EXC of DFT

Scuola Internazionale Superiore di Studi Avanzati

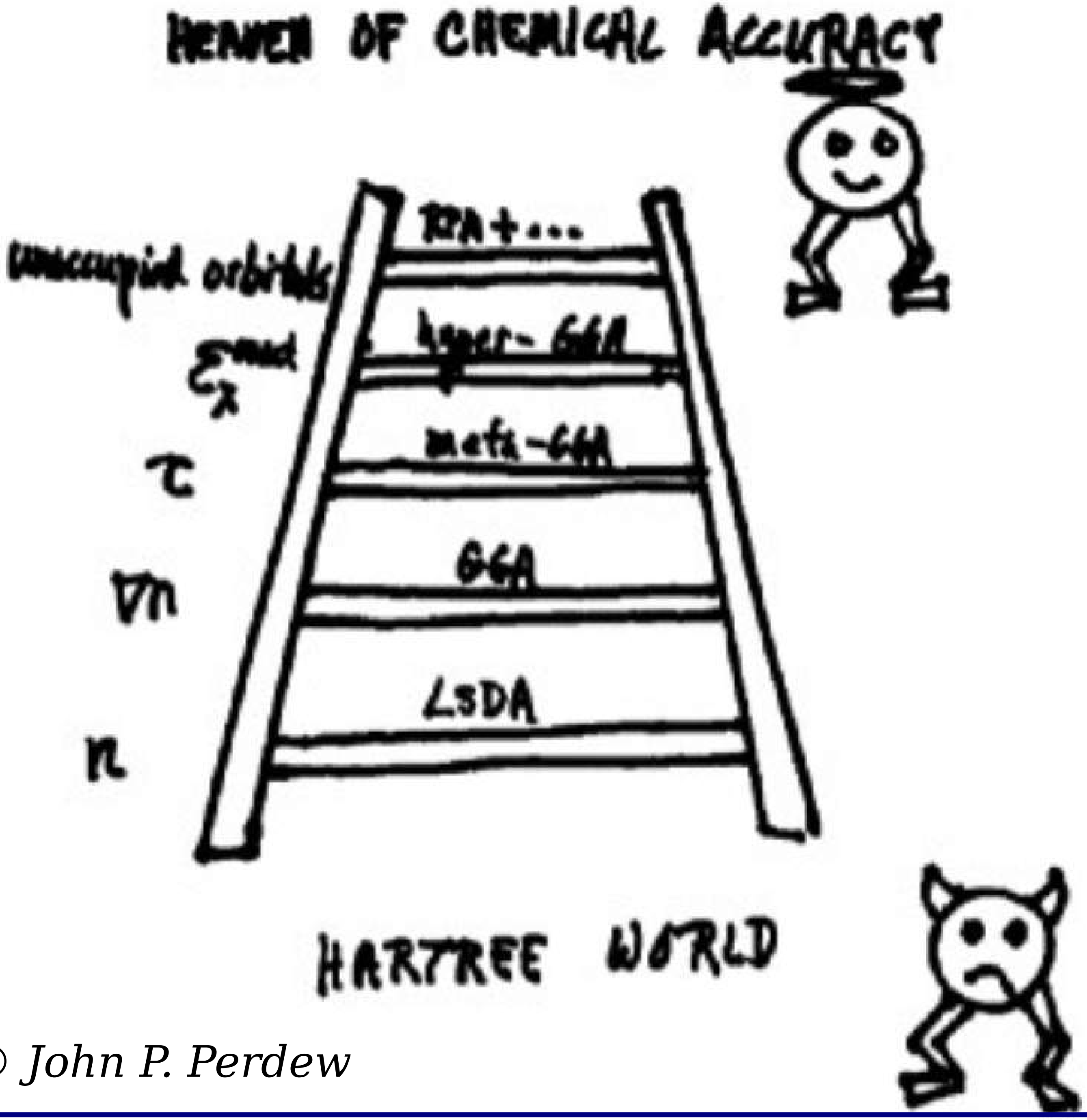
ma per seguir virtute e conoscenza

Exchange-Correlation functionals

FIG. 3. The alphabet soup of approximate functionals available in a code near you. Figure used with permission from Peter Elliott.

Kieron Burke, “Perspective on density functional theory” JCP 136 (2012) 150901

Jacob's ladder of Density Functional Theory



® *John P. Perdew*

LDA and LSDA
simple and well defined. good geometry, overbinding

GGA : PW91, PBE, revPBE, RPBE, BLYP
many options, improved energetics, good geometry

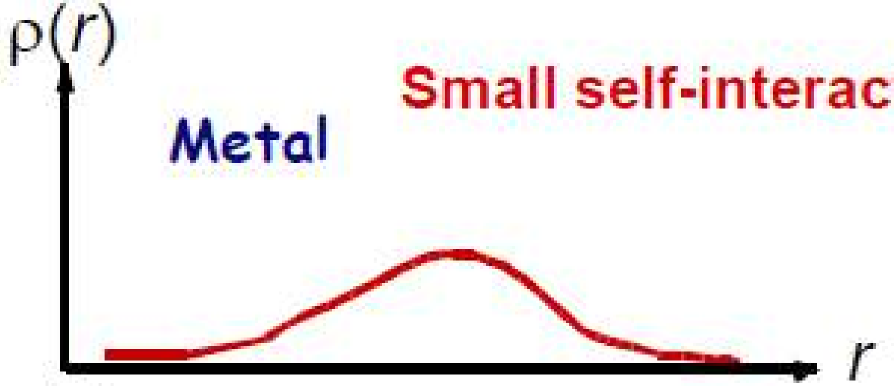
META-GGA: PKZB, TPSS,
more complicated, not very much used

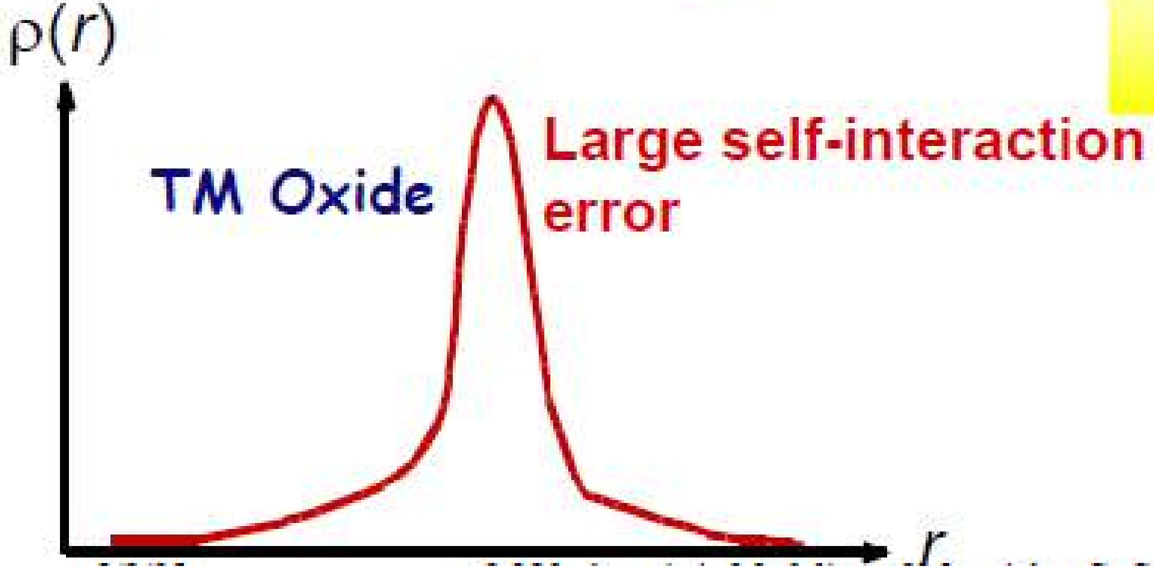
SIC, DFT+U, Hybrids
address the self-interaction error with some drawback

Van der Waals functionals
truly non local, very active field

In standard DFT an electron interacts with the effective potential generated by all the electrons (including itself)

$$H = \sum_i H_i = \sum_{i=1}^{N_e} \nabla_i^2 + \sum_{i=1}^{N_e} V_{nuclear}(r_i) + \sum_{i=1}^{N_e} V_{effective}(r_i)$$





Self interaction in DFT is key problem in transition metal oxides

Redox Reactions can be more Problematic

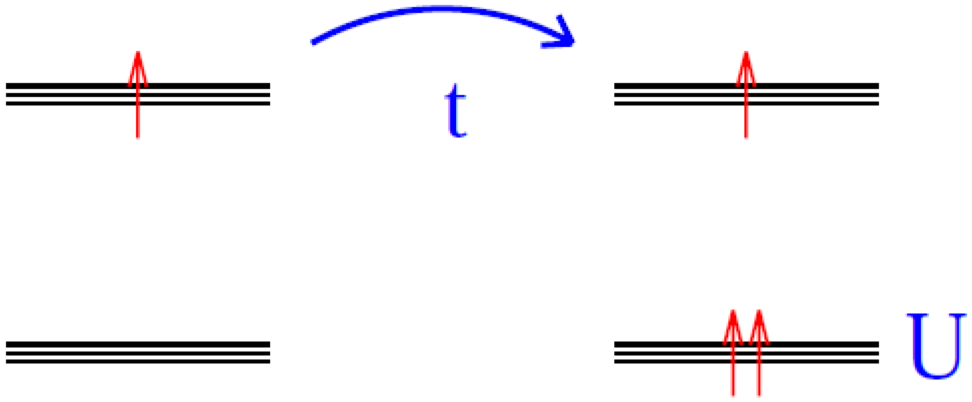
	GGA	Exp
$FePO_4$ + Li -> $LiFePO_4$	2.8 eV	3.5 eV
MnO_2 + Li -> $LiMn_2O_4$	3.6 eV	4.1 eV
$V_2(PO_4)_3$ + Li -> $LiV_2(PO_4)_3$	3.3 eV	4.6 eV

All these reactions involve the transfer of an electron from a delocalized state in Li metal to a localized state in the transition metal oxide (phosphate)

Self Interaction Error

One important source of error in LDA/GGA that can lead to qualitatively wrong results is the only approximate cancellation of self interaction coming from the approximate treatment of exchange

Mott insulators: what is missing in LDA ?

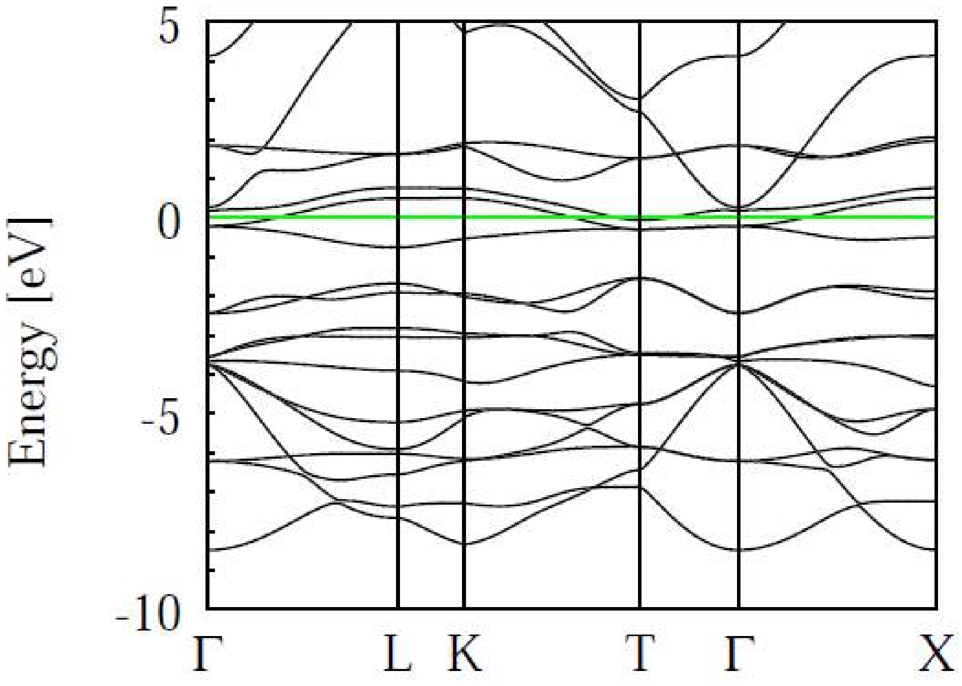


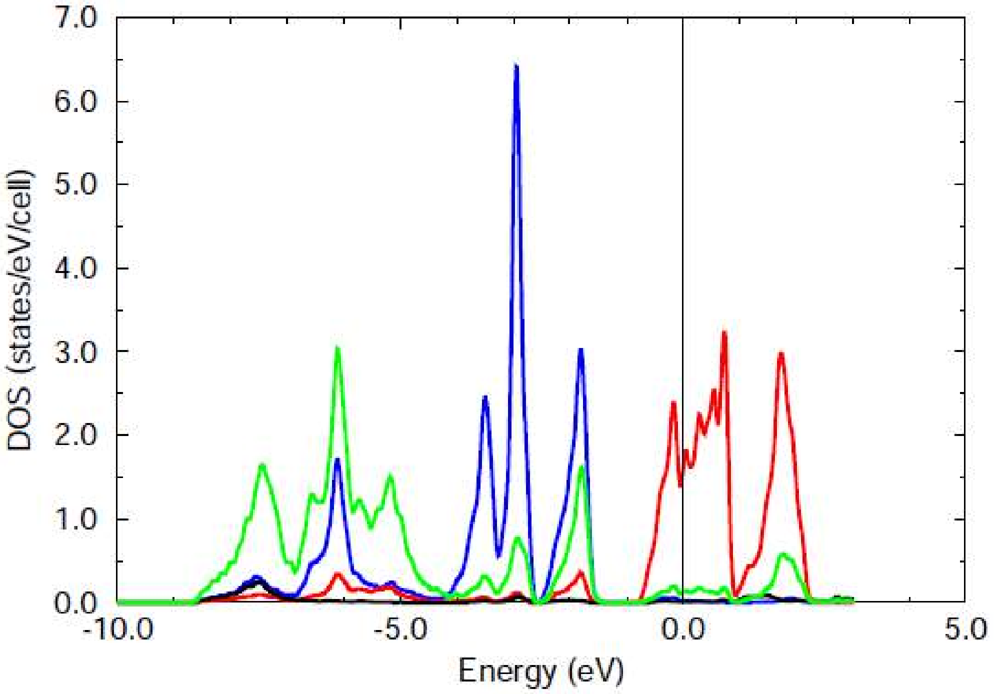
is OK in LDA

is wrong in LDA

LDA / GGA can badly fail for TMO and in 4f- systems

Electronic Structure of FeO





SIC, DFT+U, Hybrids

Self interaction correction was proposed as early as in 1981 by Perdew-Zunger. Conceptually important but not widely used.

Hybrid functionals (like PBE0, B3LYB) mix a fraction of Self-interaction-free HF with LDA/GGA functionals.
Is the method preferred by chemists.
It is very expensive in a plane-wave basis.

DFT+U has been introduced by Anisimov, Zaanen and Andersen as an approximation to treat strongly correlated materials. It has been more recently been applied also in more normal system with encouraging results.

PHYSICAL REVIEW B VOLUME 23, NUMBER 10 15 MAY 1981

Self-interaction correction to density-functional approximations for many-electron systems

J. P. Perdew
Department of Physics and Quantum Theory Group, Tulane University, New Orleans, Louisiana 70118

Alex Zunger
Solar Energy Research Institute, Golden, Colorado 80401
and Department of Physics, University of Colorado, Boulder, Colorado 80302

(Received 31 October 1980)

The exact density functional for the ground-state energy is strictly self-interaction-free (i.e., orbitals demonstrably do not self-interact), but many approximations to it, including the local-spin-density (LSD) approximation for exchange and correlation, are not. We present two related methods for the self-interaction correction (SIC) of any density functional for the energy; correction of the self-consistent one-electron potenial follows naturally from the variational principle. Both methods are sanctioned by the Hohenberg-Kohn theorem. Although the first method introduces an orbital-dependent single-particle potential, the second involves a local potential as in the Kohn-Sham scheme. We apply the first method to LSD and show that it properly conserves the number content of the exchange-correlation hole, while substantially improving the description of its shape. We apply this method to a number of physical problems, where the uncorrected LSD approach produces systematic errors. We find systematic improvements, qualitative as well as quantitative, from this simple correction. Benefits of SIC in atomic calculations include (i) improved values for the total energy and for the separate exchange and correlation pieces of it, (ii) accurate binding energies of negative ions, which are wrongly unstable in LSD, (iii) more accurate electron densities, (iv) orbital eigenvalues that closely approximate physical removal energies, *including* relaxation, and (v) correct long-range behavior of the potential and density. It appears that SIC can also remedy the LSD underestimate of the band gaps in insulators (as shown by numerical calculations for the rare-gas solids and CuCl), and the LSD overestimate of the cohesive energies of transition metals. The LSD spin splitting in atomic Ni and *s*-*d* interconfigurational energies of transition elements are almost unchanged by SIC. We also discuss the admissibility of fractional occupation numbers, and present a parametrization of the electron-gas correlation energy at any density, based on the recent results of Ceperley and Alder.

$$Q[n_\uparrow, n_\downarrow] = T[n_\uparrow, n_\downarrow] + U[n] + E_{\mathrm{xc}}[n_\uparrow, n_\downarrow] ,$$

$$E_{\mathrm{xc}}^{\mathrm{SIC}} = E_{\mathrm{xc}}^{\mathrm{approx}}[n_\uparrow, n_\downarrow] - \sum_{\alpha\sigma} \delta_{\alpha\sigma} ,$$

$$\delta_{\alpha\sigma} = U[n_{\alpha\sigma}] + E_{\mathrm{xc}}^{\mathrm{approx}}[n_{\alpha\sigma}, 0]$$

Derivation

Full-Interacting Hamiltonian

$$H = T + W + v_{ext} \quad \Rightarrow \quad |\Psi^{GS}\rangle,\ n(\mathbf{r})$$

Non-Interacting (Khon-Sham) Hamiltonian

$$H_{KS} = T_s + v_{KS} \quad \Rightarrow \quad |\Phi^{GS}_{KS}\rangle,\ n(\mathbf{r})$$

then we introduce fictitious systems with **scaled interaction** λW wich connect the KS ($\lambda = 0$) with the Many-Body system ($\lambda = 1$)

Adiabatic Connection

$$H_\lambda = T + \lambda W + v^{\lambda}_{ext}$$

$$v^{\lambda=0}_{ext} = v_{KS}$$

$$v^{\lambda=1}_{ext} = v_{ext}$$

$$n_\lambda(\mathbf{r}) = \langle \Psi^{GS}_\lambda | \hat{n}(\mathbf{r}) | \Psi^{GS}_\lambda \rangle = n(\mathbf{r})$$

Derivation

According to **Hellmann-Feynman** theorem

$$\frac{dE_\lambda}{d\lambda} = \langle \Psi_\lambda | \frac{dH_\lambda}{d\lambda} | \Psi_\lambda \rangle = \langle \Psi_\lambda | W | \Psi_\lambda \rangle + \langle \Psi_\lambda | \frac{\partial v_{ext}}{\partial \lambda} | \Psi_\lambda \rangle$$

Integrating over λ beetween 0 and 1

$$E_{\lambda=1} = E_{\lambda=0} + \int_0^1 d\lambda \, \langle \Psi_\lambda | W | \Psi_\lambda \rangle + \int d\mathbf{r} \, n(\mathbf{r})[v_{ext}(\mathbf{r}) - v_{KS}(\mathbf{r})]$$

With the usual decomposition of energy functional

$$E_{\lambda=1} = T_s + E_H + E_{xc} + \int d\mathbf{r} \, n(\mathbf{r}) v_{ext}(\mathbf{r})$$

$$E_{\lambda=0} = T_s + \int d\mathbf{r} \, n(\mathbf{r}) v_{KS}(\mathbf{r})$$

we end up with

$$E_H + E_{xc} = \int_0^1 d\lambda \, \langle \Psi_\lambda | W | \Psi_\lambda \rangle$$

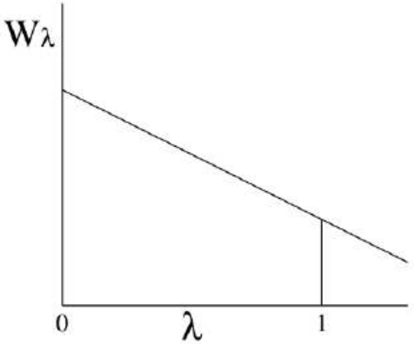
J. Chem. Phys. **96**, 2155 (1992)

A new mixing of Hartree–Fock and local density-functional theories

Axel D. Becke
Department of Chemistry, Queen's University, Kingston, Ontario, Canada K7L 3N6

(Received 12 August 1992; accepted 8 October 1992)

Previous attempts to combine Hartree–Fock theory with local density-functional theory have been unsuccessful in applications to molecular bonding. We derive a new coupling of these two theories that maintains their simplicity and computational efficiency, and yet greatly improves their predictive power. Very encouraging results of tests on atomization energies, ionization potentials, and proton affinities are reported, and the potential for future development is discussed.

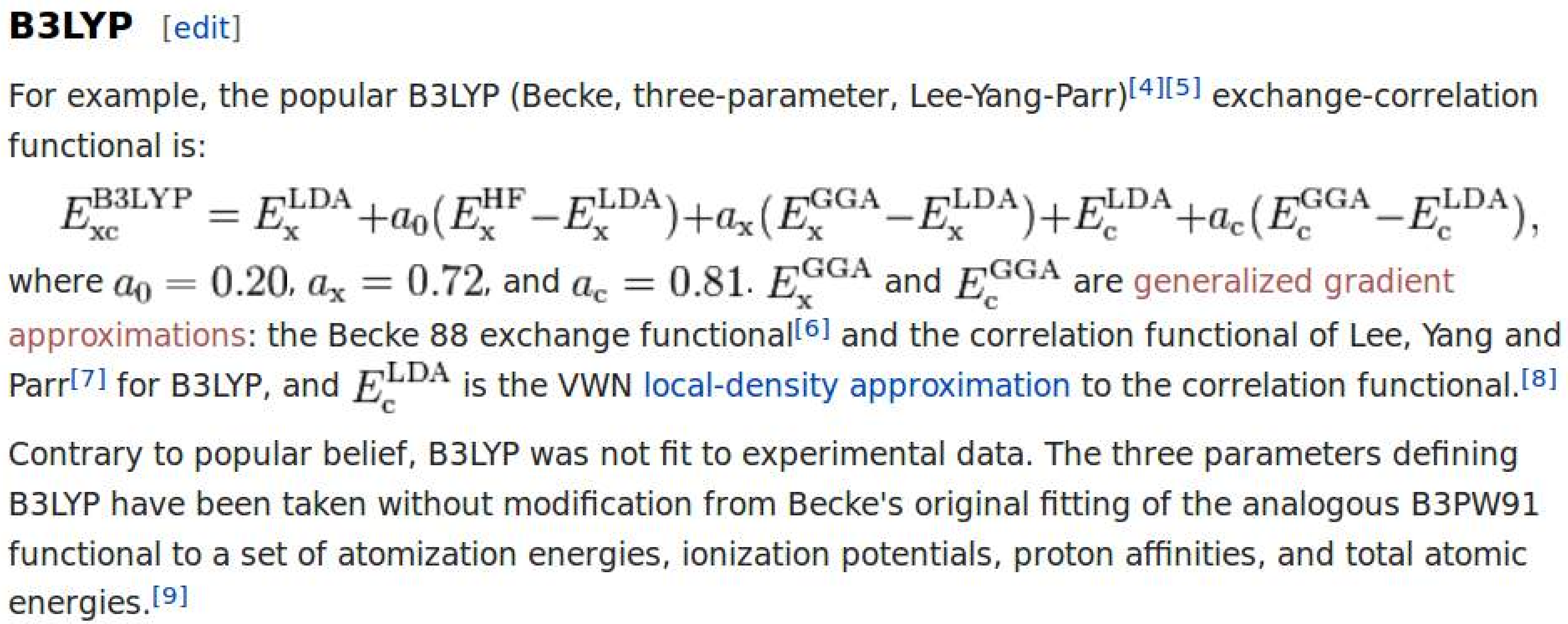


Half-Half

$$E_{\mathrm{XC}} \simeq \tfrac{1}{2} U^0_{\mathrm{XC}} + \tfrac{1}{2} U^1_{\mathrm{XC}},$$

$$U^0_{XC} = E_X = -\frac{1}{2} \sum_{ij}^{N} \iint \frac{\psi_i(\mathbf{r}_1)\psi_j(\mathbf{r}_2)\psi_j(\mathbf{r}_1)\psi_i(\mathbf{r}_2)}{r_{12}} d^3\mathbf{r}_1 d^3\mathbf{r}_2$$

$$U^1_{\mathrm{XC}} \simeq U^{\mathrm{LSDA}}_{\mathrm{XC}} = \int u_{\mathrm{XC}}[\rho_\alpha(\mathbf{r}), \rho_\beta(\mathbf{r})] d^3\mathbf{r},$$



B3LYP [edit]

For example, the popular B3LYP (Becke, three-parameter, Lee-Yang-Parr)[4][5] exchange-correlation functional is:

$$E_{\mathrm{xc}}^{\mathrm{B3LYP}} = E_{\mathrm{x}}^{\mathrm{LDA}} + a_0 (E_{\mathrm{x}}^{\mathrm{HF}} - E_{\mathrm{x}}^{\mathrm{LDA}}) + a_{\mathrm{x}} (E_{\mathrm{x}}^{\mathrm{GGA}} - E_{\mathrm{x}}^{\mathrm{LDA}}) + E_{\mathrm{c}}^{\mathrm{LDA}} + a_{\mathrm{c}} (E_{\mathrm{c}}^{\mathrm{GGA}} - E_{\mathrm{c}}^{\mathrm{LDA}}),$$

where $a_0 = 0.20$, $a_{\mathrm{x}} = 0.72$, and $a_{\mathrm{c}} = 0.81$. $E_{\mathrm{x}}^{\mathrm{GGA}}$ and $E_{\mathrm{c}}^{\mathrm{GGA}}$ are generalized gradient approximations: the Becke 88 exchange functional[6] and the correlation functional of Lee, Yang and Parr[7] for B3LYP, and $E_{\mathrm{c}}^{\mathrm{LDA}}$ is the VWN local-density approximation to the correlation functional.[8]

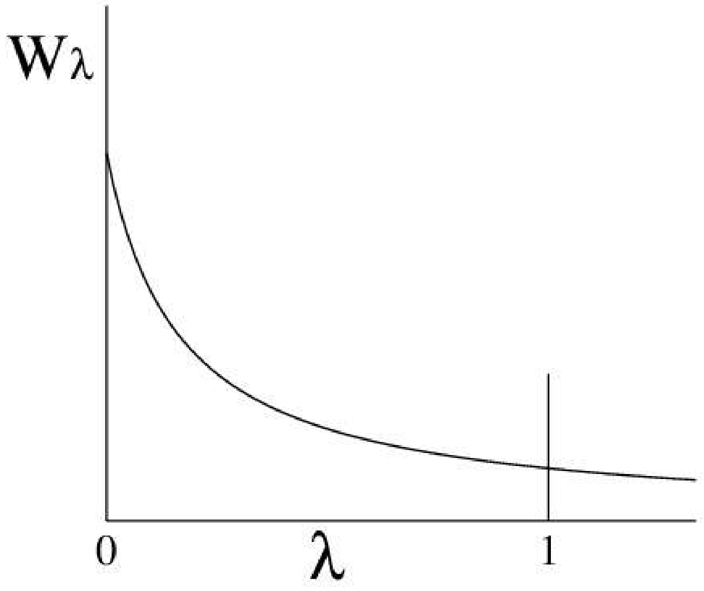
Contrary to popular belief, B3LYP was not fit to experimental data. The three parameters defining B3LYP have been taken without modification from Becke's original fitting of the analogous B3PW91 functional to a set of atomization energies, ionization potentials, proton affinities, and total atomic energies.[9]

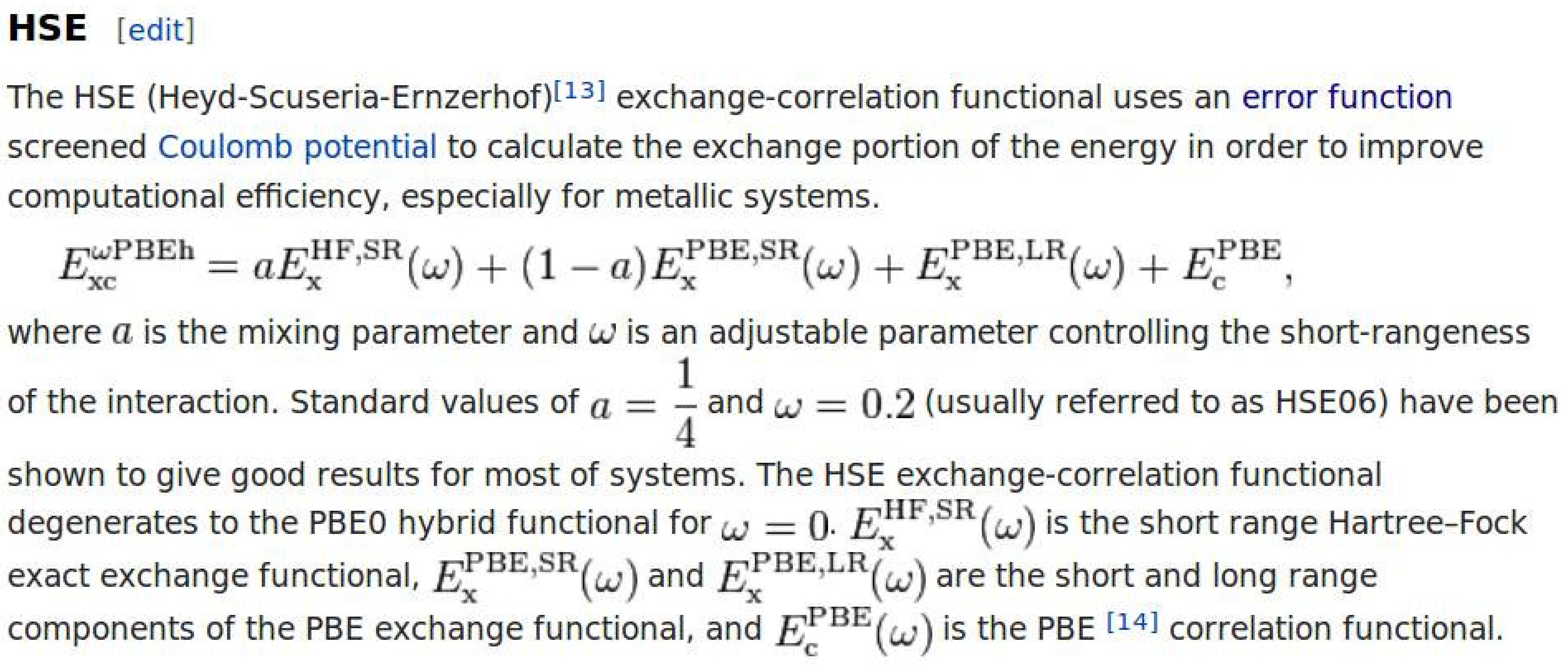
PBE0 [edit]

The PBE0 functional[10] [11] mixes the PBE exchange energy and Hartree-Fock exchange energy in a set 3 to 1 ratio, along with the full PBE correlation energy:

$$E_{\mathrm{xc}}^{\mathrm{PBE0}} = \frac{1}{4}E_{\mathrm{x}}^{\mathrm{HF}} + \frac{3}{4}E_{\mathrm{x}}^{\mathrm{PBE}} + E_{\mathrm{c}}^{\mathrm{PBE}},$$

where $E_{\mathrm{x}}^{\mathrm{HF}}$ is the Hartree–Fock exact exchange functional, $E_{\mathrm{x}}^{\mathrm{PBE}}$ is the PBE exchange functional, and $E_{\mathrm{c}}^{\mathrm{PBE}}$ is the PBE correlation functional.[12]





HSE [edit]

The HSE (Heyd-Scuseria-Ernzerhof)[13] exchange-correlation functional uses an error function screened Coulomb potential to calculate the exchange portion of the energy in order to improve computational efficiency, especially for metallic systems.

$$E_{\mathrm{xc}}^{\omega\mathrm{PBEh}} = aE_{\mathrm{x}}^{\mathrm{HF,SR}}(\omega) + (1-a)E_{\mathrm{x}}^{\mathrm{PBE,SR}}(\omega) + E_{\mathrm{x}}^{\mathrm{PBE,LR}}(\omega) + E_{\mathrm{c}}^{\mathrm{PBE}},$$

where a is the mixing parameter and ω is an adjustable parameter controlling the short-rangeness of the interaction. Standard values of $a = \frac{1}{4}$ and $\omega = 0.2$ (usually referred to as HSE06) have been shown to give good results for most of systems. The HSE exchange-correlation functional degenerates to the PBE0 hybrid functional for $\omega = 0$. $E_{\mathrm{x}}^{\mathrm{HF,SR}}(\omega)$ is the short range Hartree–Fock exact exchange functional, $E_{\mathrm{x}}^{\mathrm{PBE,SR}}(\omega)$ and $E_{\mathrm{x}}^{\mathrm{PBE,LR}}(\omega)$ are the short and long range components of the PBE exchange functional, and $E_{\mathrm{c}}^{\mathrm{PBE}}(\omega)$ is the PBE [14] correlation functional.

The LDA+U energy functional

$$E_{LDA+U}[n(\mathbf{r})] = E_{LDA}[n(\mathbf{r})] + \Delta E_{Hub}[\{n^{I\sigma}_{mm'}\}]$$

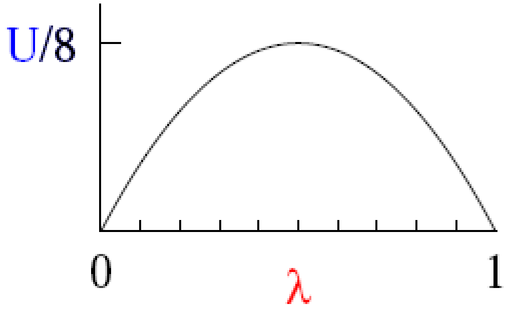
[Anisimov, Zaanen and Andersen, *PRB* **44**, 943 (1991).]

A simplified LDA+U model:

$$\Delta E_{Hub}[\{n^{I\sigma}_{mm'}\}] = \frac{U}{2}\sum_{I,\sigma} \mathrm{Tr}[\mathbf{n}^{I\sigma}(\mathbf{1} - \mathbf{n}^{I\sigma})].$$

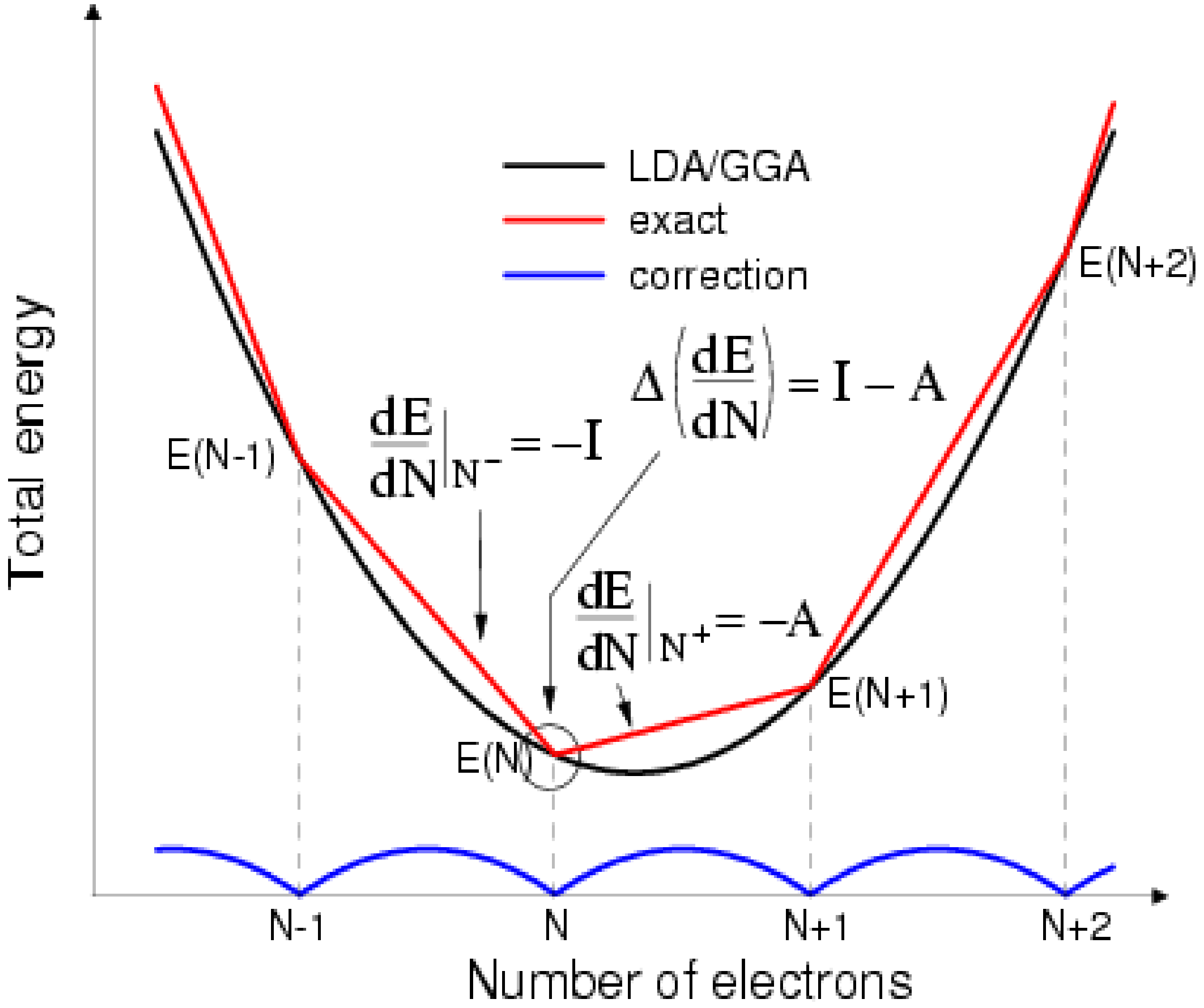
In the diagonal basis, where $\mathbf{n}^{I\sigma} \cdot \overrightarrow{v}^{I\sigma}_{\alpha} = \lambda^{I\sigma}_{\alpha}\overrightarrow{v}^{I\sigma}_{\alpha}$, the LDA+U correction is simply

$$\Delta E_{Hub}[\{n^{I\sigma}_{mm'}\}] = \frac{U}{2}\sum_{I,\sigma,\alpha} \lambda^{I\sigma}(1 - \lambda^{I\sigma})$$



Fractional occupation are strongly discouraged for large U.

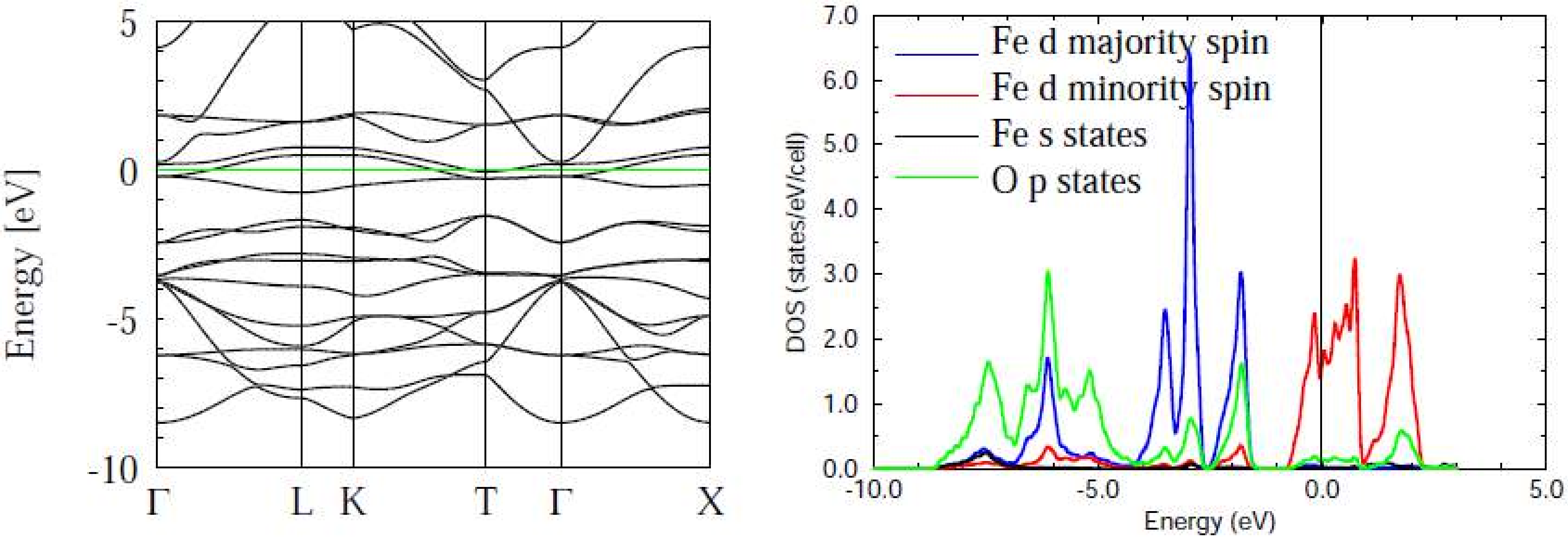
LDA/GGA failure in the atomic limit



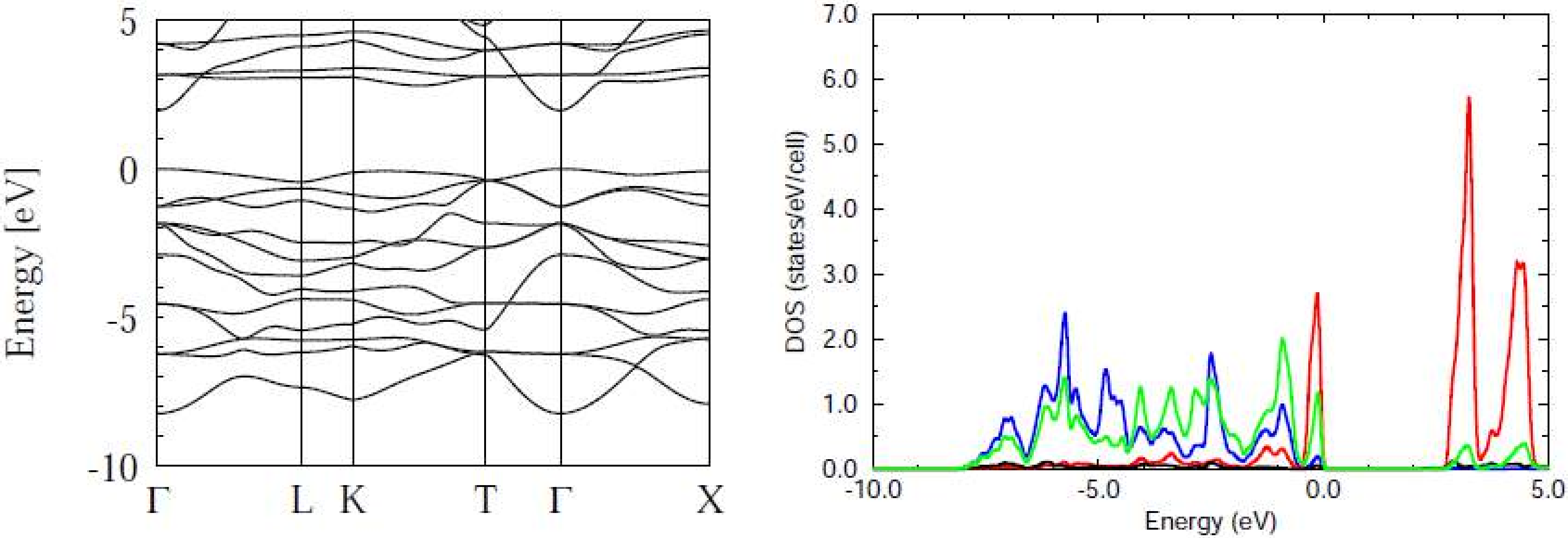
A correction is needed to remove spurious self-interaction

Electronic Structure of FeO

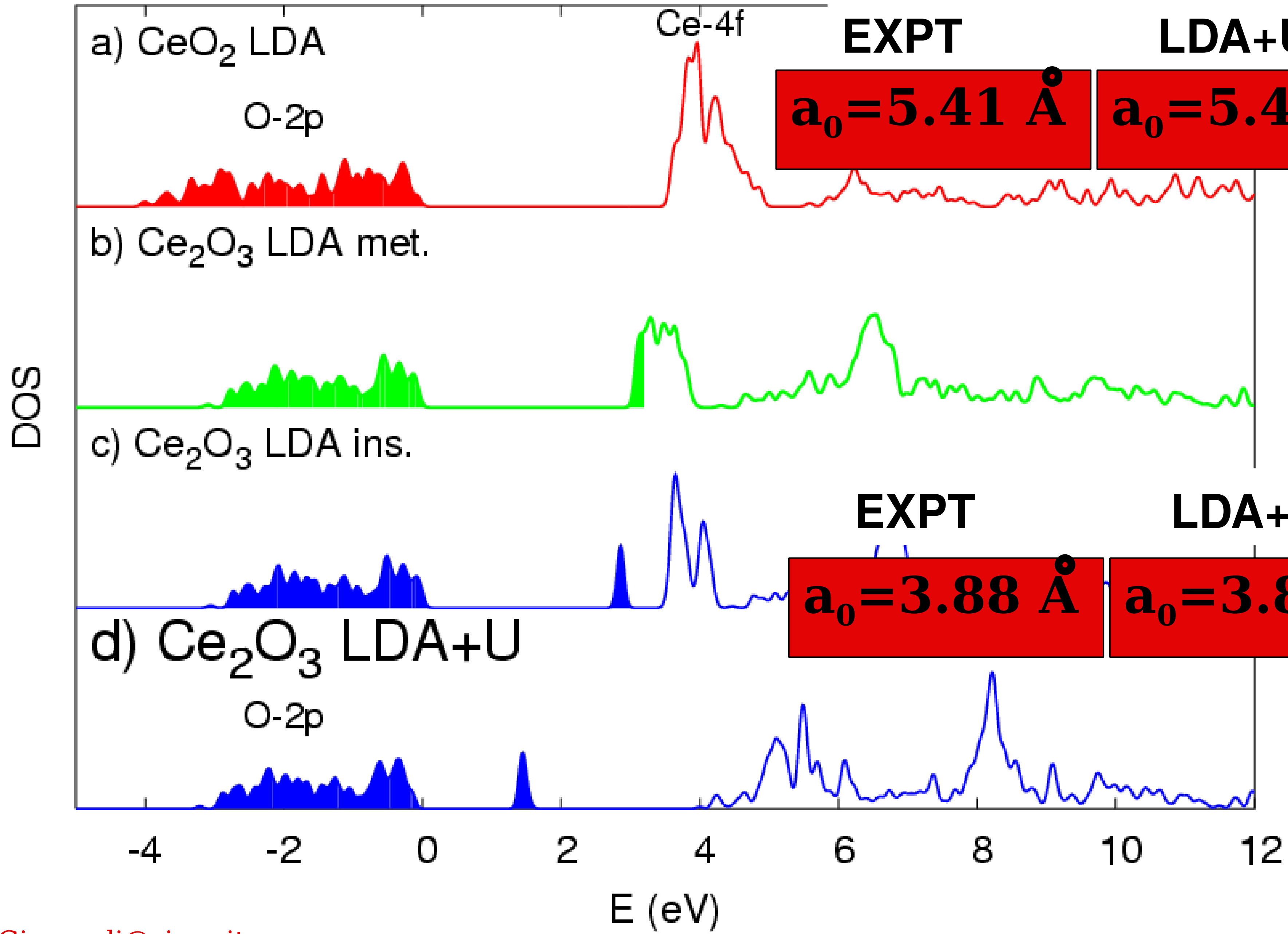
GGA



$LDA+U^{SIC}$



Electronic Structure of Ceria



EXPT	LDA+U
a_0=5.41 Å	a_0=5.41 Å

EXPT	LDA+U
a_0=3.88 Å	a_0=3.89 Å

deGironcoli@sissa.it

Evaluating the U parameter

In atoms: U is the (wrong) LDA/GGA curvature of the total energy as a function of occupation number.

In solids: U should be extracted from the curvature of E^{LDA} with respect to occupation number, after correcting for band structure effects present also for-non interacting system :

$$U = \frac{d^2 E^{LDA}}{d(n_d^I)^2} - \frac{d^2 E_0^{LDA}}{d(n_d^I)^2}$$

M. Cococcioni (SISSA PhD 2002)

Evaluating the U parameter

$$U = \frac{d^2 E^{LDA}}{d(n_d^I)^2} - \frac{d^2 E_0^{LDA}}{d(n_d^I)^2}$$

In practice: we introduce localized perturbations in large supercells

$$V_{ext} + \sum_I \alpha_I P_d^I \xrightarrow[SCF]{} \{n_d^J\} \Longrightarrow \chi_{IJ} = \frac{dn_d^I}{d\alpha_J}; \quad \frac{d^2 E^{LDA}}{d(n_d^I)^2} = -\frac{d\alpha_I}{dn_d^I}$$

$$V_{KS} + \sum_I \alpha_I P_d^I \xrightarrow[NOSCF]{} \{n_d^J\} \Longrightarrow \chi_{0IJ} = \frac{dn_d^I}{d\alpha_J}; \quad \frac{d^2 E_0^{LDA}}{d(n_d^I)^2} = -\frac{d\alpha_I}{dn_d^I}$$

and compute the variation of the energies with respect to occupation numbers, via inversion of the response function:

The Hubbard U thus results: $U = \left({\chi_0}^{-1} - \chi^{-1}\right)_{II}$

M.Cococcioni and S. deGironcoli, PRB 71, 035105 (2005)

Hartree-Fock energy

$$\mathbf{E}_{HF} = -\frac{e^2}{2}\sum_{\substack{\mathbf{k}v\\ \mathbf{k}'v'}} \int \frac{\phi^*_{\mathbf{k}v}(\mathbf{r})\phi_{\mathbf{k}'v'}(\mathbf{r})\phi^*_{\mathbf{k}'v'}(\mathbf{r}')\phi_{\mathbf{k}v}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}d\mathbf{r}'$$

- Hartree-Fock
- Exact Exchange (OEP)
- Hybrid Functionals: HH, B3LYP, PBE0
  (range separated) HSE

HF Vx using PWs

- **FFT pseudo wfc to real space**

$$\phi_{\mathbf{k}v}(\mathbf{k}+\mathbf{G}) \quad \xrightarrow{FFT} \quad \phi_{\mathbf{k}v}(\mathbf{r})$$

- **For each qpoint and each occupied band build “charge density”**

$$\rho_{\mathbf{q}}(\mathbf{r}) = \phi^*_{\mathbf{k}-\mathbf{q}v'}(\mathbf{r})\phi_{\mathbf{k}v}(\mathbf{r})$$

- **FFT charge to recip.space and solve Poisson eq.**

$$\rho_{\mathbf{q}}(\mathbf{r}) \quad \xrightarrow{FFT} \quad \rho_{\mathbf{q}}(\mathbf{q}+\mathbf{G}) \quad \Longrightarrow \quad V_{\mathbf{q}}(\mathbf{q}+\mathbf{G}) = \frac{4\pi e^2}{|\mathbf{q}+\mathbf{G}|^2} \quad \rho_{\mathbf{q}}(\mathbf{q}+\mathbf{G})$$

- **FFT back to real space, multiply by wfc and add to result**

$$V_{\mathbf{q}}(\mathbf{q}+\mathbf{G}) \quad \xrightarrow{FFT} \quad V_{\mathbf{q}}(\mathbf{r}) \quad \Longrightarrow \quad V_x\phi_{\mathbf{k}v}(\mathbf{r}) = V_x\phi_{\mathbf{k}v}(\mathbf{r}) + \phi_{\mathbf{k}-\mathbf{q}v'}(\mathbf{r})V_{\mathbf{q}}(\mathbf{r})$$

The q+G=0 divergence

- Gygi-Baldereschi PRB 34, 4405 (1986)

$$\rho_{\substack{\mathbf{k}-\mathbf{q},v' \\ \mathbf{k},v}}(\mathbf{r}) = \phi^*_{\mathbf{k}-\mathbf{q},v'}(\mathbf{r})\phi_{\mathbf{k},v}(\mathbf{r}) \quad \Longrightarrow \quad A(\mathbf{q}+\mathbf{G}) = \frac{\Omega}{(2\pi)^3}\int d\mathbf{k}\ |\rho^{\mathbf{k}-\mathbf{q},v'}_{\mathbf{k},v}(\mathbf{q}+\mathbf{G})|^2$$

$$= \frac{1}{N_{\mathbf{k}}}\sum_{\mathbf{k}} |\rho^{\mathbf{k}-\mathbf{q},v'}_{\mathbf{k},v}(\mathbf{q}+\mathbf{G})|^2$$

$$E_{HF} = -\frac{4\pi e^2}{2\Omega} \times \frac{\Omega}{(2\pi)^3}\int d\mathbf{q} \sum_{\mathbf{G}} \frac{A(\mathbf{q}+\mathbf{G})}{|\mathbf{q}+\mathbf{G}|^2}$$

Integrable divergence

The q+G=0 divergence

- Gygi-Baldereschi PRB 34, 4405 (1986)

$$\rho^{\mathbf{k}-\mathbf{q},v'}_{\mathbf{k},v}(\mathbf{r}) = \phi^*_{\mathbf{k}-\mathbf{q},v'}(\mathbf{r})\phi_{\mathbf{k},v}(\mathbf{r}) \quad\Longrightarrow\quad A(\mathbf{q}+\mathbf{G}) = \frac{\Omega}{(2\pi)^3}\int d\mathbf{k}\;\left|\rho^{\mathbf{k}-\mathbf{q},v'}_{\mathbf{k},v}(\mathbf{q}+\mathbf{G})\right|^2$$

$$= \frac{1}{N_\mathbf{k}}\sum_{\mathbf{k}}\left|\rho^{\mathbf{k}-\mathbf{q},v'}_{\mathbf{k},v}(\mathbf{q}+\mathbf{G})\right|^2$$

$$E_{HF} = -\frac{4\pi e^2}{2\Omega}\times\left\{\frac{\Omega}{(2\pi)^3}\int d\mathbf{q}\sum_{\mathbf{G}}\frac{A(\mathbf{q}+\mathbf{G}) - A(0)e^{-\alpha|\mathbf{q}+\mathbf{G}|^2}}{|\mathbf{q}+\mathbf{G}|^2} + \frac{\Omega}{(2\pi)^3}\int d\mathbf{q}\sum_{\mathbf{G}}\frac{e^{-\alpha|\mathbf{q}+\mathbf{G}|^2}}{|\mathbf{q}+\mathbf{G}|^2}A(0)\right\}$$

The q+G=0 divergence

- Gygi-Baldereschi PRB 34, 4405 (1986)

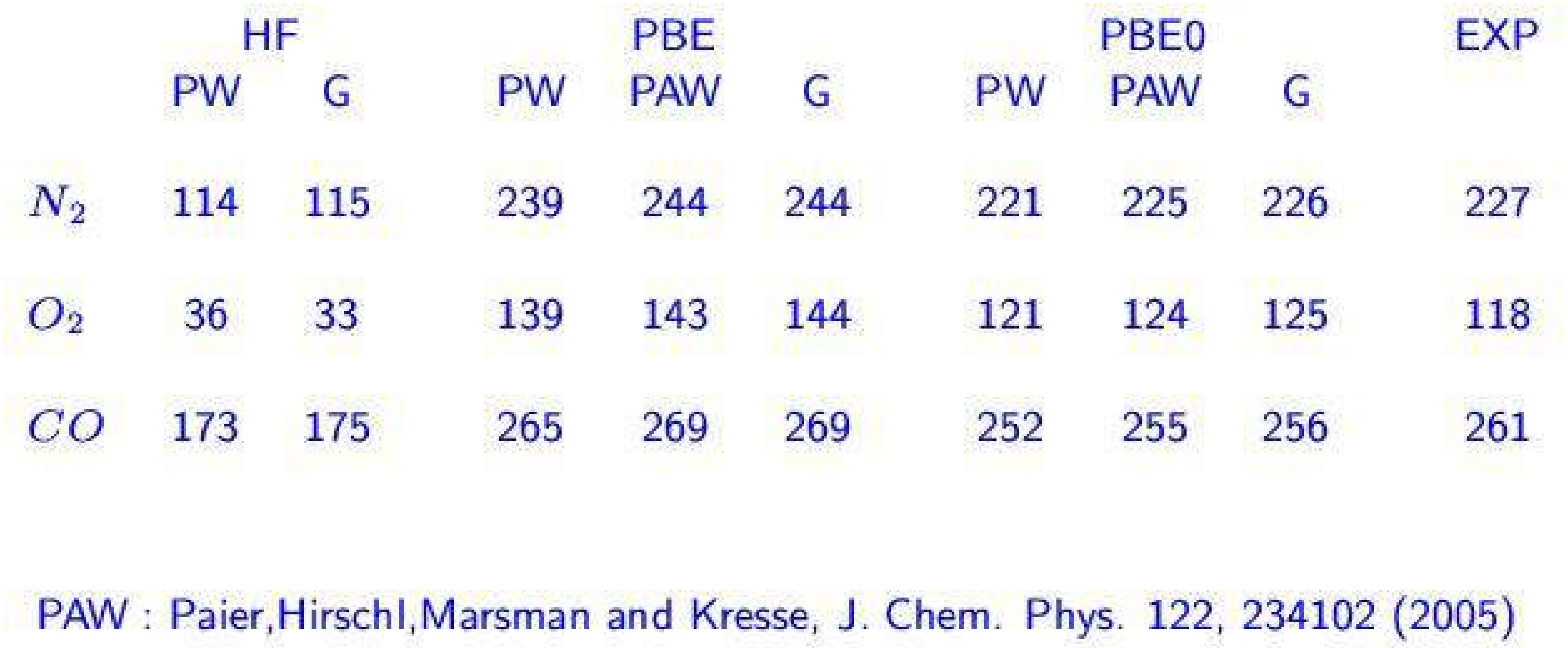
$$\rho^{\mathbf{k}-\mathbf{q},v'}_{\mathbf{k},v}(\mathbf{r}) = \phi^*_{\mathbf{k}-\mathbf{q},v'}(\mathbf{r})\,\phi_{\mathbf{k},v}(\mathbf{r}) \quad\Longrightarrow\quad A(\mathbf{q}+\mathbf{G}) = \frac{\Omega}{(2\pi)^3}\int d\mathbf{k}\ \ |\rho^{\mathbf{k}-\mathbf{q},v'}_{\mathbf{k},v}(\mathbf{q}+\mathbf{G})|^2$$

$$= \frac{1}{N_{\mathbf{k}}}\sum_{\mathbf{k}} |\rho^{\mathbf{k}-\mathbf{q},v'}_{\mathbf{k},v}(\mathbf{q}+\mathbf{G})|^2$$

$$E_{HF} = -\frac{4\pi e^2}{2\Omega}\times\left\{\frac{1}{N_{\mathbf{q}}}\left[{\sum_{\mathbf{q},\mathbf{G}}}' \frac{A(\mathbf{q}+\mathbf{G})}{|\mathbf{q}+\mathbf{G}|^2} + \lim_{\mathbf{q}\to 0}\frac{A(\mathbf{q})-A(0)}{\mathbf{q}^2}\right] + D\times A(0)\right\}$$

$$D = \frac{1}{N_{\mathbf{q}}}\left[-{\sum_{\mathbf{q},\mathbf{G}}}' \frac{e^{-\alpha|\mathbf{q}+\mathbf{G}|^2}}{|\mathbf{q}+\mathbf{G}|^2} + \alpha\right] + \frac{\Omega}{(2\pi)^3}\sqrt{\frac{\pi}{\alpha}}$$

Simple Molecules



	HF		PBE			PBE0			EXP
	PW	G	PW	PAW	G	PW	PAW	G	
N_2	114	115	239	244	244	221	225	226	227
O_2	36	33	139	143	144	121	124	125	118
CO	173	175	265	269	269	252	255	256	261

PAW : Paier,Hirschl,Marsman and Kresse, J. Chem. Phys. 122, 234102 (2005)

Energies in kcal/mol = 43.3 meV

Scaling

- Kinetic energy and local Potential

$$NPW + 2 * FFT + NRXX$$

- Non local potential

$$2 * NBND * NPW$$

- Fock operator

$$2 * FFT + NBND * NQ * (NRXX + FFT) + 2 * NRXX$$

Scaling

- Kinetic energy and local Potential

$$NPW + 2 * FFT + NRXX$$

- Non local potential

$$2 * NBND * NPW$$

- Fock operator

$$2 * FFT + NBND * NQ * (NRXX + FFT) + 2 * NRXX$$

From 10 to 100 times slower than standard case

Moore's law: computer power doubles every 18 months
(a factor of 10 in 5 yrs)

Scaling

- Kinetic energy and local Potential

$$NPW + 2 * FFT + NRXX$$

- Non local potential

$$2 * NBND * NPW$$

- Fock operator

$$2 * FFT + NBND * NQ * (NRXX + FFT) + 2 * NRXX$$

From 10 to 100 times slower than standard case

Separation of long- and short-range part in X can help

Scaling

- Kinetic energy and local Potential

$$NPW + 2 * FFT + NRXX$$

- Non local potential

$$2 * NBND * NPW$$

- Fock operator

$$2 * FFT + NBND * NQ * (NRXX + FFT) + 2 * NRXX$$

From 10 to 100 times slower than standard case

LDA and LSDA
simple and well defined. good geometry, overbinding

GGA : PW91, PBE, revPBE, RPBE, BLYP
many options, improved energetics, good geometry

META-GGA: PKZB, TPSS,
more complicated, not very much used

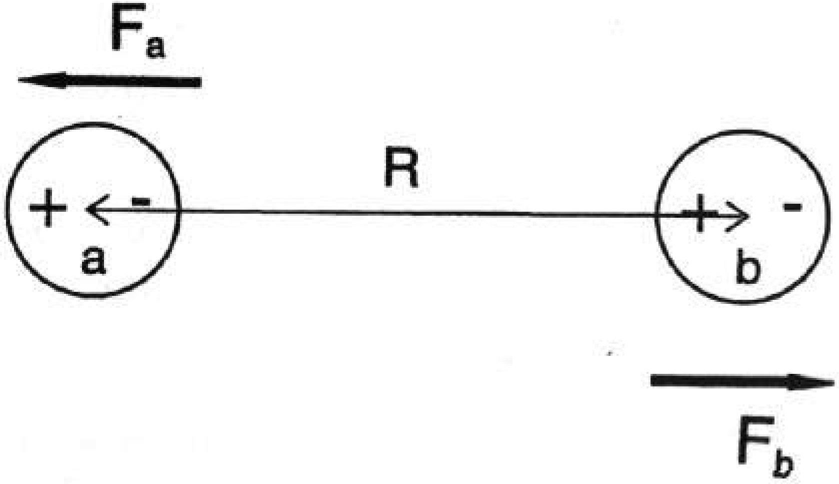
SIC, DFT+U, Hybrids
address the self-interaction error with some drawback

Van der Waals functionals
truly non local, very active field

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.

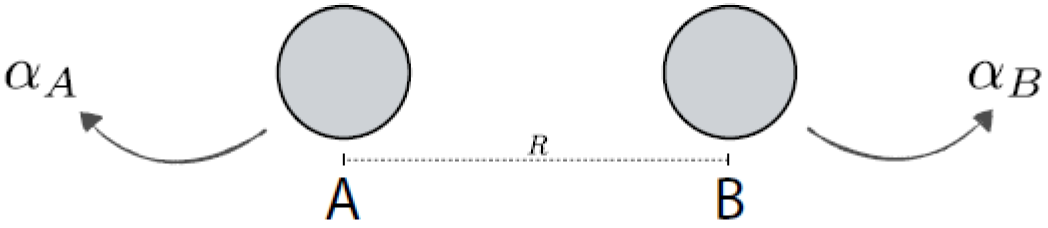


van der Waals

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.

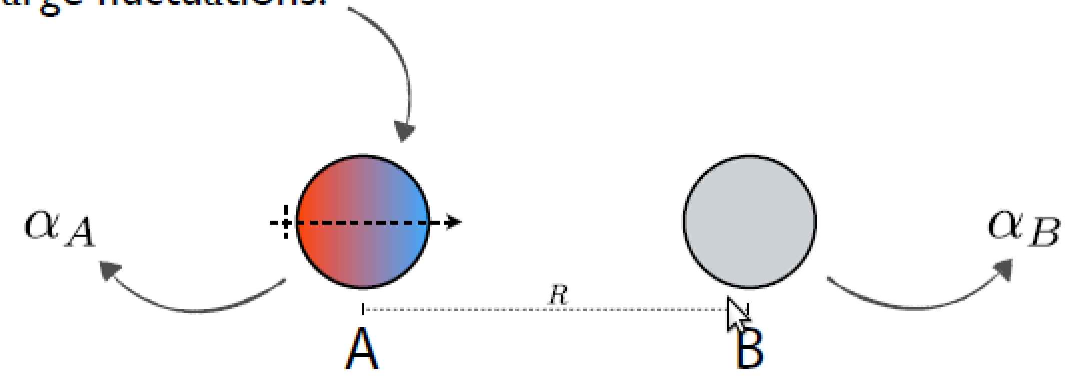
It is due to truly non-local correlation effects.
It is contained in the true XC functional but LDA/GGA/MetaGGA and Hybrids do not describe it properly.

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

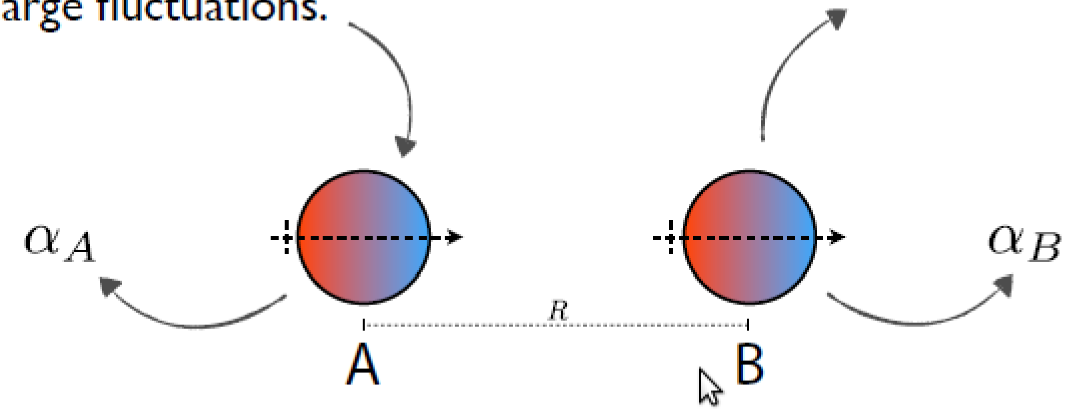
vdW : non local correlation



Instantaneous dipole d_A generated from charge fluctuations.

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.

Induced dipole

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

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

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

Density Functional Theory

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

KS self consistent eqs.

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

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

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

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

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

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

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.

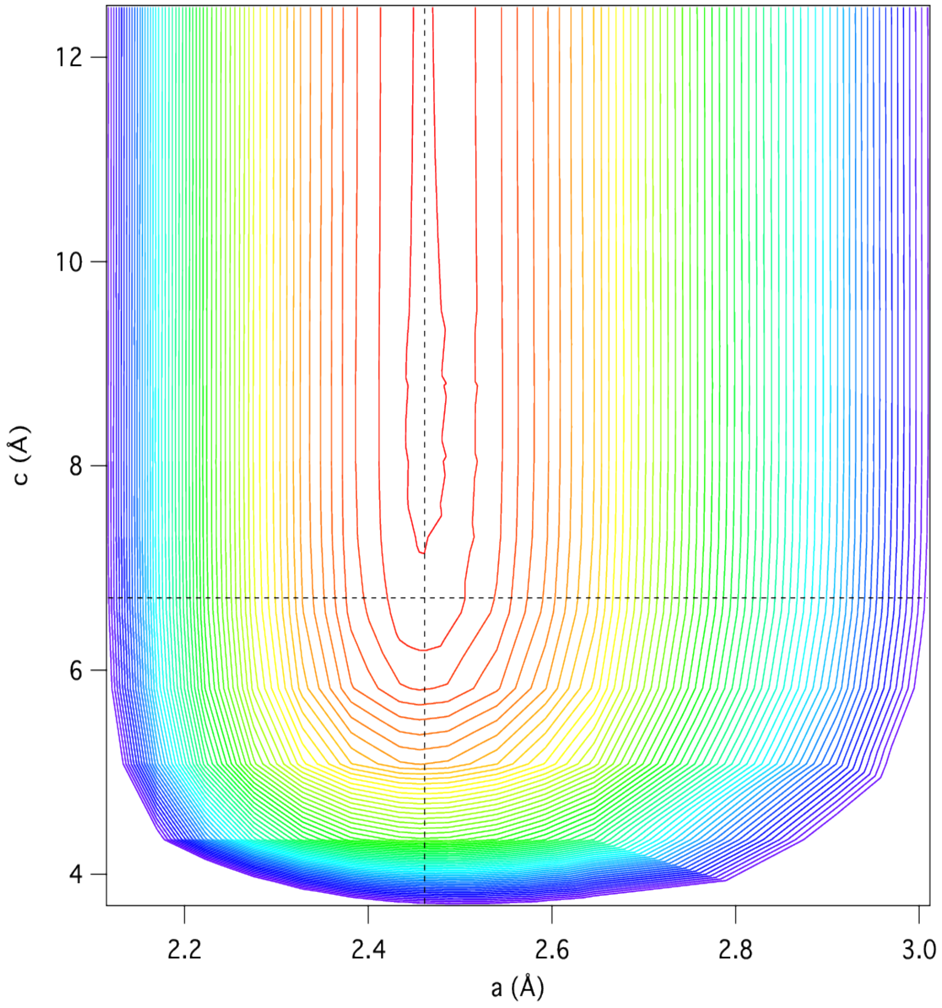
$$E_{xc}^{LDA} = \int n(r)\epsilon_{xc}^{hom}(n(r))dr \qquad E_{xc}^{GGA} = \int n(r)F_{xc}^{GGA}(n(r)), |\nabla n(r)|)dr$$

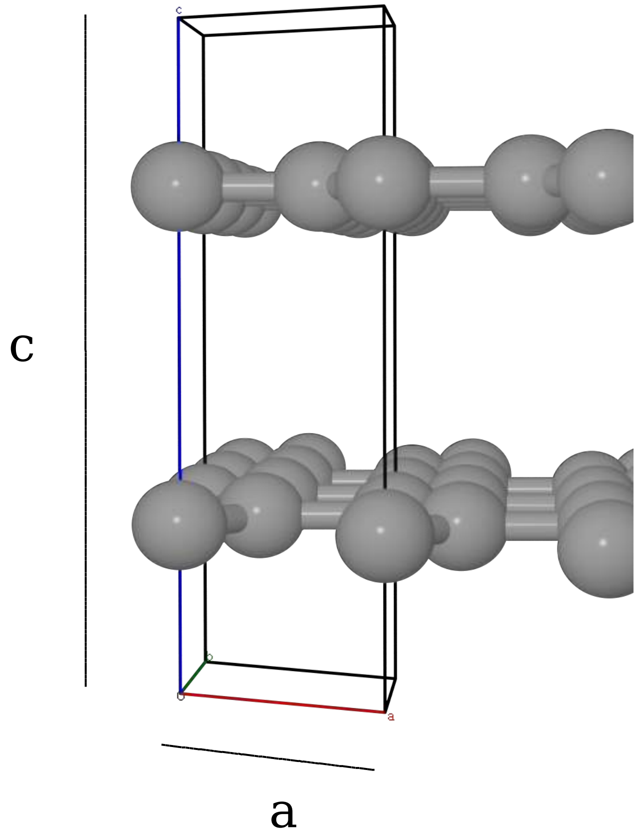
As such they do not describe vdW interaction.

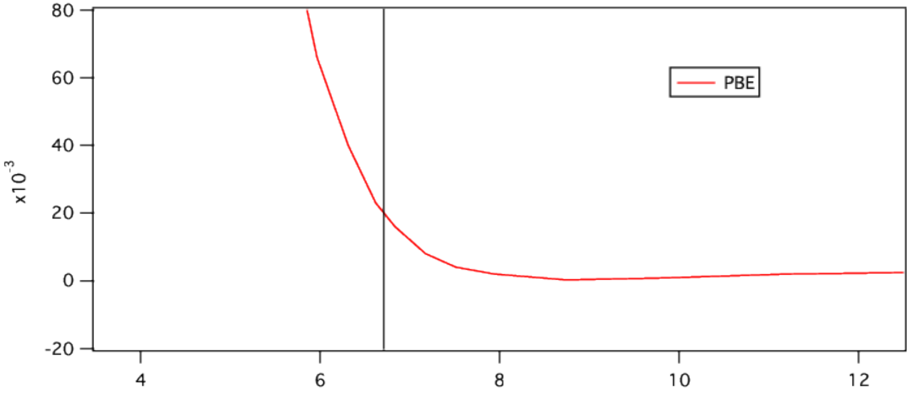
The same is true for Hybrids, DFT+U and SIC etc...

Failure of semilocal functionals

Graphite







How to deal with van der Waals ?

- neglect it

- add an empirical damped dispersion correction
  Grimme, Tkatchenko-Scheffler, MBD

- develop a truly non local XC functional starting from the
  Adiabatic Coupling Fluctuation Dissipation formula
  Vdw-DF, vdw-DF2, VV09, VV10

- RPA and beyond RPA

How to deal with van der Waals ?

- add an empirical damped dispersion correction

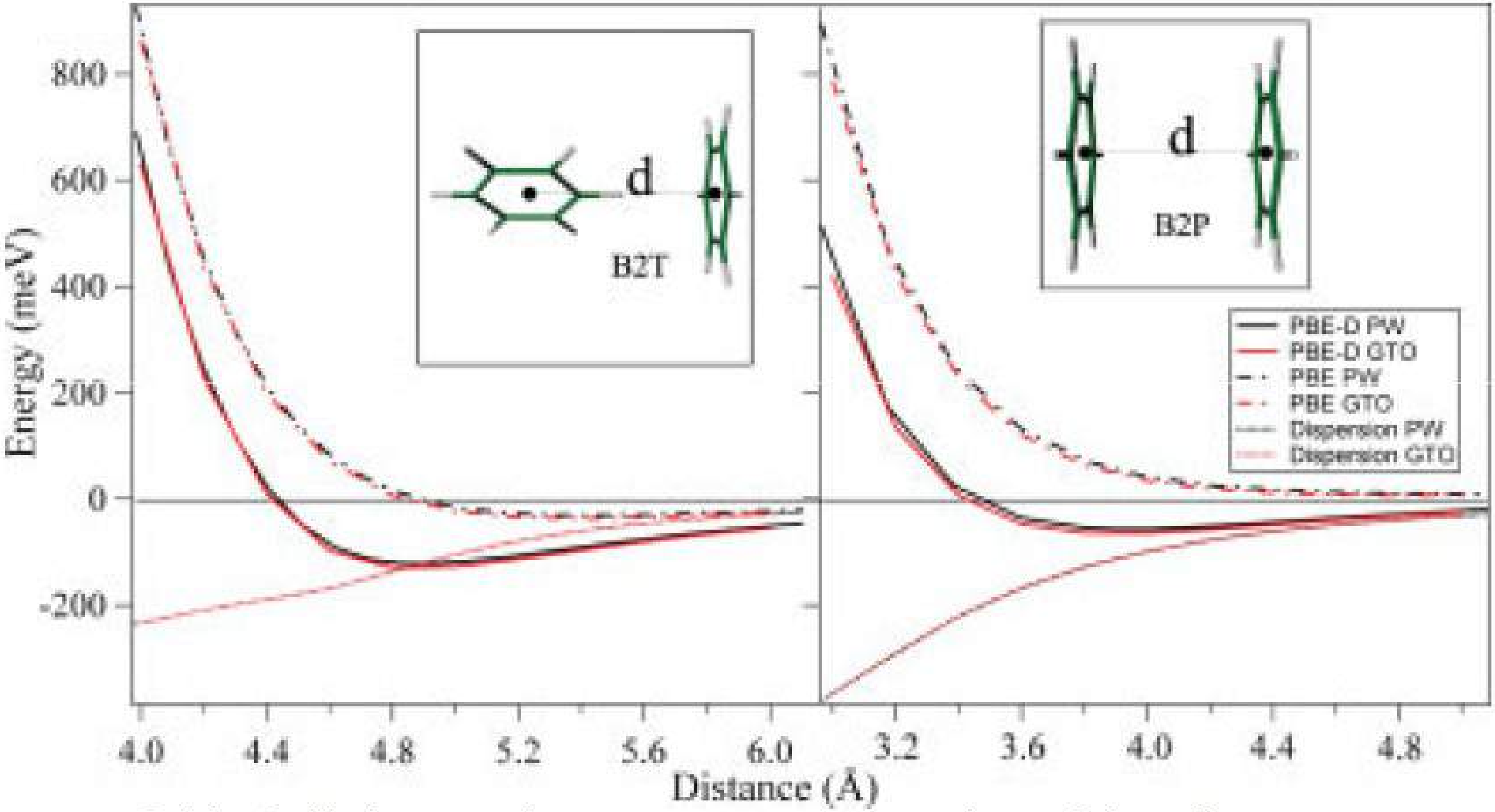
S. Grimme , J. Comp. Chem 27, 1787 (2006)

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

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

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*

$$C_6^{ij} = \sqrt{C_6^i C_6^j} \qquad f_{\text{dmp}}(R_{ij}) = \frac{1}{1 + e^{-d(R_{ij}/R_r - 1)}}$$



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)

How to deal with van der Waals ?

- add an empirical damped dispersion correction

A Tkatchenko and M Scheffler, PRL 102, 073005 (2009)

$$E_{\mathrm{vdW}} = -\frac{1}{2}\sum_{A,B} f_{\mathrm{damp}}(R_{AB}, R_A^0, R_B^0) C_{6AB} R_{AB}^{-6},$$

$$f_{\mathrm{damp}}(R_{AB}, R_{AB}^0) = \frac{1}{1 + \exp[-d(\frac{R_{AB}}{s_R R_{AB}^0} - 1)]},$$

where $R_{AB}^0 = R_A^0 + R_B^0$, d and s_R are free parameters.

$$C_{6AA}^{\mathrm{eff}} = \left(\frac{V_A^{\mathrm{eff}}}{V_A^{\mathrm{free}}}\right)^2 C_{6AA}^{\mathrm{free}}.$$

$$\frac{\kappa_A^{\mathrm{eff}}}{\kappa_A^{\mathrm{free}}} \frac{\alpha_A^{\mathrm{eff}}}{\alpha_A^{\mathrm{free}}} = \frac{V_A^{\mathrm{eff}}}{V_A^{\mathrm{free}}} = \left(\frac{\int r^3 w_A(\mathbf{r}) n(\mathbf{r}) d^3\mathbf{r}}{\int r^3 n_A^{\mathrm{free}}(\mathbf{r}) d^3\mathbf{r}}\right),$$

$$w_A(\mathbf{r}) = \frac{n_A^{\mathrm{free}}(\mathbf{r})}{\sum_B n_B^{\mathrm{free}}(\mathbf{r})},$$

Hirshfeld partition

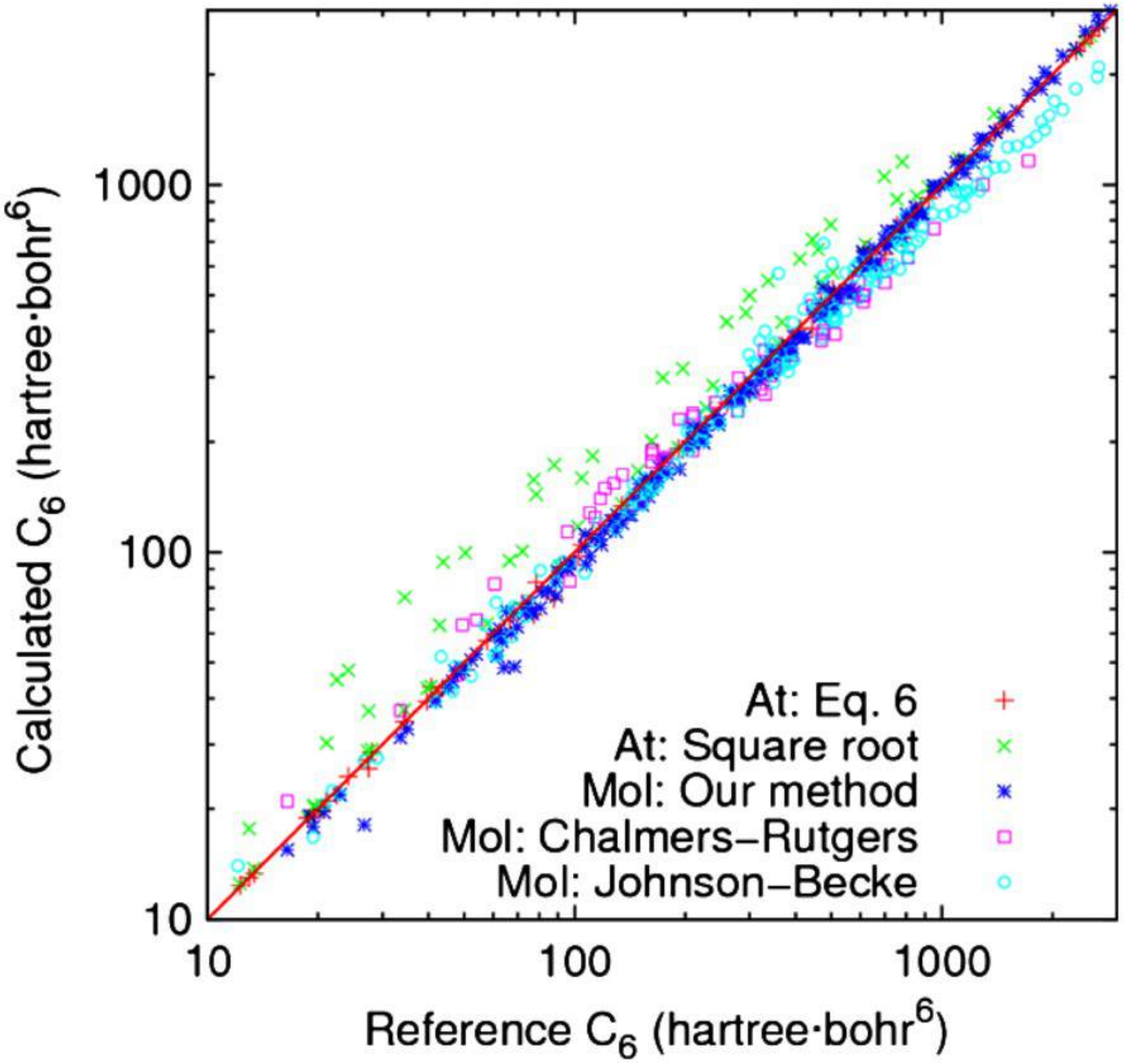


FIG. 1 (color online). Comparison of the C_6 coefficients for atom-atom interaction (At) and atom-molecule and molecule-molecule interaction (Mol). The reference results for atom-atom interaction are from accurate wave function calculations [26–28]. For molecules, DOSD results are taken as a reference [5,8,20,21]. Our results (only 211 values out of 1225 are shown) are compared to those of Chalmers-Rutgers collaboration [15] and Johnson-Becke [8]. The only outliers for our method are cases involving the H_2 molecule (20–44% deviation).

How to deal with van der Waals ?

- add an empirical damped dispersion correction + long-range many-body dispersion correction

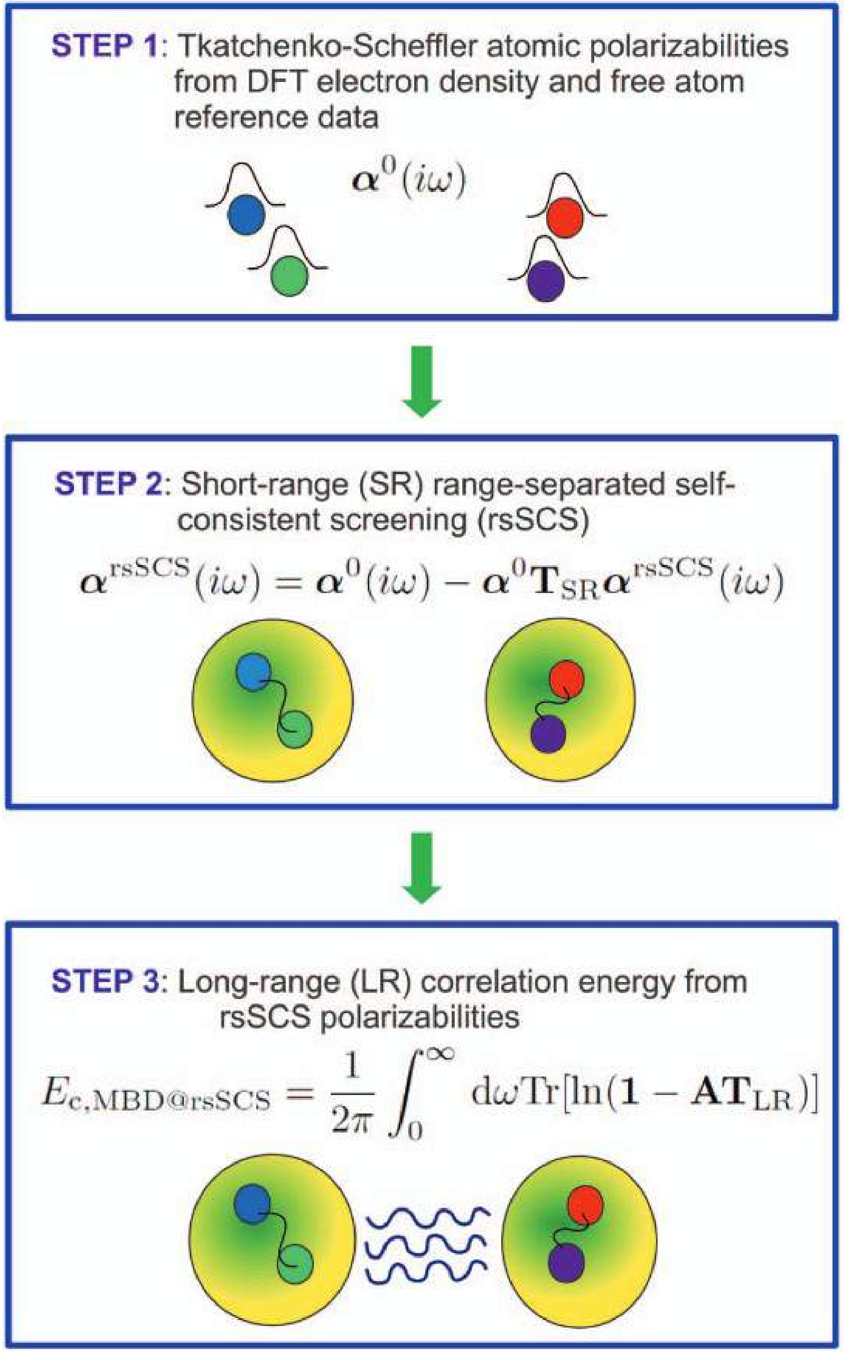
A Tkatchenko, RA Di Stasio, R Car, and M Scheffler, ``Accurate and efficient method for many-body van der waals interactions'', PRL 108, 236402 (2012).

A Ambrosetti, AM Reilly, RA DiStasio, and A Tkatchenko, ``Long-range correlation energy calculated from coupled atomic response functions'', JCP 140, 018A508 (2014).

Random Phase Approximation

$$E_c = \int_0^\infty \frac{d\omega}{2\pi} \quad \mathrm{Tr}\left\{\ln(1 - v\chi_0(i\omega)) + v\chi_0(i\omega)\right\},$$

MBD@rsSCS long-range correlation energy



STEP 1: Tkatchenko-Scheffler atomic polarizabilities from DFT electron density and free atom reference data

$$\boldsymbol{\alpha}^0(i\omega)$$

STEP 2: Short-range (SR) range-separated self-consistent screening (rsSCS)

$$\boldsymbol{\alpha}^{\mathrm{rsSCS}}(i\omega) = \boldsymbol{\alpha}^0(i\omega) - \boldsymbol{\alpha}^0 \mathbf{T}_{\mathrm{SR}} \boldsymbol{\alpha}^{\mathrm{rsSCS}}(i\omega)$$

STEP 3: Long-range (LR) correlation energy from rsSCS polarizabilities

$$E_{\mathrm{c,MBD@rsSCS}} = \frac{1}{2\pi} \int_0^\infty \mathrm{d}\omega \mathrm{Tr}[\ln(\mathbf{1} - \mathbf{A}\mathbf{T}_{\mathrm{LR}})]$$

$$E_{\mathrm{c}} \simeq E_{\mathrm{c}}^{\mathrm{SR}} + E_{\mathrm{c}}^{\mathrm{LR}},$$

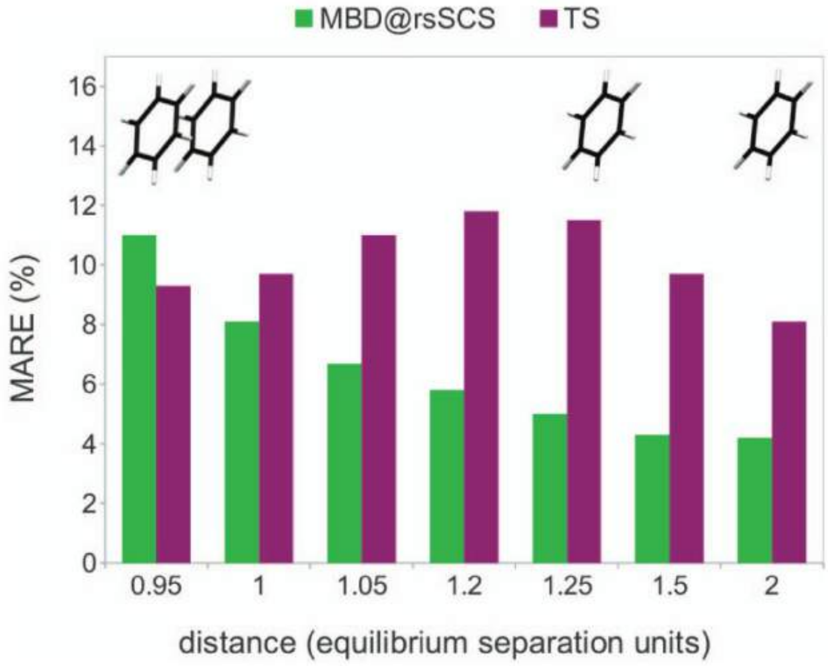


FIG. 2. The mean absolute relative error of PBE0+MBD@rsSCS and PBE0+TS (in %) at each of the S66×7 inter-fragment separations.

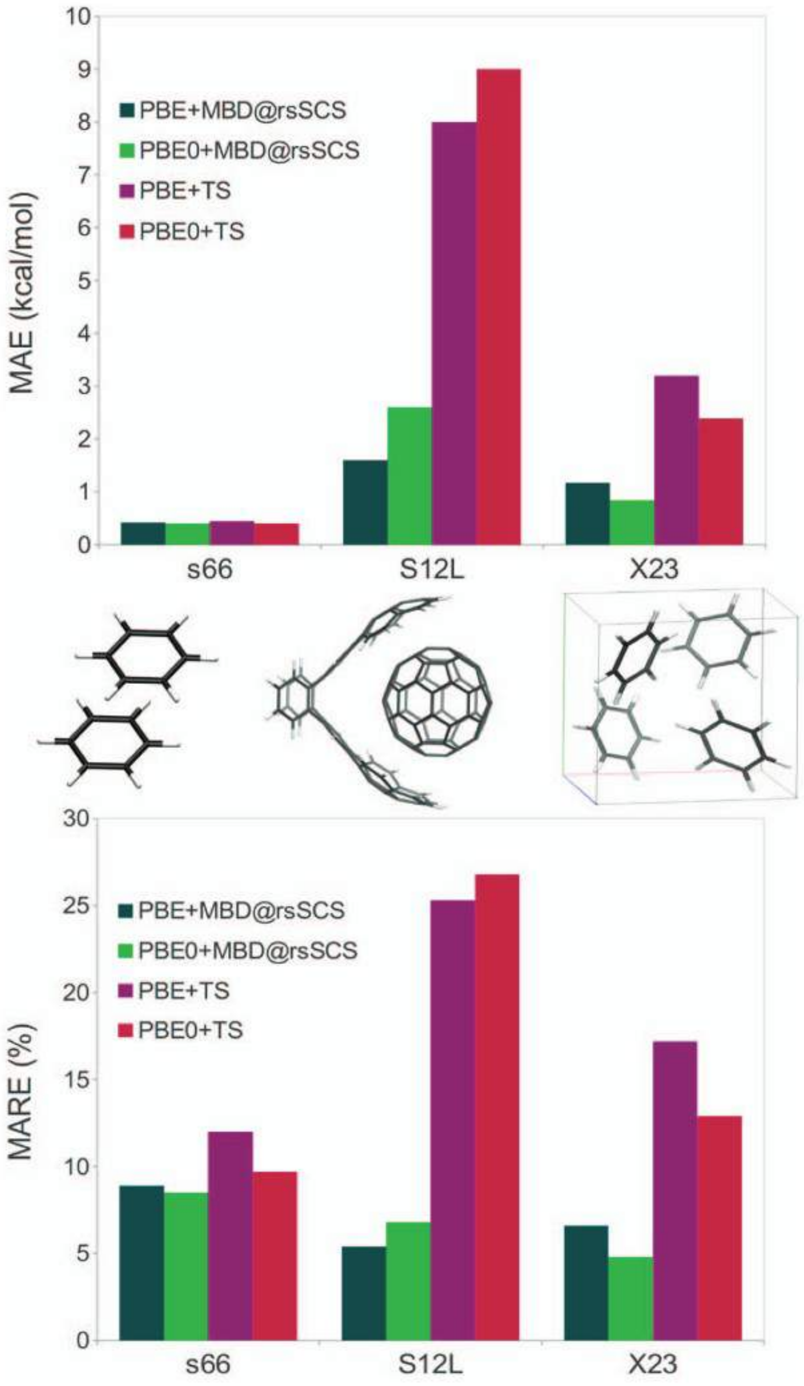


FIG. 3. MAE (upper panel in kcal/mol) and MARE (lower panel in %) for the S66, S12L, and X23 databases computed with MBD@rsSCS and TS combined with both the PBE and PBE0 functionals.

Derivation

Replacing χ_λ with $\chi_{KS} = \chi_0$

$$E_x = -\frac{1}{2}\int d\mathbf{r}d\mathbf{r}'\frac{|\sum_i^{occ}\phi_i^*(\mathbf{r})\phi_i(\mathbf{r}')|^2}{|\mathbf{r}-\mathbf{r}'|}$$

The exchange-correlation energy can thus be separated

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

Adiabatic connection formula for correlation energy

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

$$\chi_\lambda(iu) = \chi_0(iu) + \chi_\lambda(iu)[\lambda\upsilon_c + f_{xc}^\lambda(iu)]\chi_0(iu)$$

How to deal with van der Waals ?

- develop a truly non local XC functional

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

$$\phi(\ n(\mathbf{r}), \nabla n(\mathbf{r}), n(\mathbf{r}'), \nabla n(\mathbf{r}'), |\mathbf{r}-\mathbf{r}'|\ )$$

-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)

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 Integra l !

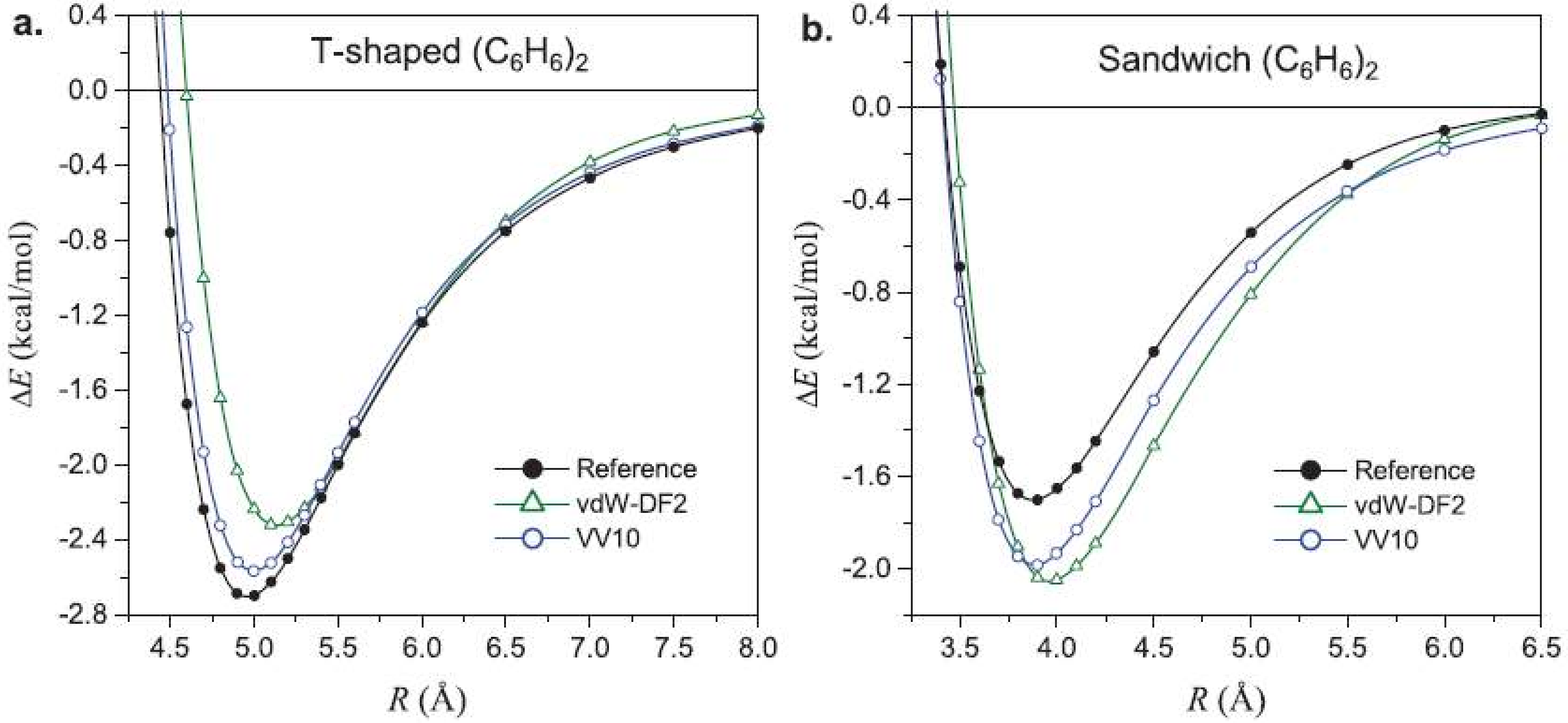
$$\Phi \longrightarrow -\frac{3e^4}{2m^2}\frac{1}{\omega_0(r)\omega_0(r')[\omega_0(r)+\omega_0(r')]|r-r'|^6}$$

How to deal with van der Waals ?

- develop a truly non local XC functional

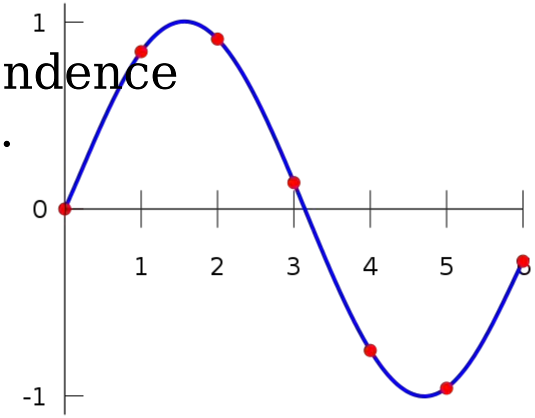
$$E_{\mathrm{c}}^{\mathrm{nl}} = \frac{1}{2}\int d^3r\, d^3r'\, n(\vec{r})\phi(\vec{r},\vec{r}\,')n(\vec{r}\,'),$$

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



Efficient integration

Roman-Rerez 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 ...



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

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

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

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

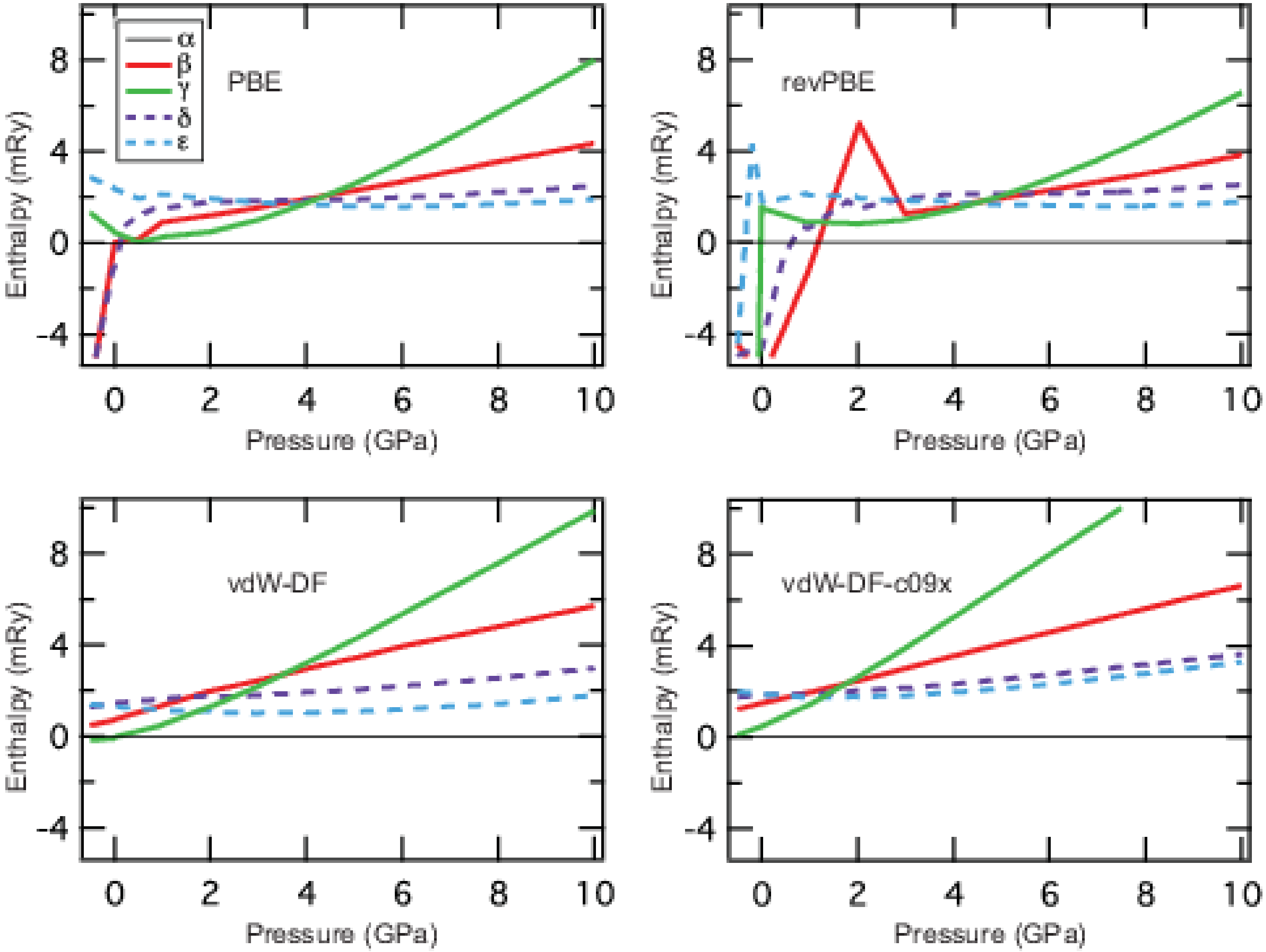
The vdW energy can be expressed as a sum of simple 3d integrals

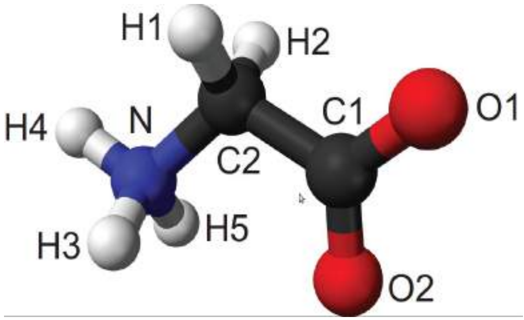
Several Non-Local Functionals

	ω_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	$\sqrt{\frac{\omega_p^2}{3} + C\frac{\hbar^2}{m^2}\left\vert\frac{\nabla n}{n}\right\vert^4}$ 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

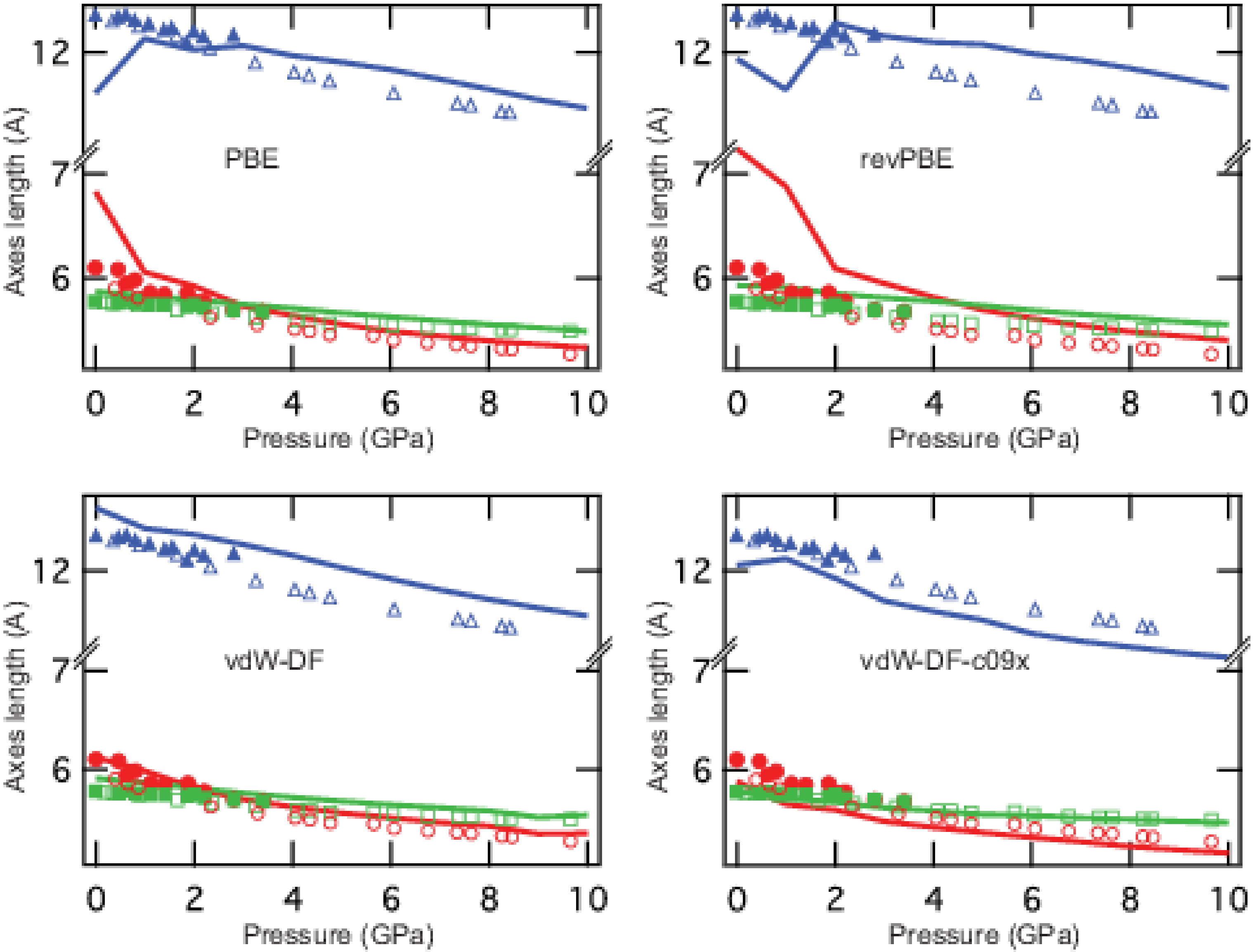
Glycine polymorphes

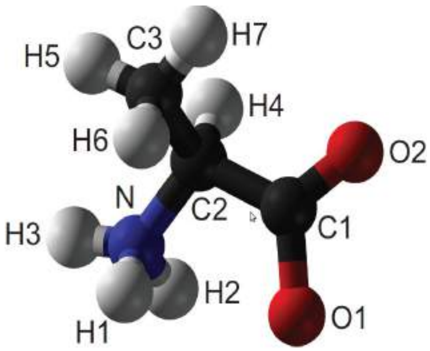




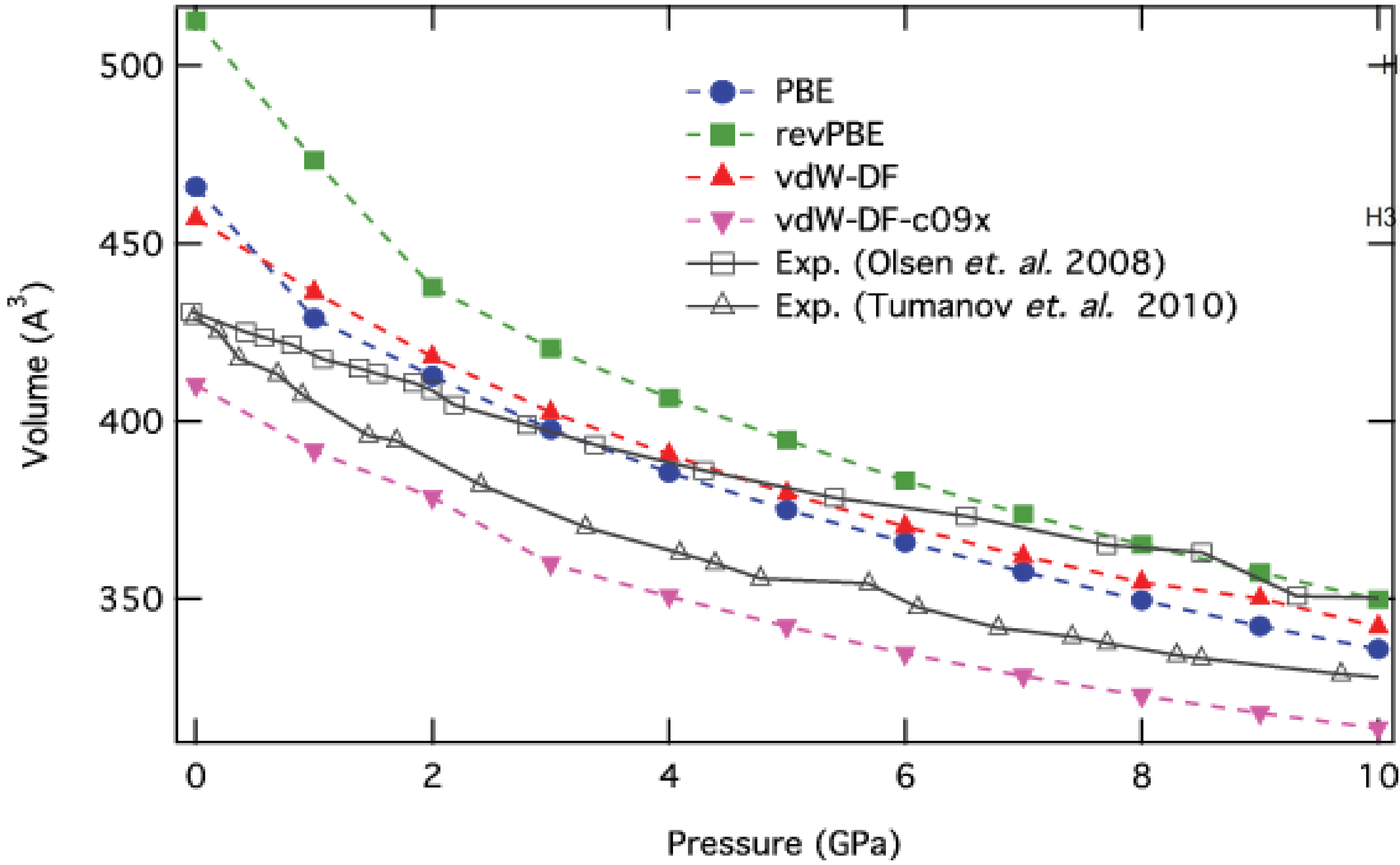
$$\gamma < \alpha < \beta < \ldots$$

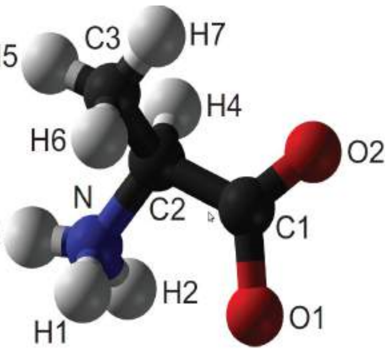
Alanine evolution with Pressure





Alanine evolution with P





VV10 functional

$$\Phi^{VV10}(r,r') = -\frac{3e^4}{2m^2}\frac{1}{gg'(g+g')} \qquad k(r) = 3\pi b\left(\frac{n}{9\pi}\right)^{\frac{1}{6}}$$

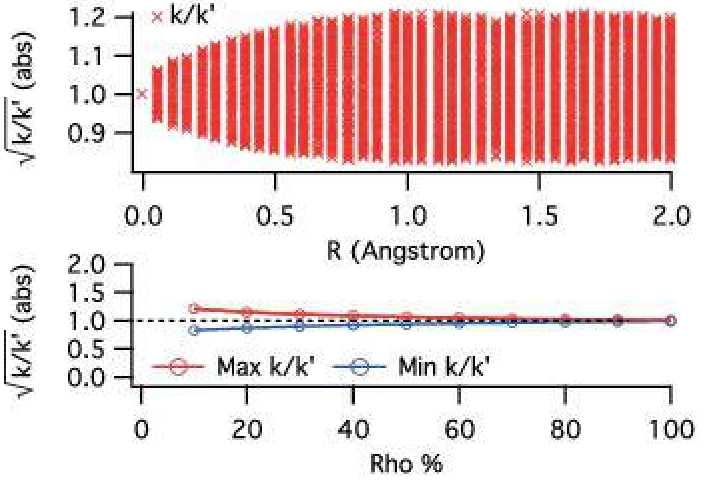
$$g = \omega_0(r)R^2 + k(r)$$

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

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

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

$$q(r) = \omega_0(n(r),\nabla n(r))/k(n(r))$$

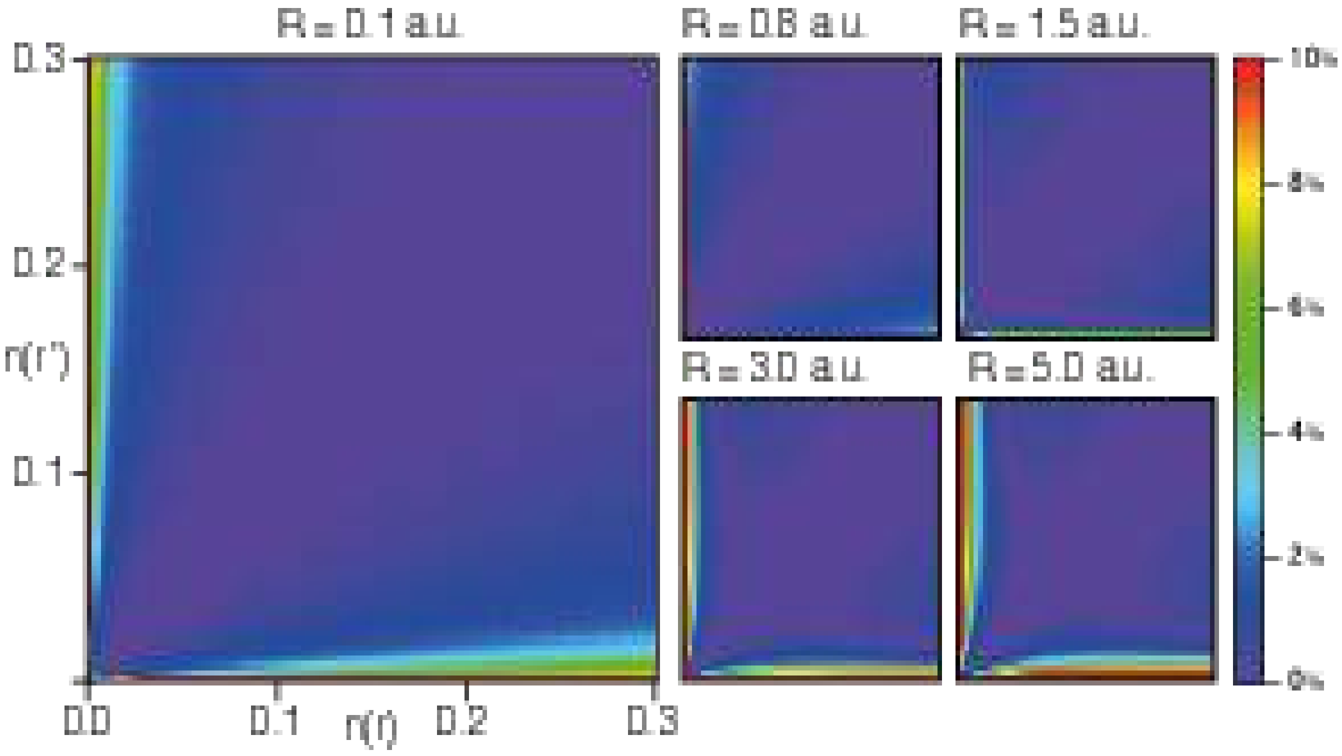


$$\Phi^{rVV10}(r,r') = -\frac{3e^4}{2m^2}\frac{1}{k^{3/2}k'^{3/2}}\frac{1}{(qR^2+1)(q'R^2+1)(qR^2+q'R^2+2)}$$

Separable !

VV10 vs rVV10

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



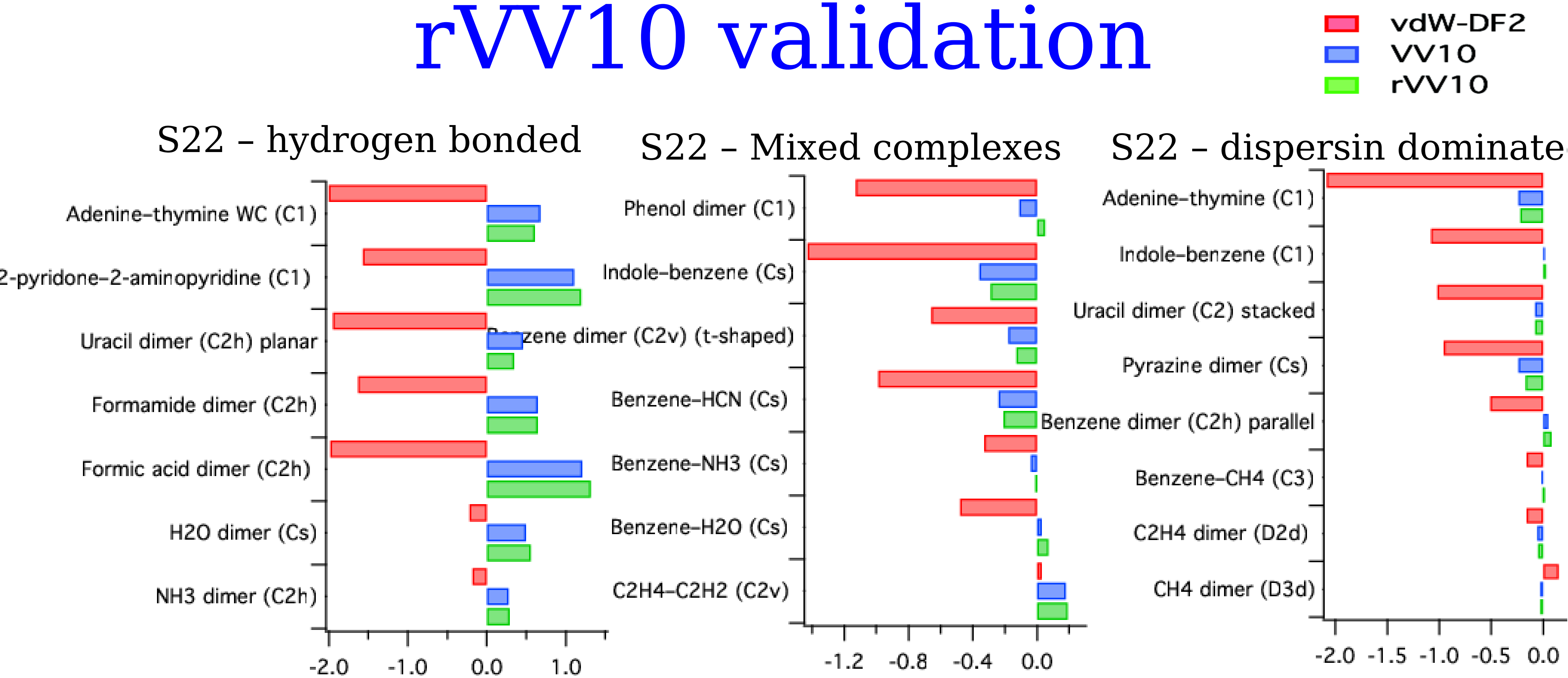
The error in the kernel is small except when the density itself is very small !

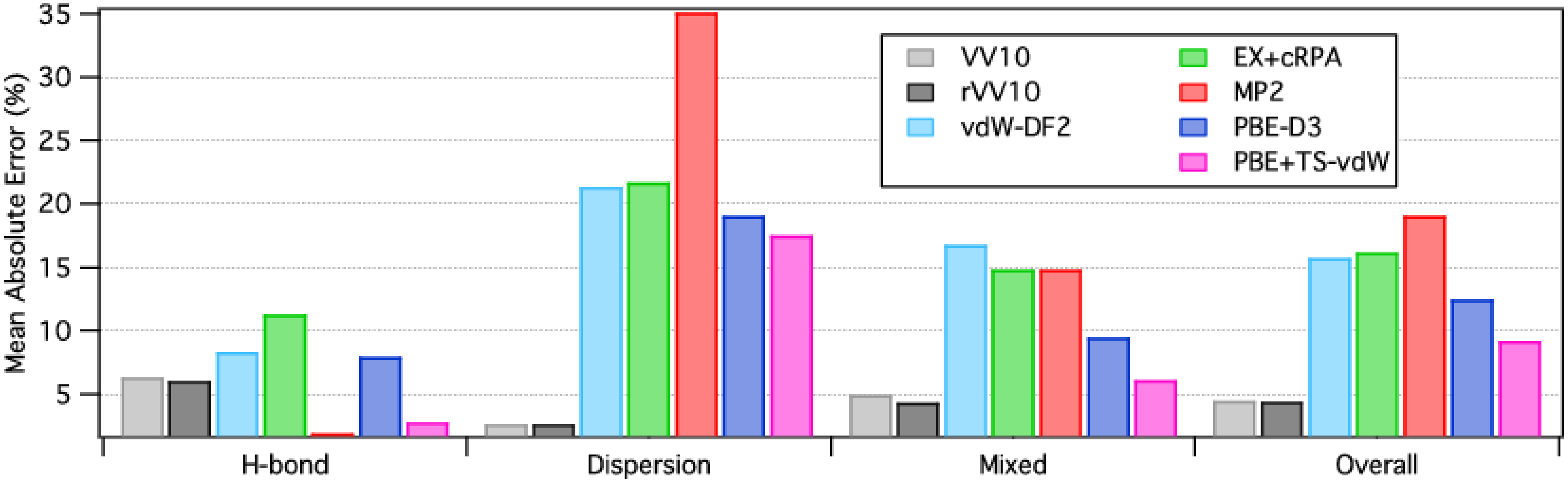
rVV10 validation

S22 – hydrogen bonded

S22 – Mixed complexes

S22 – dispersin dominate

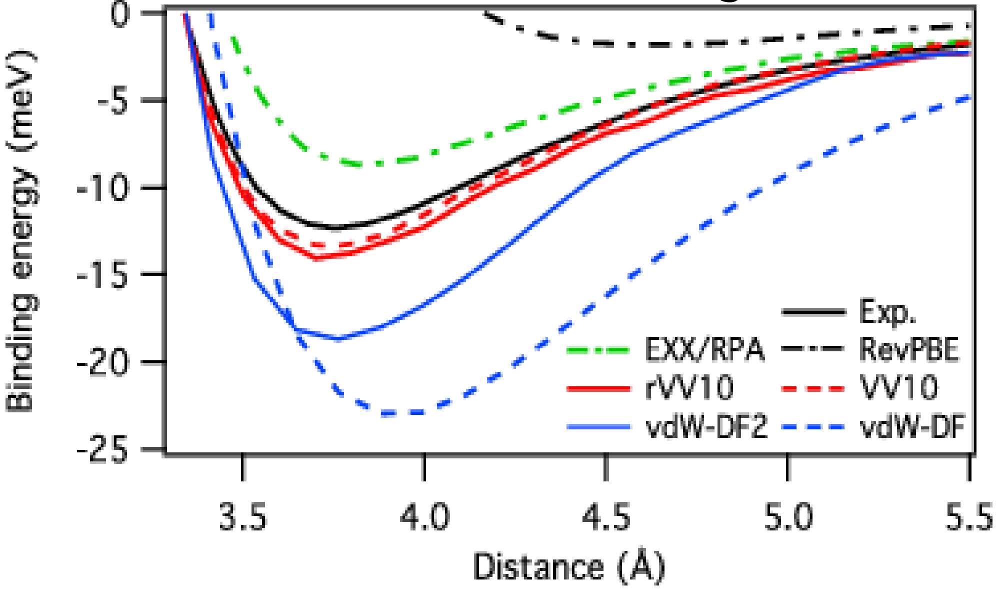


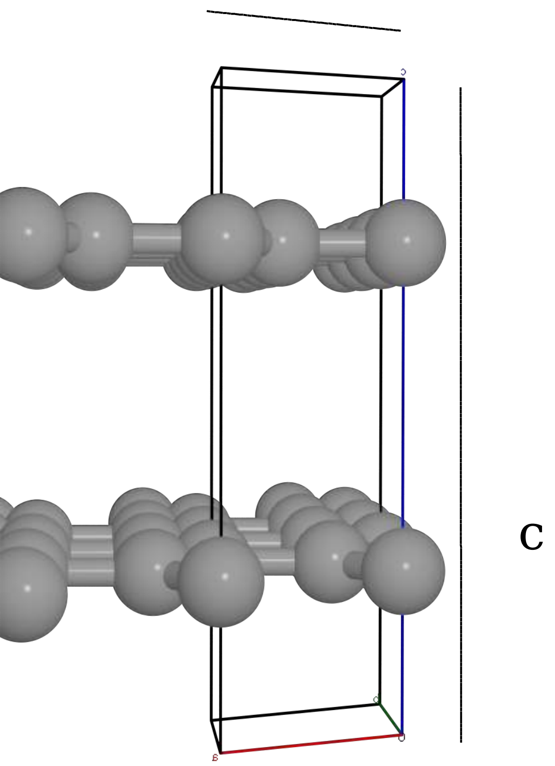


rVV10 applications

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

Argon dimer

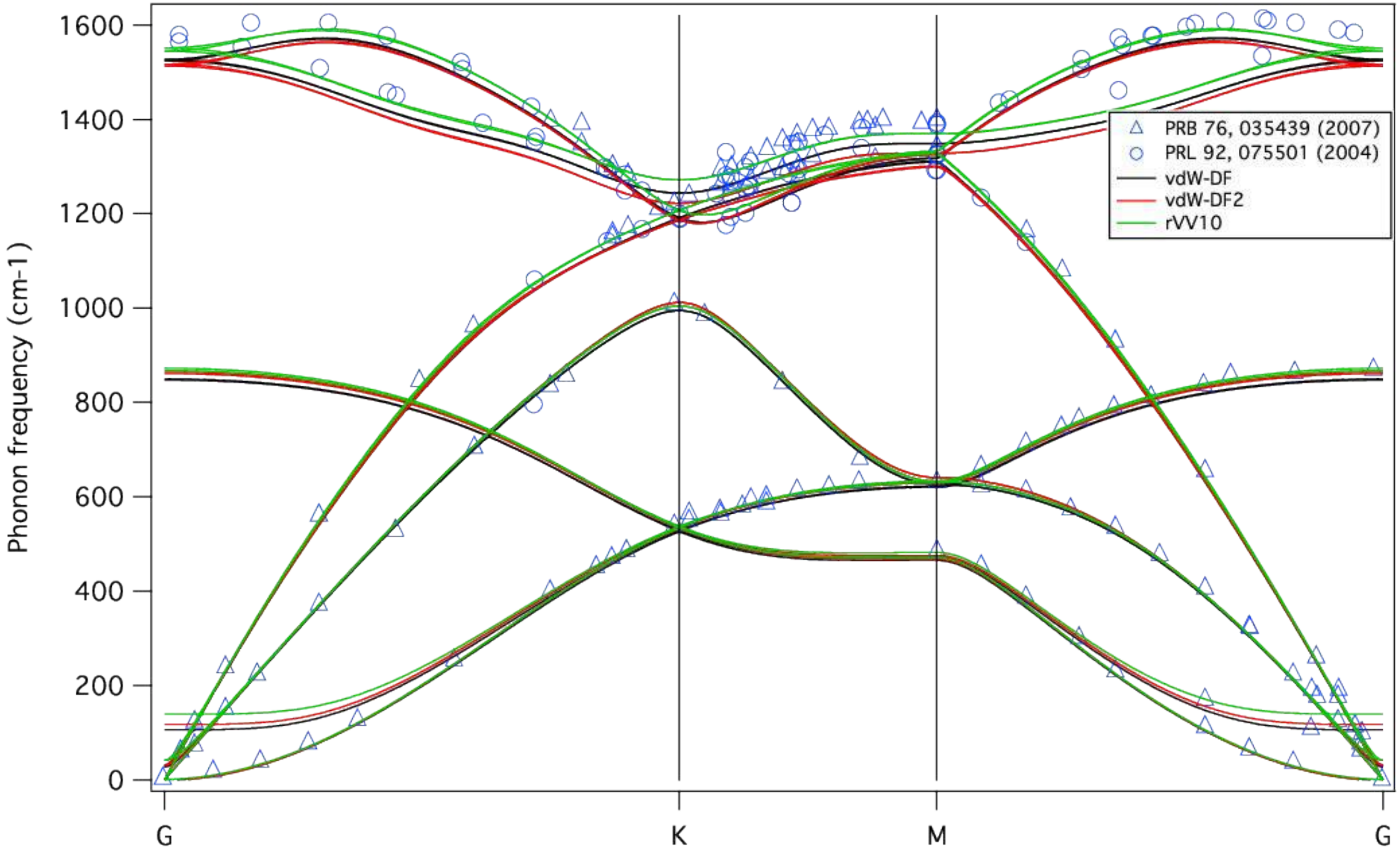


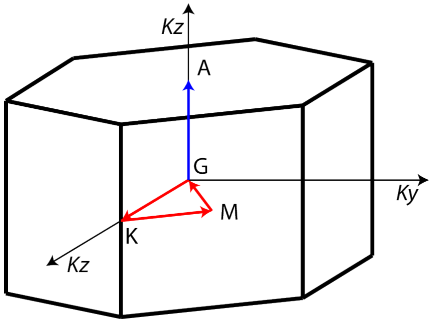


Graphite cel parameters (A)

	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



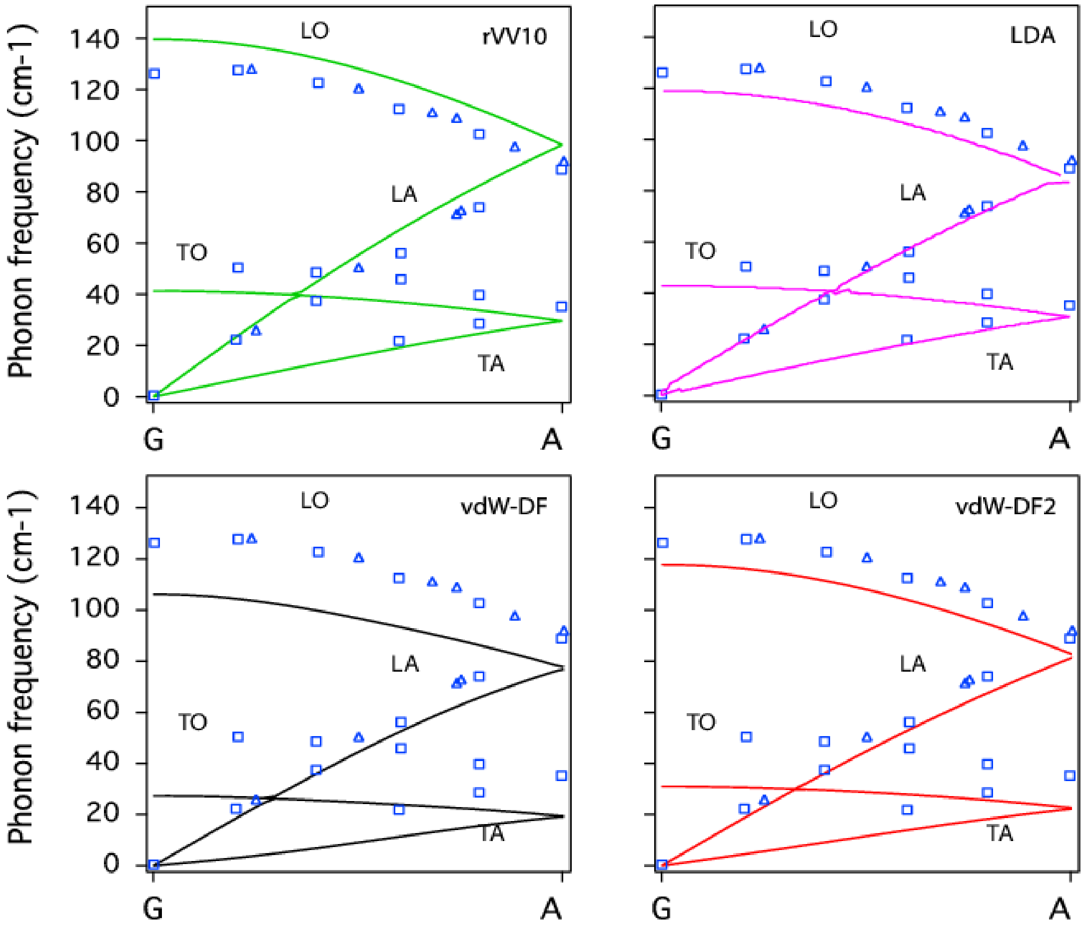


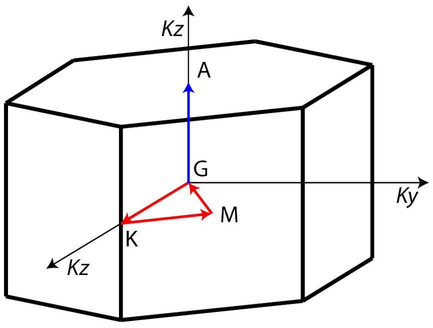
Stiff intralayer
modes

	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

SUMMARY

LDA and LSDA
  simple and well defined. good geometry, overbinding

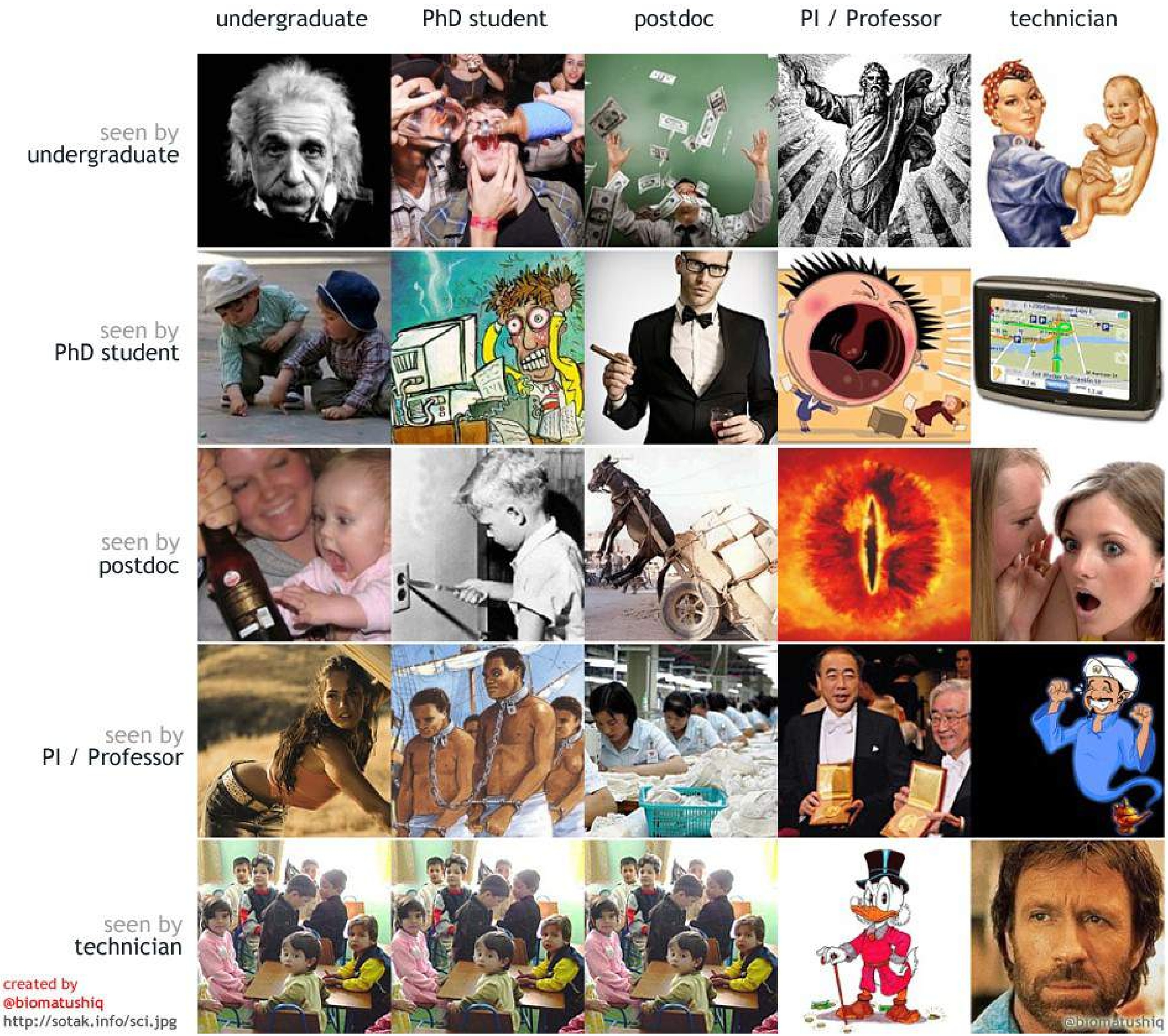
GGA : PW91, PBE, revPBE, RPBE, BLYP
  many options, improved energetics, good geometry

META-GGA: PKZB, TPSS,
  more complicated, not very much used

SIC, DFT+U, Hybrids
  address the self-interaction error with some drawback

Van der Waals functionals
  truly non local, very active field

How people in science see each other



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@biomatushiq
http://sotak.info/sci.jpg

THE END

Some Remarks on DFT Calculations

- DFT is an exact theory BUT approximations for the exchange-correlation energy are required for practical applications
- LDA, GGAs succesfully predict properties of a wide class of electronic systems

Local or Semi-Local nature of LDA, GGAs functionals

$$E_{xc}^{LDA} = \int d\mathbf{r}\, \varepsilon_{xc}^{LDA}[n(\mathbf{r})]\, n(\mathbf{r})$$

$$E_{xc}^{GGA} = \int d\mathbf{r}\, \varepsilon_{xc}^{GGA}[n(\mathbf{r}), \nabla n(\mathbf{r})]\, n(\mathbf{r})$$

- There are many systems where DFT within LDA and GGAs fails e.g. **strongly correlated materials AND weakly vdW bonded compounds**

ACFDT : an exact definition for the correlation energy

Adiabatic Connection formula for correlation energy:

$$E_c = -\frac{1}{2\pi}\int_0^1 d\lambda \int d\mathbf{r}d\mathbf{r}'\frac{1}{|\mathbf{r}-\mathbf{r}'|}\left\{\int_0^\infty du\,[\chi_\lambda(iu) - \chi_{KS}(iu)]\right\}$$

where $\chi_\lambda(iu)$ is given by

$$\chi_\lambda(iu) = \chi_{KS}(iu) + \chi_\lambda(iu)\left[\lambda v_c + {f_{xc}}^\lambda(iu)\right]\chi_{KS}(iu)$$

ADVANTAGES

- practical (so to speak) way to calculate xc-energy explicitely
- theoretical framework for **systematic** development of functionals

LIMITATIONS

- computationally very demanding
- affected by a circular argument?

Derivation

Full-Interacting Hamiltonian

$$H = T + W + v_{ext} \quad \Rightarrow \quad |\Psi^{GS}\rangle, \, n(\mathbf{r})$$

Non-Interacting (Khon-Sham) Hamiltonian

$$H_{KS} = T_s + v_{KS} \quad \Rightarrow \quad |\Phi^{GS}_{KS}\rangle, \, n(\mathbf{r})$$

then we introduce fictitious systems with **scaled interaction** λW wich connect the KS ($\lambda = 0$) with the Many-Body system ($\lambda = 1$)

Adiabatic Connection

$$H_\lambda = T + \lambda W + v^{\lambda}_{ext}$$

$$v^{\lambda=0}_{ext} = v_{KS}$$

$$v^{\lambda=1}_{ext} = v_{ext}$$

$$n_\lambda(\mathbf{r}) = \langle \Psi^{GS}_{\lambda} | \hat{n}(\mathbf{r}) | \Psi^{GS}_{\lambda} \rangle = n(\mathbf{r})$$

Derivation

According to **Hellmann-Feynman** theorem

$$\frac{dE_\lambda}{d\lambda} = \langle \Psi_\lambda | \frac{dH_\lambda}{d\lambda} | \Psi_\lambda \rangle = \langle \Psi_\lambda | W | \Psi_\lambda \rangle + \langle \Psi_\lambda | \frac{\partial v_{ext}}{\partial \lambda} | \Psi_\lambda \rangle$$

Integrating over λ beetween 0 and 1

$$E_{\lambda=1} = E_{\lambda=0} + \int_0^1 d\lambda \, \langle \Psi_\lambda | W | \Psi_\lambda \rangle + \int d\mathbf{r} \, n(\mathbf{r}) [v_{ext}(\mathbf{r}) - v_{KS}(\mathbf{r})]$$

With the usual decomposition of energy functional

$$E_{\lambda=1} = T_s + E_H + E_{xc} + \int d\mathbf{r} \, n(\mathbf{r}) v_{ext}(\mathbf{r})$$

$$E_{\lambda=0} = T_s + \int d\mathbf{r} \, n(\mathbf{r}) v_{KS}(\mathbf{r})$$

we end up with

$$E_H + E_{xc} = \int_0^1 d\lambda \, \langle \Psi_\lambda | W | \Psi_\lambda \rangle$$

Derivation

$$\langle \Psi_\lambda | W | \Psi_\lambda \rangle = \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} n_\lambda^{(2)}(\mathbf{r}, \mathbf{r}')$$

$$n_\lambda^{(2)}(\mathbf{r}, \mathbf{r}') = \langle \delta\hat{n}(\mathbf{r}) \delta\hat{n}(\mathbf{r}') \rangle_\lambda + n(\mathbf{r}) n(\mathbf{r}') - \delta(\mathbf{r} - \mathbf{r}') n(\mathbf{r})$$

Inserting a resolution of the identity in the expectation value and using

$$\frac{2}{\pi} \int_0^\infty du \frac{\gamma}{\gamma^2 + u^2} = 1, \qquad \text{for all } \gamma > 0$$

Fluctuation-Dissipation Theorem

Density Fluctuation ⇒ Energy Dissipation i.e. $Im[\chi]$

$$n_\lambda^{(2)}(\mathbf{r}, \mathbf{r}') = -\int_0^\infty \frac{du}{\pi} \chi_\lambda(\mathbf{r}, \mathbf{r}'; iu) + n(\mathbf{r}) n(\mathbf{r}') - \delta(\mathbf{r} - \mathbf{r}') n(\mathbf{r})$$

Derivation

$$\langle \Psi_\lambda | W | \Psi_\lambda \rangle = \frac{1}{2}\int d\mathbf{r}d\mathbf{r}' \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} n_\lambda^{(2)}(\mathbf{r},\mathbf{r}')$$

$$n_\lambda^{(2)}(\mathbf{r},\mathbf{r}') = \langle \delta\hat{n}(\mathbf{r})\delta\hat{n}(\mathbf{r}')\rangle_\lambda + n(\mathbf{r})n(\mathbf{r}') - \delta(\mathbf{r}-\mathbf{r}')n(\mathbf{r})$$

Fluctuation-Dissipation Theorem

$$n_\lambda^{(2)}(\mathbf{r},\mathbf{r}') = -\int_0^\infty \frac{du}{\pi}\chi_\lambda(\mathbf{r},\mathbf{r}';iu) + n(\mathbf{r})n(\mathbf{r}') - \delta(\mathbf{r}-\mathbf{r}')n(\mathbf{r})$$

Exchange-Correlation Energy from ACFDT

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

Derivation

Replacing χ_λ with $\chi_{KS} = \chi_0$

$$E_x = -\frac{1}{2}\int d\mathbf{r}d\mathbf{r}' \frac{|\sum_i^{occ} \phi_i^*(\mathbf{r})\phi_i(\mathbf{r}')|^2}{|\mathbf{r}-\mathbf{r}'|}$$

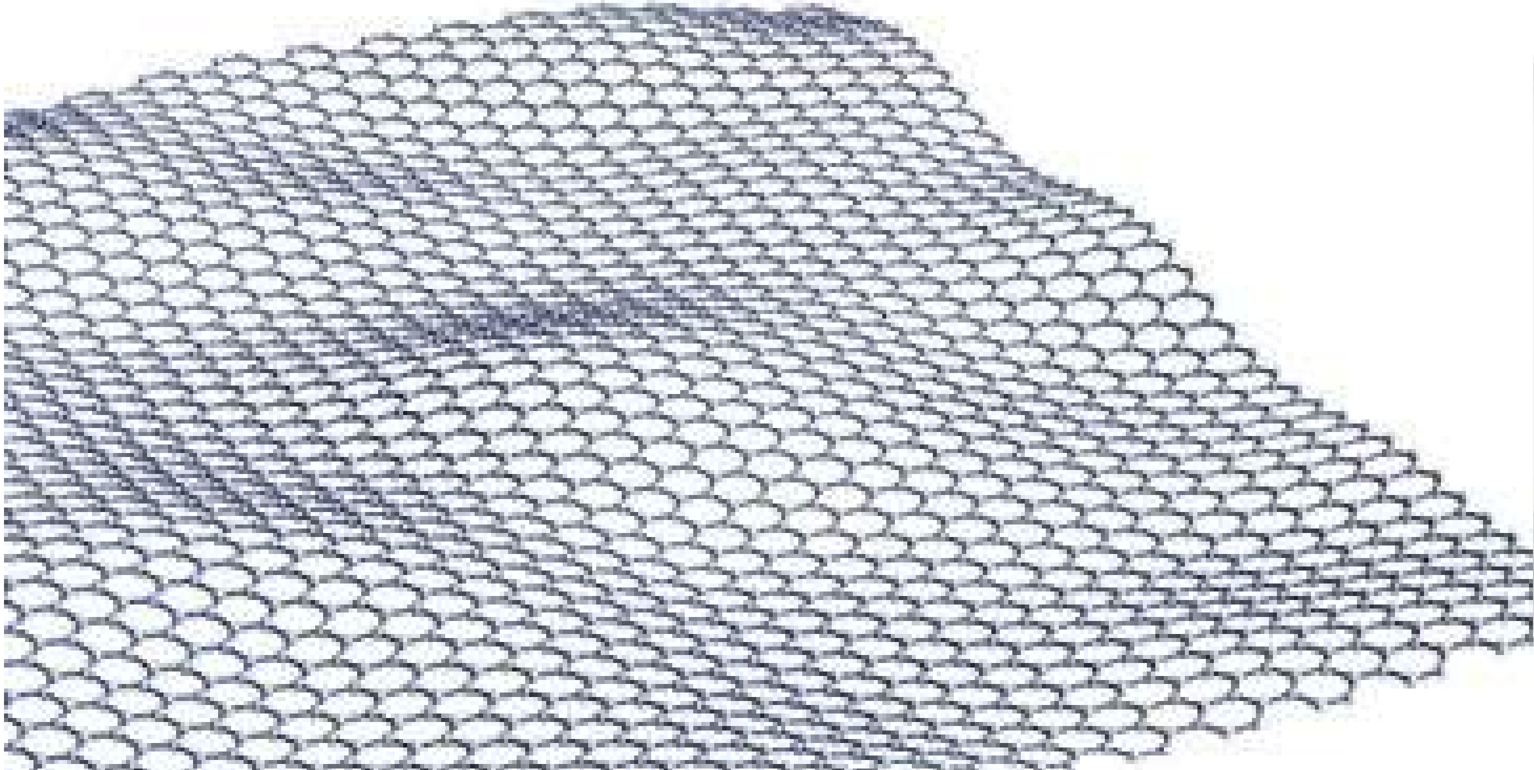
The exchange-correlation energy can thus be separated

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

Adiabatic connection formula for correlation energy

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

$$\chi_\lambda(iu) = \chi_0(iu) + \chi_\lambda(iu)[\lambda\upsilon_c + f_{xc}^\lambda(iu)]\chi_0(iu)$$



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