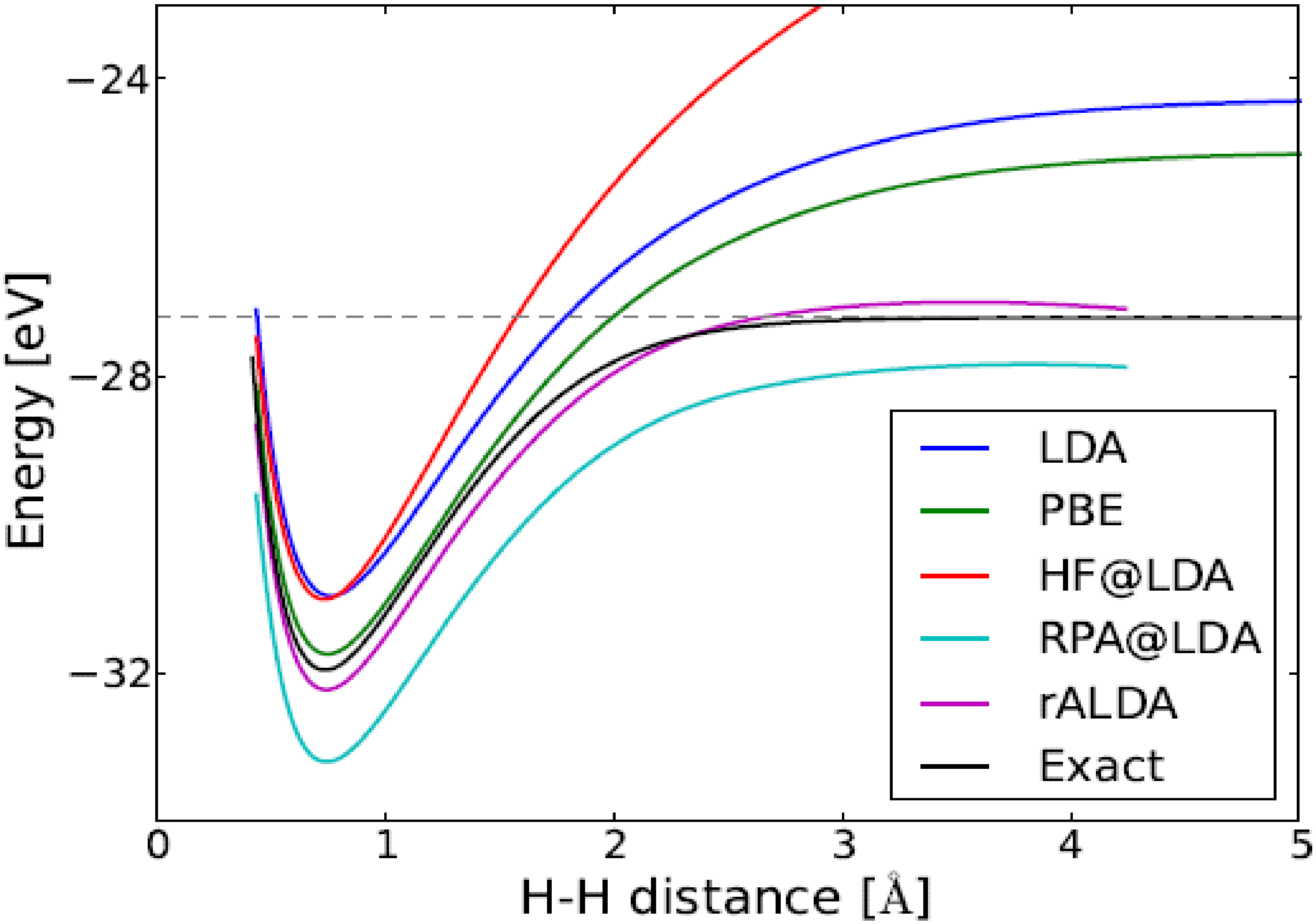


For semiconductors results are much better than RPA, but not for metals...

[T. Olsen and K. S. Thygesen, in preparation]

rALDA - Static Correlation

Dissociation of H2



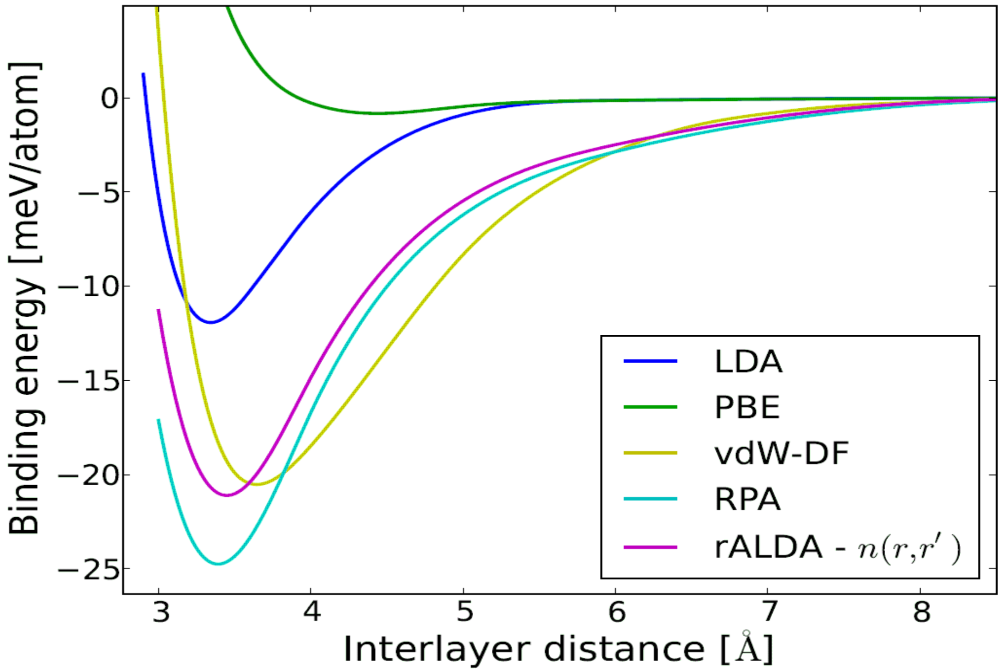
rALDA results are similar to RPA but offset is much better

[T. Olsen and K. S. Thygesen, in preparation]

rALDA – van der Waals

For van der Waals interactions the rALDA kernel gives results similar to RPA

Bilayer graphene



We have also tested four members of the s22 set of molecular dimers where rALDA and RPA produce identical results

[T. Olsen and K. S. Thygesen, in preparation]

Summary and Outlook

- Compared to RPA, the rALDA kernel significantly improves absolute correlation energies

- Atomization energies are significantly improved for small molecules and solids

- The rALDA kernel conserves the RPA description of dispersive interactions and static correlation

- The method allows for straightforward generalizations to renormalized adiabatic GGAs
  - preliminary rAPBE results gives a correlation energy for H < 1 meV

- Include correlation part of the adiabatic kernel