RPA total energies for solids with ABINIT

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Outline

I. Some fancy applications of Abinit

II. Implementation of the RPA functional with k-points

III. Testing the implementation

IV. Range-separation for RPA

Abinit can run (easily) 4096 atoms!

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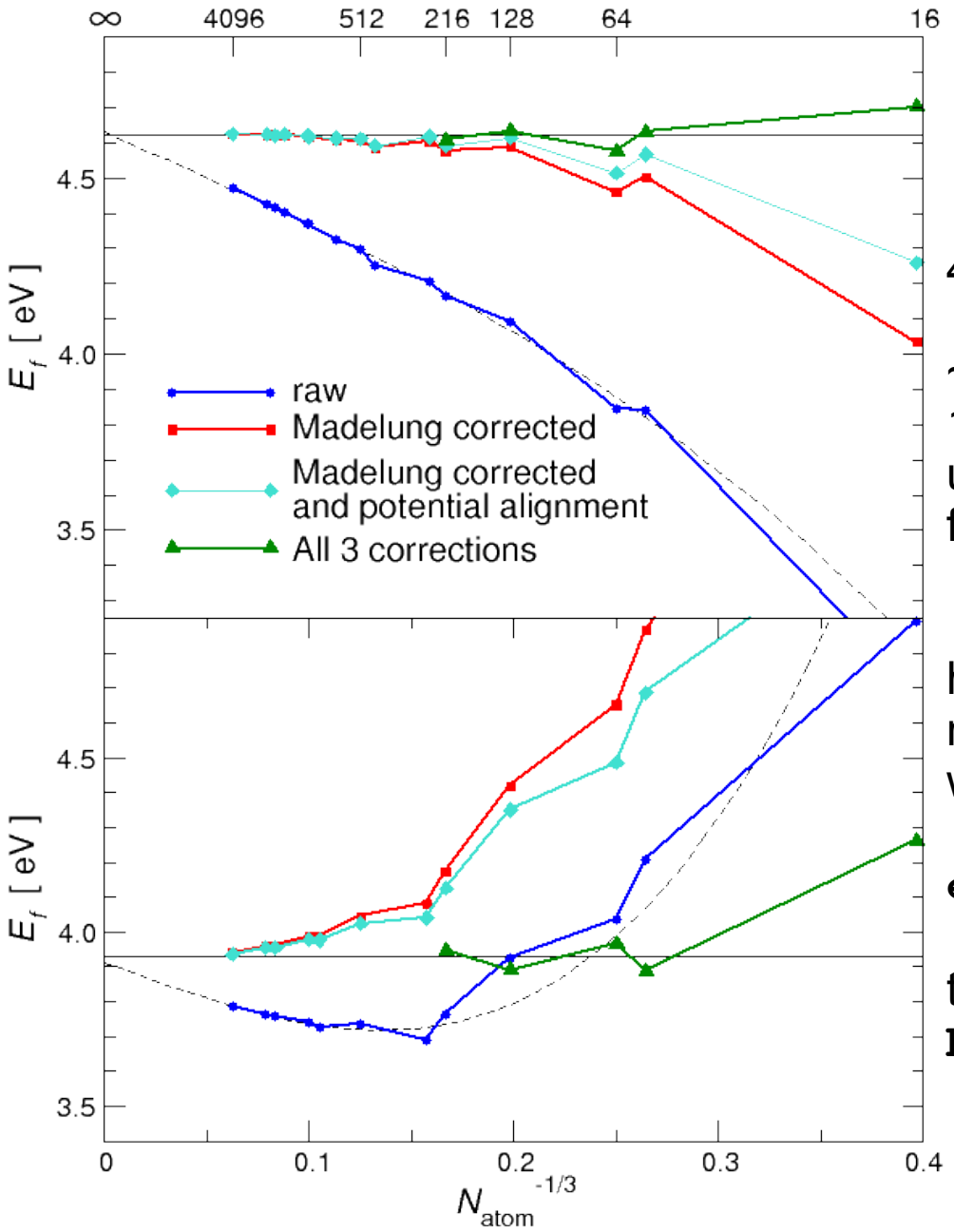
Charged Silicon interstitial Si_{tet}^{2+}



Charged Silicon vacancy V_{Si}^{2+}

4096 atom energy calculation:

~ 10 hours on
120 nodes
using only 4 cores out of 8
for memory issue (36 Gb/node)

home-made crude
norm-conserving pseudo
with rcut = 4.0 bohr

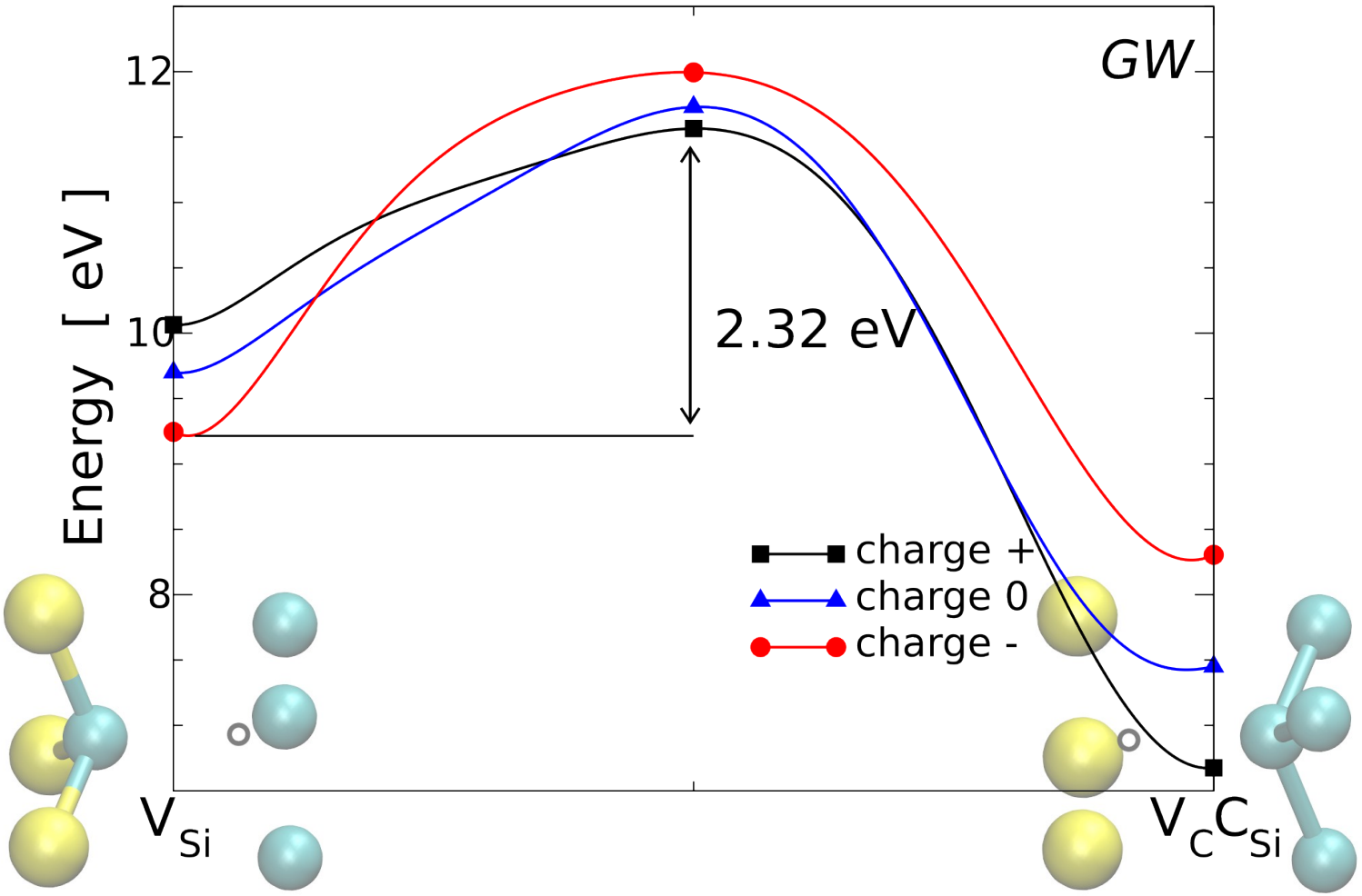
`ecut` = 2.0 Ha

tuning the FFT grids with
`boxcutmin` (as VASP™)

S. Taylor and F. Bruneval *on the desk of the referees*

GW calculations for 216 atom supercells

GW correction of a migration path of a vacancy in SiC



NEB paths performed with Quantum-Espresso
GW (Γ-point only) performed with Abinit with the same pseudos

F. Bruneval and G. Roma *accepted in PRB*

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Why implementing today the RPA functional?

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Because it's fashionable!

Furche
PRB

Fuchs-Gonze
PRB

Fuchs-Gonze
PRL Comment

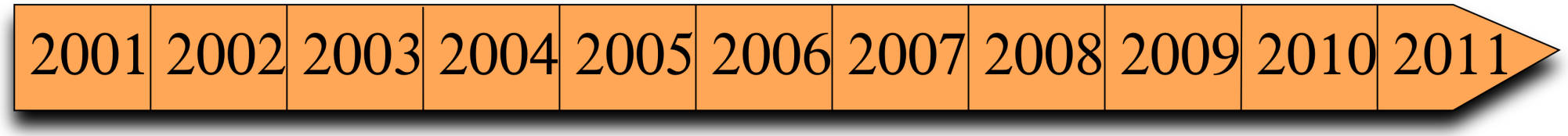
Aryasetiawan, Miyake
PRL, PRB

Marini-Rubio
PRL

NGuyen-de Gironcoli
PRB

NGuyen-Galli
JCP

Ren-Scheffler
PRB



Harl-Kresse
PRL, JCP

Harl-Kresse
PRB, PRL
Nature Mat.

Toulouse-Savin
PRL

And also because one gets

Correct vanderWaals interactions:

graphite interlayer distance, rare-gas solids,
ad-atoms on surfaces

ACFD Theorem

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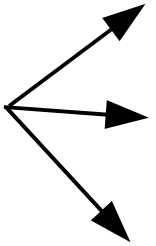
Adiabatic connection

$$E_{\text{interacting}} - E_{\text{non-interacting}} = \int_0^1 d\lambda \frac{dE(\lambda)}{d\lambda}$$

Hellman-Feynman theorem

$$E_{Hxc} = \int_0^1 d\lambda \left\langle \Psi(\lambda) \middle| v \middle| \Psi(\lambda) \right\rangle$$



Hartree

Exchance

Correlation

Fluctuation-dissipation

$$E_c = -\frac{1}{2}\int_0^1 d\lambda \, \mathrm{Tr}\left[v\chi_\lambda(t=0) - v\chi_0(t=0) \right]$$

Polarizabilities

$$= -\frac{1}{4\pi}\int_0^1 d\lambda \int_{-\infty}^{+\infty} d\omega \, \mathrm{Tr}\left[v\chi_\lambda(\omega) - v\chi_0(\omega) \right]$$

$$= -\frac{1}{2\pi}\int_0^1 d\lambda \int_0^{+\infty} du \, \mathrm{Tr}\left[v\chi_\lambda(iu) - v\chi_0(iu) \right]$$

A definition of the correlation energy which is **DFT compliant** and so far **exact.**

SRMP

Formulas implemented and input parameters

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Independant particle polarizability:

$$\chi^0_{\boldsymbol{G}\boldsymbol{G}'}(\boldsymbol{q},iu)=\sum_{\boldsymbol{k}ij}(f_{\boldsymbol{k}+\boldsymbol{q}j}-f_{\boldsymbol{k}i})\frac{\langle \boldsymbol{k}i|e^{-i(\boldsymbol{q}+\boldsymbol{G}).\boldsymbol{r}}|\boldsymbol{k}+\boldsymbol{q}j\rangle\langle \boldsymbol{k}+\boldsymbol{q}j|e^{i(\boldsymbol{q}+\boldsymbol{G}').\boldsymbol{r}}|\boldsymbol{k}i\rangle}{iu-(\epsilon_{\boldsymbol{k}i}-\epsilon_{\boldsymbol{k}+\boldsymbol{q}j})}$$

ecuteps **nband** **nfreqim**

RPA polarizability for each coupling constant λ:

$$\chi^\lambda(\boldsymbol{q},iu) = \chi^0(\boldsymbol{q},iu)+\chi^0(\boldsymbol{q},iu)\lambda v(\boldsymbol{q})\chi^\lambda(\boldsymbol{q},iu)$$

RPA correlation energy:

$$E_c^{\mathrm{RPA}} = -\frac{1}{2\pi}\int_0^1 d\lambda \int_0^{+\infty} du \sum_{\boldsymbol{q}\boldsymbol{G}} v(\boldsymbol{q}+\boldsymbol{G})\left[\chi^\lambda_{\boldsymbol{G}\boldsymbol{G}}(\boldsymbol{q},iu)-\chi^0_{\boldsymbol{G}\boldsymbol{G}}(\boldsymbol{q},iu)\right]$$

RPA total energy

$$E^{\mathrm{RPA}} = E^{\mathrm{LDA}} - E_{xc}^{\mathrm{LDA}} + E_x + E_c^{\mathrm{RPA}}$$

```
optdriver       4
gwcalctyp       5
ecutsigx      ecut
ecutwfn       ecut

icutcoul        0
rcut           -1
.............................
grep "New Exchange" abinit.out
```

Hartree-Foch calculation using the usual *GW* code

Spencer-Alavi scheme speeds up convergence with respect to k-points

usual screening calculation for imaginary frequencies

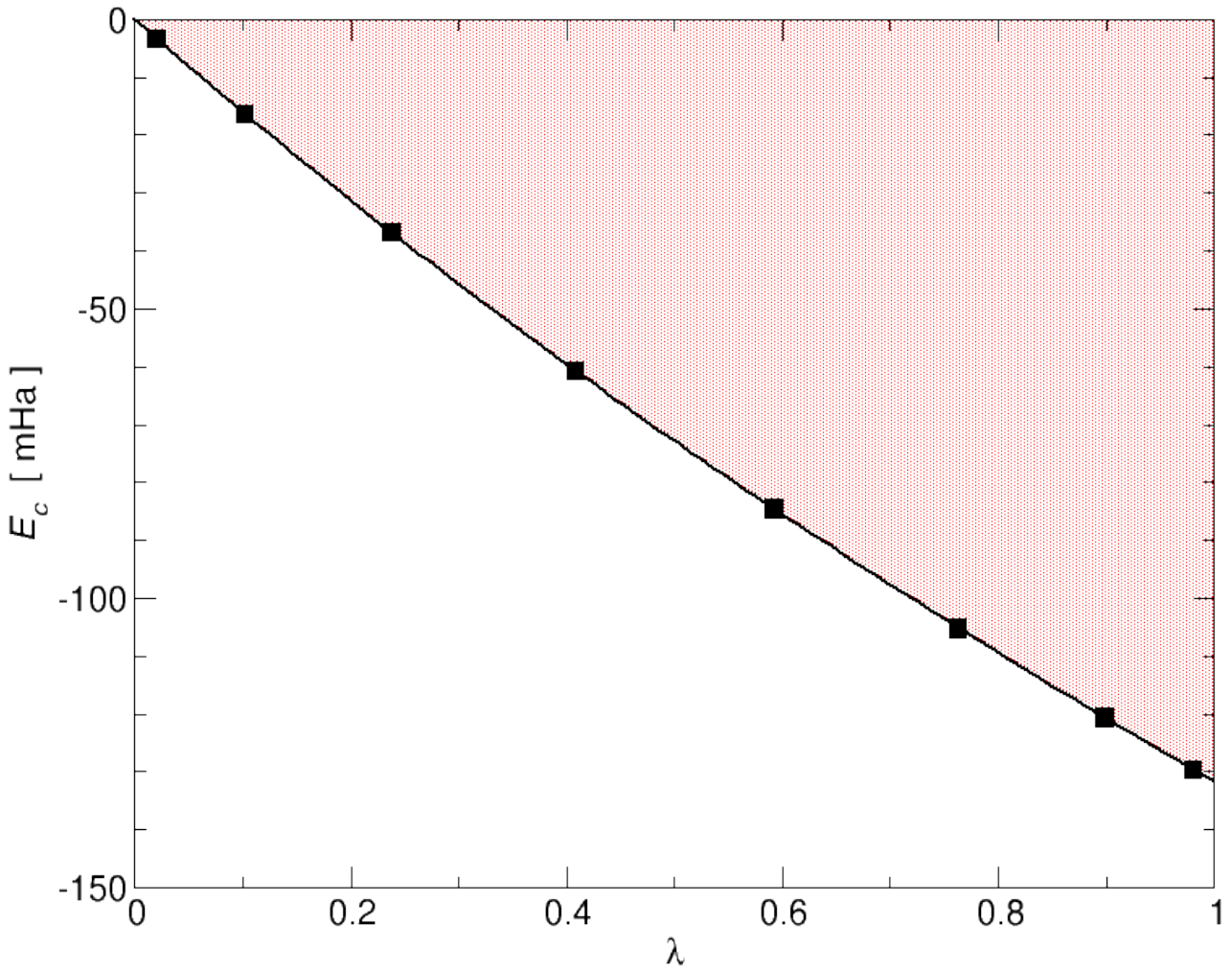
```
optdriver       3
gwcalctyp       1
nfreqim         6
ecutwfn       ecut
ecuteps       convergence study
nband       convergence study or npw

gwrpacorr       N
.............................
grep "RPA" abinit.out
```

New post-treatment of

$$\chi^0_{GG'}(\boldsymbol{q}, iu)$$

Integration over λ

$$E_c^{\mathrm{RPA}} = \int_0^1 d\lambda\, e_c^{\mathrm{RPA}}(\lambda)$$



Number of points for λ governed by

`gwrpacorr N`

requires N inversions

Exact integration over λ

`gwrpacorr 1`

requires 1 diagonalization

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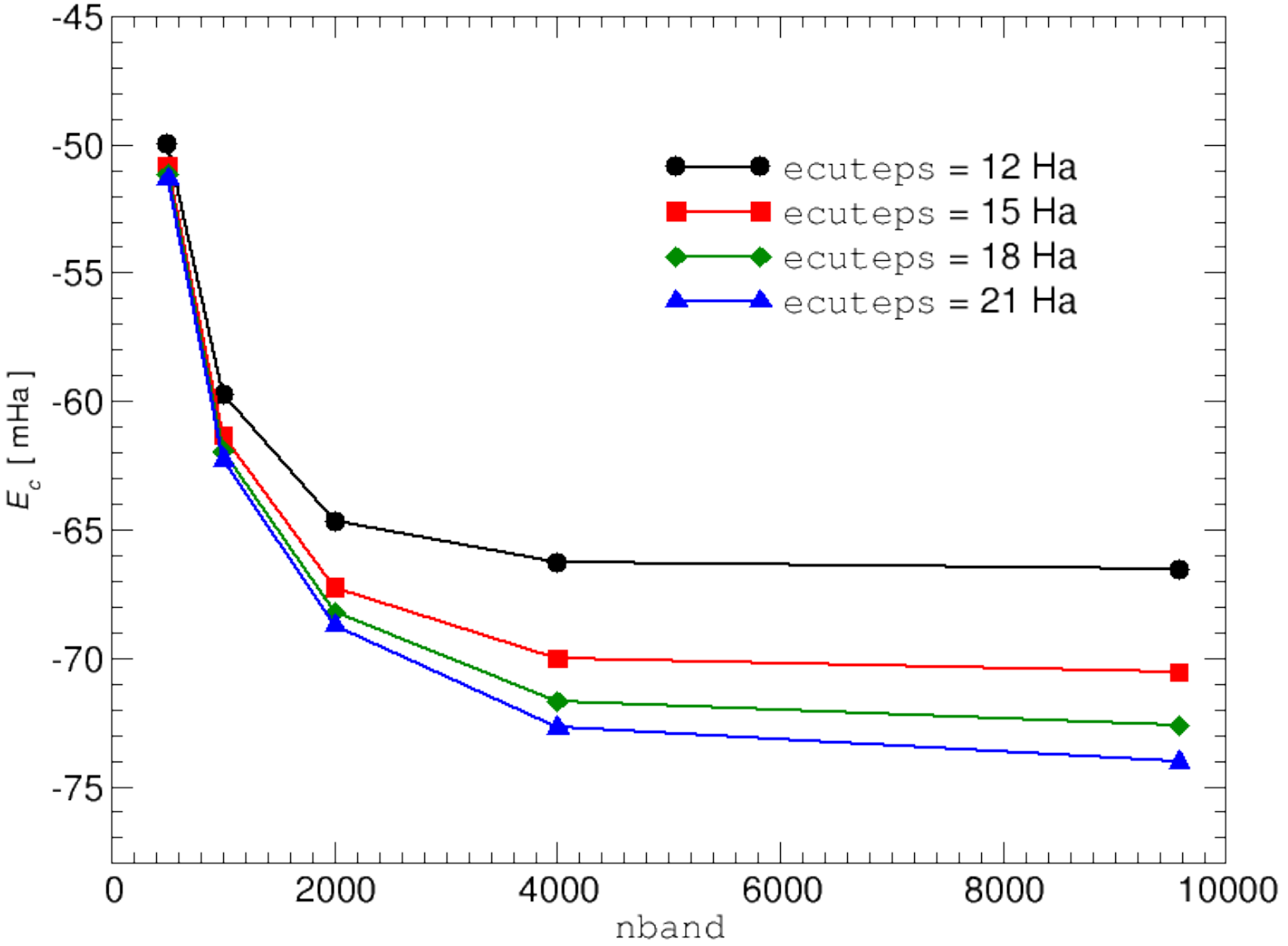
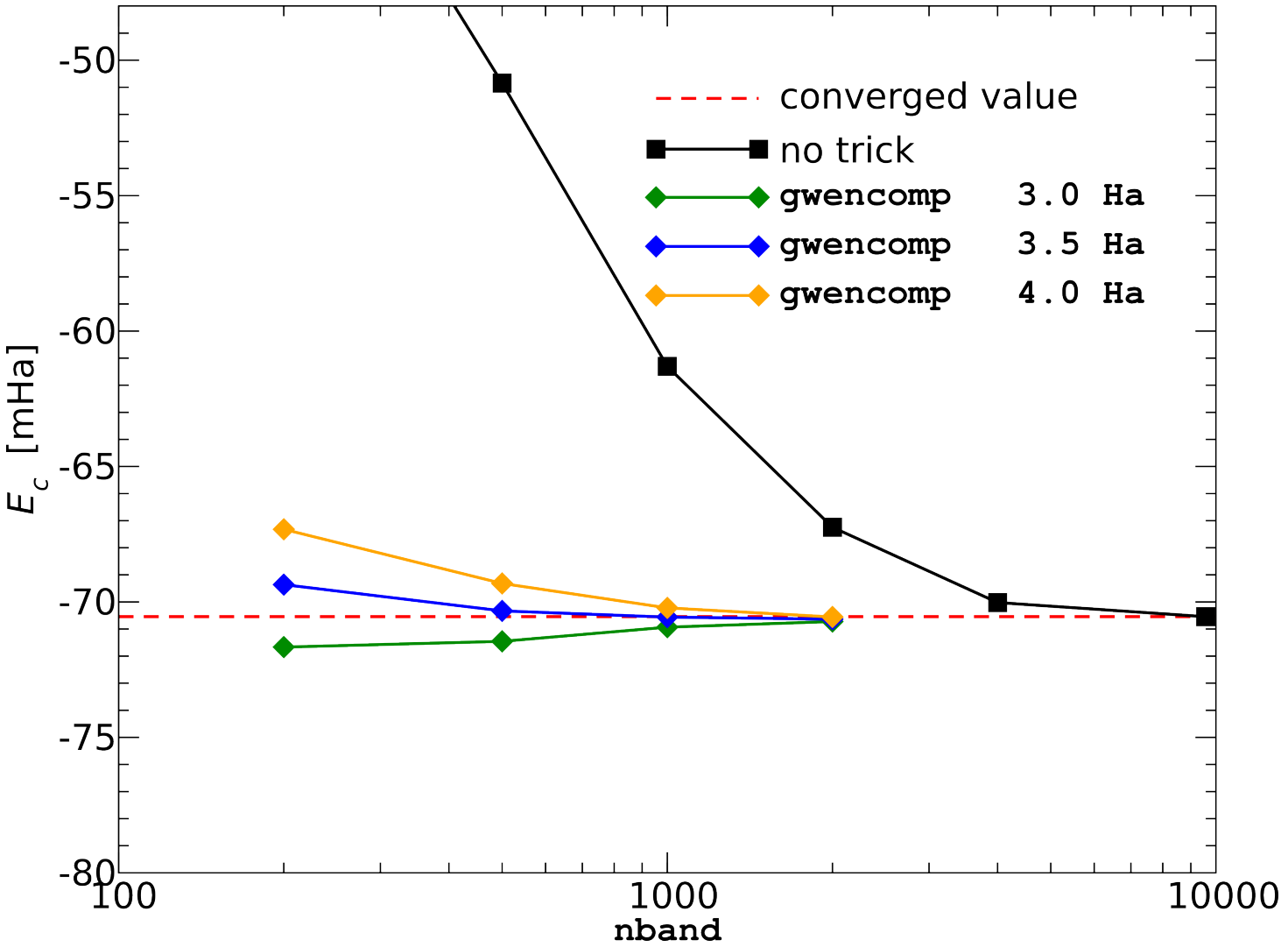
Benchmark for the helium atom



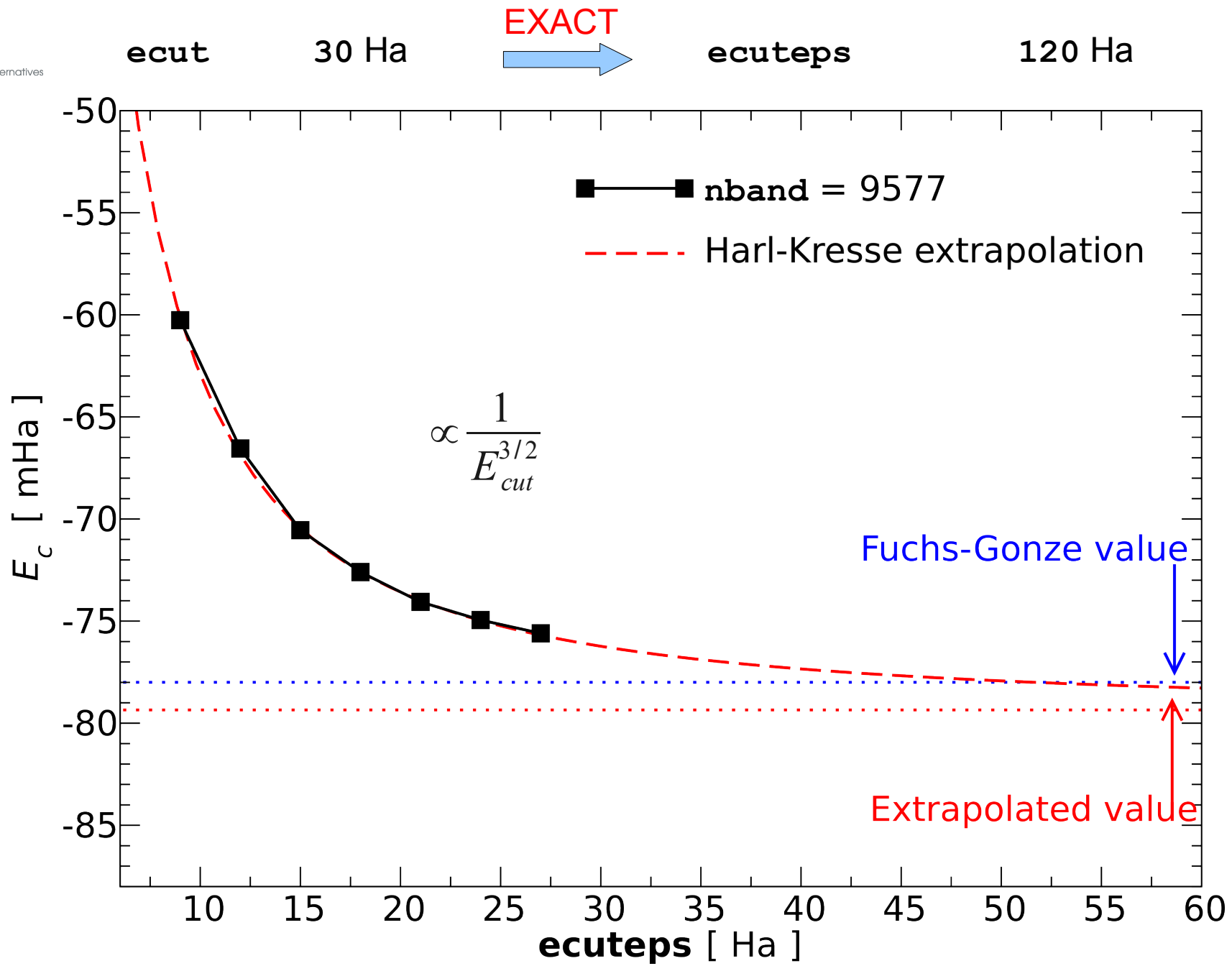
Accelerating the convergence with number of bands



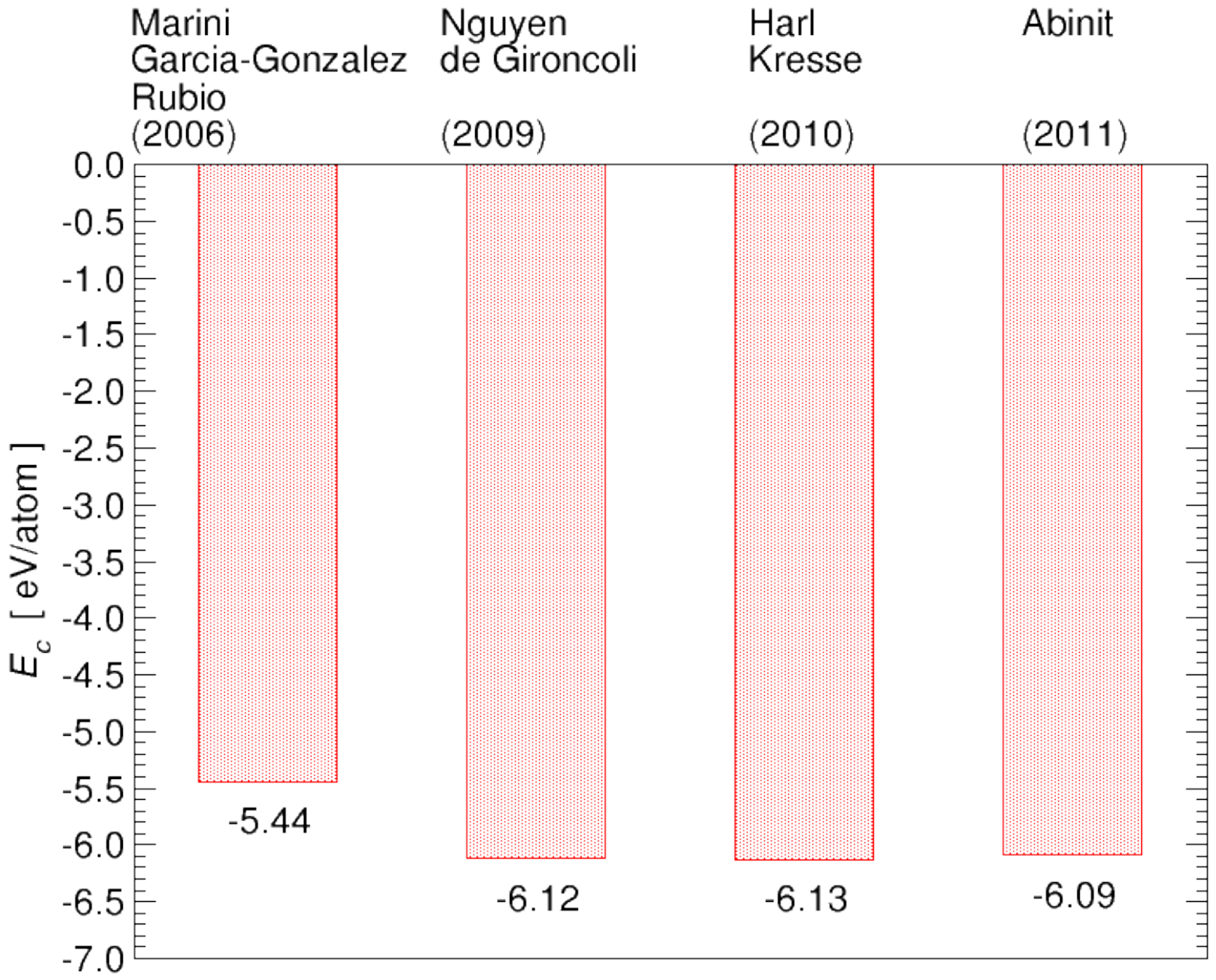
The **Bruneval-Gonze trick** requires one parameter: **`gwencomp`**

What about the Berger-Sottile-Reining trick?

Benchmark for the helium atom

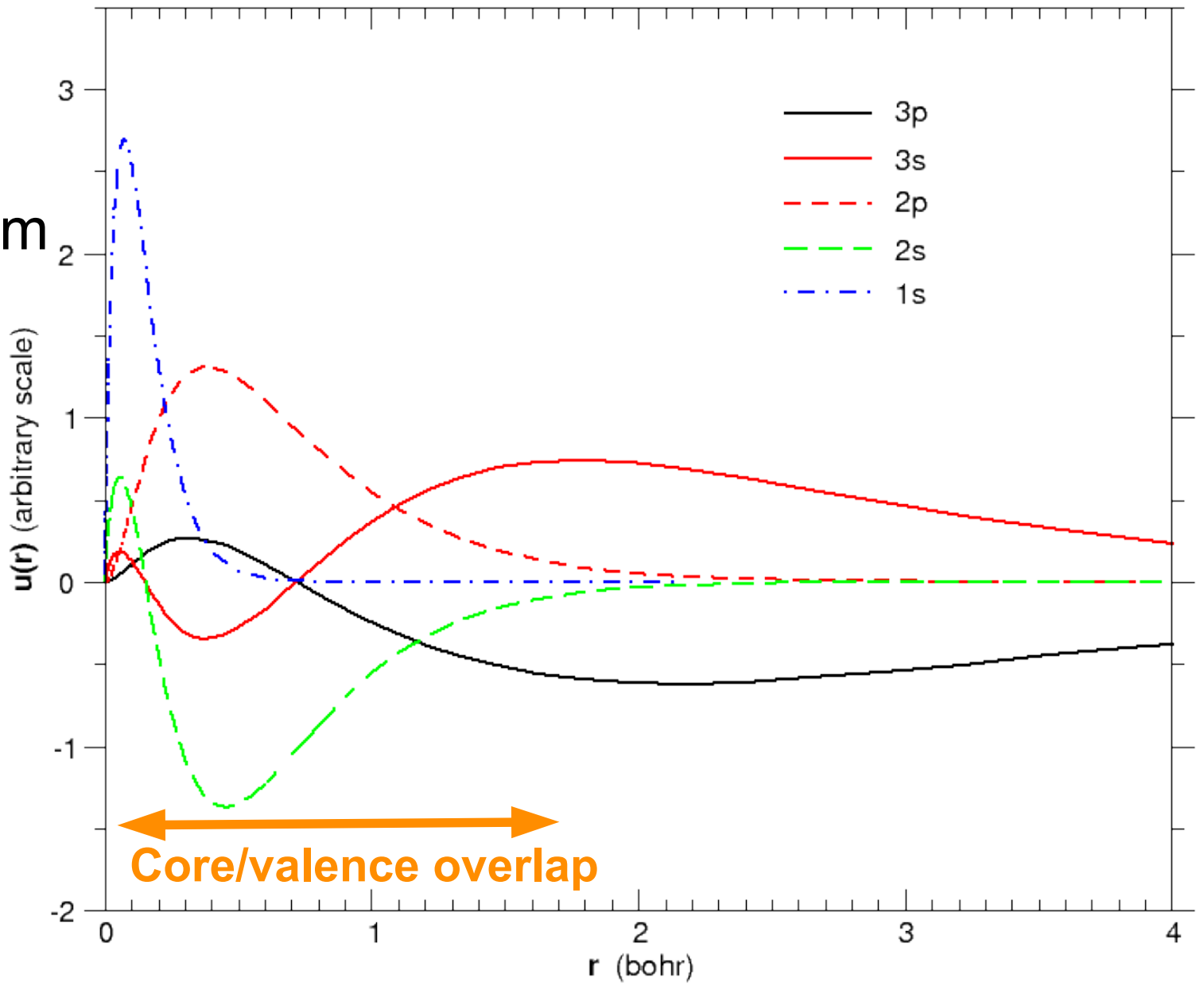


Correlation energy of bulk silicon



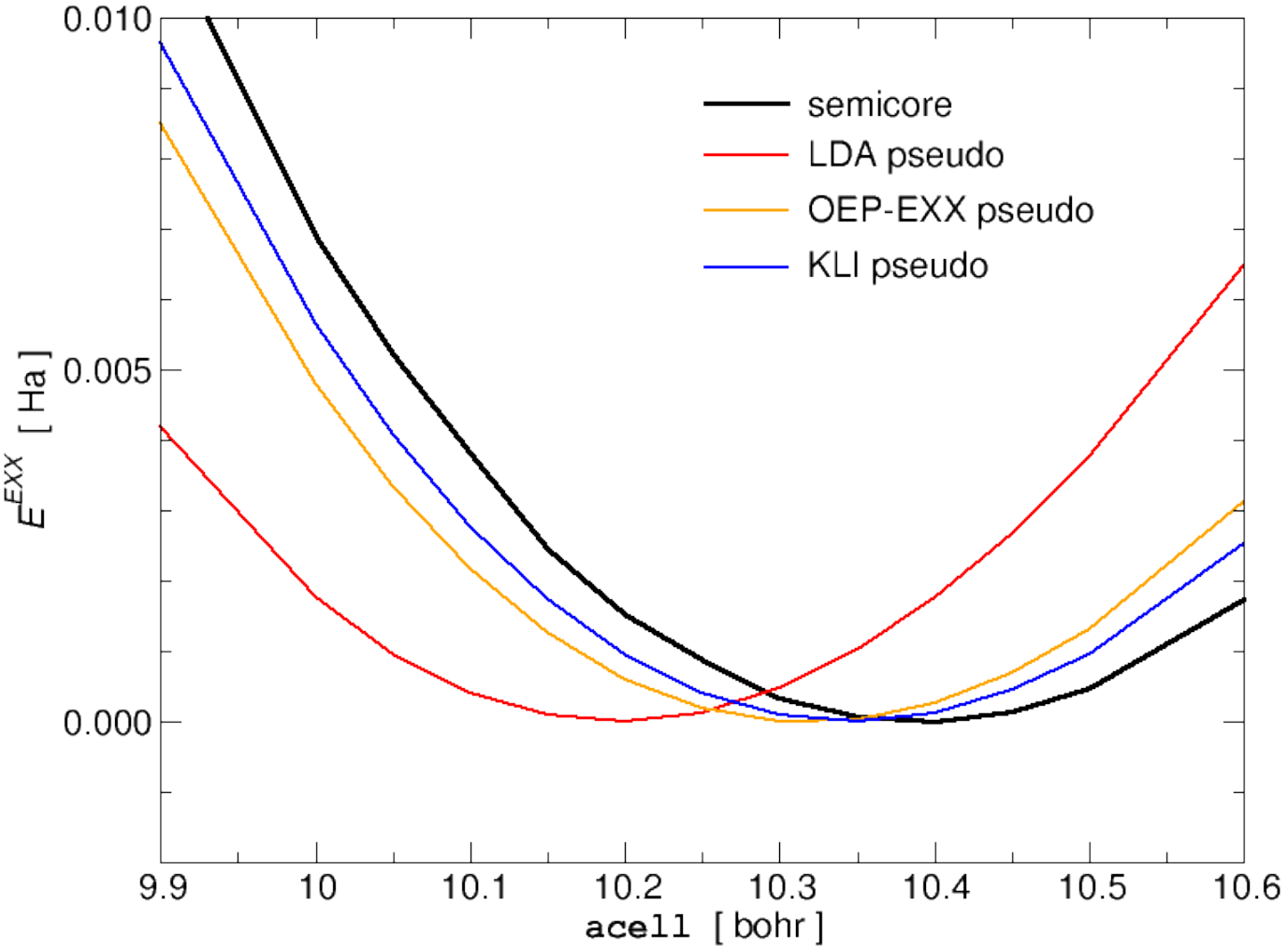
The issue of Exact-Exchange

Silicon atom



EXX lattice parameter

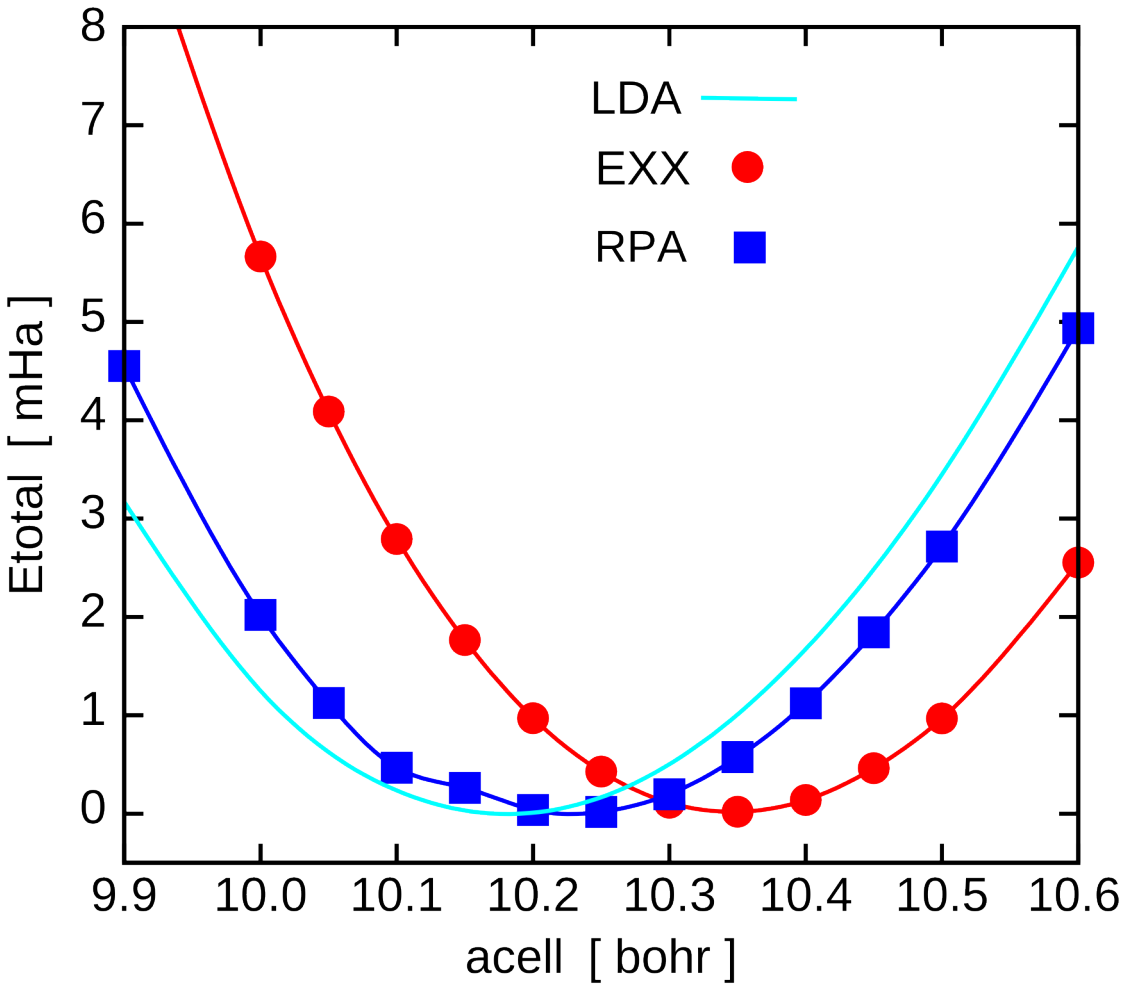
$$E^{\mathrm{EXX}} = E^{\mathrm{LDA}} - E_{xc}^{\mathrm{LDA}} + E_x$$



I'm using **KLI pseudos in the following**

In the future, one should employ the PAW implementation of Matteo for core/valence EXX.

RPA Lattice parameter of silicon



	a_{LDA}	a_{EXX}	a_{RPA}	a_{Expt}
ABINIT	10.18	10.35	10.23	10.24
VASP [1]		10.35	10.26	

[1] J. Harl, L. Schimka, G. Kresse, **PRB** (2010).

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Long-range/short-range splitting

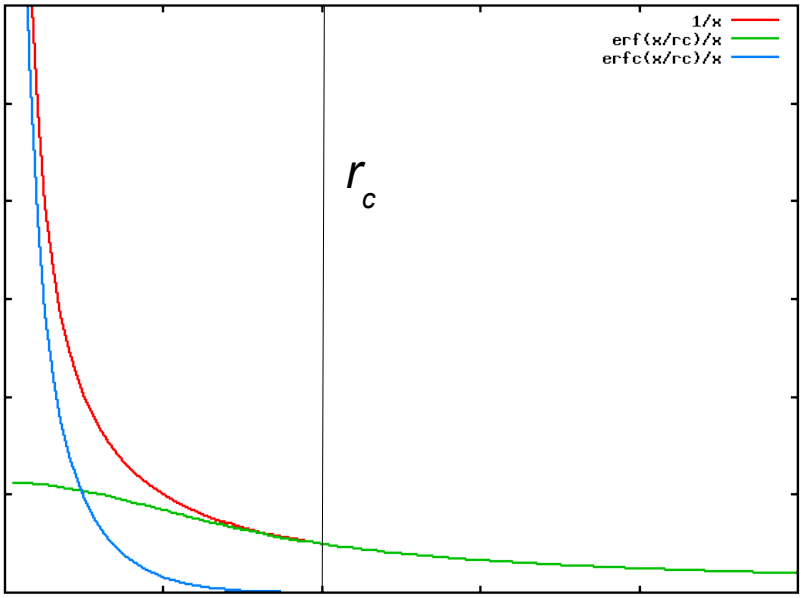
Full Coulomb interaction $\frac{1}{r} = \frac{\mathrm{erf}(r/r_c)}{r} + \frac{1-\mathrm{erf}(r/r_c)}{r}$

Long-Range

Short-Range

After Savin *et al.*

Also used in HSE



$$\mathrm{FT}\left\{\frac{1}{r}\right\} = \frac{4\pi}{\boldsymbol{G}^2}$$

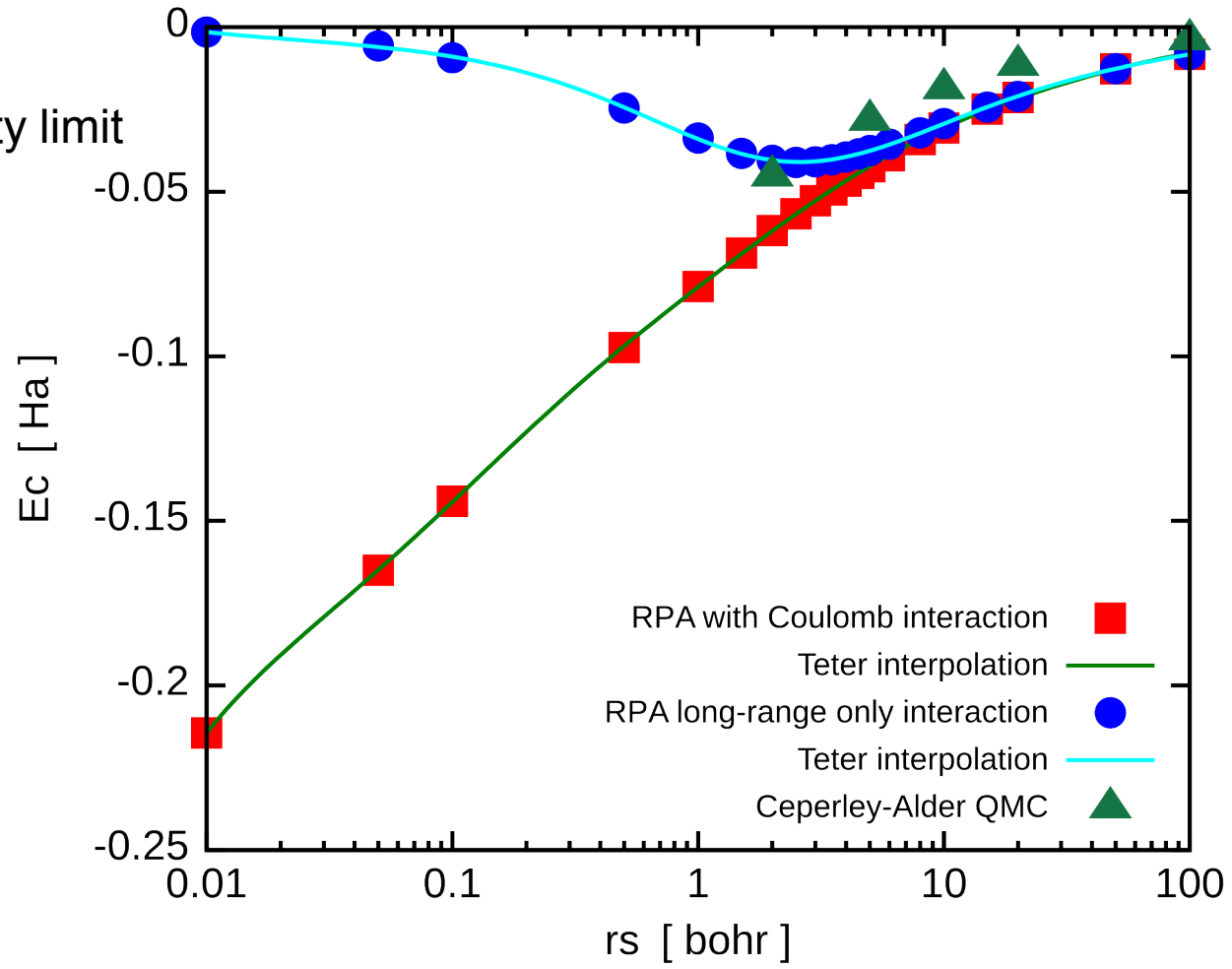
$$\mathrm{FT}\left\{\frac{\mathrm{erf}(r/rc)}{r}\right\} = \frac{4\pi}{\boldsymbol{G}^2} \times e^{-\frac{1}{4}r_c^2\boldsymbol{G}^2}$$ ⟸ Attenuated Coulomb interaction

RPA for the long-range Coulomb interaction

Long-range only RPA calculation for jellium:

High density limit

Low density limit



Goedecker, Teter, Hutter parametrization:

$$\epsilon_{xc} = -\frac{a_0 + a_1 r_s + a_2 r_s^2 + a_3 r_s^3}{b_1 r_s + b_2 r_s^2 + b_3 r_s^3 + b_4 r_s^4}$$

Local density approximations to any quantity!

The usual LDA to the total correlation energy:

$$E_c^{\mathrm{LDA}} = \int d\boldsymbol{r}\ \ n(\boldsymbol{r})\epsilon_c^{\mathrm{LDA}}(n(\boldsymbol{r}))$$

from QMC for jellium

LDA approximation to the RPA energy:

$$E_c^{\text{local RPA}} = \int d\boldsymbol{r}\ \ n(\boldsymbol{r})\epsilon_c^{\mathrm{RPA}}(n(\boldsymbol{r}))$$

can be evaluated for jellium

LDA approximation to the long range RPA energy:

$$E_c^{\text{local LR-RPA}} = \int d\boldsymbol{r}\ \ n(\boldsymbol{r})\epsilon_c^{\mathrm{LR\text{-}RPA}}(n(\boldsymbol{r}))$$

Strategy

Replace the nasty behaved RPA

$$E^{\mathrm{RPA}} = E^{\mathrm{LDA}} - E_{xc}^{LDA} + E_{EXX} + E_c^{\mathrm{RPA}}$$

by the gentle terms

$$E^{\mathrm{RPA}} = E^{\mathrm{LDA}} - E_{xc}^{LDA} + E_{EXX} + E_c^{\mathrm{local\ RPA}} - E_c^{\mathrm{local\ LR\text{-}RPA}} + E_c^{\mathrm{LR\text{-}RPA}}$$

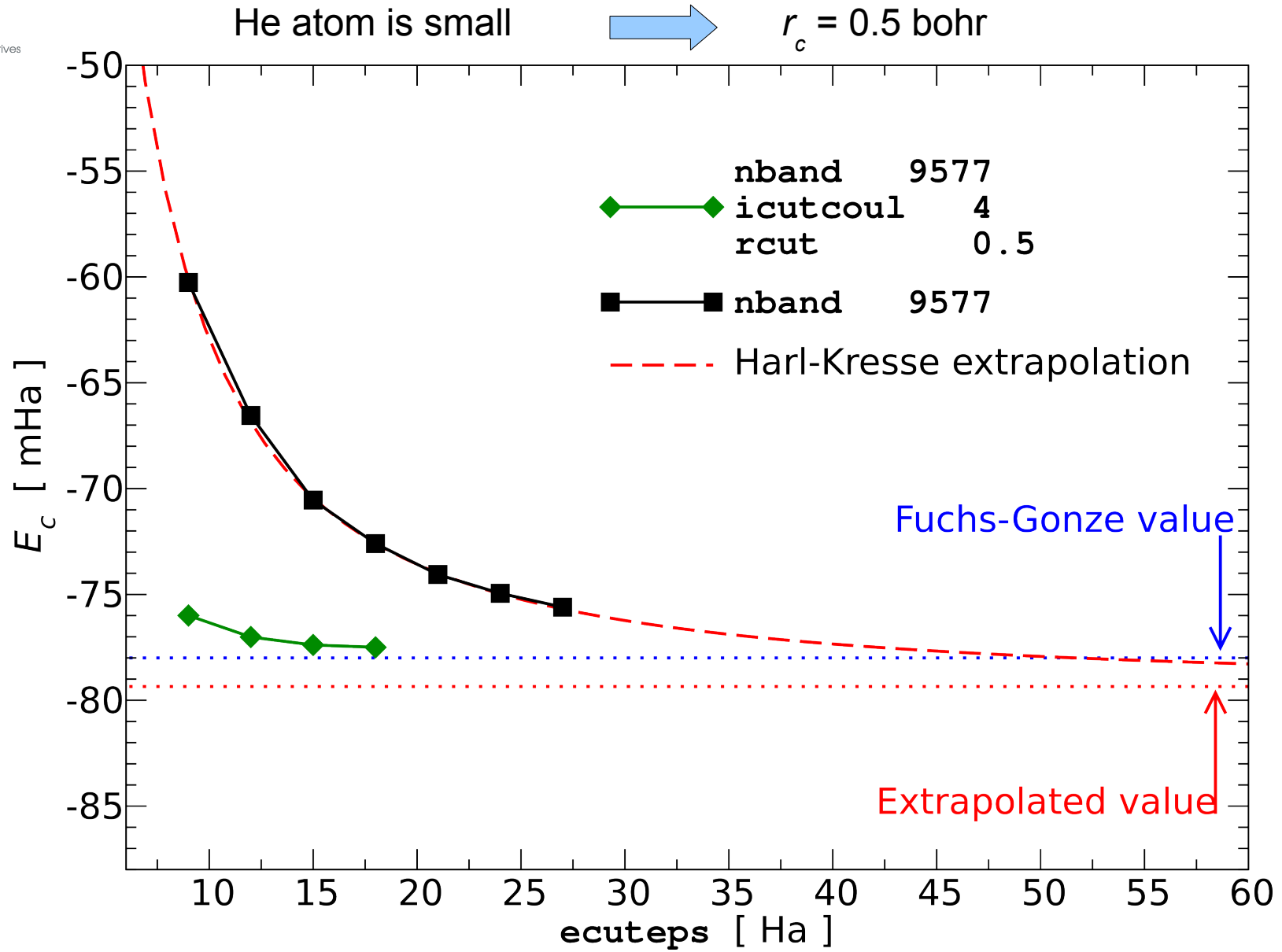
obtained from jellium

Truly calculated,
but converges fast

The scheme is governed by the cutoff radius r_c :

usual complete RPA functional $0 < r_c < +\infty$ usual LDA correlation

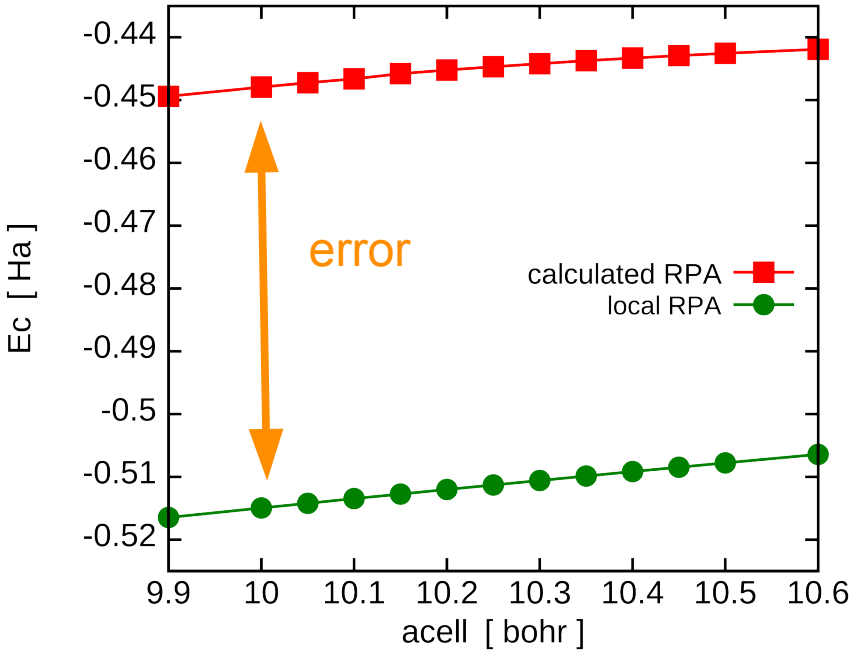
Helium convergence



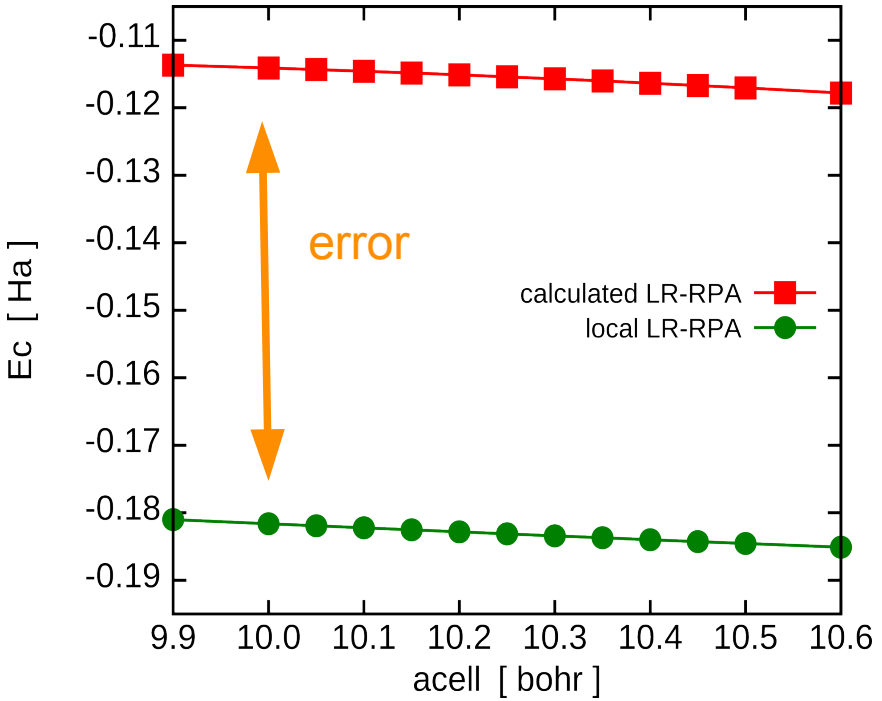
converges **very fast** to a constant value...

Test for bulk silicon with r_c = 2 bohr

Full RPA



Long-Range RPA



Almost all the error contained in the **local approximation** is contained in the **Long-Range** part!

Test for bulk silicon with r_c = 2 bohr

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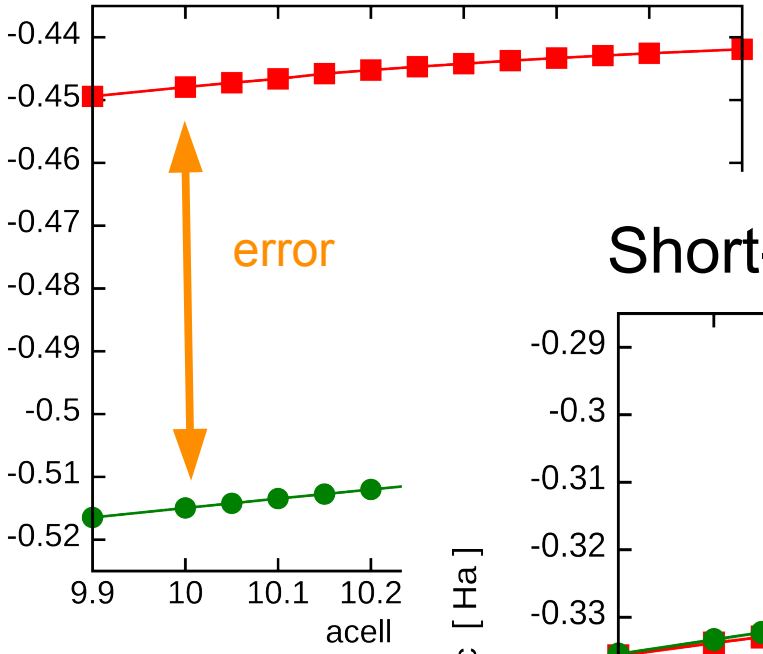
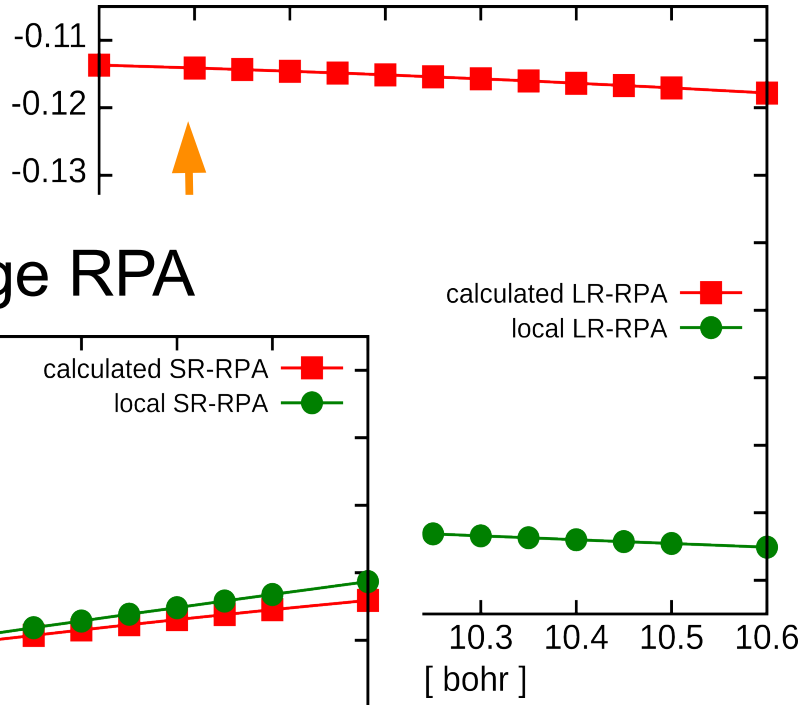
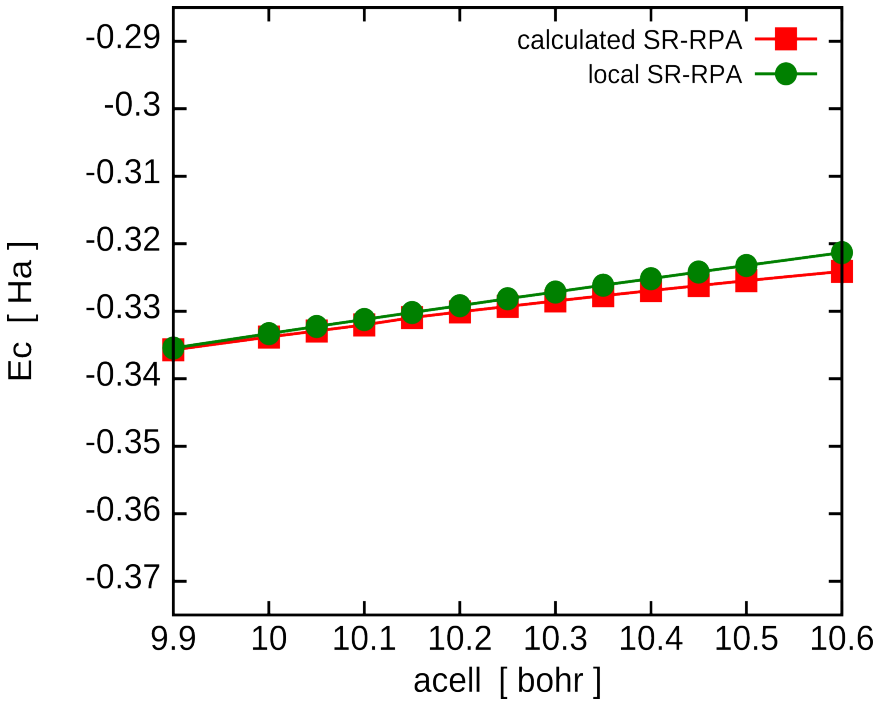
Full RPA



Long-Range RPA



Short-Range RPA



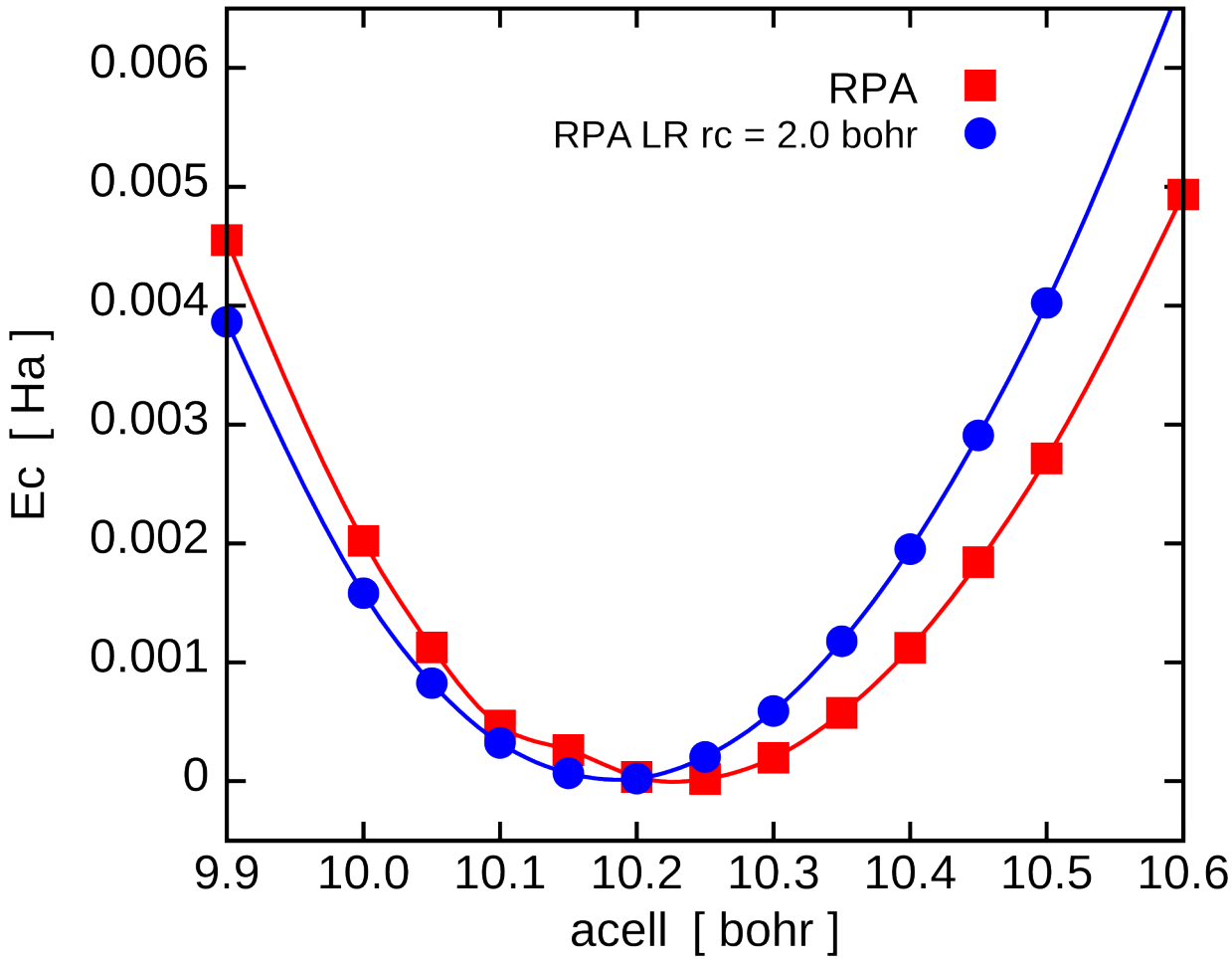
Almost all the

Long-Range

is contained in the

The local approximation works fine for the short range part

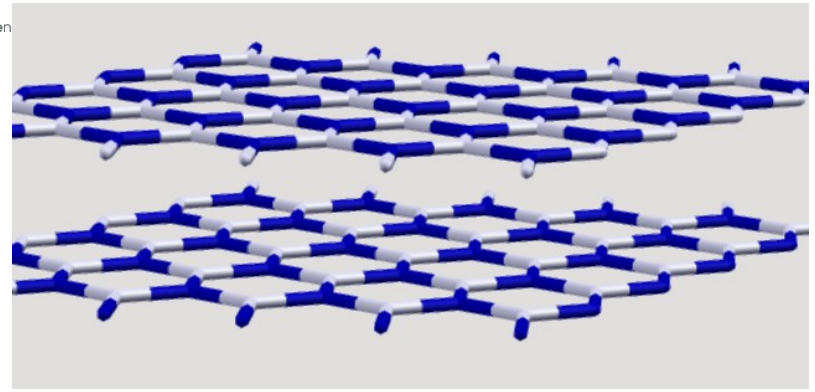
Lattice parameter of bulk silicon



A small discrepancy, however **a lot easier** to converge

ecuteps	**2.0 Ha**	instead of	**ecuteps**	**10.0 Ha**
nband	**100**	instead of	**nband**	**350**

h-BN interlayer distance



Interlayer distance

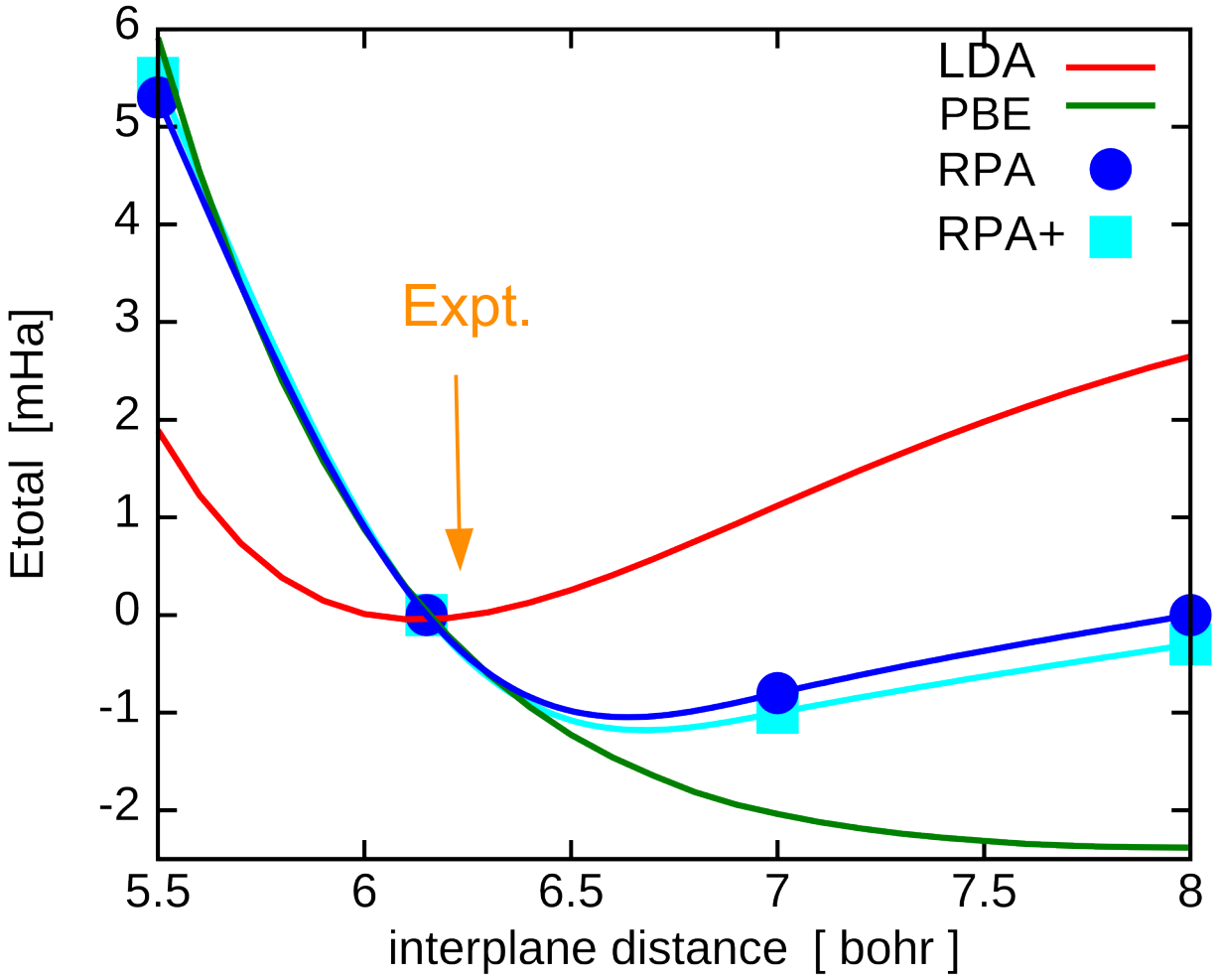
A van der Waals bonded system

Long-range only RPA

```
icutcoul      4
rcut          4.0   bohr
```

Wrong RPA in-plane interaction

Correct RPA plane-plane interaction



Summary / Perspertives

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The RPA functional with **k**-points has been implemented in ABINIT.

It re-uses the *GW* subroutines.
Only one subroutine added: `src/70_gw/calc_rpa_functional.F90`

The final RPA calculation is **parallelized over frequencies** (~ 6-10 freq).
Should be parallelized with scalapack...

The Exact-Exchange is **not easy** to calculate

- Slow **k**-points convergence (S. Lebègue [**PRL** 2010] reports 26x26x8 for graphite)
- Strong core/valence interaction:
  Use of Matteo's approach of frozen cores within the PAW spheres

Promising approach using **range-separation**:
the **short-range** is accounted with a local density approximation
the **long-range** is really calculated