# Going beyond Local Density and Gradient Corrected XC functionals in Quantum-ESPRESSO

Stefano de Gironcoli

SISSA and INFM DEMOCRITOS

# Jacob's laddder of Density Functional Theory

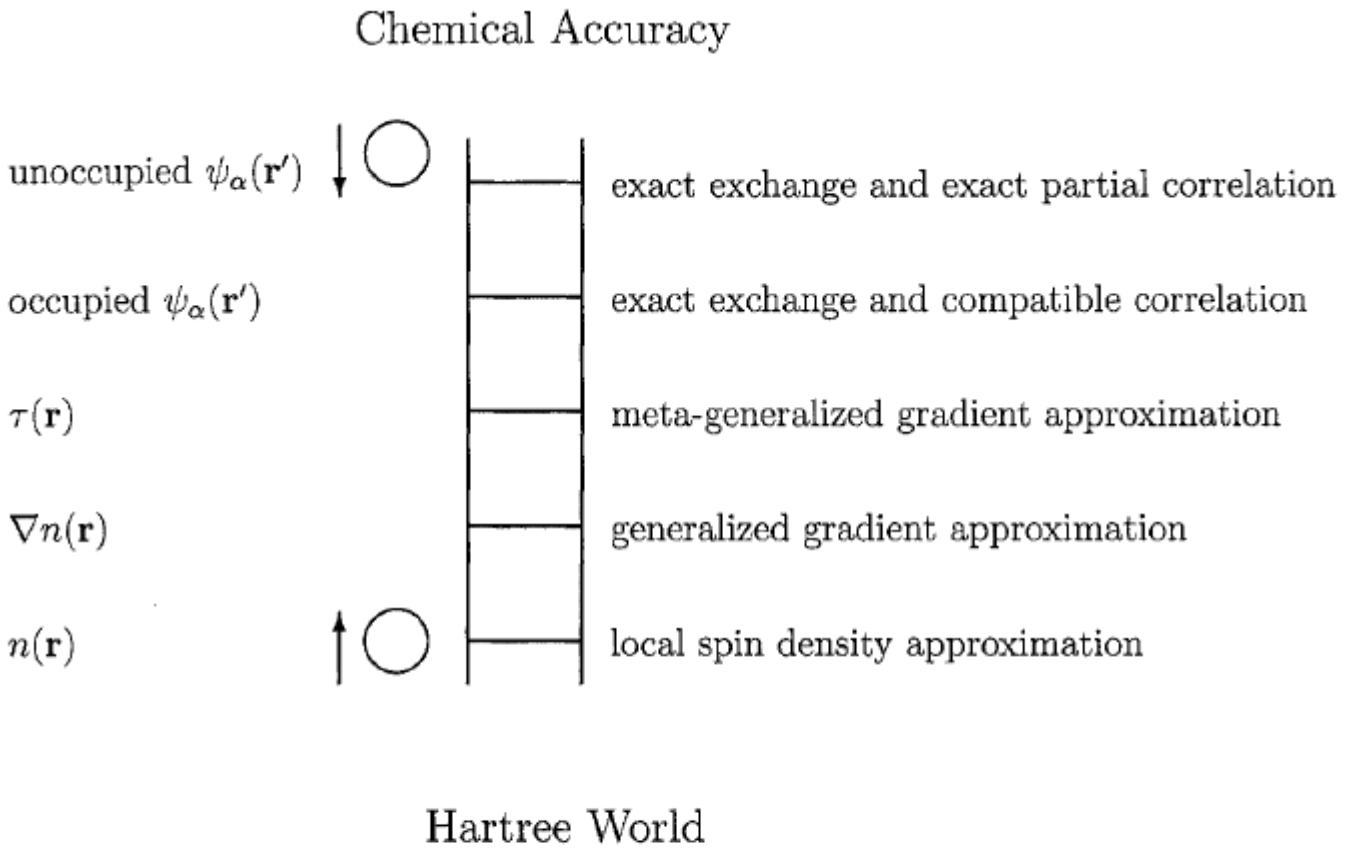



**FIGURE 1.** Jacob's ladder of density functional approximations. Any resemblance to the Tower of Babel is purely coincidental. Also shown are angels in the spherical approximation, ascending and descending. Users are free to choose the rungs appropriate to their accuracy requirements and computational resources. However, at present their safety can be guaranteed only on the two lowest rungs.

LDA and LSDA ✓

GGA : PW91, PBE, revPBE, RPBE, BLYP ✓

~~META-GGA: PKZB, TPSS,~~

~~SIC, DFT+U,~~ hybrids ✓

van der Waals functionals

...

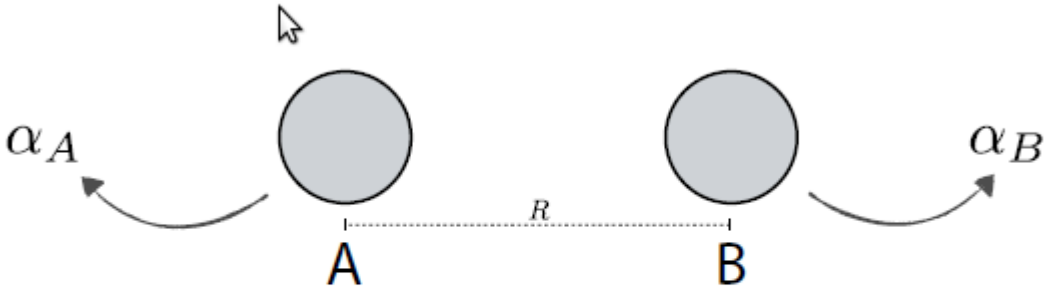
*exact DFT*

# van der Waals

van der Waals interaction is relatively weak but widespread in nature.
An important source of stability for molecular solids and physisorption of molecules on surfaces.

It is due to truly non-local correlation effects.
It is contained in the true XC functional but LDA/GGA/MetaGGA and Hybrids do not describe it properly.

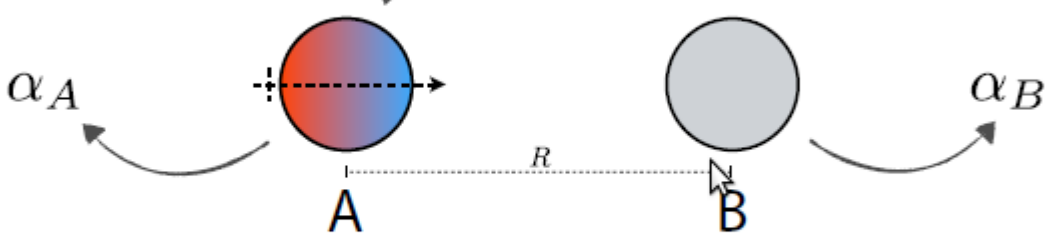
# vdW : non local correlation




Two neutral atoms separated by R much larger than the atomic size, a limit that ensure that the corresponding wavefunctions are not overlapping

# vdW : non local correlation

Instantaneous dipole $d_A$ generated from charge fluctuations.

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Induced dipole

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

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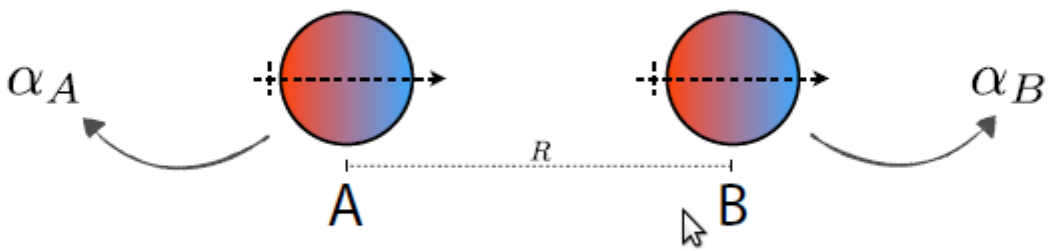



Two neutral atoms separated by R much larger than the atomic size, a limit that ensure that the corresponding wavefunctions are not overlapping

$$E = \underbrace{(K\hbar\omega_0\alpha_A\alpha_B)}_{C_6^{AB}} \, R^{-6}$$

# LDA/GGA
# Semilocal Density Functionals

DFT within LDA and GGA functionals has been extremely successful in predicting structural, elastic, vibrational properties of materials bound by metallic, ionic, covalent bonds.

These functionals focus on the properties of the electron gas around a single point in space.

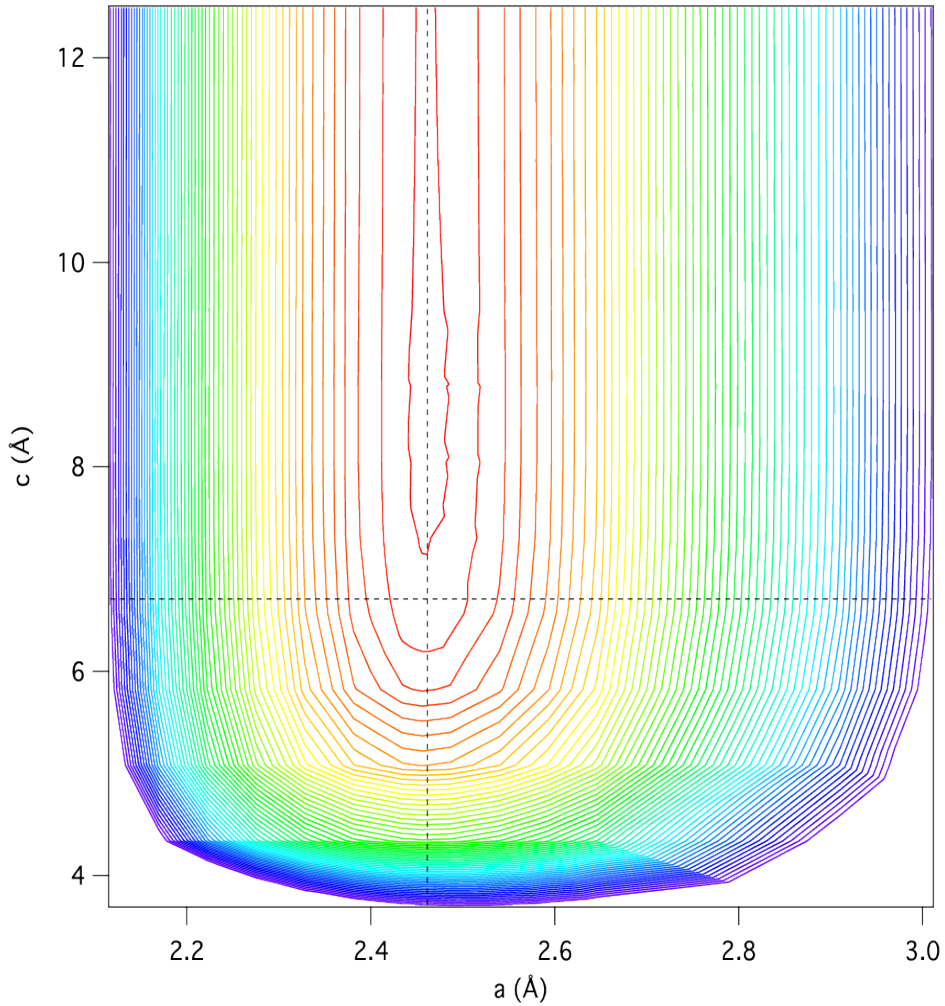
$$E_{xc}^{LDA} = \int n(r)\epsilon_{xc}^{hom}(n(r))dr \qquad E_{xc}^{GGA} = \int n(r)F_{xc}^{GGA}(n(r)), |\nabla n(r)|)dr$$

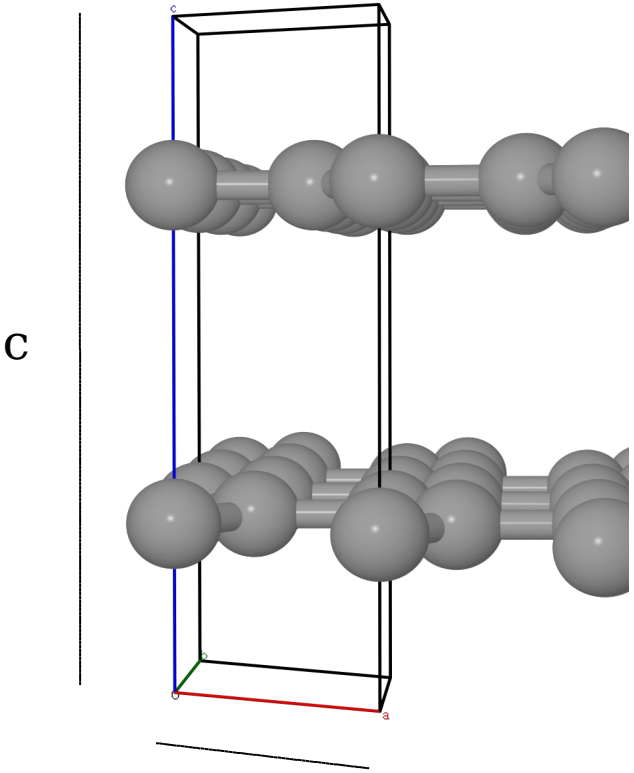
As such they do not describe vdW interaction.

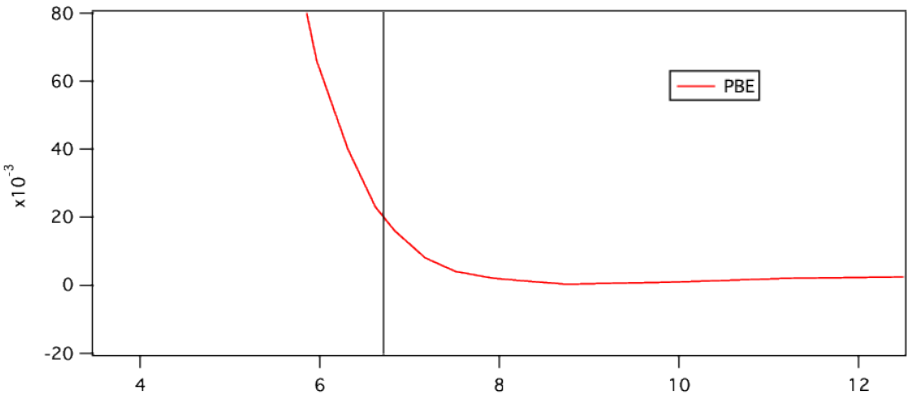
The same is true for Hybrids, DFT+U and SIC etc...

# Failure of semilocal functionals

Graphite



# How to deal with van der Waals ?

- neglect it

- add an empirical damped dispersion correction
  Grimme, Tatckenko-Scheffler

- develop a truly non local XC functional
  Vdw-DF, vdw-DF2, VV09, VV10

- RPA and beyond RPA

# How to deal with van der Waals ?

- add an empirical damped dispersion correction

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

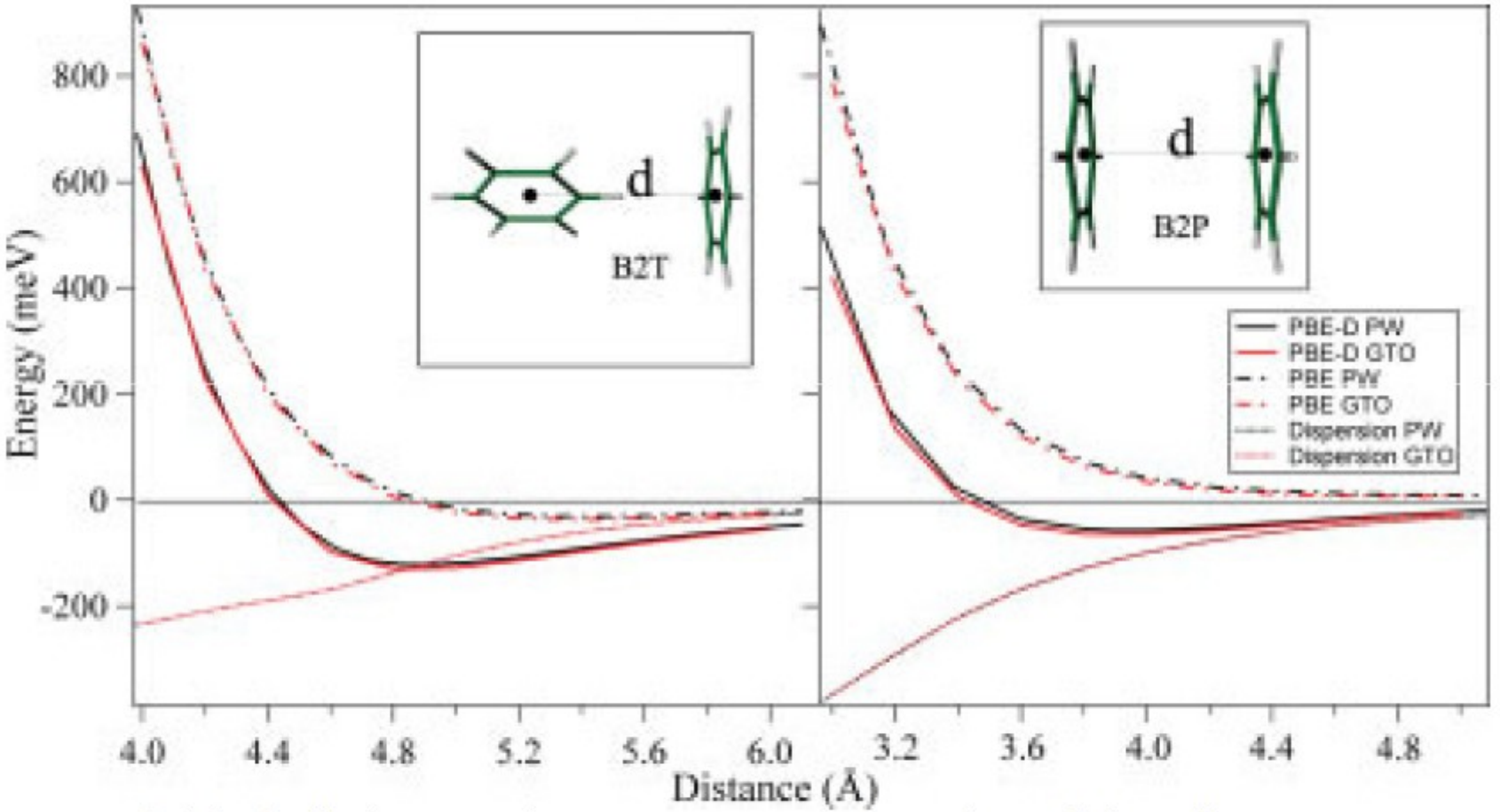
- $E_{DFT\text{-}D} = E_{DFT} + E_{disp}$

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

Here, $N_{at}$ *is the number of atoms in the system,* $C^{ij}_6$ denotes the dispersion coefficient for atom pair *ij,* $s_6$ *is a global scaling factor* that only depends on the DF used, and $R_{ij}$ *is an interatomic distance.* In order to avoid near-singularities for small *R, a damping function* $f_{dmp}$ *must be used*

$$C_6^{ij} = \sqrt{C_6^i C_6^j}$$

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




$C_6H_6$-$C_6H_6$ interaction energy as a function of the distance between centers of mass: red (black) lines refer to Gaussian (PWscf) calculations. GTO results were not corrected for BSSE.

Barone et al. J. Comput. Chem. 30, 934-939 (2009)

# Density Functional Theory

$$E(\{R\}) = T_s[n(r)] + \frac{1}{2}\int \frac{n(r)n(r')}{|r-r'|}drdr' + E_{xc}[n(r)] + \int V_{ext}(r)n(r)dr + E_N(\{R\})$$

$$n(r) = 2\sum_{i=1}^{N/2} |\phi_n(r)|^2$$

KS self consistent eqs.

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{KS}(r)\right]\phi_n(r) = \varepsilon_{nn}(r)$$

$$V_{KS}(r) = V_{ext}(r) + \int \frac{n(r')}{|r-r'|}dr' + v_{xc}(r)$$

$$v_{xc}(r) = \frac{\delta E_{xc}}{\delta n(r)}$$

$$E_{xc}^{LDA} = \int n(r)\epsilon_{xc}^{hom}(n(r))dr$$

$$E_{xc}^{GGA} = \int n(r)F_{xc}^{GGA}(n(r)), |\nabla n(r)|)dr$$

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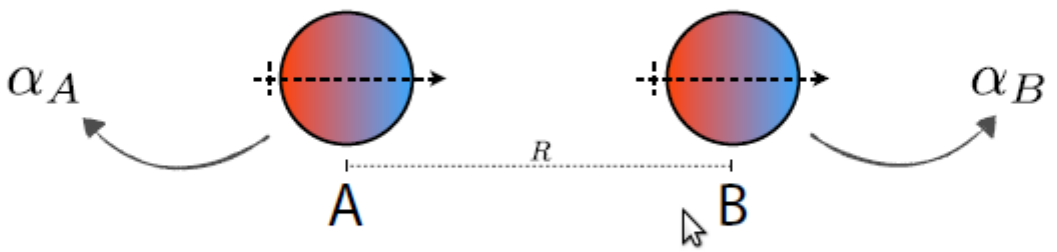


Two neutral atoms separated by R much larger than the atomic size, a limit that ensure that the corresponding wavefunctions are not overlapping

$$E = \underbrace{(K\hbar\omega_0\alpha_A\alpha_B)}_{C_6^{AB}} \, R^{-6}$$

# Truly non-local functionals

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

$$\overline{\alpha}(iu) = \int \alpha(r,iu)$$

$$u \longrightarrow \infty : \overline{\alpha}(iu) = Ne^2/mu^2$$

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

$$E^{(2)} = -\frac{3\hbar e^4}{2m^2}\int dr \int dr' \frac{n(r)n(r')}{\omega_0(r)\omega_0(r')[\omega_0(r)+\omega_)(r')]|r-r'|^6}$$

$$E_c = E_c^0 + E_c^{nl}$$

$$E_c^{nl} = \frac{\hbar}{2}\int dr \int dr' \;\; n(r)\Phi(r,r')n(r')$$

**6 dim integral !**

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

# How to deal with van der Waals in DFT?

- develop a truly non local XC functional

$$E_c^{nl} = \frac{1}{2}\int d^3r\, d^3r'\, n(\vec{r})\phi(\vec{r},\vec{r}\,')n(\vec{r}\,'),$$

Phi(n(r),grad n, n(r'), grad n', |r-r'|)

A number of functionals have been proposed

-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**, 244103 (2010)

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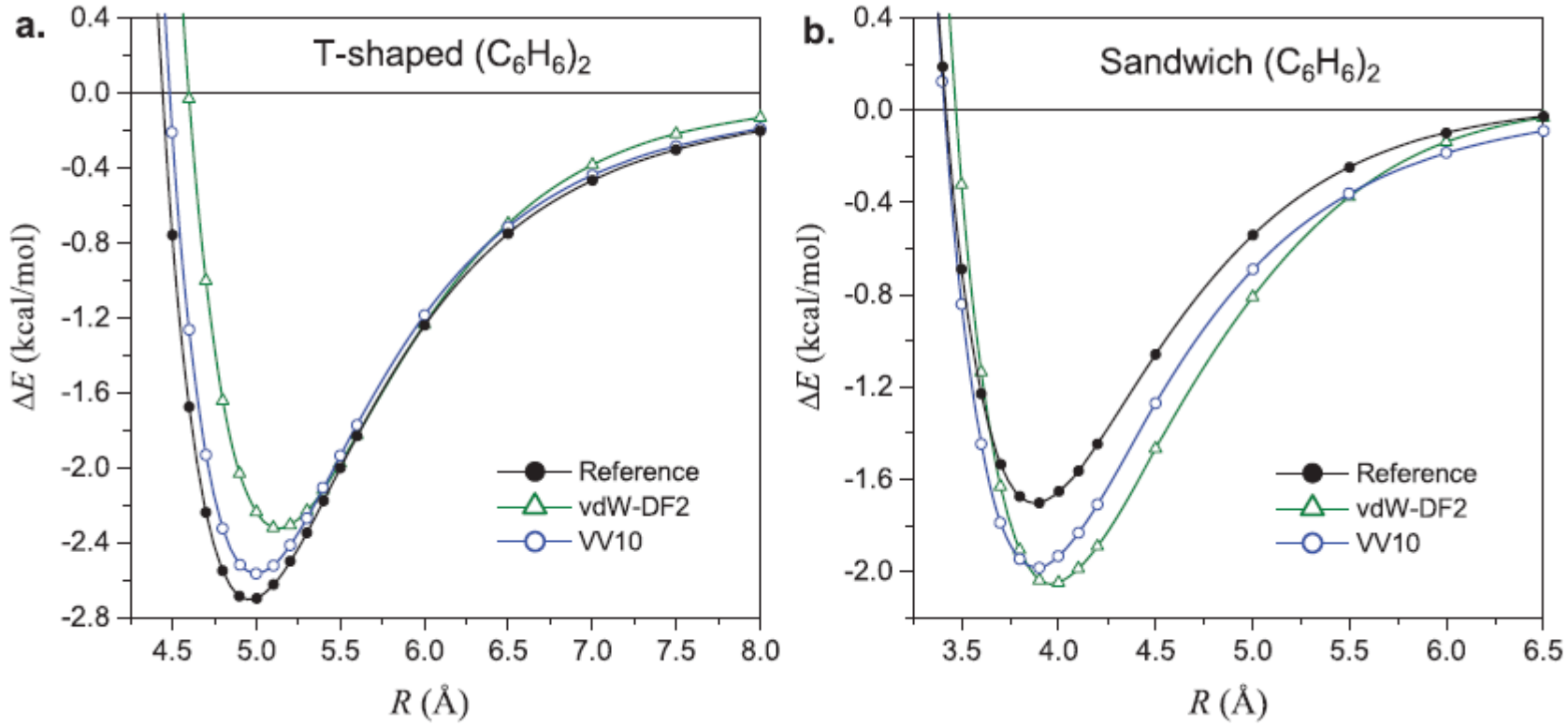


How to compute efficiently van der Waals functionals ?

- for

$$E_c^{nl} = \frac{1}{2} \int d^3r \, d^3r' \, n(\vec{r}) \phi(\vec{r}, \vec{r}\,') n(\vec{r}\,'),$$

Phi( n(r), grad n, n(r'), grad n', |r-r'| )

If the kernel depends separately on densities and gradients in the two points the integral is a 6-dimesional object very expensive to calculate

How to compute efficiently van der Waals functionals ?

- for

$$E_c^{nl} = \frac{1}{2}\int d^3r\, d^3r'\, n(\vec{r})\phi(\vec{r},\vec{r}\,')n(\vec{r}\,'),$$

Phi( n(r), grad n, n(r'), grad n', |r-r'| )

If the kernel does not depend separately on the densities and gradient in the two points but only through a combined function q(n(r),grad n) (true for vDW-DF/vdW-dF2)

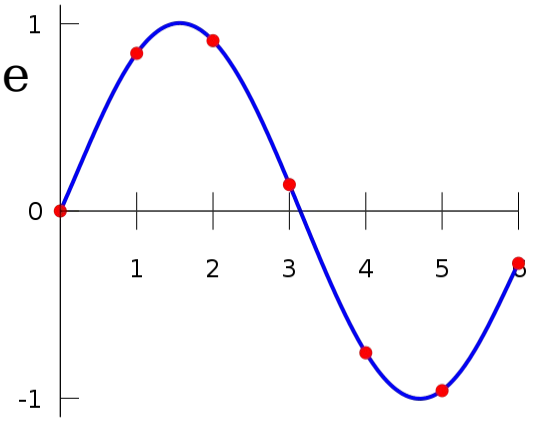
Phi( q(n(r),grad n), q(n(r'), grad n'), |r-r'|)

one can precalculate the value of the kernel for a number of Points in a 2D q-grid and interpolate in between

G. Roman-Perez & J.M. Soler, *PRL 103, 096102 (2009)*

# an efficient integration

Roman-Perez & Soler interpolation scheme
If it's possible to express the complex density dependence on r, r' via a single q(r) ( and q(r') ) function then ...




$$\Phi(q_1, q_2, r_{12}) \approx \sum_{\alpha,\beta} \Phi(q_\alpha, q_\beta, r_{12}) P_\alpha(q_1) P_\beta(q_2)$$

$$E_c^{nl} = \frac{1}{2} \sum_{\alpha,\beta} \int \int \Theta_\alpha(r) \Phi(q_\alpha, q_\beta, |r - r'|) \Theta_\beta(r') \, dr dr'$$

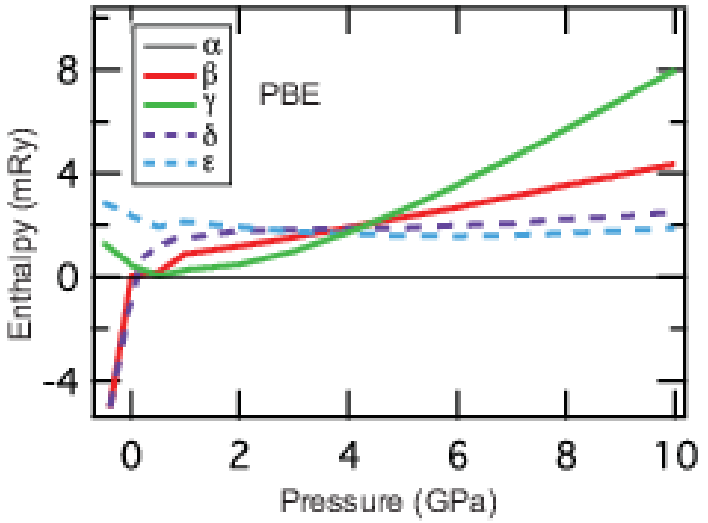
$$= \frac{\Omega}{2} \sum_{\alpha,\beta} \sum_{G} \Theta_\alpha^*(G) \Phi(q_\alpha, q_\beta, |G|) \Theta_\beta(G)$$

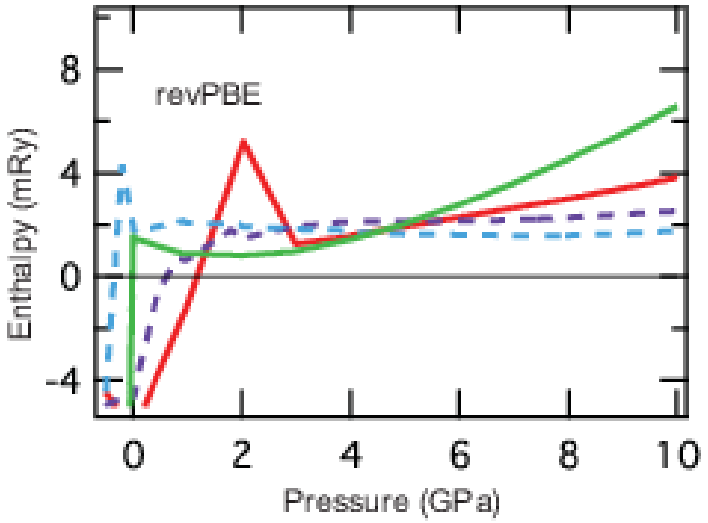
$$\Theta_\alpha(r) = n(r) P_\alpha(q(r))$$

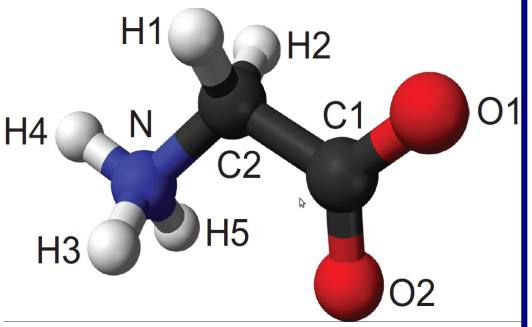
The vdW energy can be expressed as a sum of a number of convolutions
i.e. simple 3d integrals

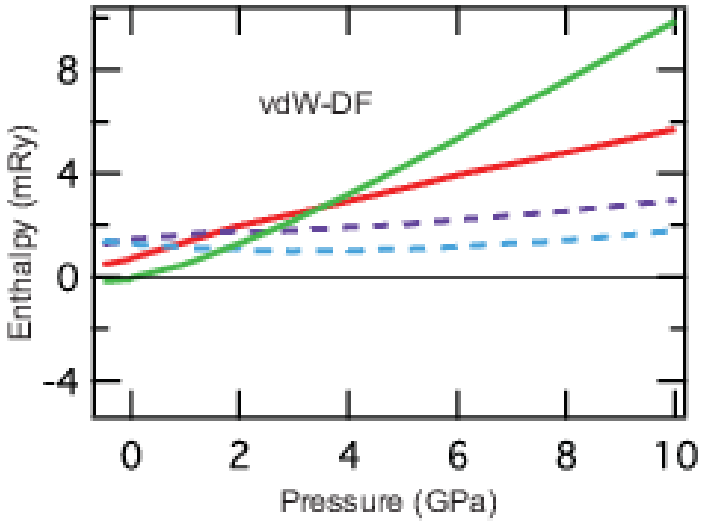
The grid dimension determines the accuracy: 20 x 20 is ok

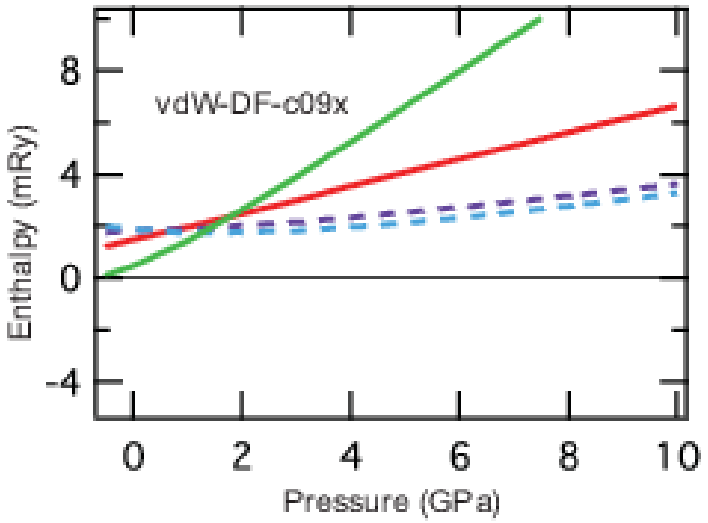
# Glycine polymorphes



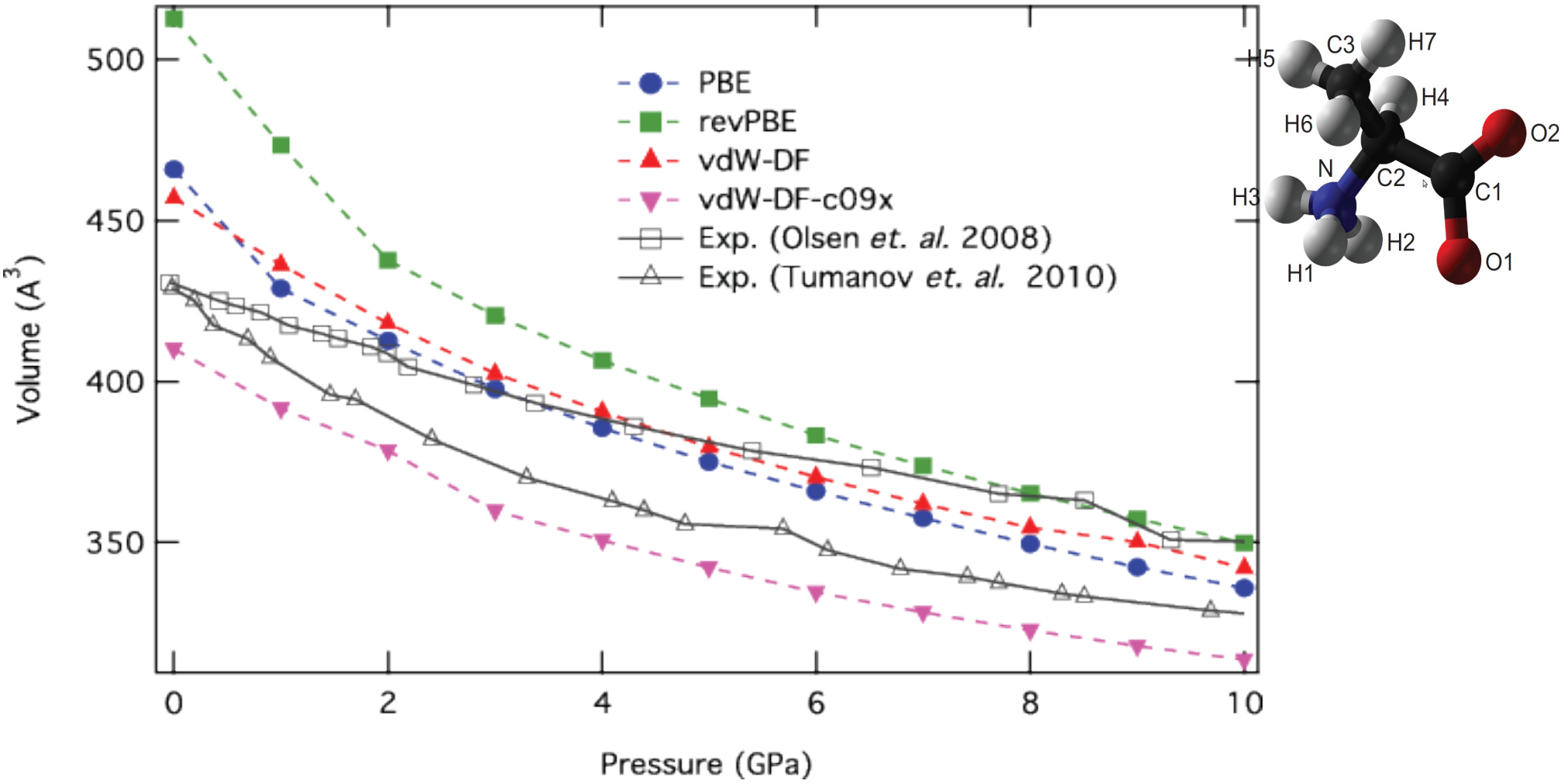




$$\gamma < \alpha < \beta < \ldots$$

# Alanine evolution with P



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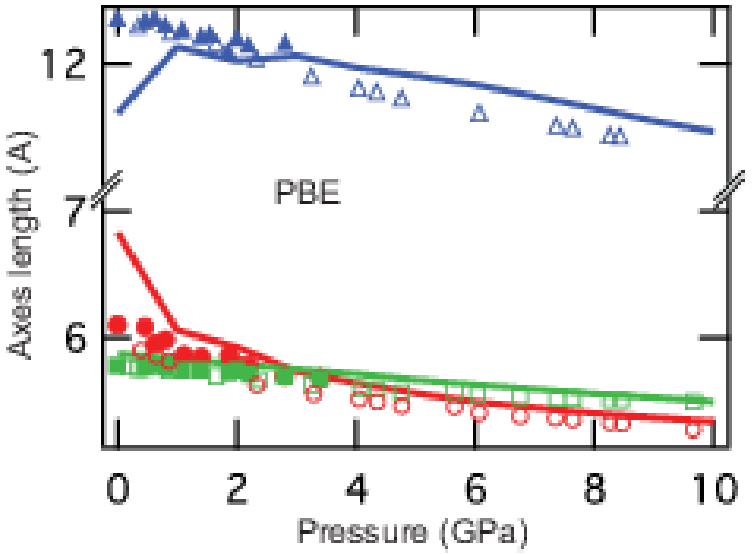


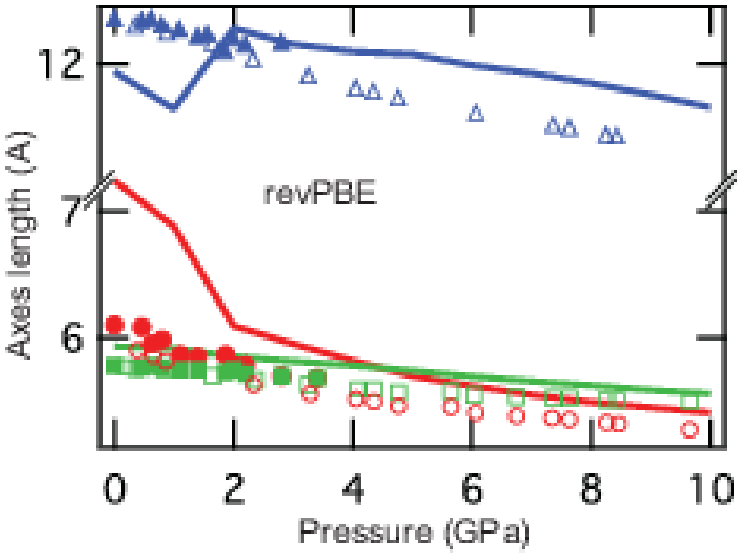


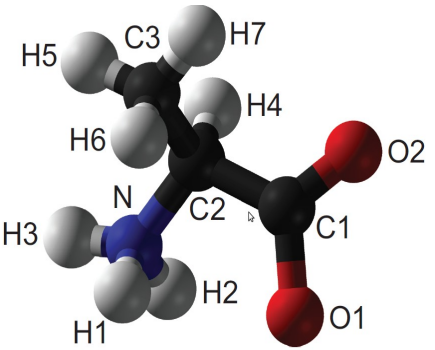


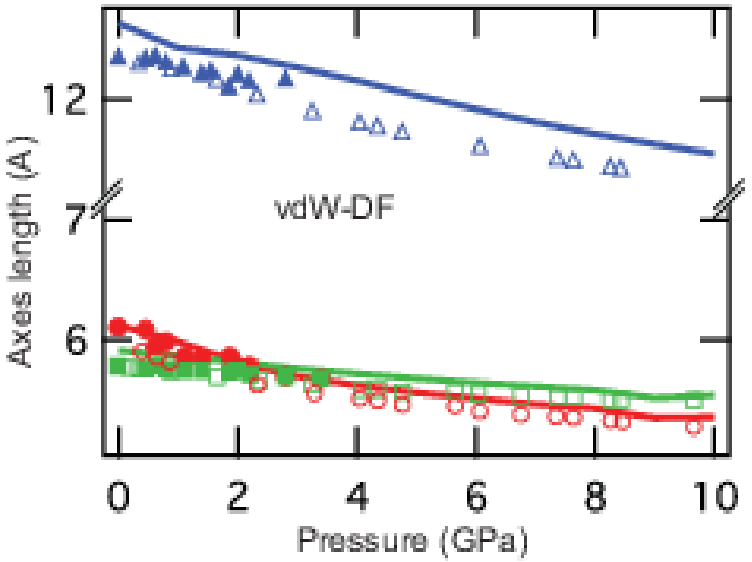


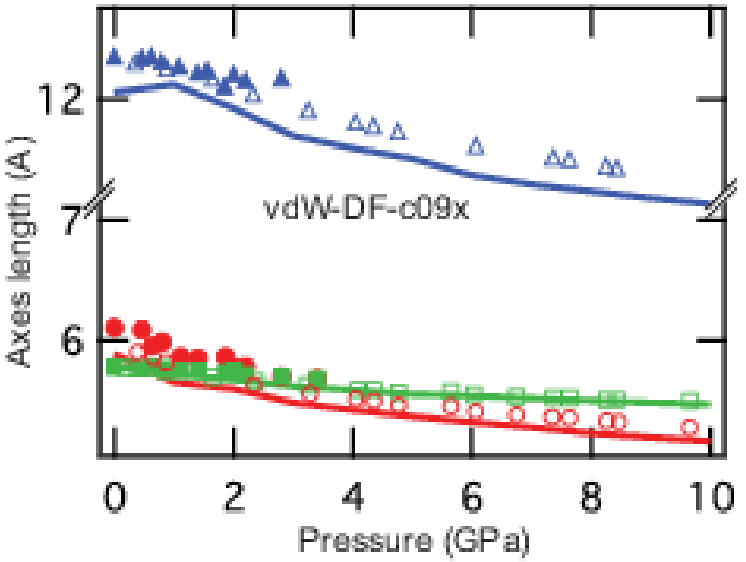

# Several Non-Local Functionals

| | $\omega_0$ in $E_c^{(2)}$ | | | $E_{xc}^{LDA/GGA}$ | $C_6$ error |
|---|---|---|---|---|---|
| vdWDF | $\frac{9\hbar}{8\pi m}\left[k_F(1+\mu s^2)\frac{4\pi}{3e^2}\varepsilon_c^{LDA}\right]$ | with | $\mu = 0.09434$ | SLA+PW+RPBE- | 18.5% |
| vdWDF2 | $\frac{9\hbar}{8\pi m}\left[k_F(1+\mu s^2)\frac{4\pi}{3e^2}\varepsilon_c^{LDA}\right]$ | with | $\mu = 0.20963$ | SLA+PW+RPW86- | 60.9% |
| vdWDF-09 | $\frac{\hbar}{3m}k_F^2(1+\mu s^2)$ | 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+PW+RPW86+PBC | 10.7% |

vdWDF – functional can exploit the Roman-Perez Soler interpolation
Vv10 – functional does not fulfill the needed conditions

# VV10 functional

$$\Phi^{VV10}(r,r') = -\frac{3e^4}{2m^2}\frac{1}{gg'(g+g')}$$

$$g = \omega_0(r)R^2 + k(r) \qquad k(r) = 3\pi b\left(\frac{n}{9\pi}\right)^{\frac{1}{6}}$$

$$\omega_0 = \sqrt{\omega_g^2 + \frac{\omega_p^2}{3}}, \quad \omega_g^2 = C\left(\frac{\hbar^2}{m^2}\right)\left|\frac{\nabla n}{n}\right|^4, \quad \omega_p^2 = \frac{4\pi n e^2}{m}$$

The original espression cannot be separared in a function of two auxiliary functions q(n,\grad n)

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reordering the terms...

$$z(r) = \frac{\omega_0(r)}{k(r)}R^2 + 1$$

$$\Phi^{VV10}(r,r') = -\frac{3e^4}{2m^2}\frac{1}{k^{3/2}k'^{3/2}}\frac{1}{zz'\left(\sqrt{\frac{k}{k'}}z + \sqrt{\frac{k'}{k}}z'\right)}$$

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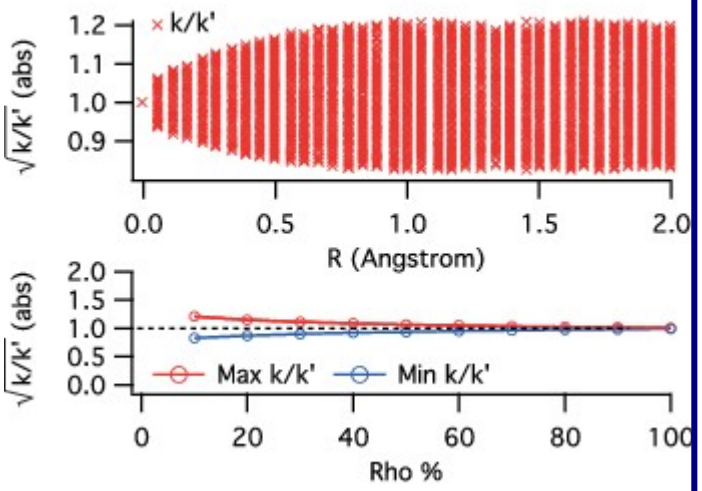

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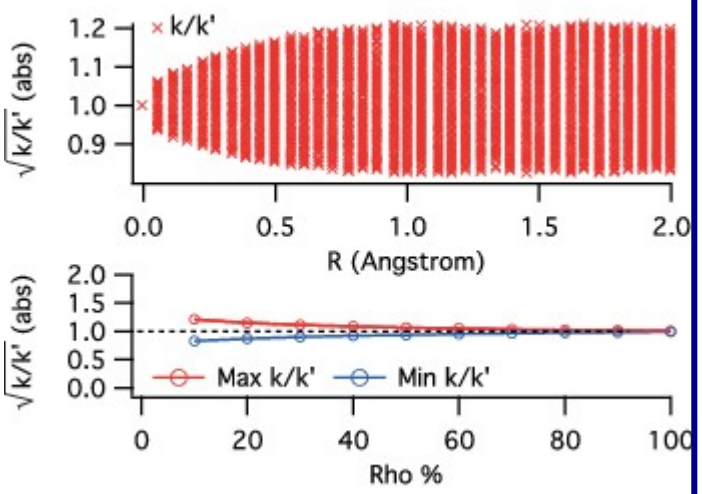
setting $\sqrt{\frac{k}{k'}} = 1$ and $q(r) = \omega_0(n(r), \nabla n(r))/k(n(r))$



# rVV10 functional

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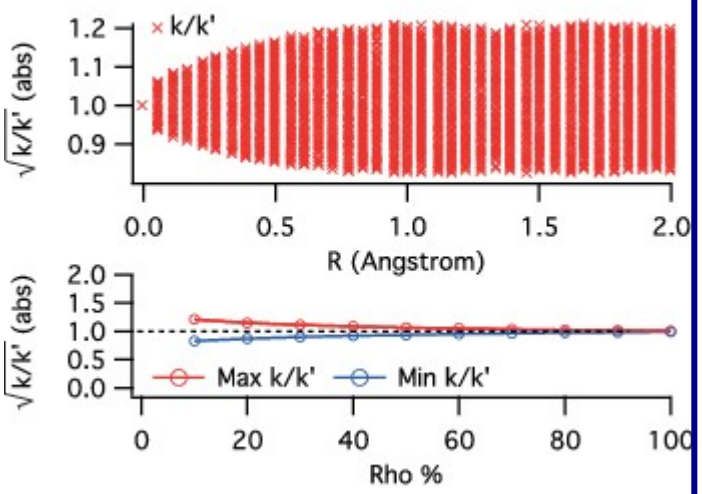
$$z(r) = \frac{\omega_0(r)}{k(r)}R^2 + 1$$

$$\Phi^{VV10}(r,r') = -\frac{3e^4}{2m^2}\frac{1}{k^{3/2}k'^{3/2}}\frac{1}{zz'\left(\sqrt{\frac{k}{k'}}z + \sqrt{\frac{k'}{k}}z'\right)}$$




setting $\sqrt{\frac{k}{k'}} = 1$ and $q(r) = \omega_0(n(r), \nabla n(r))/k(n(r))$

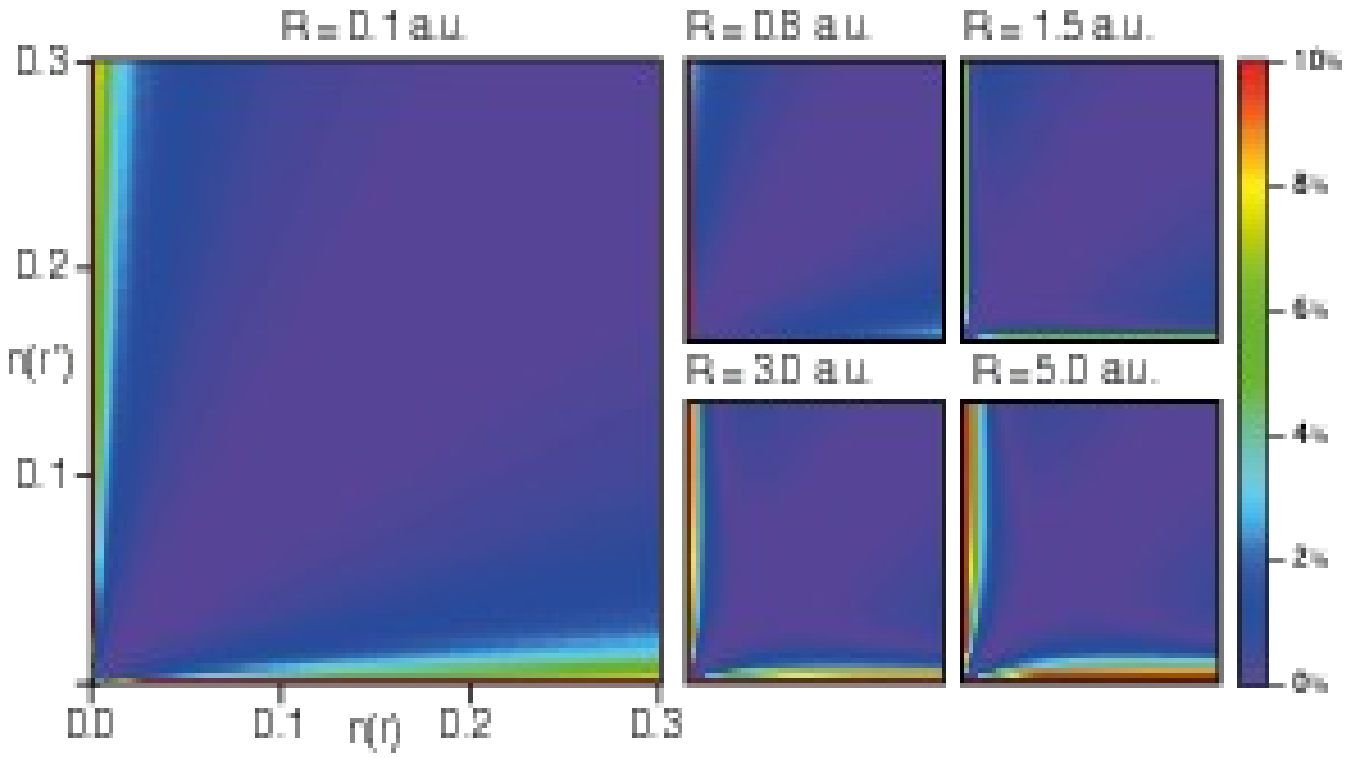
$$\Phi^{rVV10}(r,r') = -\frac{3e^4}{2m^2}\frac{1}{k^{3/2}k'^{3/2}}\frac{1}{(qR^2+1)(q'R^2+1)(qR^2+q'R^2+2)}$$

Separable !

Sabatini, Gorni & de Gironcoli, *PRB 87, 041108(R) (2013)*

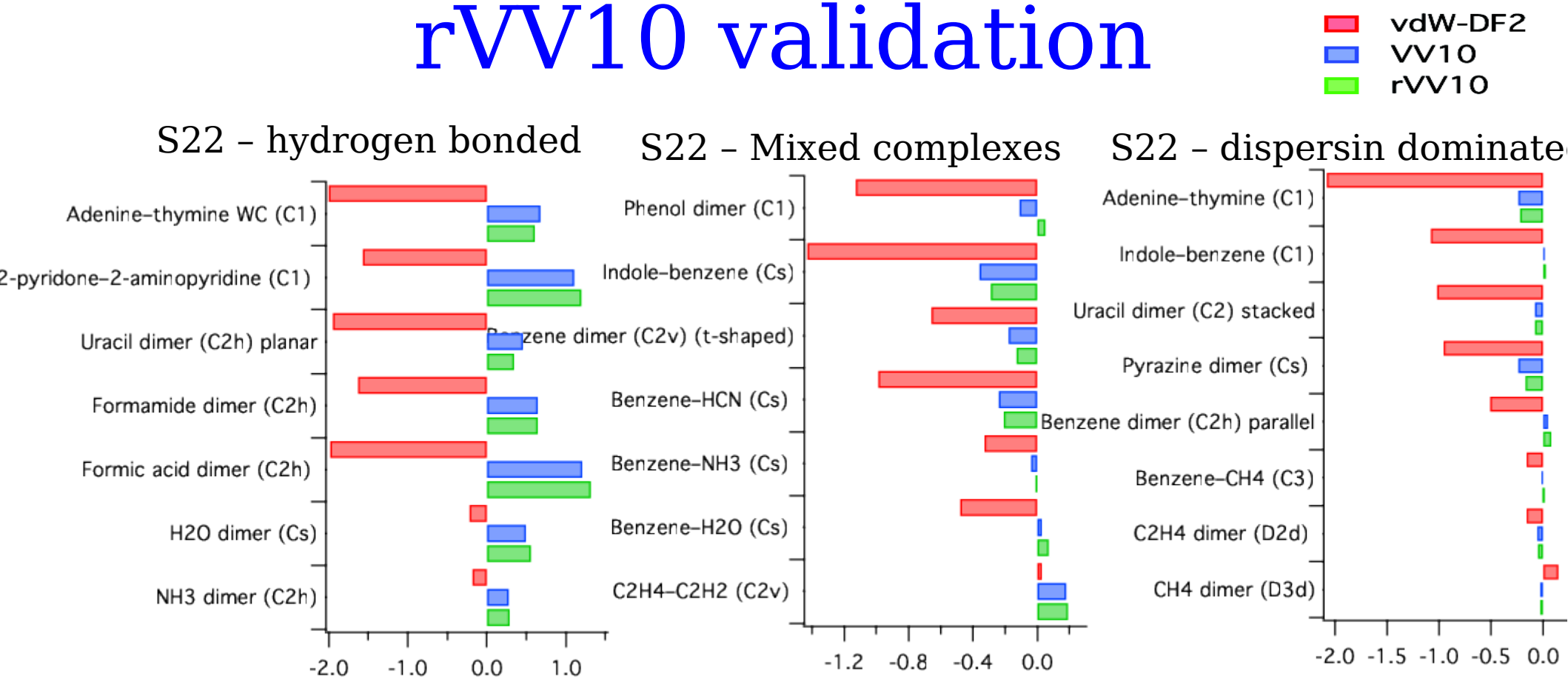
# VV10 vs rVV10

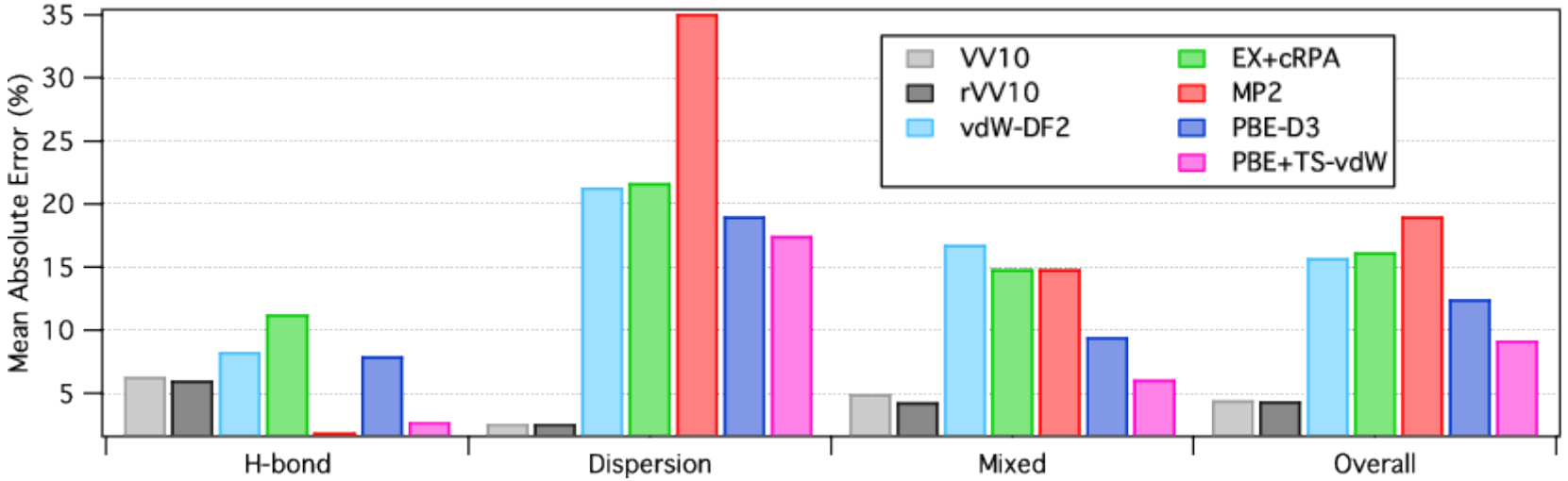
$$\Delta\Phi^{VV10} = \Phi^{VV10}(r, r') - \Phi^{rVV10}(r, r')$$




The error in the kernel is small except when the density itself is very small !

# rVV10 validation

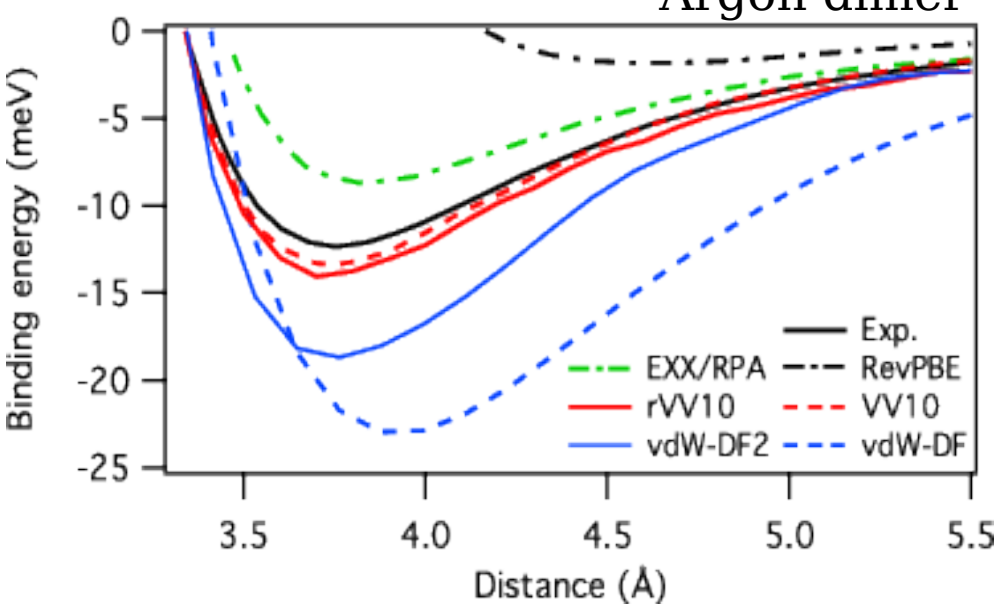


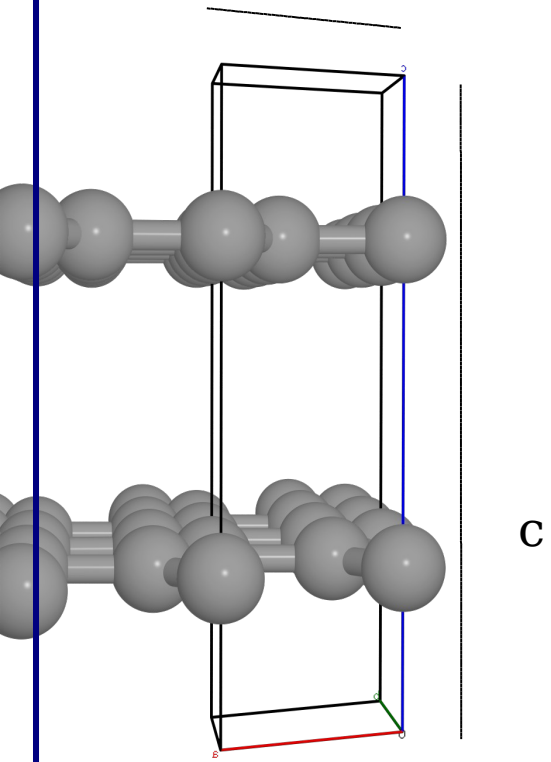



# rVV10 applications

Noble gas dimer are classical examples of dispersion dominated systems where the quality of different functionals can be explored.

Argon dimer

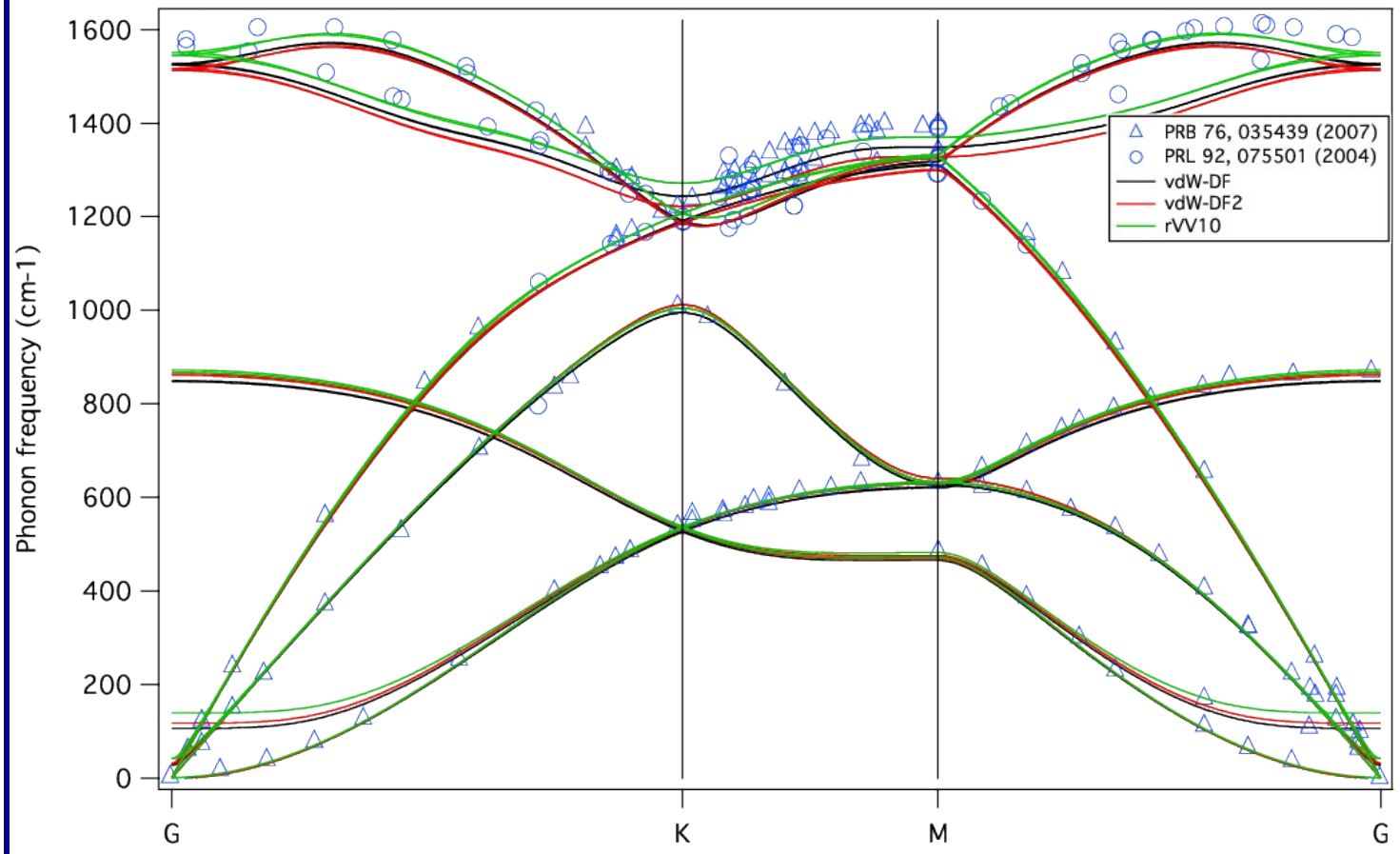


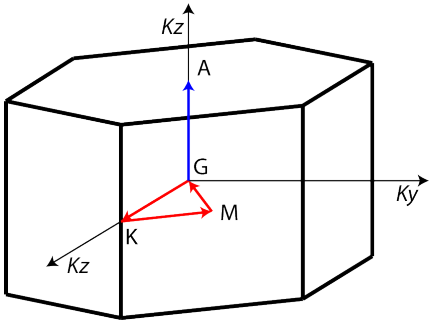




Graphite cel parameters (A)

| | a | c |
|---|---|---|
| vdW-DF | 2.48 | 7.19 |
| vdW-DF2 | 2.47 | 7.06 |
| rVV10 | 2.46 | 6.72 |
| exp | 2.46 | 6.71 |

# Phonons in Graphite



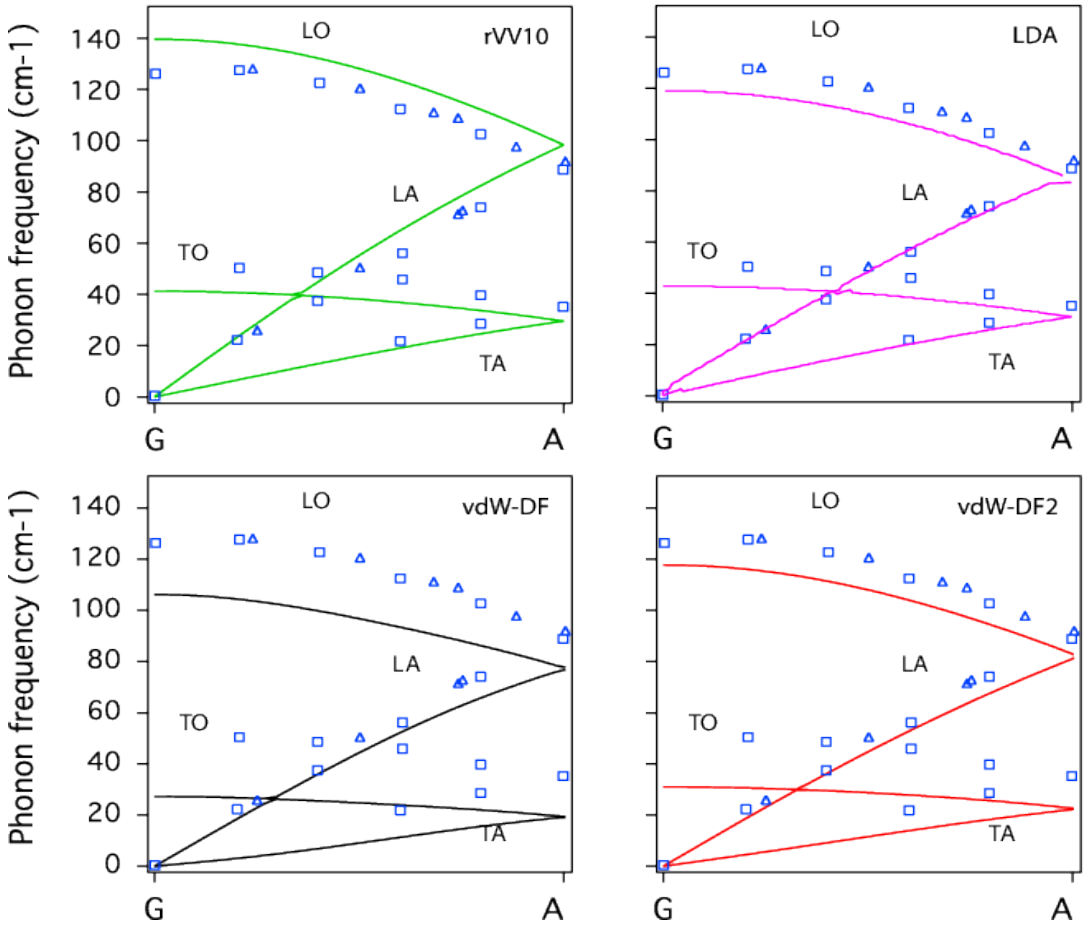



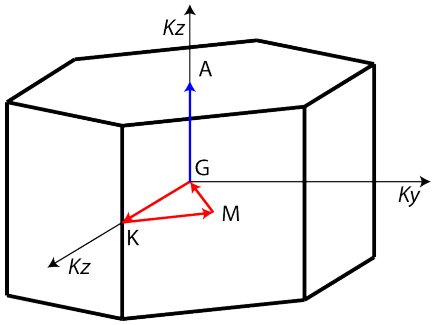

Stiff intralayer modes

| | LDA | vdW-DF | vdW-DF2 | rVV10 |
|---|---|---|---|---|
| MAE (cm-1) | 39.86 | 24.57 | 28.29 | 18.29 |
| MARE (%) | 3.21 | 1.85 | 2.04 | 1.36 |

Comparison of DFPT results at high symmetry points

# Phonons in Graphite




Soft interlayer modes

| | LDA | vdW-DF | vdW-DF2 | rVV10 |
|---|---|---|---|---|
| MAE (cm-1) | 5.50 | 13.50 | 10.00 | 7.50 |
| MARE (%) | 10.51 | 28.17 | 22.50 | 13.63 |

LDA and LSDA ✓

GGA : PW91, PBE, revPBE, RPBE, BLYP ✓

~~META-GGA: PKZB, TPSS,~~

~~SIC, DFT+U,~~ hybrids ✓

van der Waals functionals ✓

...

*exact DFT*