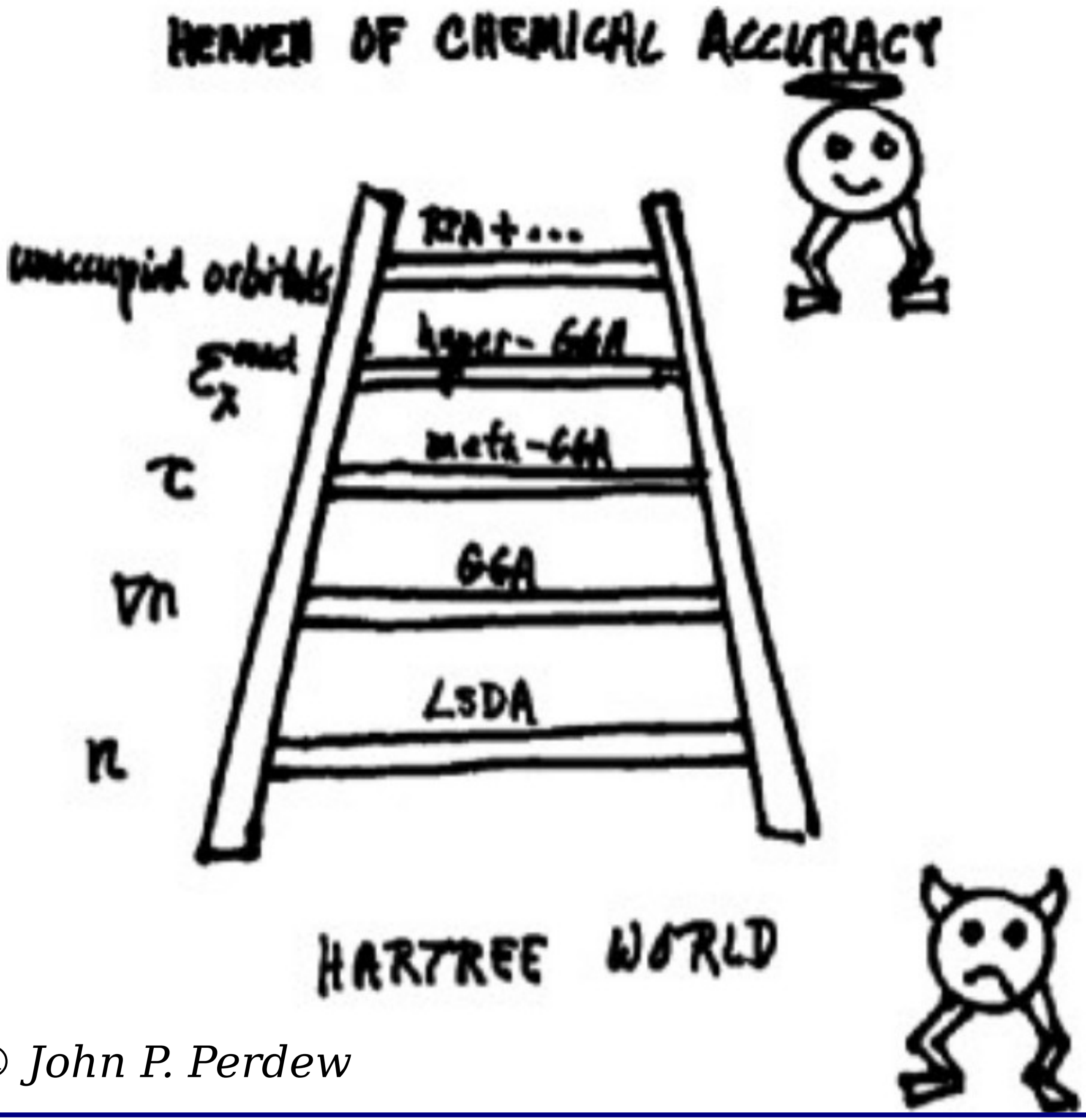
EXC of DFT

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*

Jacob's ladder of Density Functional Theory

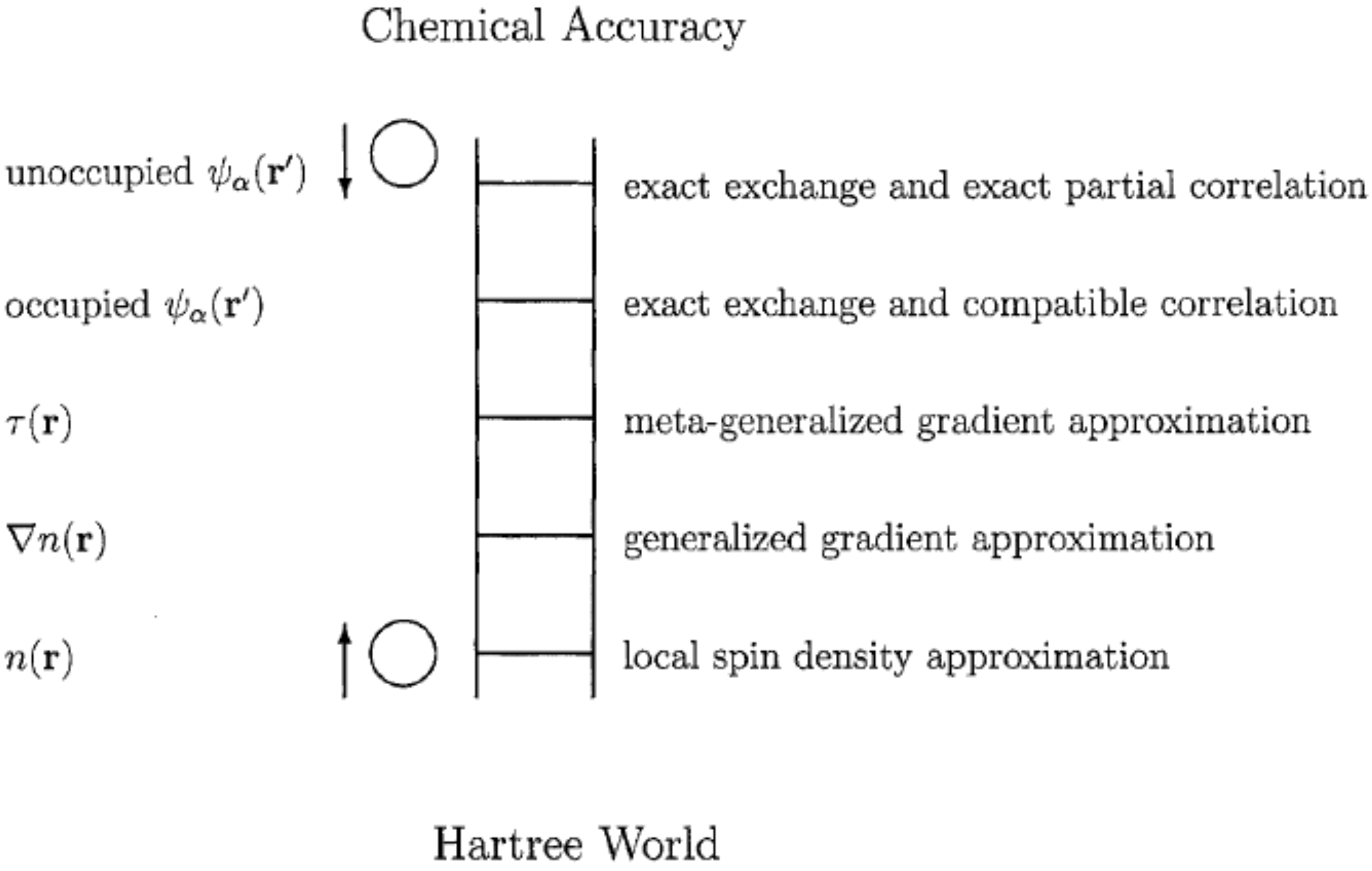
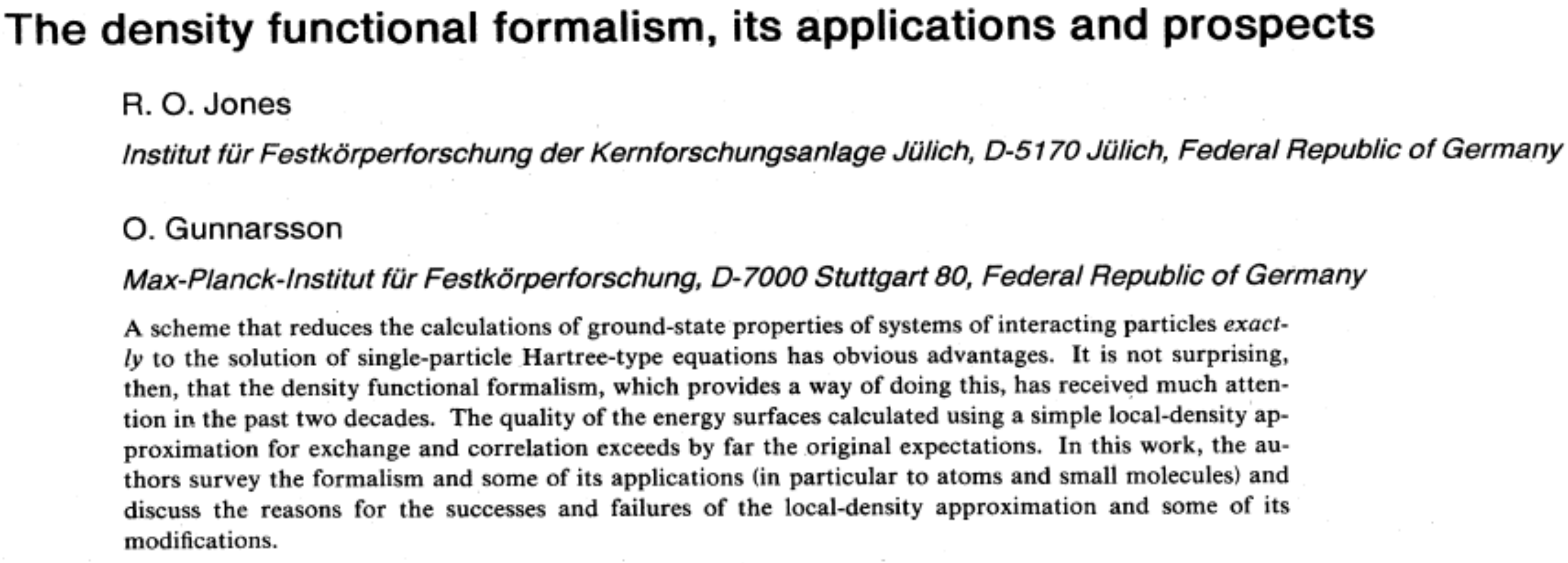


FIGURE 1. Jacob's ladder of density functional approximations. Any resemblance to the Tower of Babel is purely coincidental. Also shown are angels in the spherical approximation, ascending and descending. Users are free to choose the rungs appropriate to their accuracy requirements and computational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

Rev. Mod. Phys. **61,** 689 (1989)



The density functional formalism, its applications and prospects

R. O. Jones

Institut für Festkörperforschung der Kernforschungsanlage Jülich, D-5170 Jülich, Federal Republic of Germany

O. Gunnarsson

Max-Planck-Institut für Festkörperforschung, D-7000 Stuttgart 80, Federal Republic of Germany

A scheme that reduces the calculations of ground-state properties of systems of interacting particles *exactly* to the solution of single-particle Hartree-type equations has obvious advantages. It is not surprising, then, that the density functional formalism, which provides a way of doing this, has received much attention in the past two decades. The quality of the energy surfaces calculated using a simple local-density approximation for exchange and correlation exceeds by far the original expectations. In this work, the authors survey the formalism and some of its applications (in particular to atoms and small molecules) and discuss the reasons for the successes and failures of the local-density approximation and some of its modifications.

HK: $$n(\mathbf{r}) \longrightarrow F[n] = \min_{\Psi \to n} \langle \Psi | T_e + W_{ee} | \Psi \rangle$$

It is useful to introduce a ficticious system
of non-interacting electrons

KS: $$n(\mathbf{r}) \longrightarrow T_s[n] = \min_{\Psi \to n} \langle \Psi | T_e | \Psi \rangle$$

$$F[n] = T_s[n] + E_H[n] + E_{xc}[n]$$ This defines E_{xc}

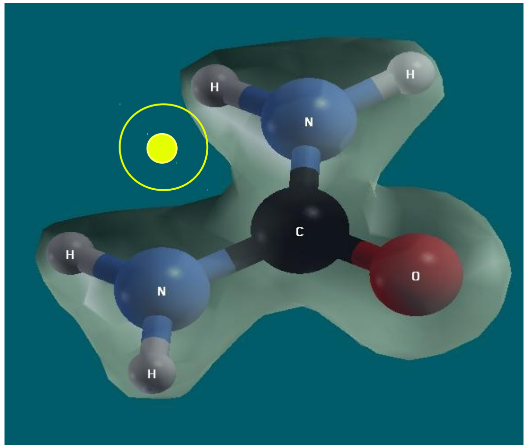
The energy becomes

$$E[n] = T_s[n] + E_H[n] + E_{xc}[n] + \int V_{ext}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r}$$

Self-consistent equations [Kohn-Sham, 1965]

$$V_{eff}(\mathbf{r},\mathbf{R}) = V_{ext}(\mathbf{r},\mathbf{R}) + e^2 \int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' + \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})}$$

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{eff}(\mathbf{r},\mathbf{R})\right]\phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r})$$



$$n(\mathbf{r}) = 2\sum_i |\phi_i(\mathbf{r})|^2$$

It is as simple as a Mean-field approach but it is exact !

$E_{xc}[n]$ is not known exactly → approximations

Simple approximations to Exc are possible

$$E[n] = T_s[n] + E_H[n] + E_{xc}[n] + \int V_{ext}(\mathbf{r})n(\mathbf{r})d\mathbf{r}$$

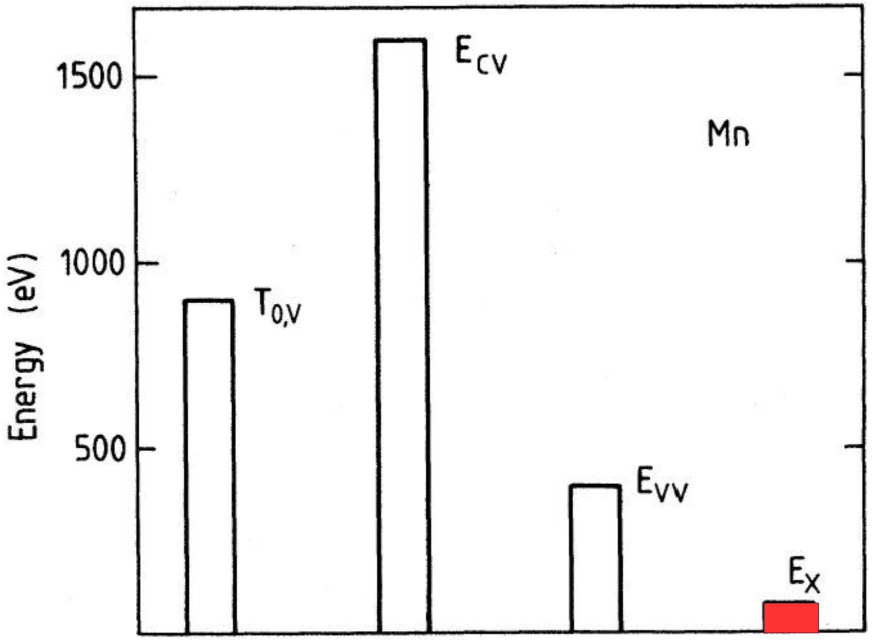
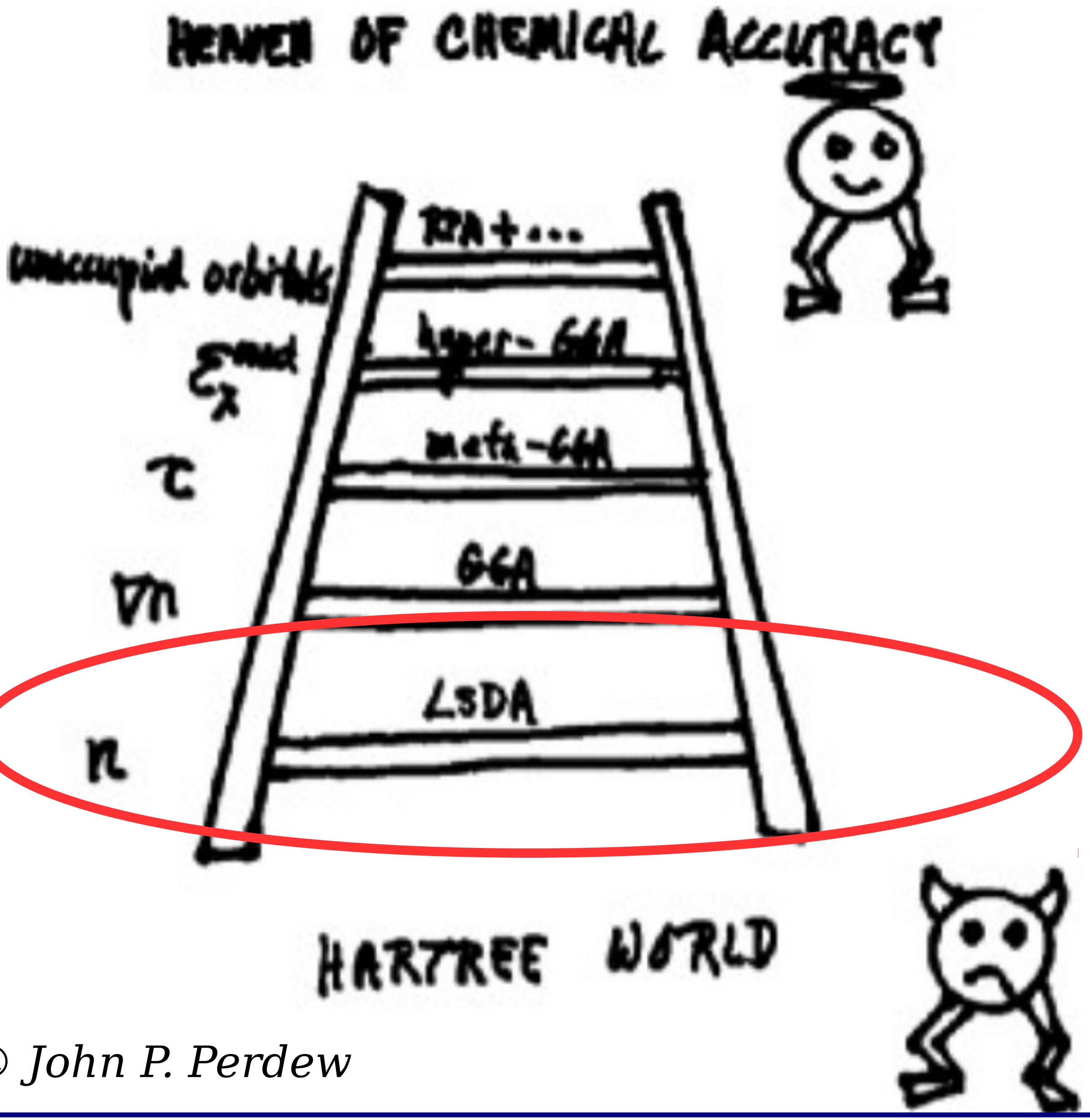


FIG. 4. Relative magnitudes of contributions to total valence energy of Mn atom (in eV).

Jacob's ladder of Density Functional Theory



® *John P. Perdew*

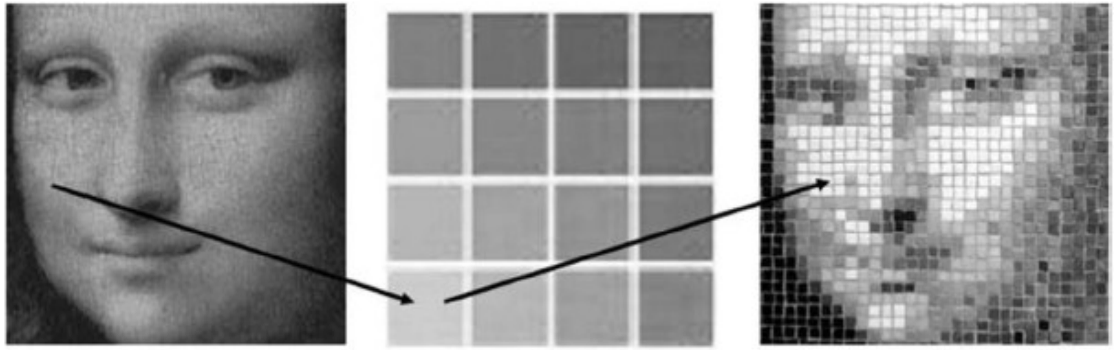
Local Density Approximation

The simplest approximation is LDA that exploits nearsightedness of the electronic matter

W. Kohn, PRL 76,3168 (1996)

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

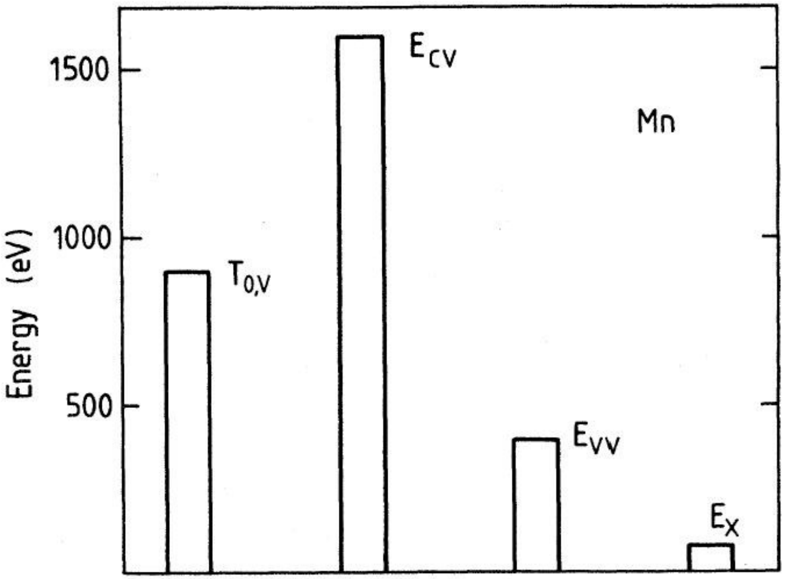
Analogous to the Thomas-Fermi approximation for the Kinetic Energy term but applied to the much smaller Exchange-Correlation term



Actual ρ
Impossible
to calculate E_{xc}

Ideal ρ for UEG
Possible
to calculate ε_{xc}

ρ for LDA/GGA
Possible
to approximate E_{xc}



A good Ground State theory

LDA/LSDA describes well a variety of materials and materials properties (amenable to an el. GS description)

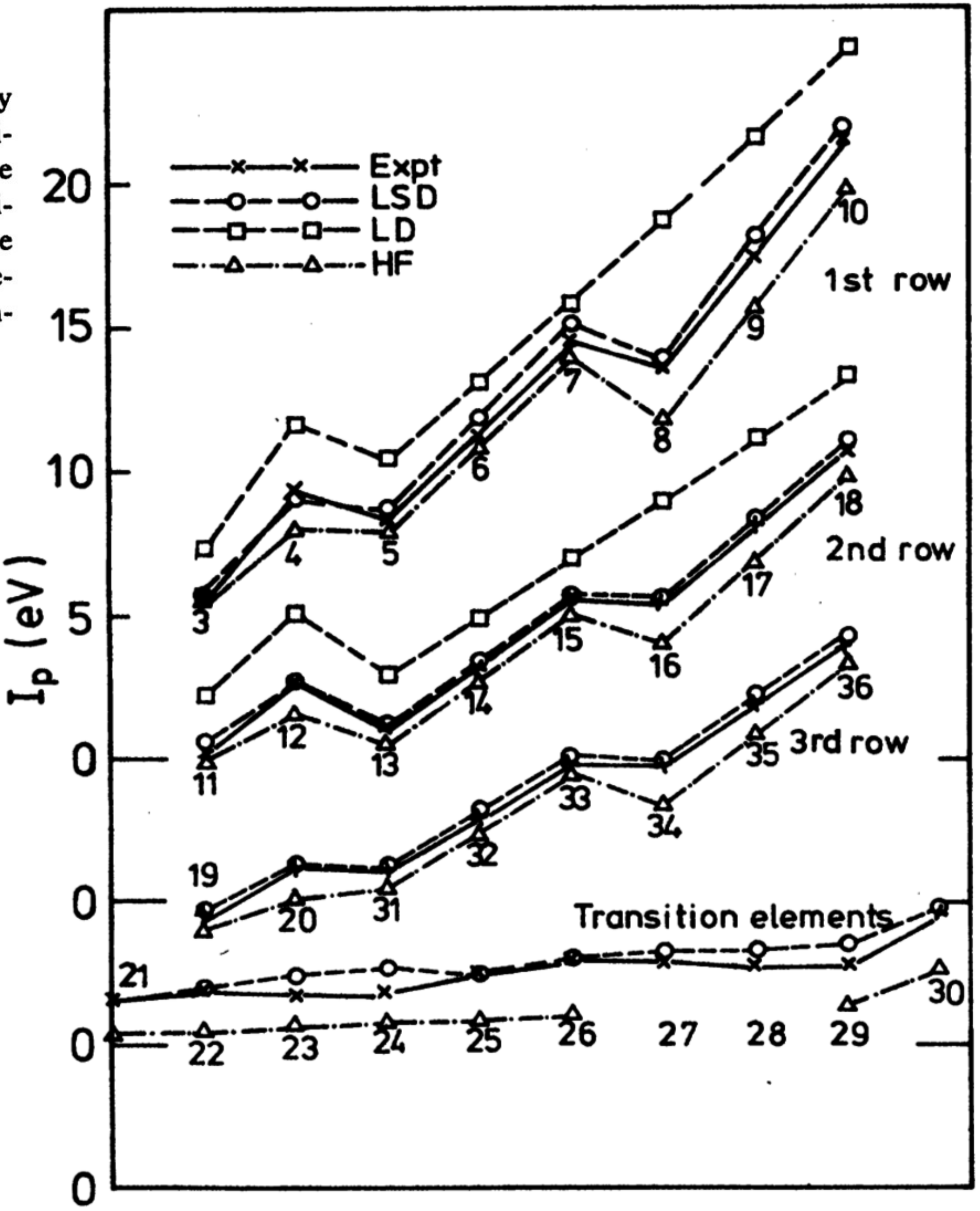
- energetics, phase stability, defects thermodynamics
- equilibrium geometries of complex systems
- response functions to external perturbations
  - *static dielectric constants*
  - *piezoelectric constants*
  - *elastic constants*
- within the adiabatic approximation lattice dymamics is a ground state property
  - *vibrational properties*
  - *defect diffusion*
  - *thermodynamic properties*

First Ionization Energies

FIG. 8. First ionization energy of atoms in the local-density (LD), local spin-density (LSD), and Hartree-Fock (HF) approximations compared with experiment. The numbers show the atomic numbers of the atoms considered. For reasons of clarity, the zero of energy is shifted by 5, 10, and 15 eV for the second row, the third row, and the transition-element row, respectively. The LD results for the first and second rows are increased by an additional 2 eV.

Rev. Mod. Phys., Vol. 61, No. 3, July 1989

Jones & Gunnarsson



s-p Transfer Energies

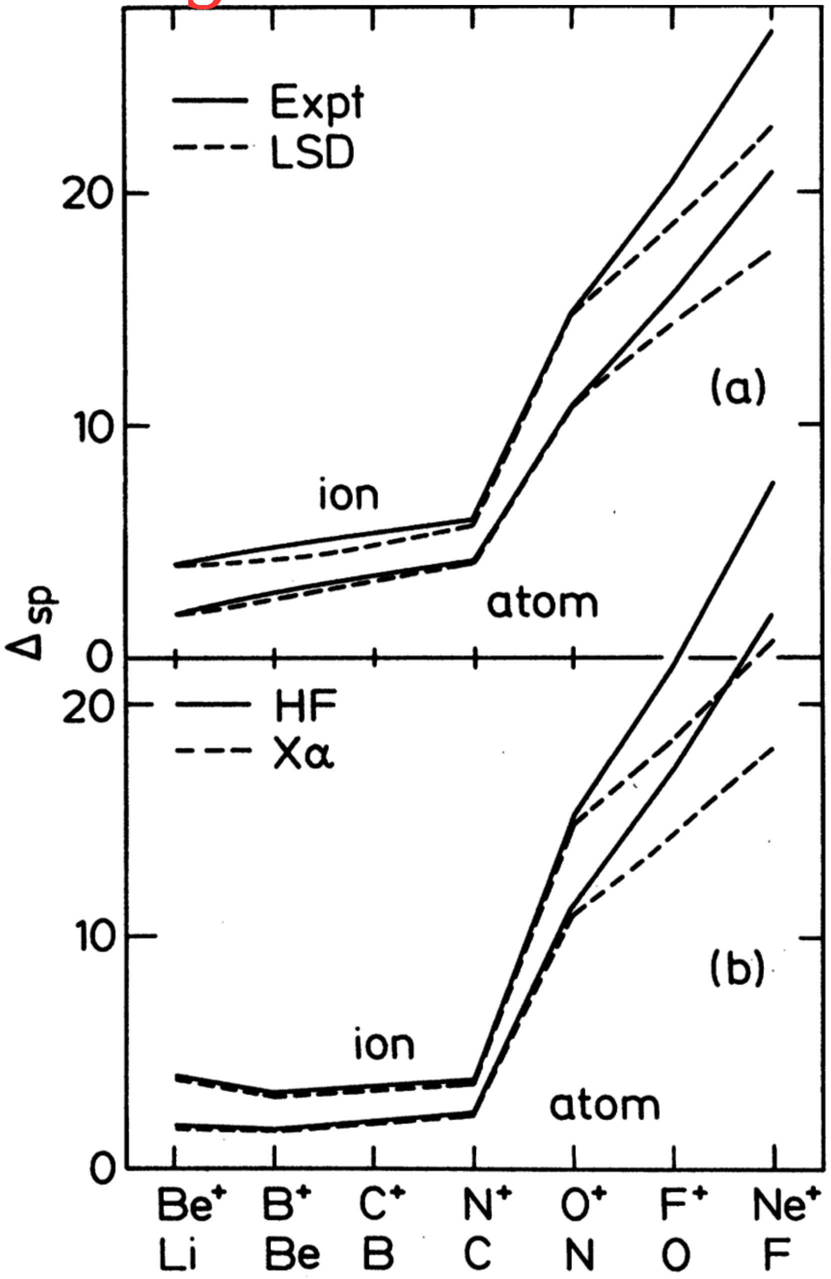
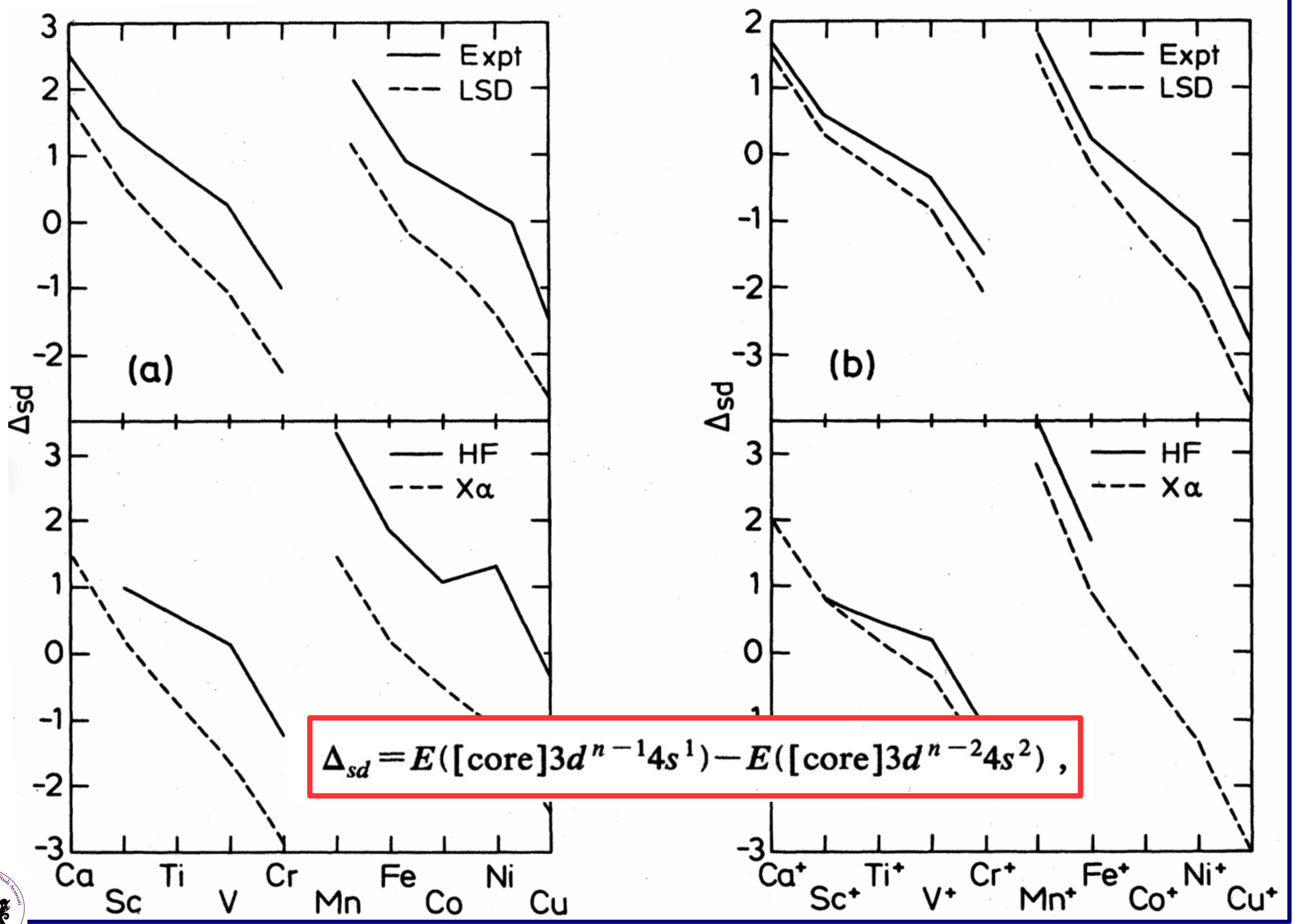


FIG. 9. The *sp* transfer energies Δ_{sp} for the first-row atom ions: (a) experimental and local spin-density (LSD) result Hartree-Fock (HF) and $X\alpha$ results. The energies are in eV.

$$\Delta_{sp} = E(1s^2 2s 2p^{n-1}) - E(1s^2 2s^2 2p^{n-2}) ,$$

s-d Transfer Energies



$$\Delta_{sd}=E([\text{core}]3d^{n-1}4s^{1})-E([\text{core}]3d^{n-2}4s^{2})\ ,$$

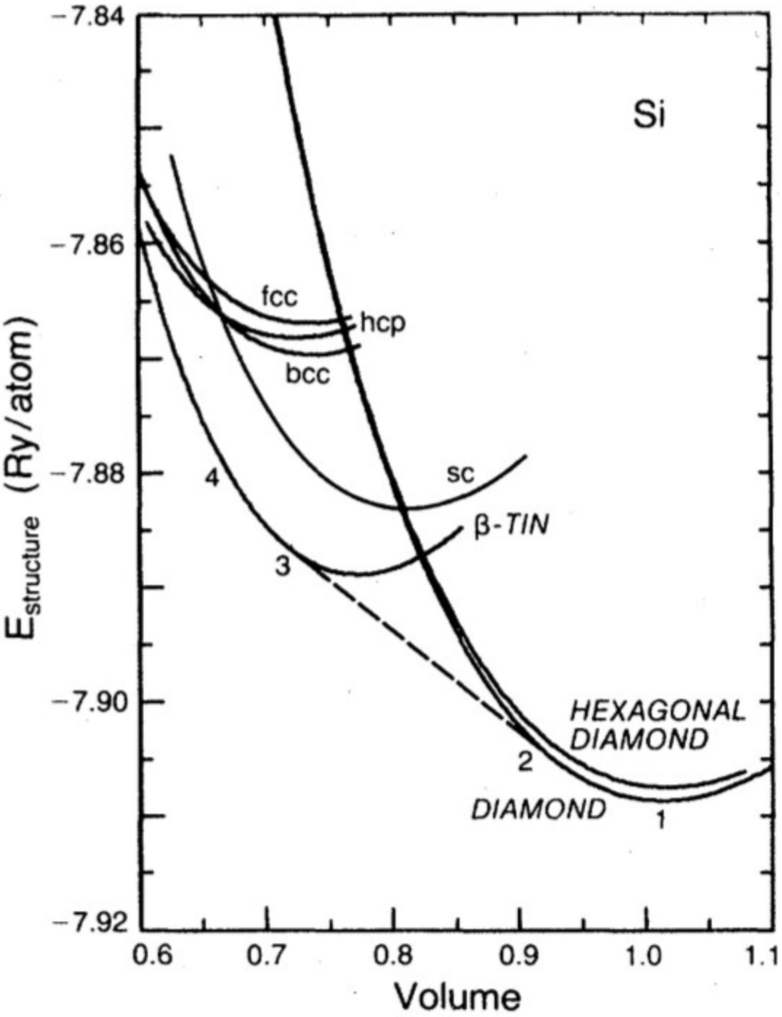


FIG. 5. Total-energy curves of the seven phases of Si as a function of the atomic volume normalized to Ω_{expt} (Ref. 31). Dashed line is the common tangent of the energy curves for the diamond phase and the β-tin phase ($c/a=0.552$).

First Row Dimers

	R_{eq} (a.u.)		BE (eV)		freq(cm-1)	
	exp	LSD	exp	LSD	exp	LSD
H_2	1.40	1.45	4.75	4.81	4400	4277
Li_2	5.05	5.12	1.06	1.01	351	347
Be_2	4.71	4.63	0.11	0.50	294	362
B_2	3.04	3.03	3.08	3.93	1051	1082
C_2	2.35	2.36	6.31	7.19	1857	1869
N_2	2.07	2.08	9.91	11.34	2358	2387
O_2	2.28	2.31	5.23	7.54	1580	1563
F_2	2.68	2.62	1.66	3.32	892	1075

Summary (LDA)

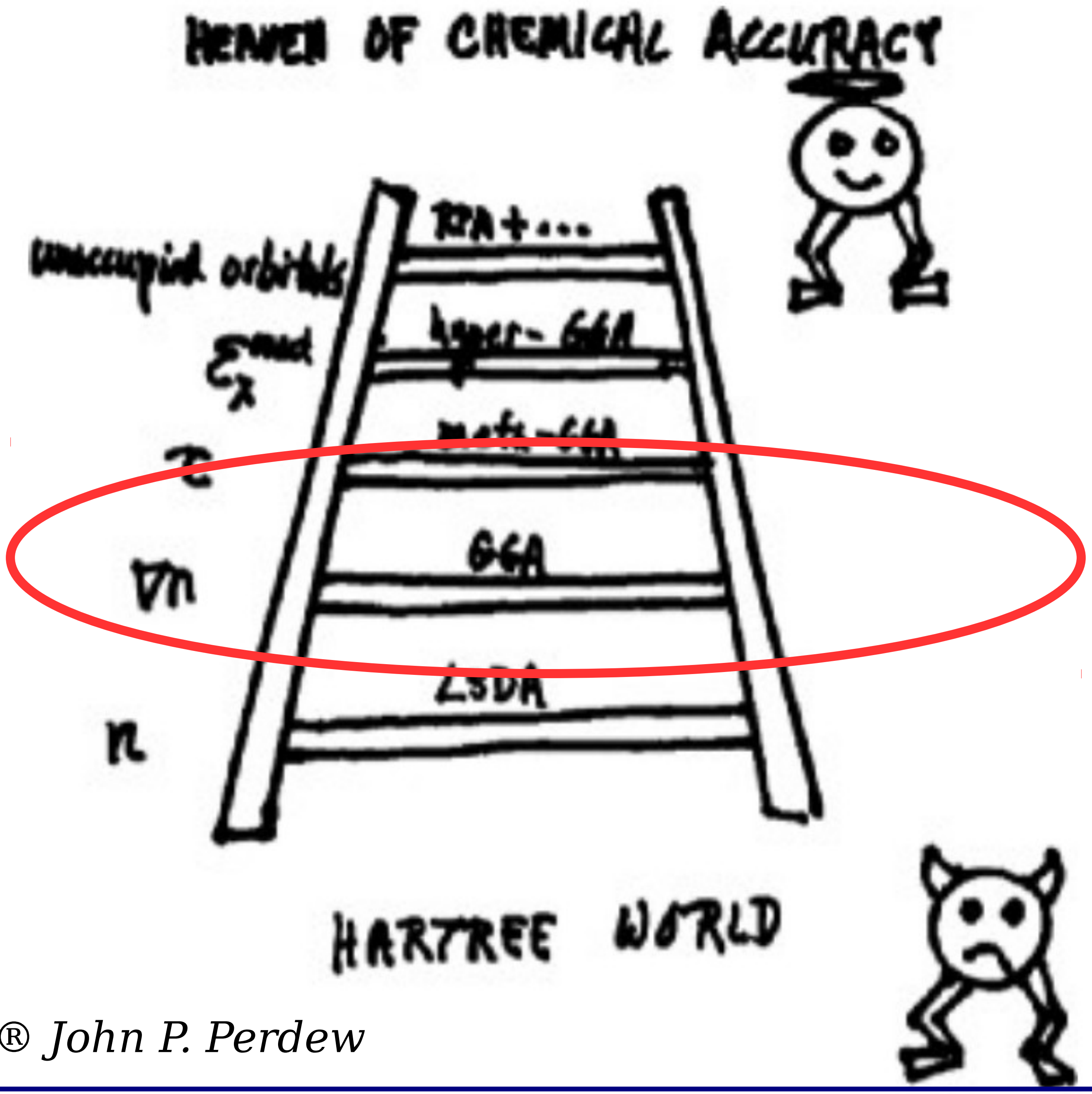
Lattice constants: 1-3% too small

Cohesive Energies: 5-20% too strongly bound

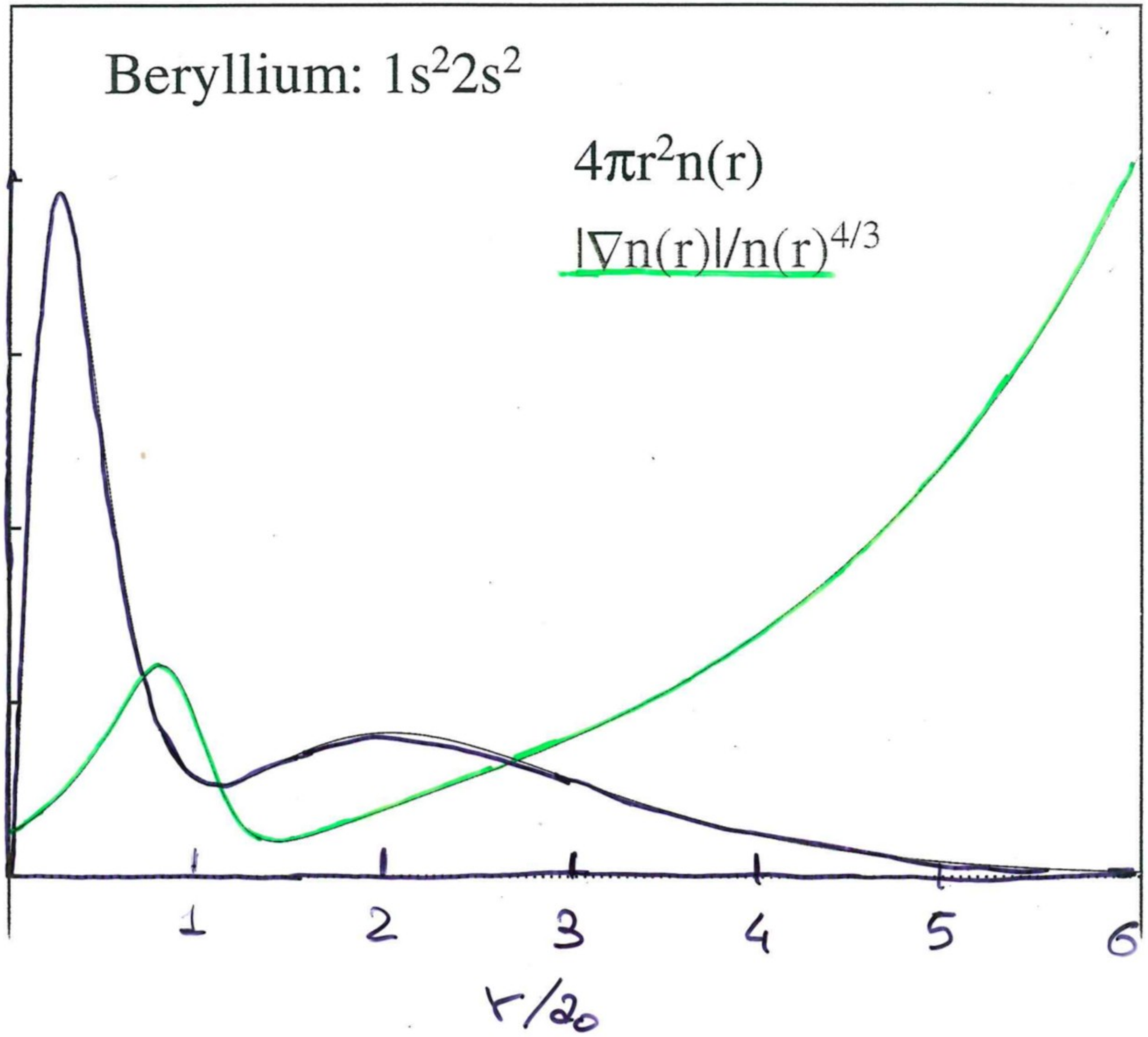
Bulk Modulus: 5-20% (largest errors for late TM)

Bandgaps: too small

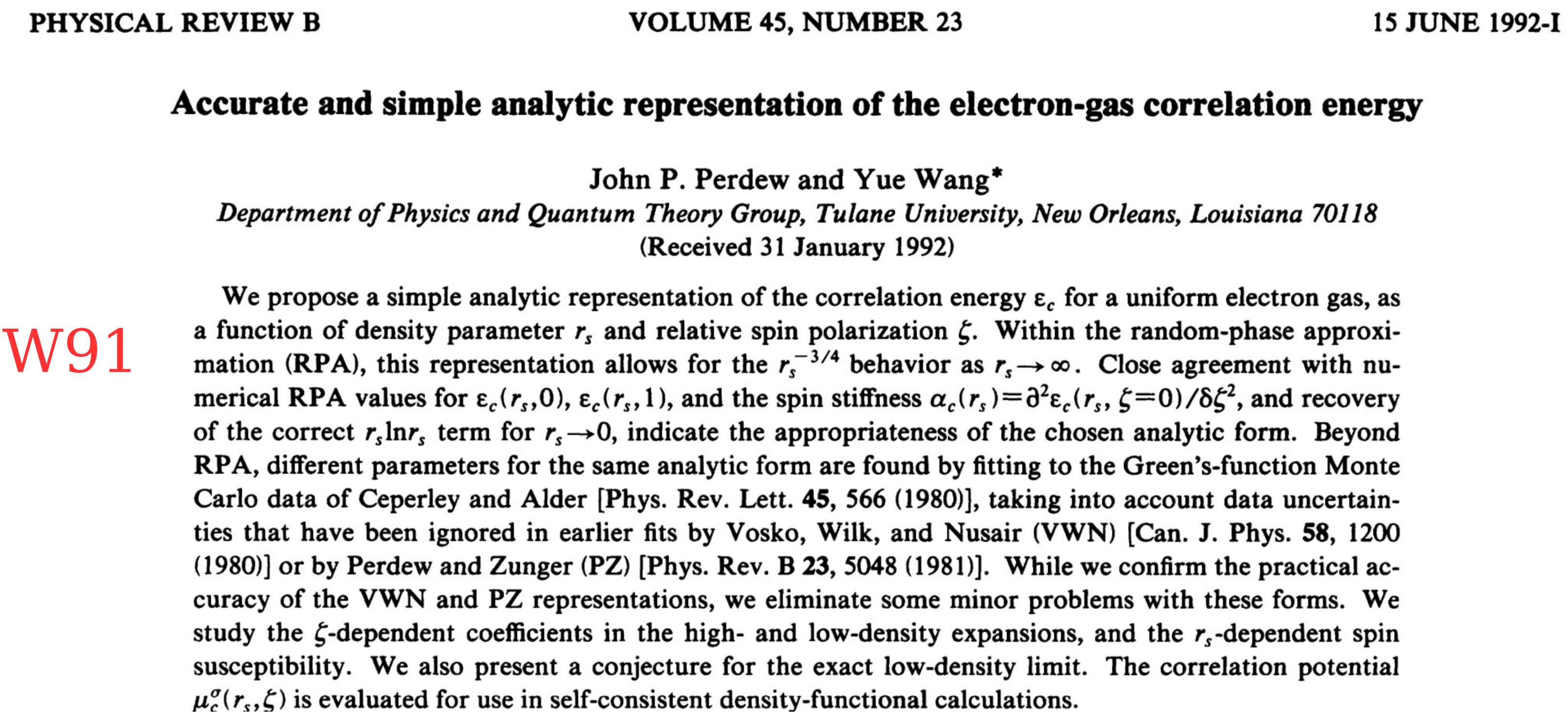
Jacob's ladder of Density Functional Theory



® *John P. Perdew*


Beryllium: $1s^2 2s^2$
$4\pi r^2 n(r)$
$|\nabla n(r)|/n(r)^{4/3}$
1
2
3
4
5
6
r/a_0

PW91



PHYSICAL REVIEW B VOLUME 45, NUMBER 23 15 JUNE 1992-I

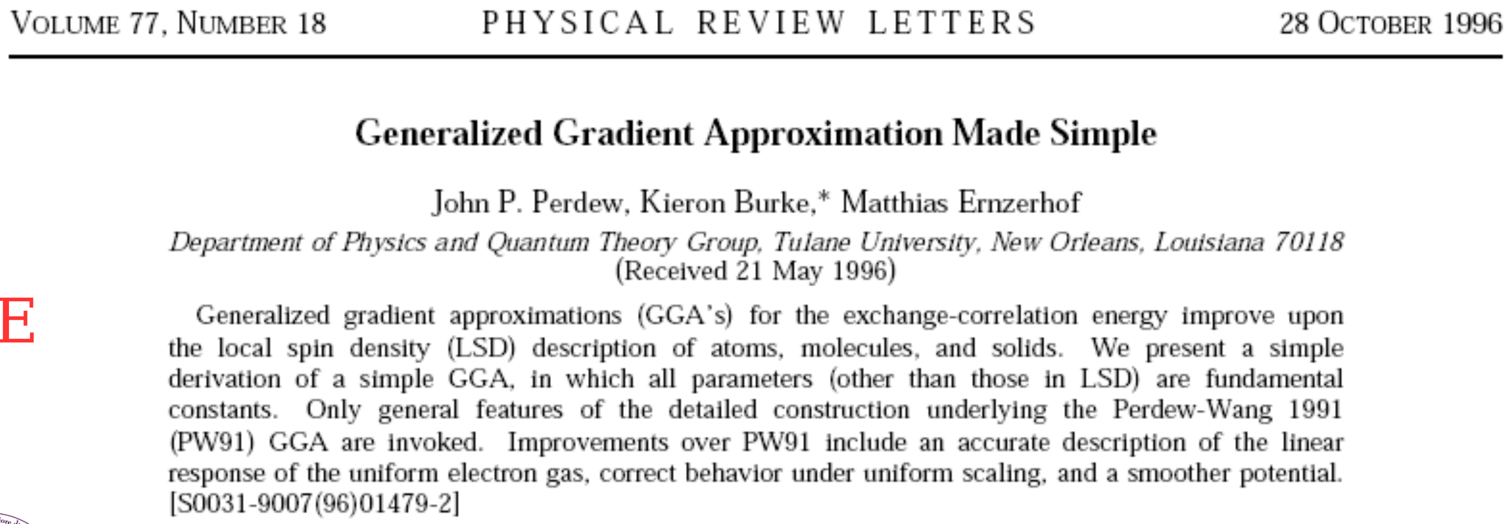
Accurate and simple analytic representation of the electron-gas correlation energy

John P. Perdew and Yue Wang*
Department of Physics and Quantum Theory Group, Tulane University, New Orleans, Louisiana 70118

(Received 31 January 1992)

We propose a simple analytic representation of the correlation energy ε_c for a uniform electron gas, as a function of density parameter r_s and relative spin polarization ζ. Within the random-phase approximation (RPA), this representation allows for the $r_s^{-3/4}$ behavior as $r_s \to \infty$. Close agreement with numerical RPA values for $\varepsilon_c(r_s,0)$, $\varepsilon_c(r_s,1)$, and the spin stiffness $\alpha_c(r_s)=\partial^2\varepsilon_c(r_s,\zeta=0)/\delta\zeta^2$, and recovery of the correct $r_s \ln r_s$ term for $r_s \to 0$, indicate the appropriateness of the chosen analytic form. Beyond RPA, different parameters for the same analytic form are found by fitting to the Green's-function Monte Carlo data of Ceperley and Alder [Phys. Rev. Lett. **45**, 566 (1980)], taking into account data uncertainties that have been ignored in earlier fits by Vosko, Wilk, and Nusair (VWN) [Can. J. Phys. **58**, 1200 (1980)] or by Perdew and Zunger (PZ) [Phys. Rev. B **23**, 5048 (1981)]. While we confirm the practical accuracy of the VWN and PZ representations, we eliminate some minor problems with these forms. We study the ζ-dependent coefficients in the high- and low-density expansions, and the r_s-dependent spin susceptibility. We also present a conjecture for the exact low-density limit. The correlation potential $\mu_c^\sigma(r_s,\zeta)$ is evaluated for use in self-consistent density-functional calculations.

PBE



VOLUME 77, NUMBER 18 PHYSICAL REVIEW LETTERS 28 OCTOBER 1996

Generalized Gradient Approximation Made Simple

John P. Perdew, Kieron Burke,* Matthias Ernzerhof
Department of Physics and Quantum Theory Group, Tulane University, New Orleans, Louisiana 70118

(Received 21 May 1996)

Generalized gradient approximations (GGA's) for the exchange-correlation energy improve upon the local spin density (LSD) description of atoms, molecules, and solids. We present a simple derivation of a simple GGA, in which all parameters (other than those in LSD) are fundamental constants. Only general features of the detailed construction underlying the Perdew-Wang 1991 (PW91) GGA are invoked. Improvements over PW91 include an accurate description of the linear response of the uniform electron gas, correct behavior under uniform scaling, and a smoother potential. [S0031-9007(96)01479-2]

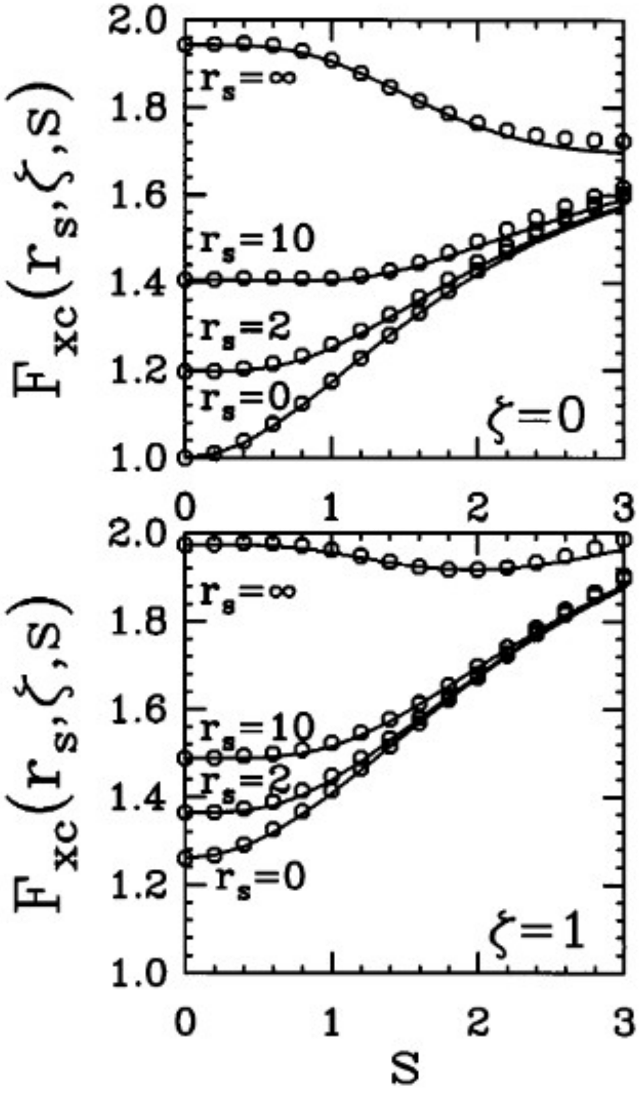
PBE

$$E_{XC}^{GGA}[n_\uparrow, n_\downarrow] = \int d^3r\, n\, \epsilon_X^{\text{unif}}(n) F_{XC}(r_s, \zeta, s).$$

$$\frac{4\pi}{3} r_s^3 = \frac{1}{n}$$

$$\zeta = \frac{n_\uparrow - n_\downarrow}{n_\uparrow + n_\downarrow}$$

$$s = \frac{|\nabla n|}{n^{4/3}}$$



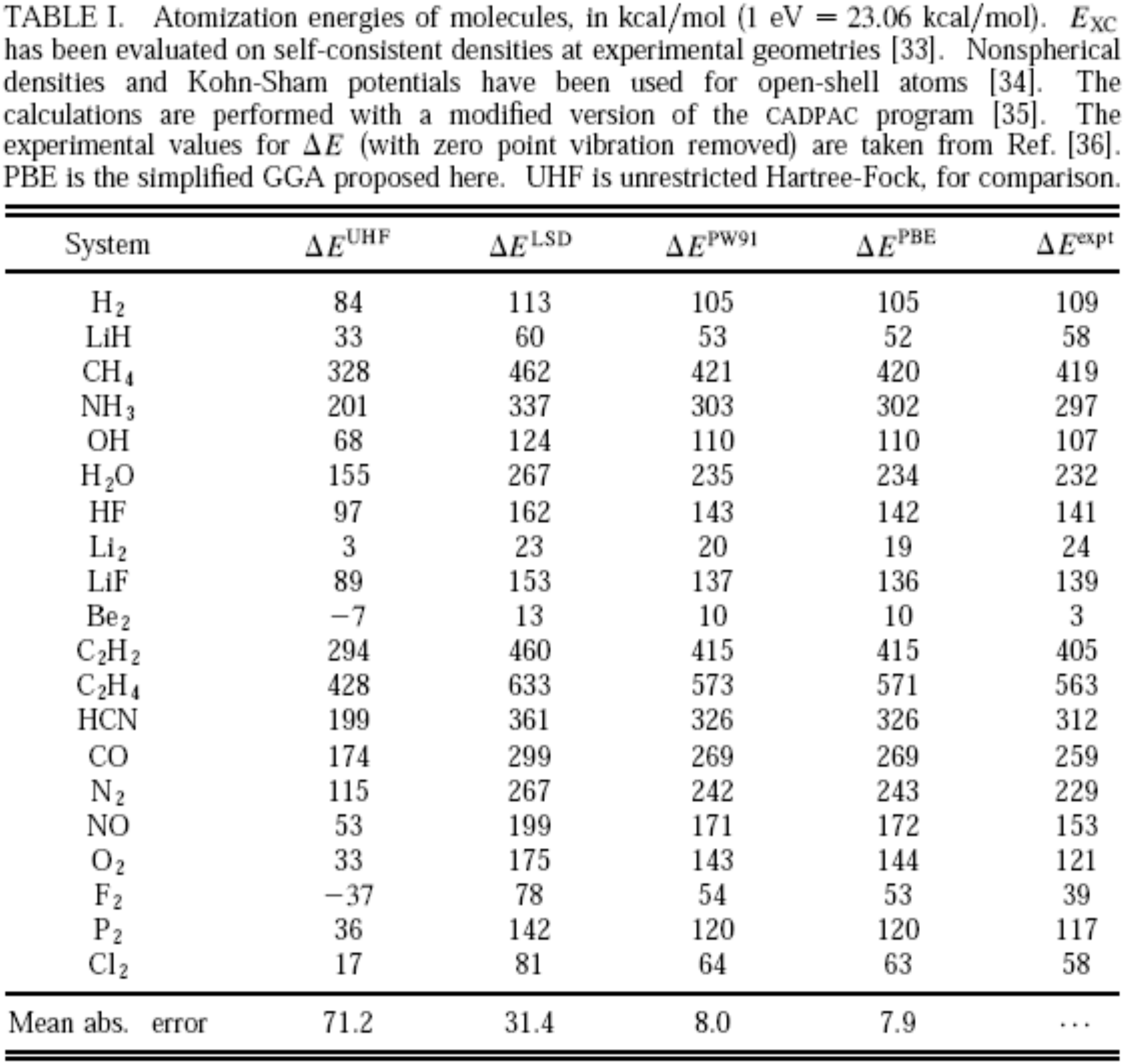


TABLE I. Atomization energies of molecules, in kcal/mol (1 eV = 23.06 kcal/mol). E_{XC} has been evaluated on self-consistent densities at experimental geometries [33]. Nonspherical densities and Kohn-Sham potentials have been used for open-shell atoms [34]. The calculations are performed with a modified version of the CADPAC program [35]. The experimental values for ΔE (with zero point vibration removed) are taken from Ref. [36]. PBE is the simplified GGA proposed here. UHF is unrestricted Hartree-Fock, for comparison.

System	ΔE^{UHF}	ΔE^{LSD}	ΔE^{PW91}	ΔE^{PBE}	ΔE^{expt}
H_2	84	113	105	105	109
LiH	33	60	53	52	58
CH_4	328	462	421	420	419
NH_3	201	337	303	302	297
OH	68	124	110	110	107
H_2O	155	267	235	234	232
HF	97	162	143	142	141
Li_2	3	23	20	19	24
LiF	89	153	137	136	139
Be_2	−7	13	10	10	3
C_2H_2	294	460	415	415	405
C_2H_4	428	633	573	571	563
HCN	199	361	326	326	312
CO	174	299	269	269	259
N_2	115	267	242	243	229
NO	53	199	171	172	153
O_2	33	175	143	144	121
F_2	−37	78	54	53	39
P_2	36	142	120	120	117
Cl_2	17	81	64	63	58
Mean abs. error	71.2	31.4	8.0	7.9	⋯

Oxides

	exp	LDA	Δ	GGA	Δ
MgO	4.21	4.17	-0.95%		
TiO2 (a)	4.59	4.548	-0.92%	4.623	0.72%
TiO2 (c)	2.958	2.944	-0.47%	2.987	0.98%
Al2O2	5.128	5.091	-0.72%	5.185	1.11%
BaTiO3	4	3.94	-1.50%		
PbTiO3	3.9	3.833	-1.72%	3.891	-0.23%
SnO2	4.737	4.637	-2.11%		
β-MnO2 (a)	4.404	4.346	-1.32%	4.444	0.91%
b-MnO2 (c)	2.876	2.81	-2.29%	2.891	0.52%

Summary (LDA & GGA)

Lattice constants: 1-3% too small

Cohesive Energies: 5-20% too strongly bound

Bulk Modulus: 5-20% (largest errors for late TM)

Bandgaps: too small

GGA gives better cohesive energies. Effect on lattice parameters is more random. GGA important for magnetic systems.

Summary of Geometry Prediction

LDA under-predicts bond lengths (always ?)

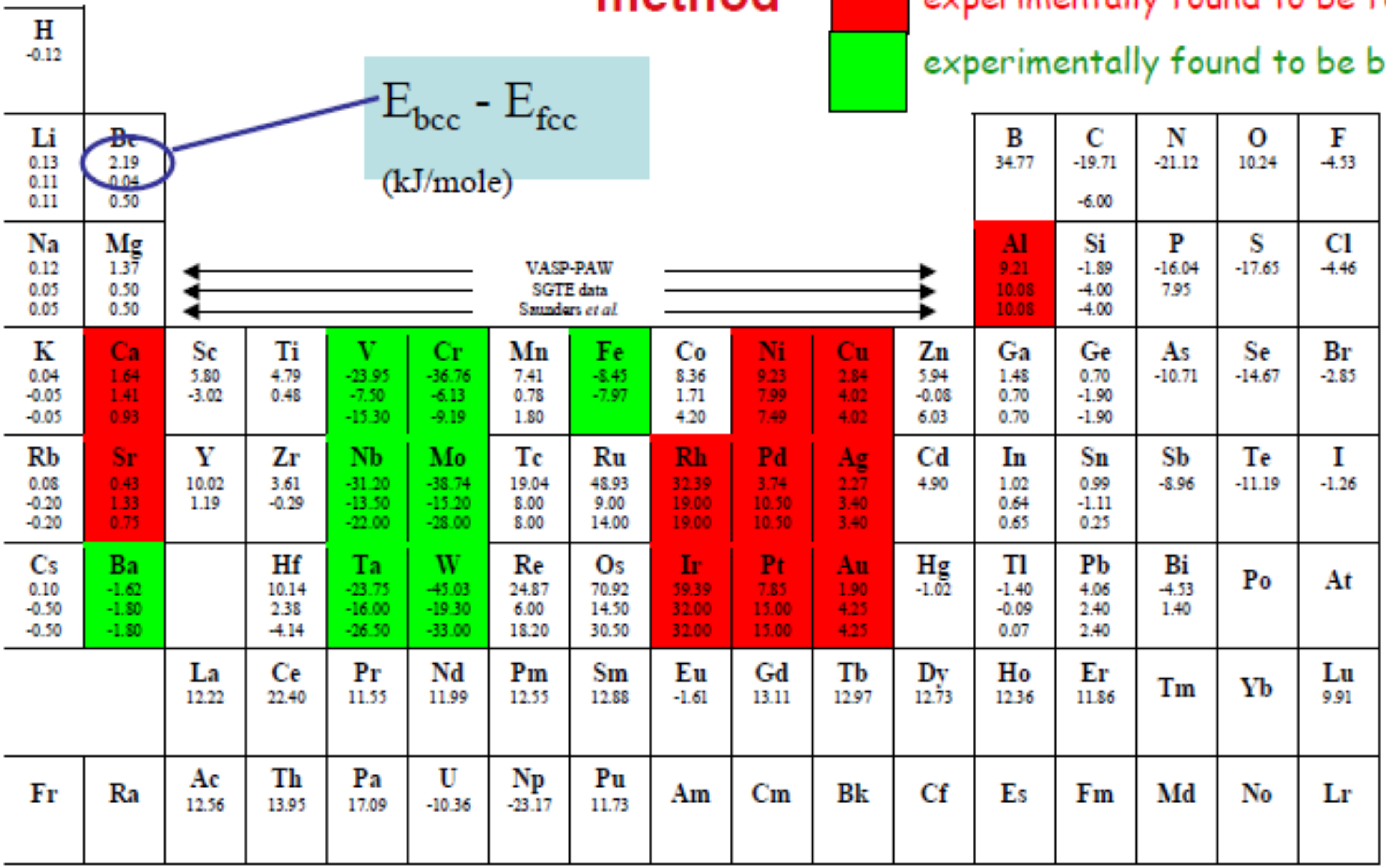
GGA error is less systematic though over-prediction is common.

errors are in many cases < 1%, for transition metal oxides < 5%

Elemental Crystal Structures: GGA pseudopotential method

🟥 experimentally found to be fcc

🟩 experimentally found to be bcc



$E_{bcc} - E_{fcc}$

(kJ/mole)

VASP-PAW
SGTE data
Saunders *et al.*

H -0.12																
Li 0.13 0.11 0.11	**Be** 2.19 0.04 0.50											**B** 34.77	**C** -19.71 -6.00	**N** -21.12	**O** 10.24	**F** -4.53
Na 0.12 0.05 0.05	**Mg** 1.37 0.50 0.50											🟥 **Al** 9.21 10.08 10.08	**Si** -1.89 -4.00 -4.00	**P** -16.04 7.95	**S** -17.65	**Cl** -4.46
K 0.04 -0.05 -0.05	🟥 **Ca** 1.64 1.41 0.93	**Sc** 5.80 -3.02	**Ti** 4.79 0.48	🟩 **V** -23.95 -7.50 -15.30	🟩 **Cr** -36.76 -6.13 -9.19	**Mn** 7.41 0.78 1.80	🟩 **Fe** -8.45 -7.97	**Co** 8.36 1.71 4.20	🟥 **Ni** 9.23 7.99 7.49	🟥 **Cu** 2.84 4.02 4.02	**Zn** 5.94 -0.08 6.03	**Ga** 1.48 0.70 0.70	**Ge** 0.70 -1.90 -1.90	**As** -10.71	**Se** -14.67	**Br** -2.85
Rb 0.08 -0.20 -0.20	🟥 **Sr** 0.43 1.33 0.75	**Y** 10.02 1.19	**Zr** 3.61 -0.29	🟩 **Nb** -31.20 -13.50 -22.00	🟩 **Mo** -38.74 -15.20 -28.00	**Tc** 19.04 8.00 8.00	**Ru** 48.93 9.00 14.00	🟥 **Rh** 32.39 19.00 19.00	🟥 **Pd** 3.74 10.50 10.50	🟥 **Ag** 2.27 3.40 3.40	**Cd** 4.90	**In** 1.02 0.64 0.65	**Sn** 0.99 -1.11 0.25	**Sb** -8.96	**Te** -11.19	**I** -1.26
Cs 0.10 -0.50 -0.50	🟩 **Ba** -1.62 -1.80 -1.80		**Hf** 10.14 2.38 -4.14	🟩 **Ta** -23.75 -16.00 -26.50	🟩 **W** -45.03 -19.30 -33.00	**Re** 24.87 6.00 18.20	**Os** 70.92 14.50 30.50	🟥 **Ir** 59.39 32.00 32.00	🟥 **Pt** 7.85 15.00 15.00	🟥 **Au** 1.90 4.25 4.25	**Hg** -1.02	**Tl** -1.40 -0.09 0.07	**Pb** 4.06 2.40 2.40	**Bi** -4.53 1.40	**Po**	**At**
		La 12.22	**Ce** 22.40	**Pr** 11.55	**Nd** 11.99	**Pm** 12.55	**Sm** 12.88	**Eu** -1.61	**Gd** 13.11	**Tb** 12.97	**Dy** 12.73	**Ho** 12.36	**Er** 11.86	**Tm**	**Yb**	**Lu** 9.91
Fr	**Ra**	**Ac** 12.56	**Th** 13.95	**Pa** 17.09	**U** -10.36	**Np** -23.17	**Pu** 11.73	**Am**	**Cm**	**Bk**	**Cf**	**Es**	**Fm**	**Md**	**No**	**Lr**

data taken from:

Y. Wang,[*a] S. Curtarolo,[et al.] *Ab Initio Lattice Stability in Comparison with CALPHAD Lattice Stability*, Computer Coupling of Phase Diagrams and T[illegible]nistry (Calphad) Vol. 28, Issue 1, March 2004, Pages 79-90.

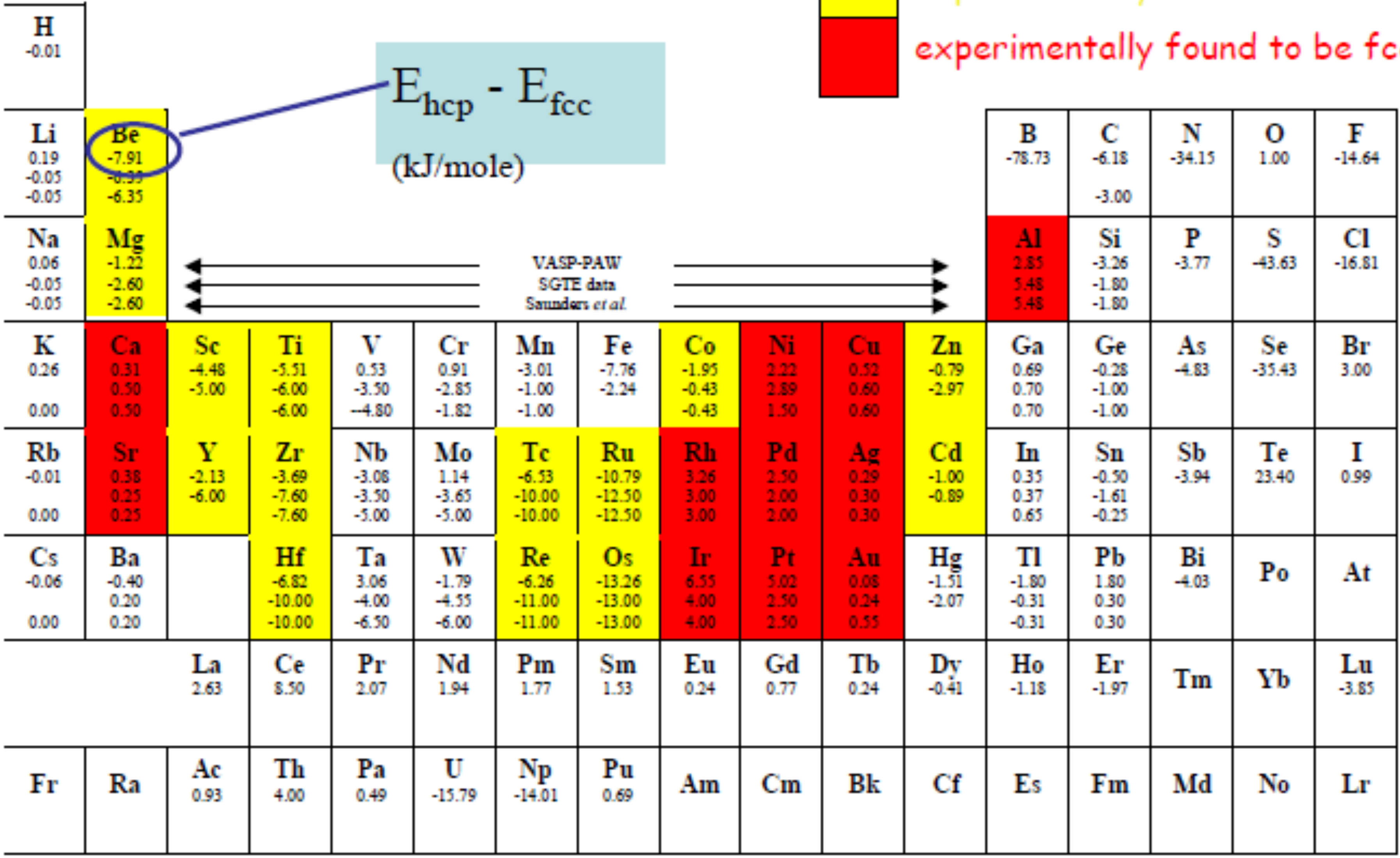
Elemental Crystal Structures: GGA pseudopotential method

🟨 experimentally found to be hcp

🟥 experimentally found to be fcc

$E_{hcp} - E_{fcc}$

(kJ/mole)



H -0.01																
Li 0.19 -0.05 -0.05	🟨 **Be** -7.91 [illegible] -6.35											**B** -78.73	**C** -6.18 -3.00	**N** -34.15	**O** 1.00	**F** -14.64
Na 0.06 -0.05 -0.05	🟨 **Mg** -1.22 -2.60 -2.60	← VASP-PAW → ← SGTE data → ← Saunders *et al.* →										🟥 **Al** 2.85 5.48 5.48	**Si** -3.26 -1.80 -1.80	**P** -3.77	**S** -43.63	**Cl** -16.81
K 0.26 0.00	🟥 **Ca** 0.31 0.50 0.50	🟨 **Sc** -4.48 -5.00	🟨 **Ti** -5.51 -6.00 -6.00	**V** 0.53 -3.50 --4.80	**Cr** 0.91 -2.85 -1.82	**Mn** -3.01 -1.00 -1.00	**Fe** -7.76 -2.24	🟨 **Co** -1.95 -0.43 -0.43	🟥 **Ni** 2.22 2.89 1.50	🟥 **Cu** 0.52 0.60 0.60	🟨 **Zn** -0.79 -2.97	**Ga** 0.69 0.70 0.70	**Ge** -0.28 -1.00 -1.00	**As** -4.83	**Se** -35.43	**Br** 3.00
Rb -0.01 0.00	🟥 **Sr** 0.38 0.25 0.25	🟨 **Y** -2.13 -6.00	🟨 **Zr** -3.69 -7.60 -7.60	**Nb** -3.08 -3.50 -5.00	**Mo** 1.14 -3.65 -5.00	🟨 **Tc** -6.53 -10.00 -10.00	🟨 **Ru** -10.79 -12.50 -12.50	🟥 **Rh** 3.26 3.00 3.00	🟥 **Pd** 2.50 2.00 2.00	🟥 **Ag** 0.29 0.30 0.30	🟨 **Cd** -1.00 -0.89	**In** 0.35 0.37 0.65	**Sn** -0.50 -1.61 -0.25	**Sb** -3.94	**Te** 23.40	**I** 0.99
Cs -0.06 0.00	**Ba** -0.40 0.20 0.20		🟨 **Hf** -6.82 -10.00 -10.00	**Ta** 3.06 -4.00 -6.50	**W** -1.79 -4.55 -6.00	🟨 **Re** -6.26 -11.00 -11.00	🟨 **Os** -13.26 -13.00 -13.00	🟥 **Ir** 6.55 4.00 4.00	🟥 **Pt** 5.02 2.50 2.50	🟥 **Au** 0.08 0.24 0.55	**Hg** -1.51 -2.07	**Tl** -1.80 -0.31 -0.31	**Pb** 1.80 0.30 0.30	**Bi** -4.03	**Po**	**At**
		La 2.63	**Ce** 8.50	**Pr** 2.07	**Nd** 1.94	**Pm** 1.77	**Sm** 1.53	**Eu** 0.24	**Gd** 0.77	**Tb** 0.24	**Dy** -0.41	**Ho** -1.18	**Er** -1.97	**Tm**	**Yb**	**Lu** -3.85
Fr	**Ra**	**Ac** 0.93	**Th** 4.00	**Pa** 0.49	**U** -15.79	**Np** -14.01	**Pu** 0.69	**Am**	**Cm**	**Bk**	**Cf**	**Es**	**Fm**	**Md**	**No**	**Lr**

data taken from:

Y. Wang,*a S. Curtarolo, et al. *Ab Initio Lattice Stability in Comparison with CALPHAD Lattice Stability*, Computer Coupling of Phase Diagram and Thermochemistry (Calphad) Vol. 28, Issue 1, March 2004, Pages 79-90.

Summary: Comparing Energy of Structures

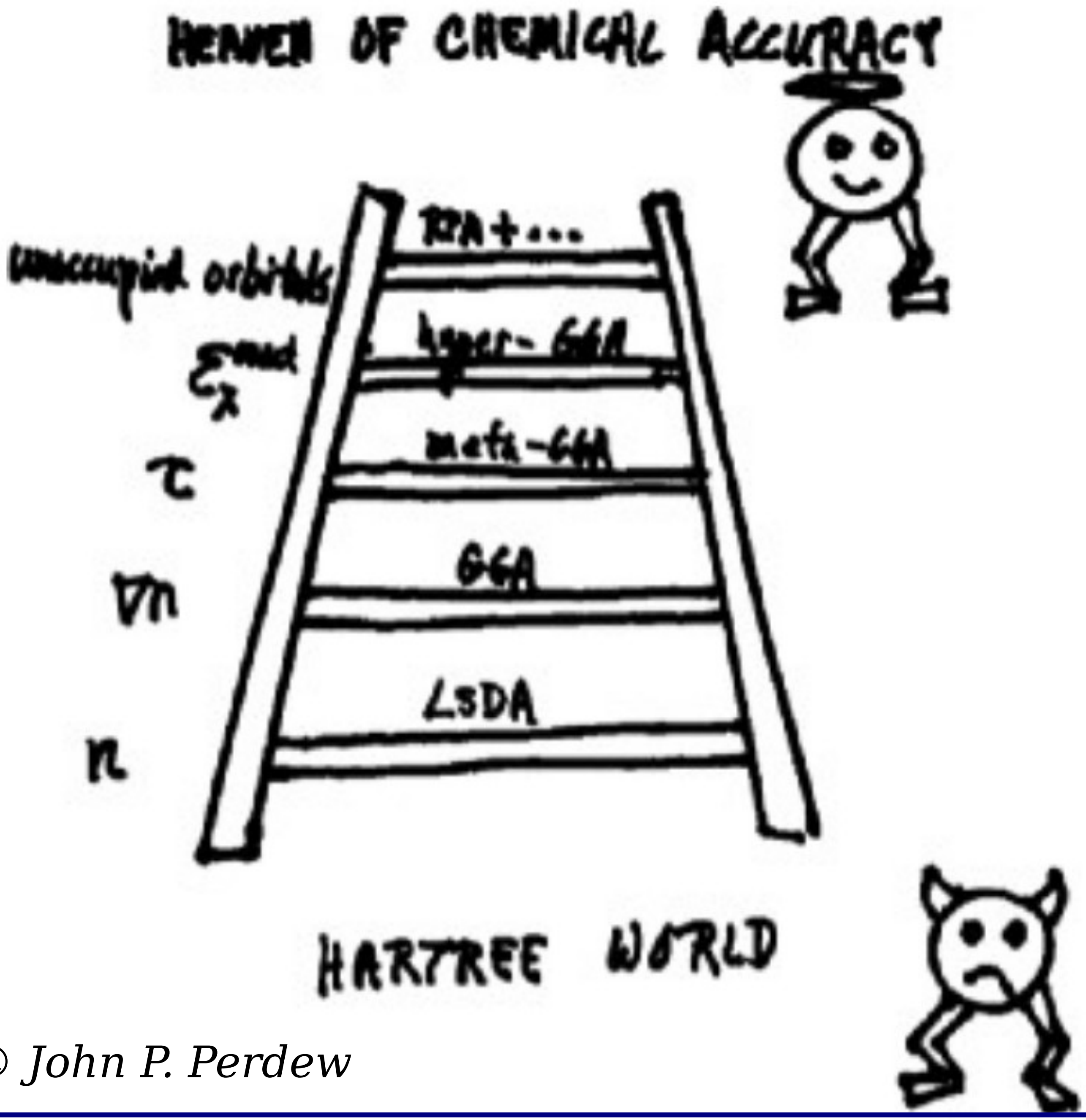
For most elements, both LDA and GGA predict the correct structure for a material (as far as we know)

Notable exceptions: Fe in LDA; materials with substantial electron correlation effects (e.g. Pu)

Problems with LDA / GGA functionals

- Chemical accuracy (1 kcal/mol) is far.
  - trends are often accurate for strong bonds (covalent, ionic,metallic)
  - weak bonds/small overlaps are problematic
- Self interaction cancellation is only approximately verified in LDA and GGA.
  - molecular dissociation limit, TMO & RE and other atom-in-solid system.
- Van der Waals interactions are not taken into account
  - occasional agreement with exp. from compensation of errors

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

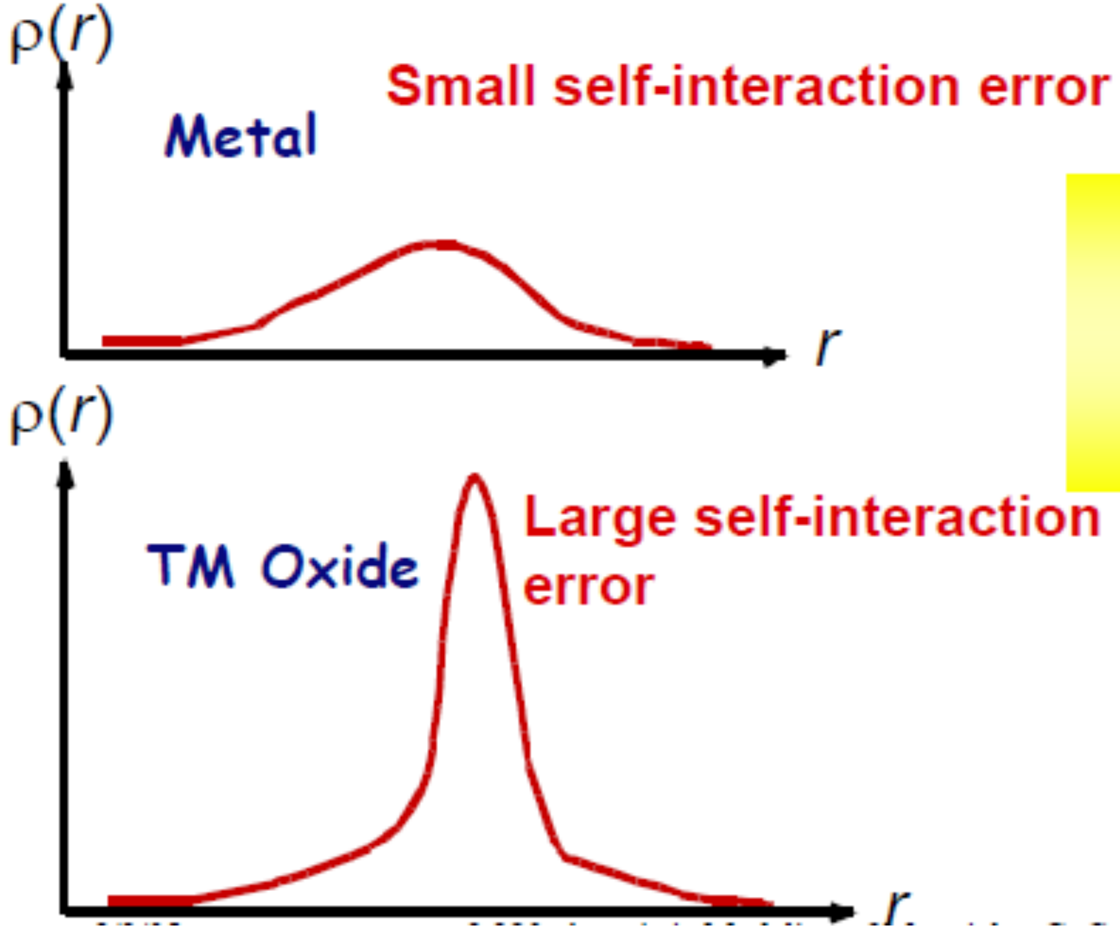
address the self-interaction error with some drawback

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)

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



Self interaction in DFT
is key problem in transition metal oxides

Redox Reactions can be more Problematic

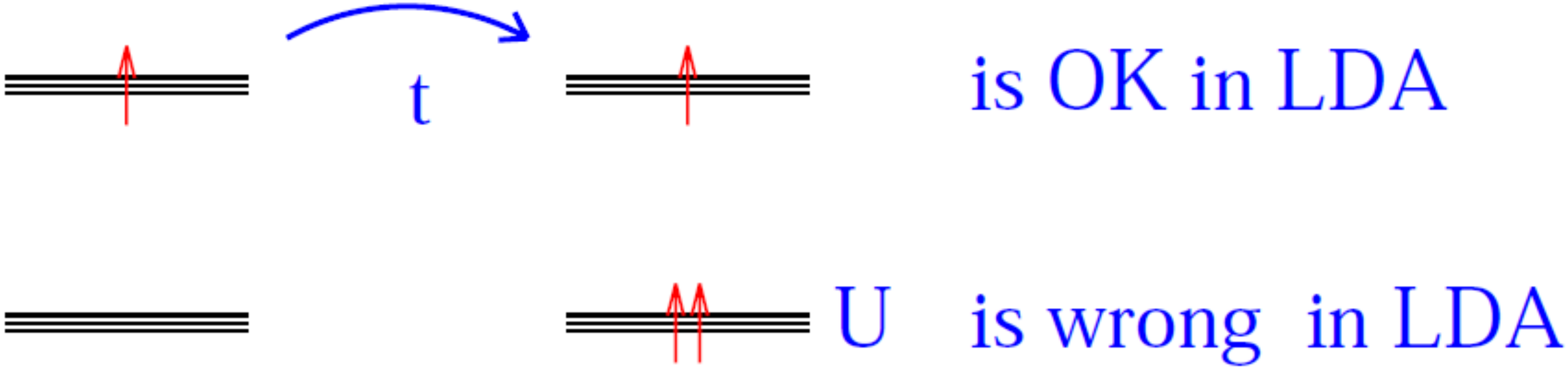
	GGA	Exp
$FePO_4$ + Li -> $LiFePO_4$	2.8 eV	3.5 eV
MnO_2 + Li -> $LiMn_2O_4$	3.6 eV	4.1 eV
$V_2(PO_4)_3$ + Li -> $LiV_2(PO_4)_3$	3.3 eV	4.6 eV

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 ?

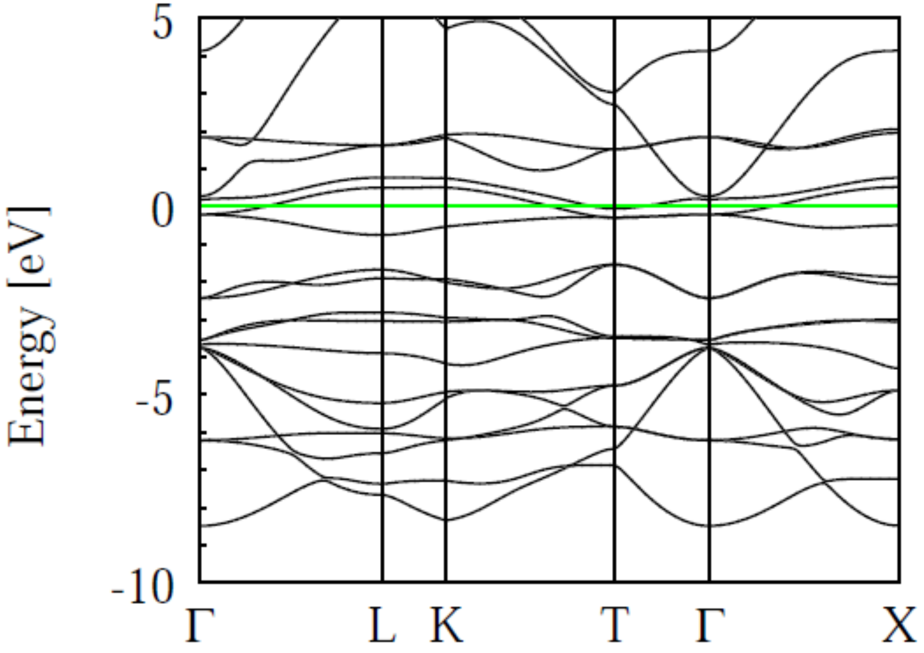


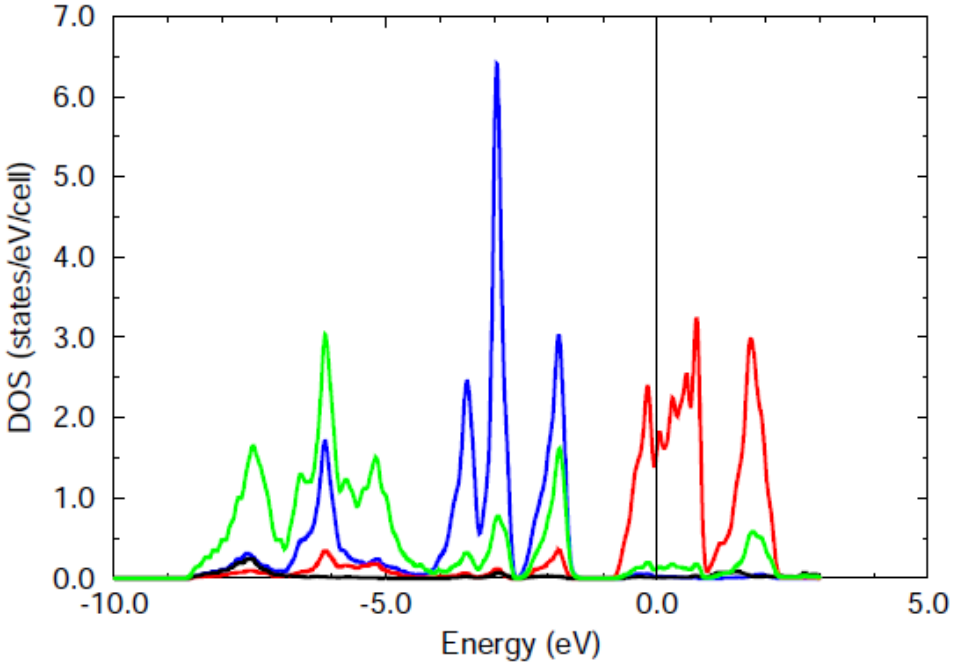
is OK in LDA

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

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

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

Adiabatic Connection

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

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

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

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

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

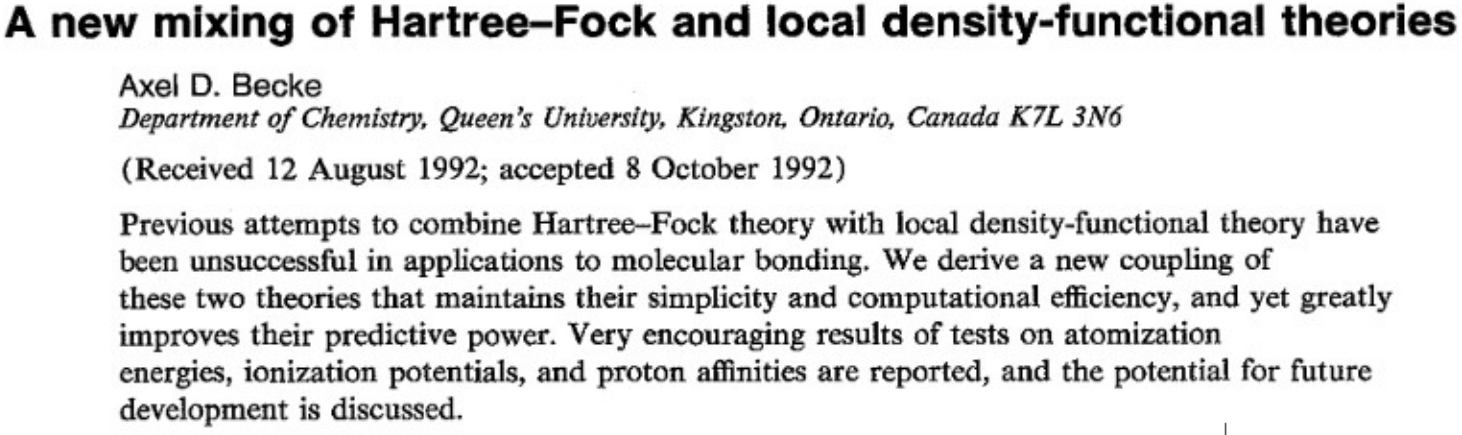
$$E_{\lambda=1} = T_s + E_H + E_{xc} + \int d\mathbf{r}\; n(\mathbf{r})v_{ext}(\mathbf{r})$$

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

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)

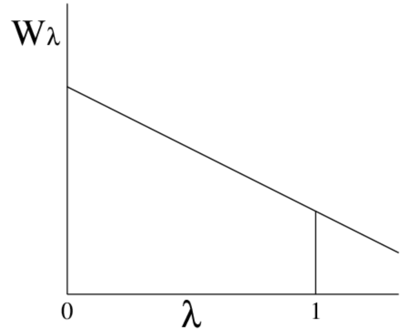


A new mixing of Hartree–Fock and local density-functional theories

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

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

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

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

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]

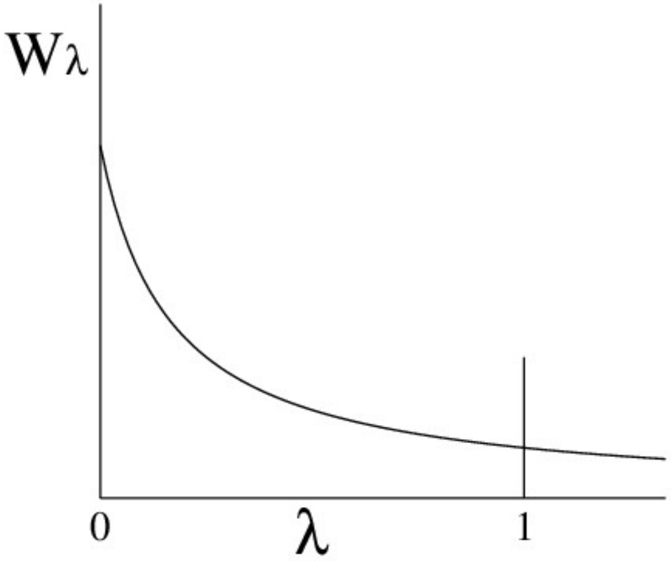
Contrary to popular belief, B3LYP was not fit to experimental data. The three parameters defining B3LYP have been taken without modification from Becke's original fitting of the analogous B3PW91 functional to a set of atomization energies, ionization potentials, proton affinities, and total atomic energies.[9]

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.

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)

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

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

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

Integrable divergence

The q+G=0 divergence

- Gygi-Baldereschi PRB 34, 4405 (1986)

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

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

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

The q+G=0 divergence

- Gygi-Baldereschi PRB 34, 4405 (1986)

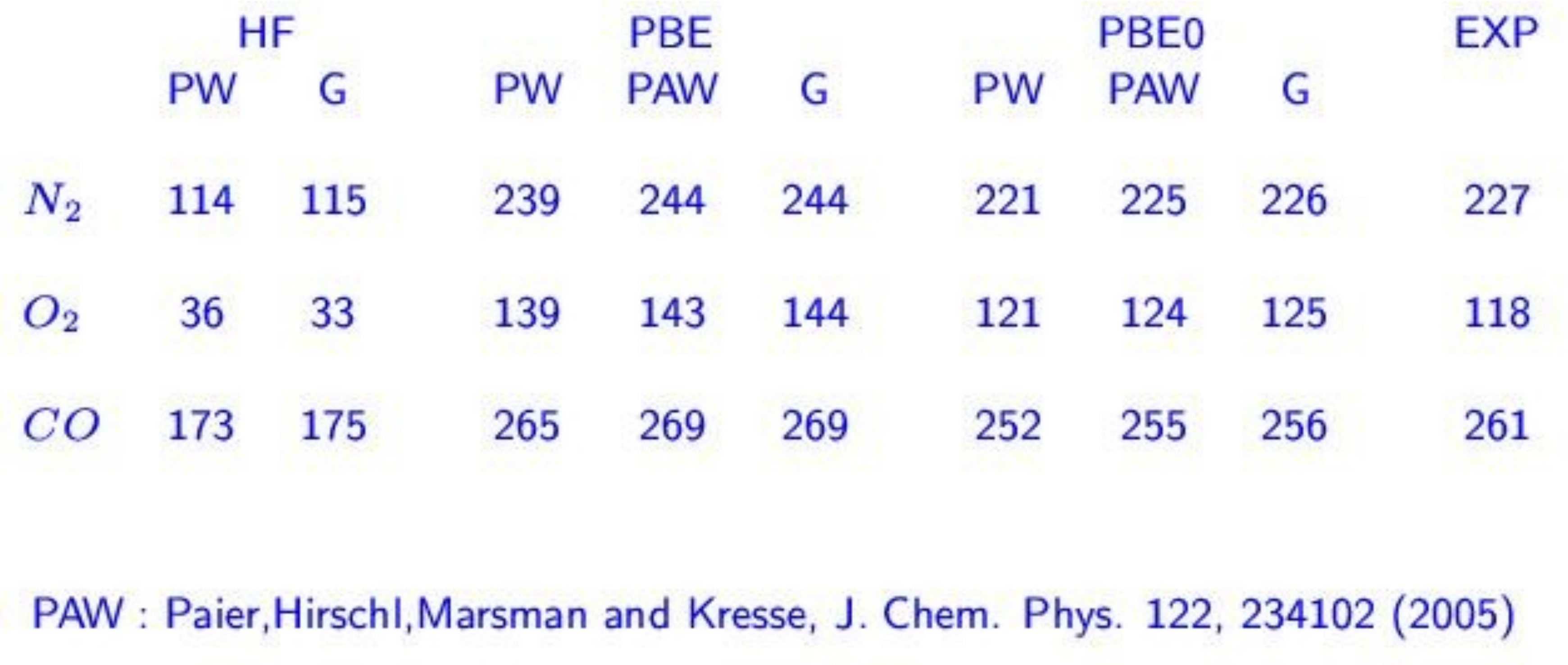
$$\rho_{\mathbf{k},v}^{\mathbf{k}-\mathbf{q},v'}(\mathbf{r}) = \phi^*_{\mathbf{k}-\mathbf{q},v'}(\mathbf{r})\phi_{\mathbf{k},v}(\mathbf{r}) \quad \Longrightarrow \quad A(\mathbf{q}+\mathbf{G}) = \frac{\Omega}{(2\pi)^3}\int d\mathbf{k}\ |\rho_{\mathbf{k},v}^{\mathbf{k}-\mathbf{q},v'}(\mathbf{q}+\mathbf{G})|^2$$

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

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

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

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

The LDA+U energy functional

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

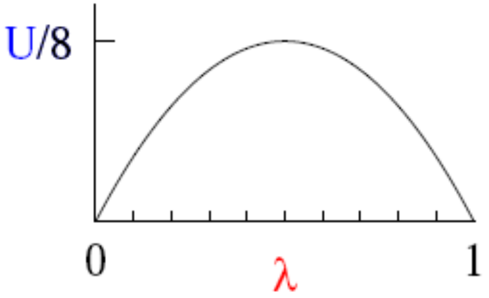
[Anisimov, Zaanen and Andersen, *PRB* **44**, 943 (1991).]

A simplified LDA+U model:

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

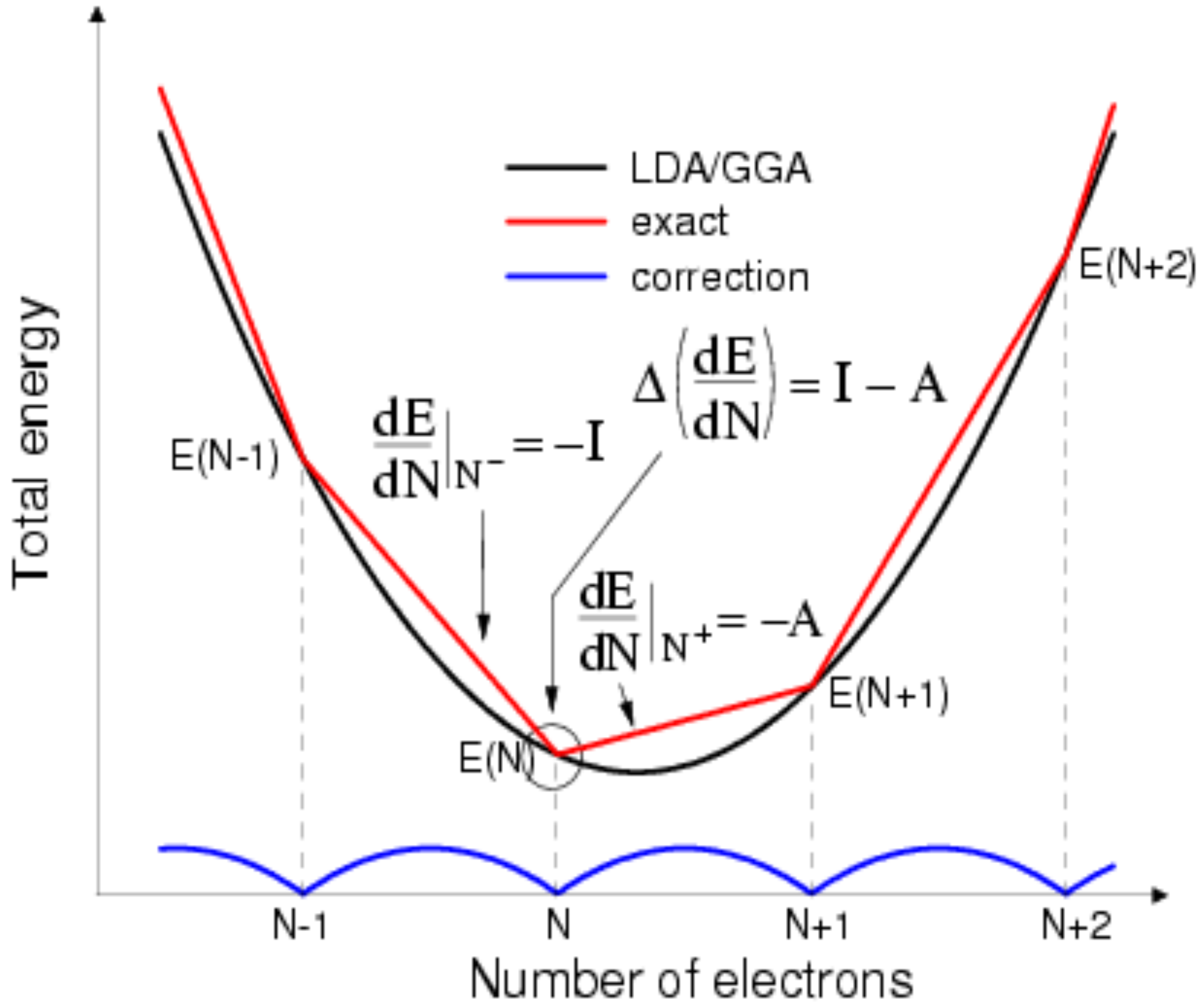
In the diagonal basis, where $\mathbf{n}^{I\sigma} \cdot \vec{v}^{I\sigma}_{\alpha} = \lambda^{I\sigma}_{\alpha} \vec{v}^{I\sigma}_{\alpha}$, the LDA+U correction is simply

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



Fractional occupation are strongly discouraged for large U.

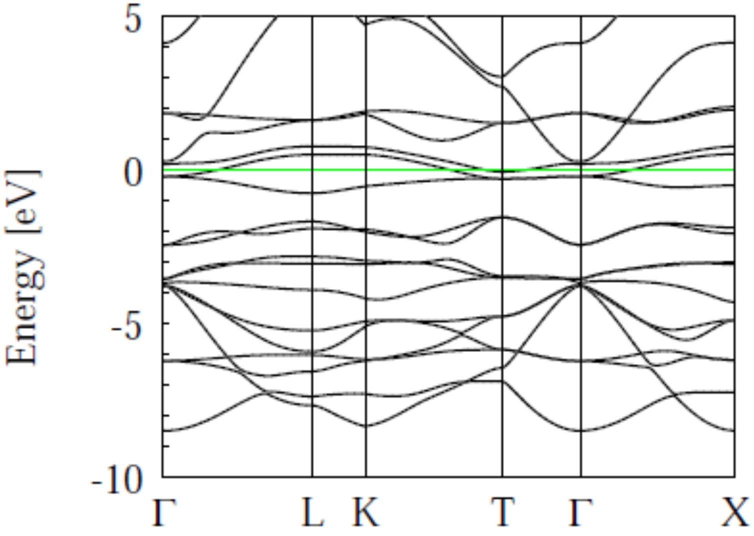
LDA/GGA failure in the atomic limit

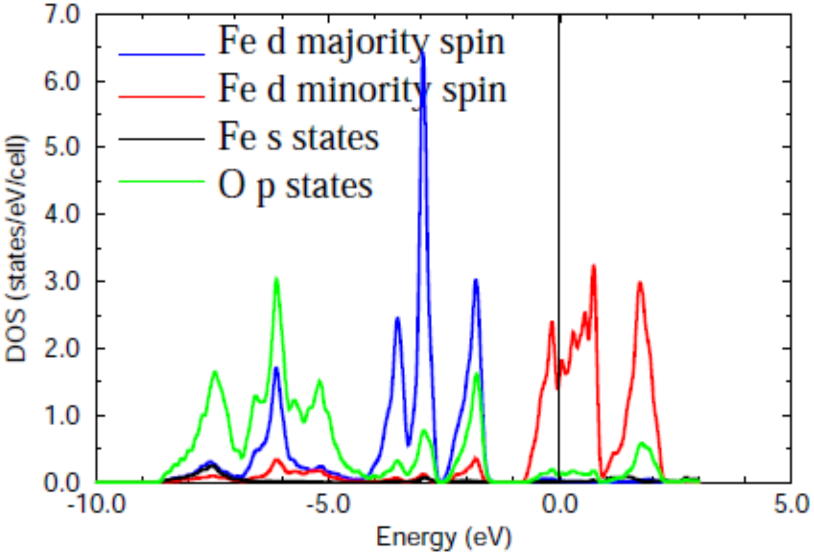


A correction is needed to remove spurious self-interaction

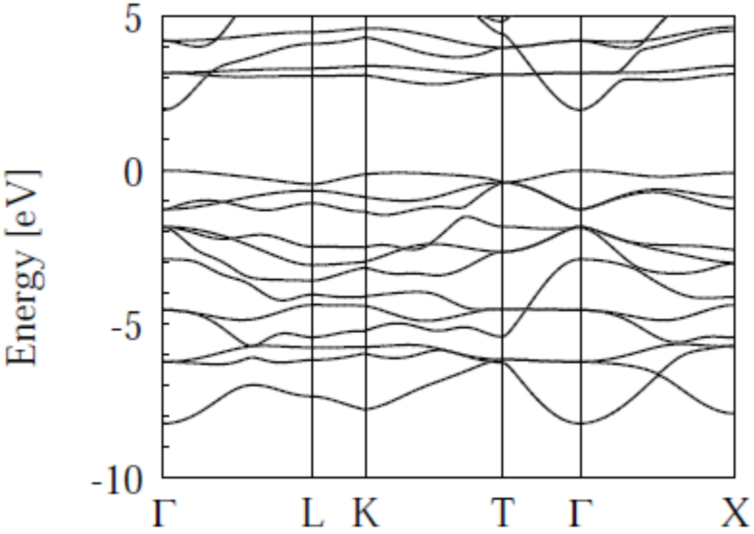
Electronic Structure of FeO

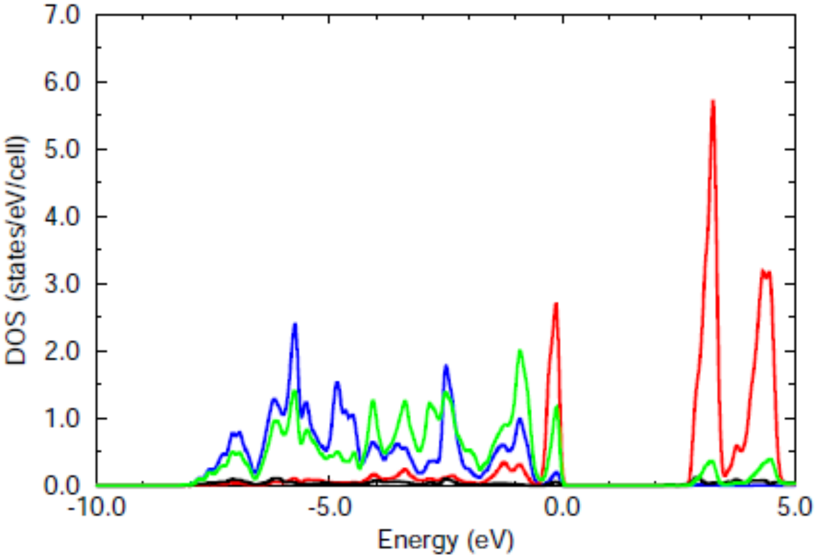
GGA



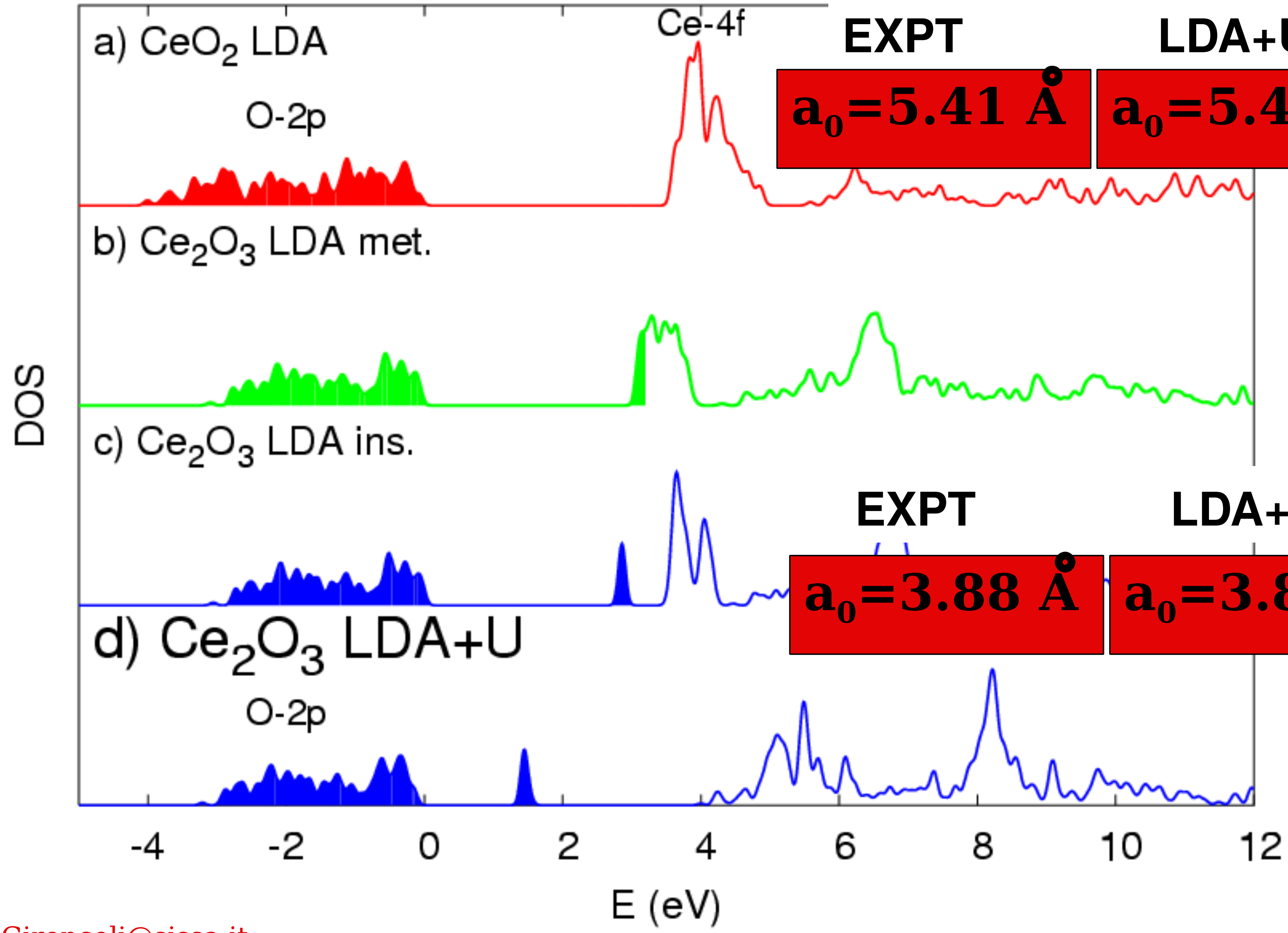


LDA+U^{SIC}





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)

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

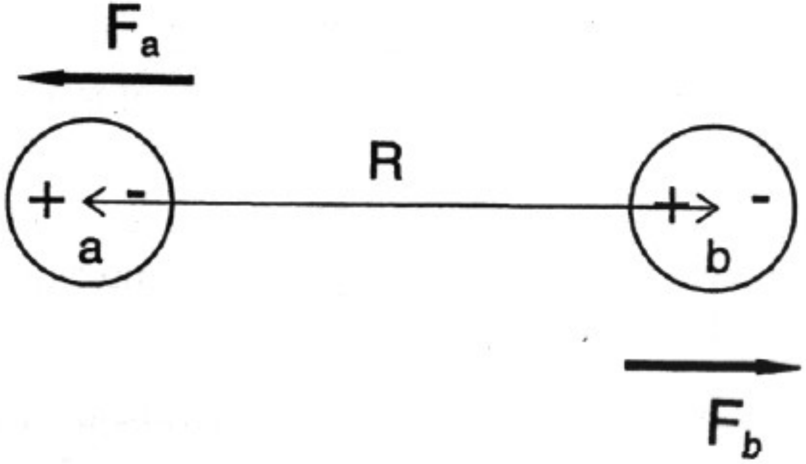
SIC, DFT+U, Hybrids
address the self-interaction error with some drawback

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.

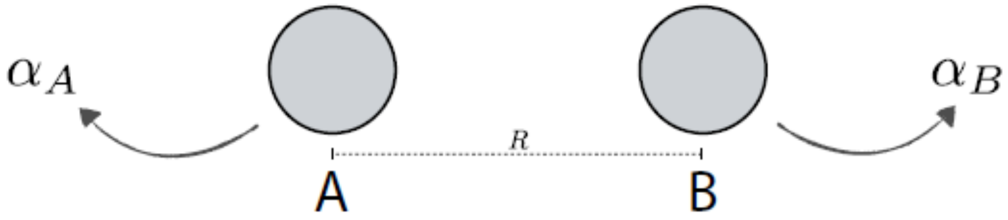


van der Waals

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.

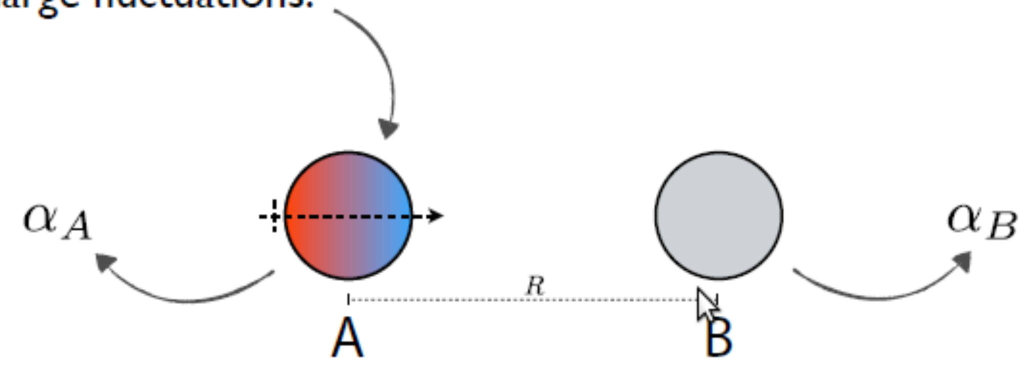
It is due to truly non-local correlation effects.
It is contained in the true XC functional but LDA/GGA/MetaGGA and Hybrids do not describe it properly.

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

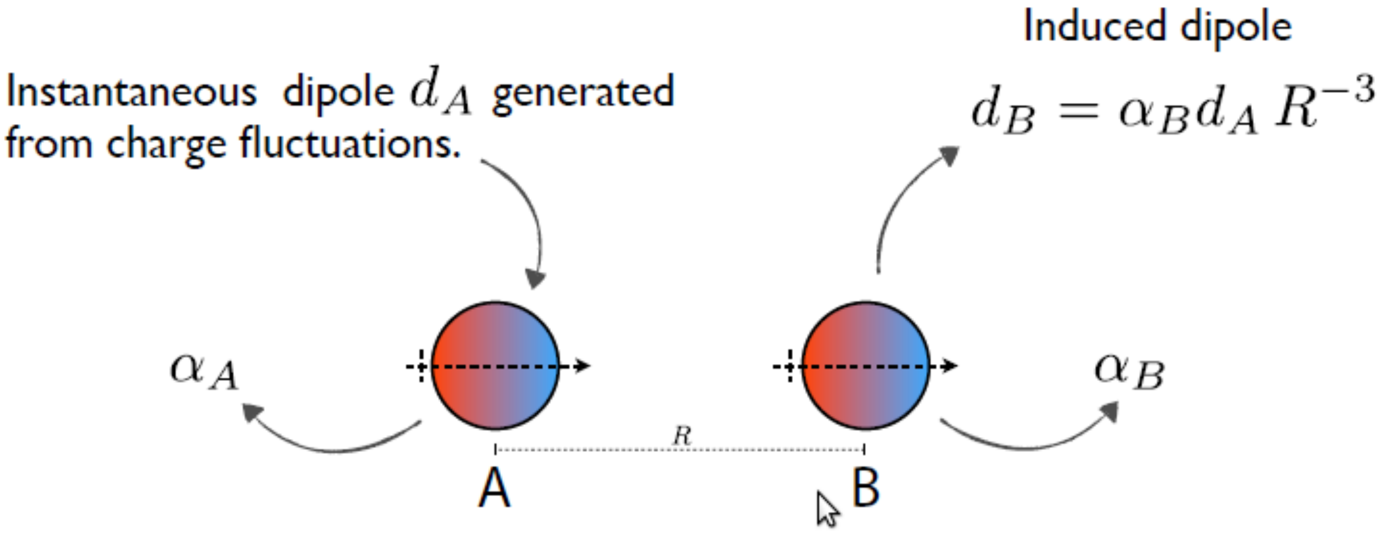
vdW : non local correlation



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.

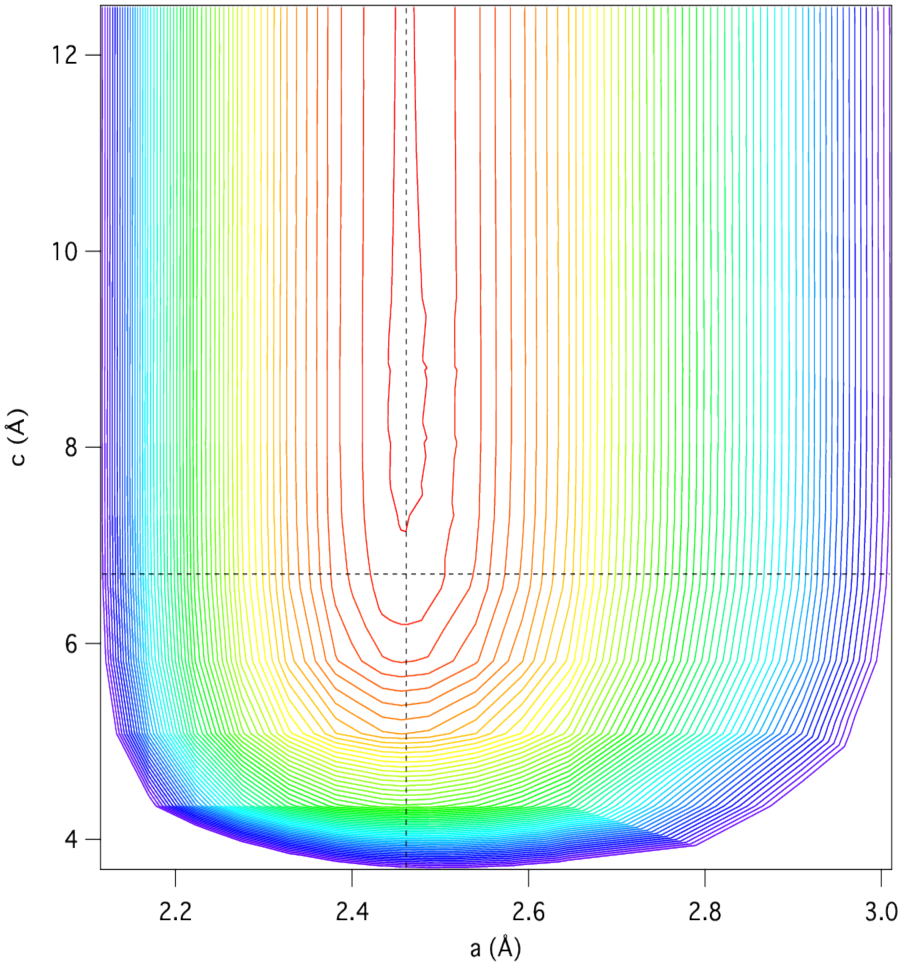
$$E_{xc}^{LDA} = \int n(r)\epsilon_{xc}^{hom}(n(r))dr \qquad E_{xc}^{GGA} = \int n(r)F_{xc}^{GGA}(n(r)), |\nabla n(r)|)dr$$

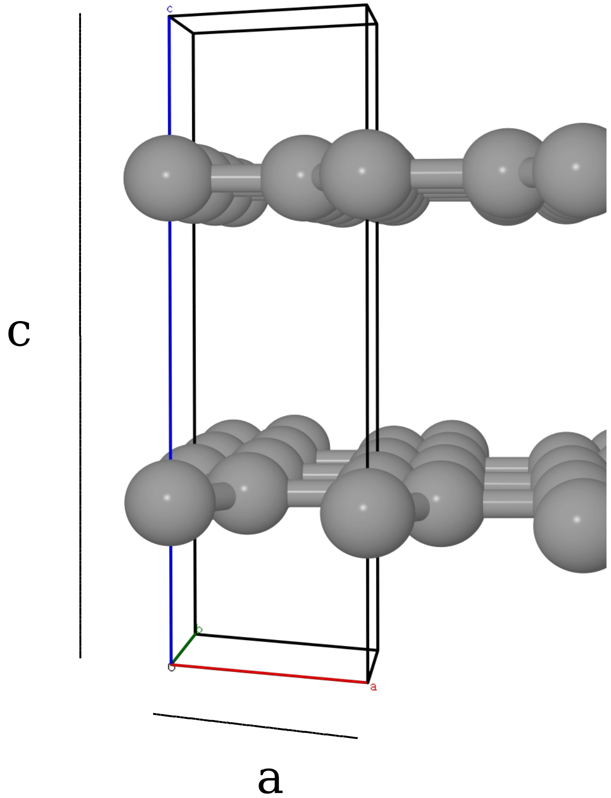
As such they do not describe vdW interaction.

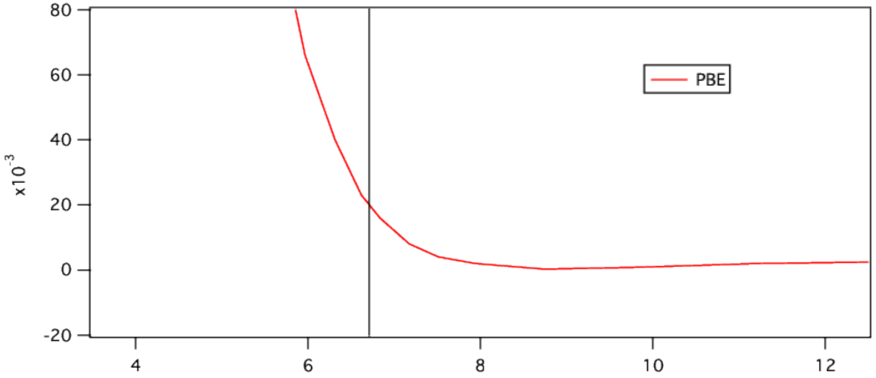
The same is true for Hybrids, DFT+U and SIC etc...

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)

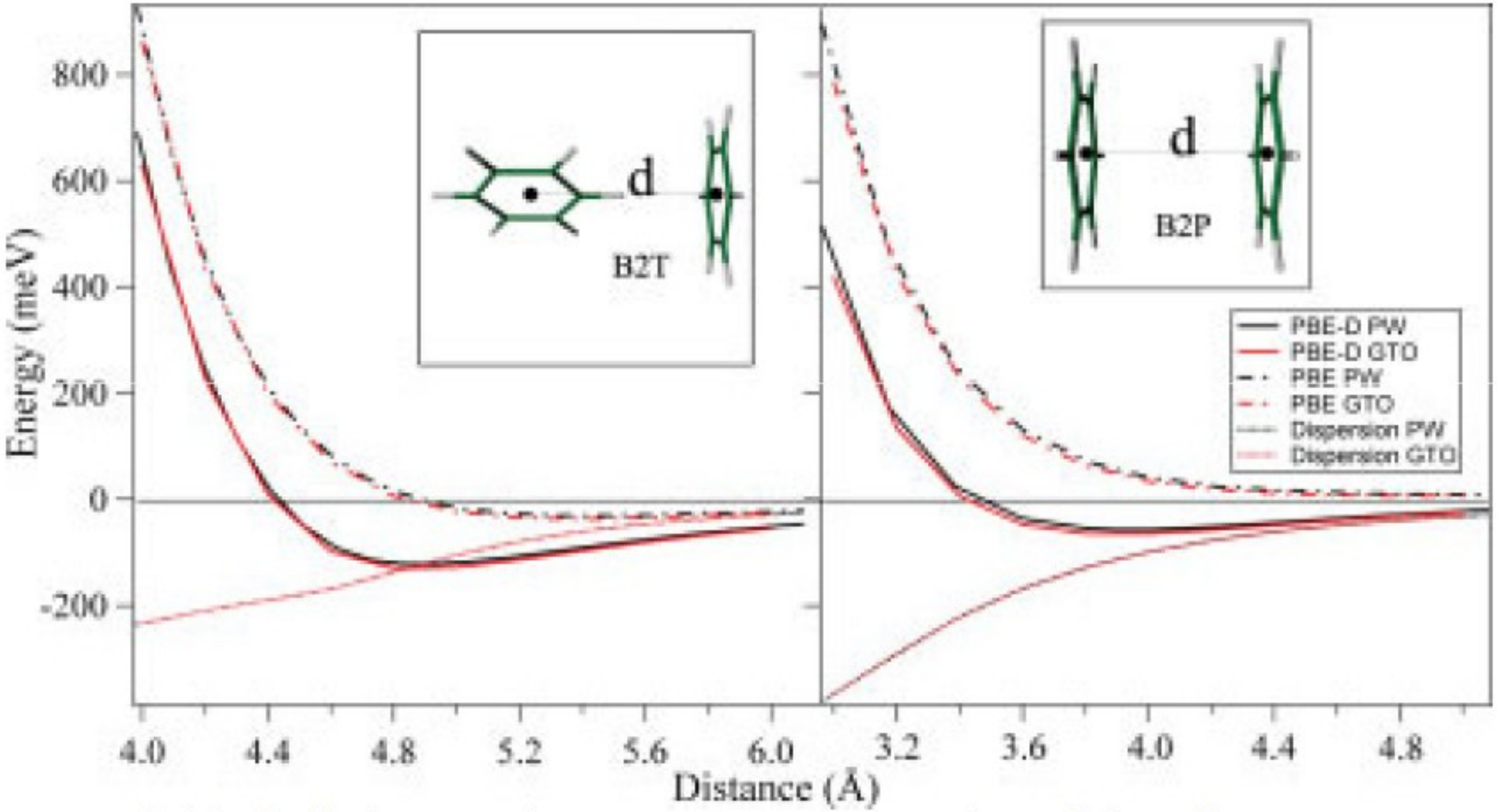
- $E_{\text{DFT-D}} = E_{\text{DFT}} + E_{\text{disp}}$

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

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*

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

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



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

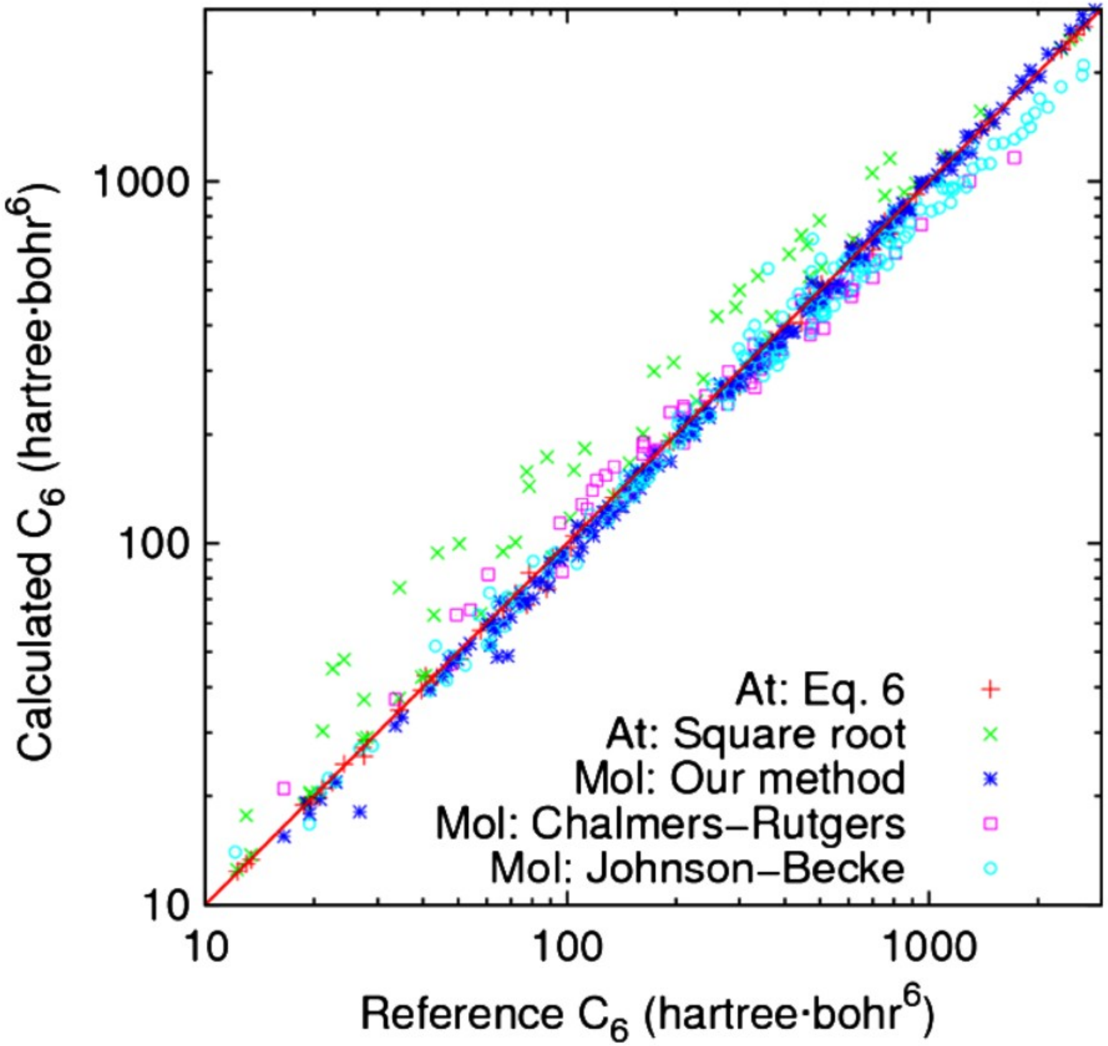


FIG. 1 (color online). Comparison of the C_6 coefficients for atom-atom interaction (At) and atom-molecule and molecule-molecule interaction (Mol). The reference results for atom-atom interaction are from accurate wave function calculations [26–28]. For molecules, DOSD results are taken as a reference [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 ?

- develop a truly non local XC functional

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

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

-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 Integral !

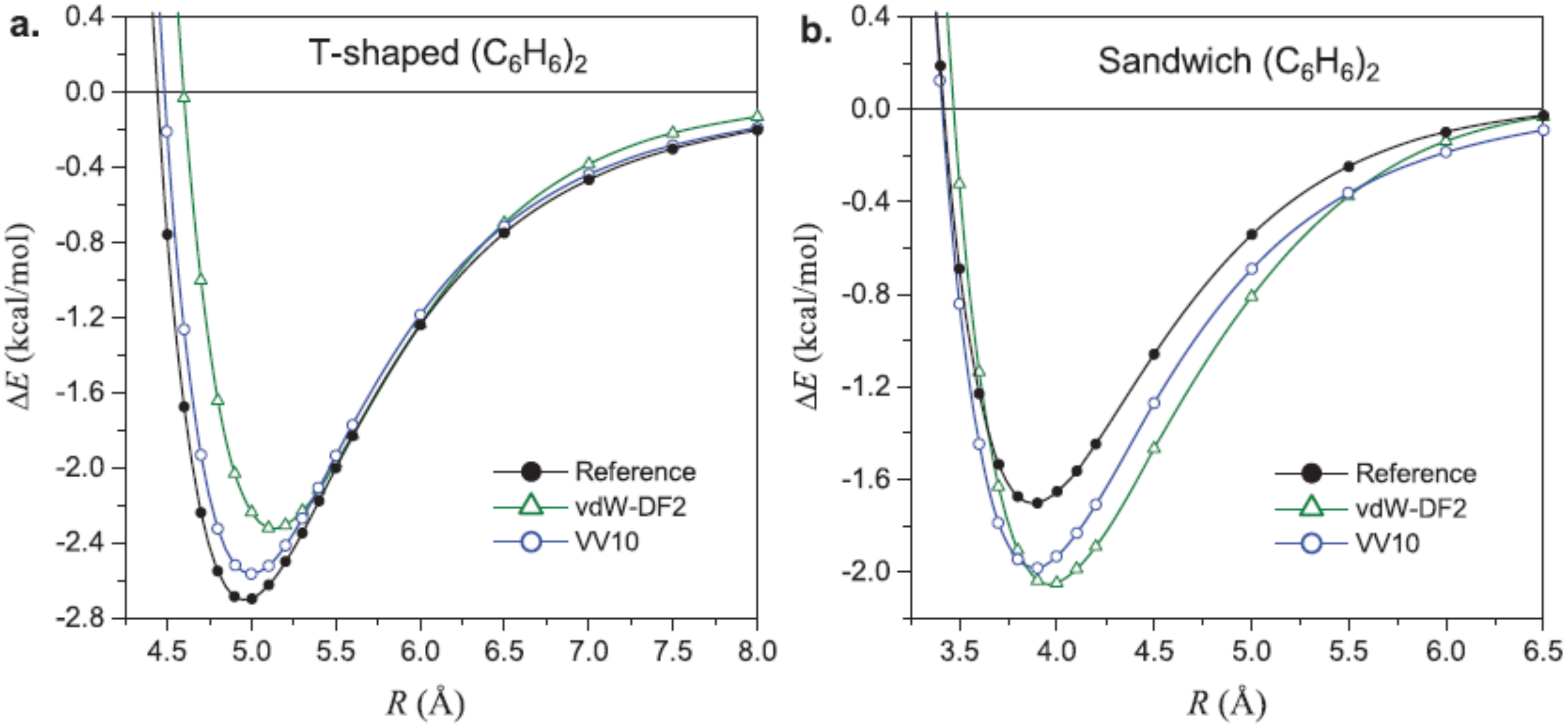
$$\Phi \longrightarrow -\frac{3e^4}{2m^2}\frac{1}{\omega_0(r)\omega_0(r')[\omega_0(r)+\omega_0(r')]|r-r'|^6}$$

How to deal with van der Waals ?

- develop a truly non local XC functional

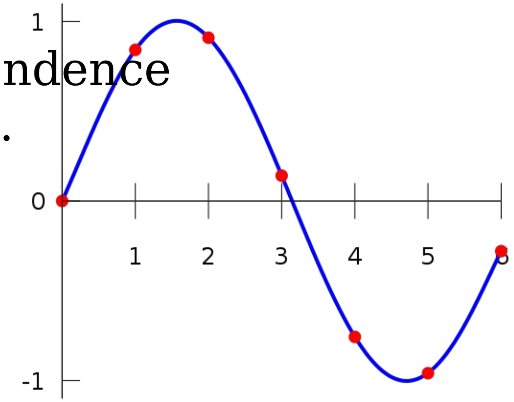
$$E_c^{\mathrm{nl}} = \frac{1}{2}\int d^3r\, d^3r'\, n(\vec{r})\phi(\vec{r},\vec{r}\,')n(\vec{r}\,'),$$

Phi(n(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 ...



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

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

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

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

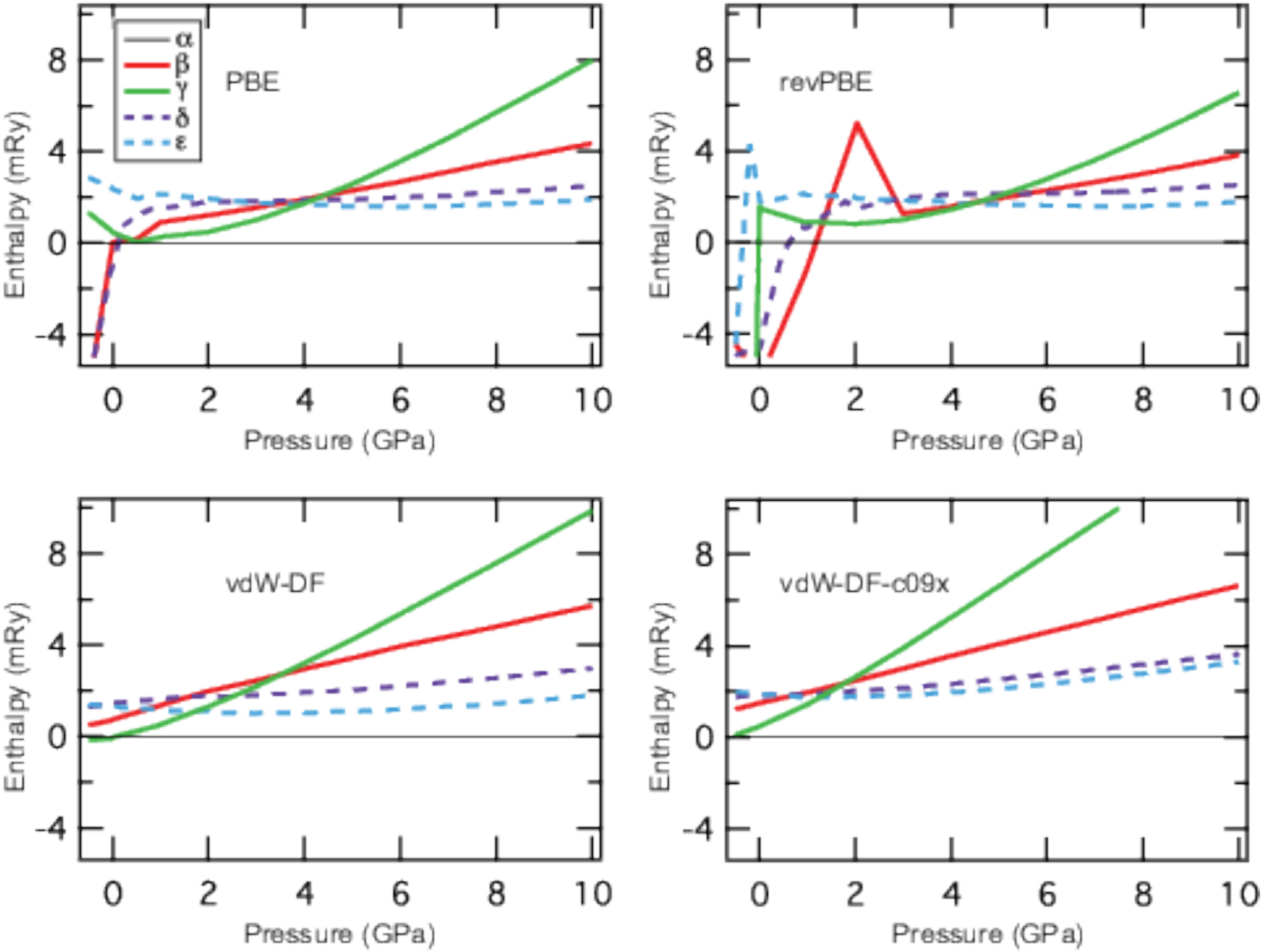
The vdW energy can be expressed as a sum of simple 3d integrals

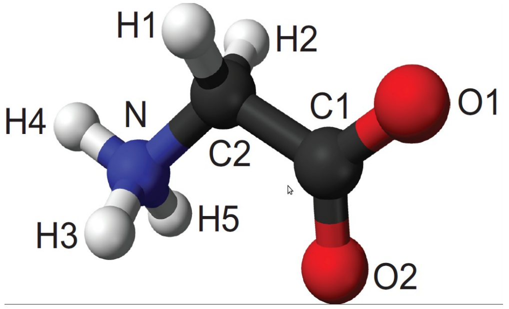
Several Non-Local Functionals

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

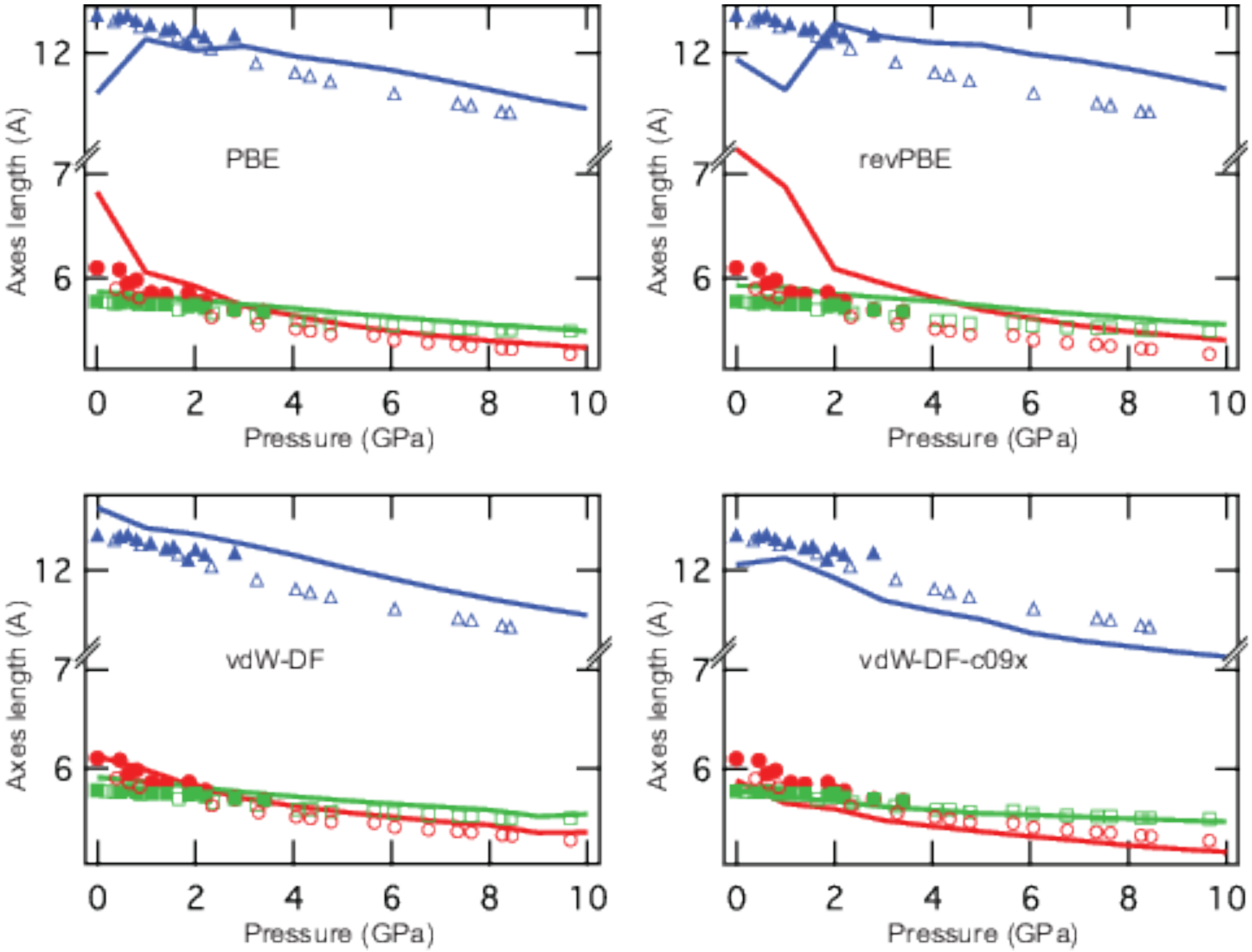
Glycine polymorphes

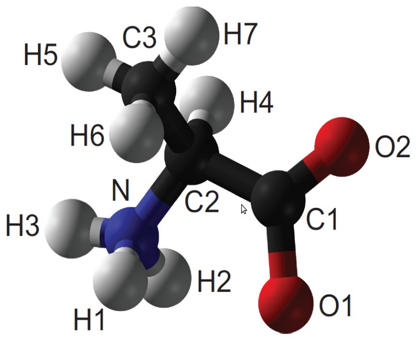




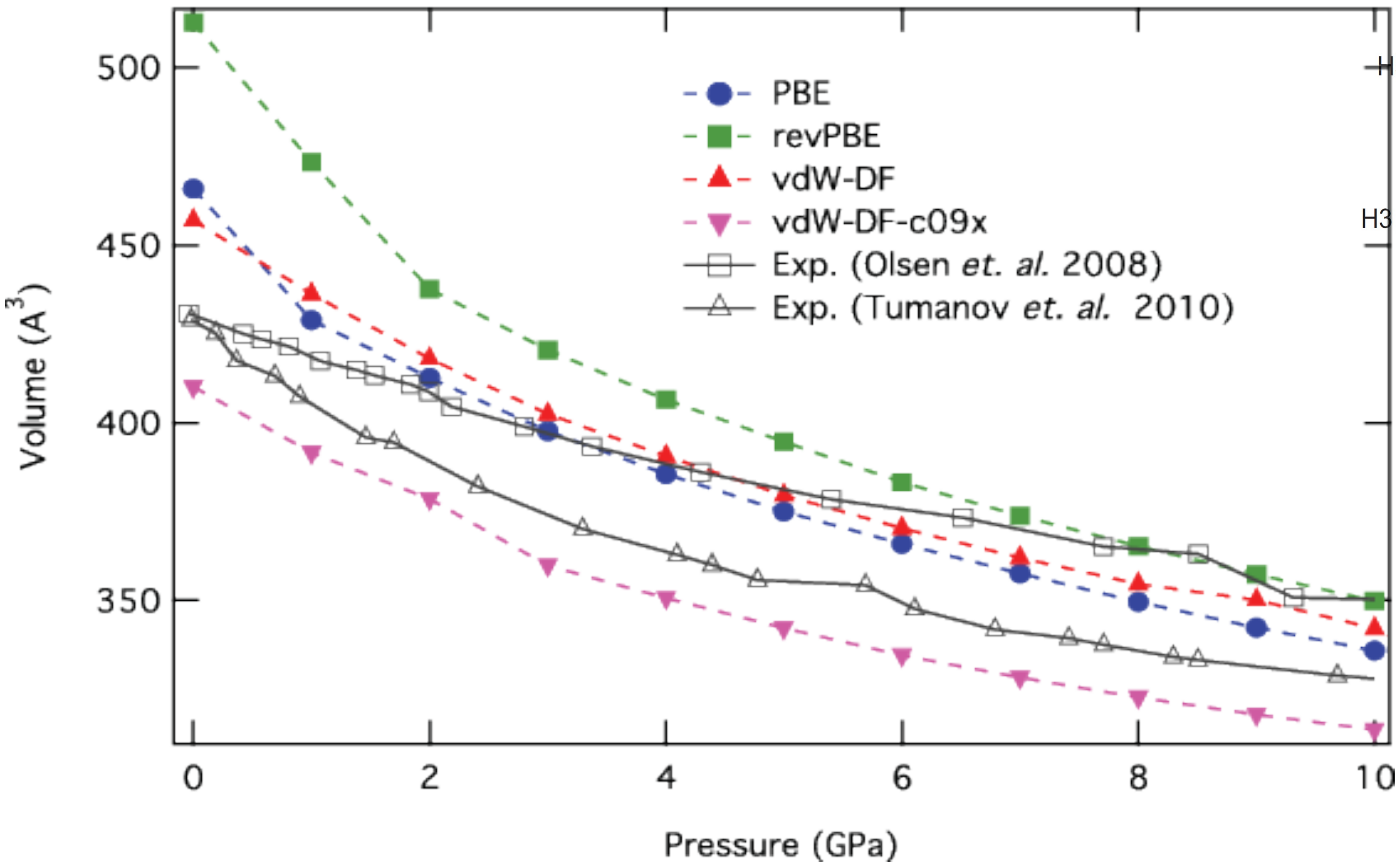
$$\gamma < \alpha < \beta < \ldots$$

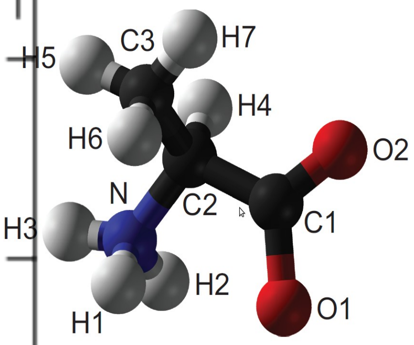
Alanine evolution with Pressure





Alanine evolution with P





VV10 functional

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

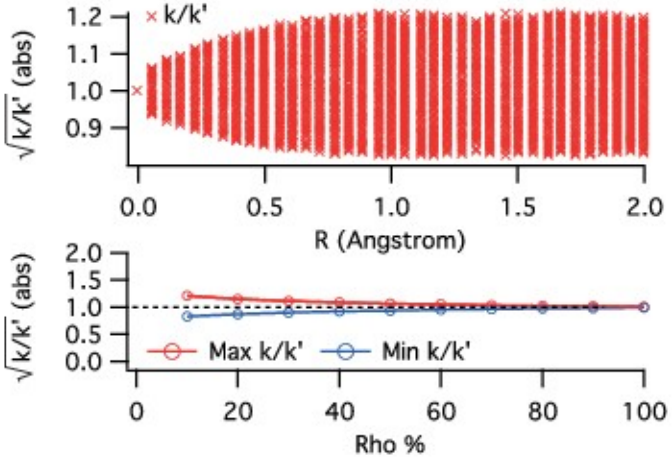
$$g = \omega_0(r)R^2 + k(r)$$

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

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

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

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

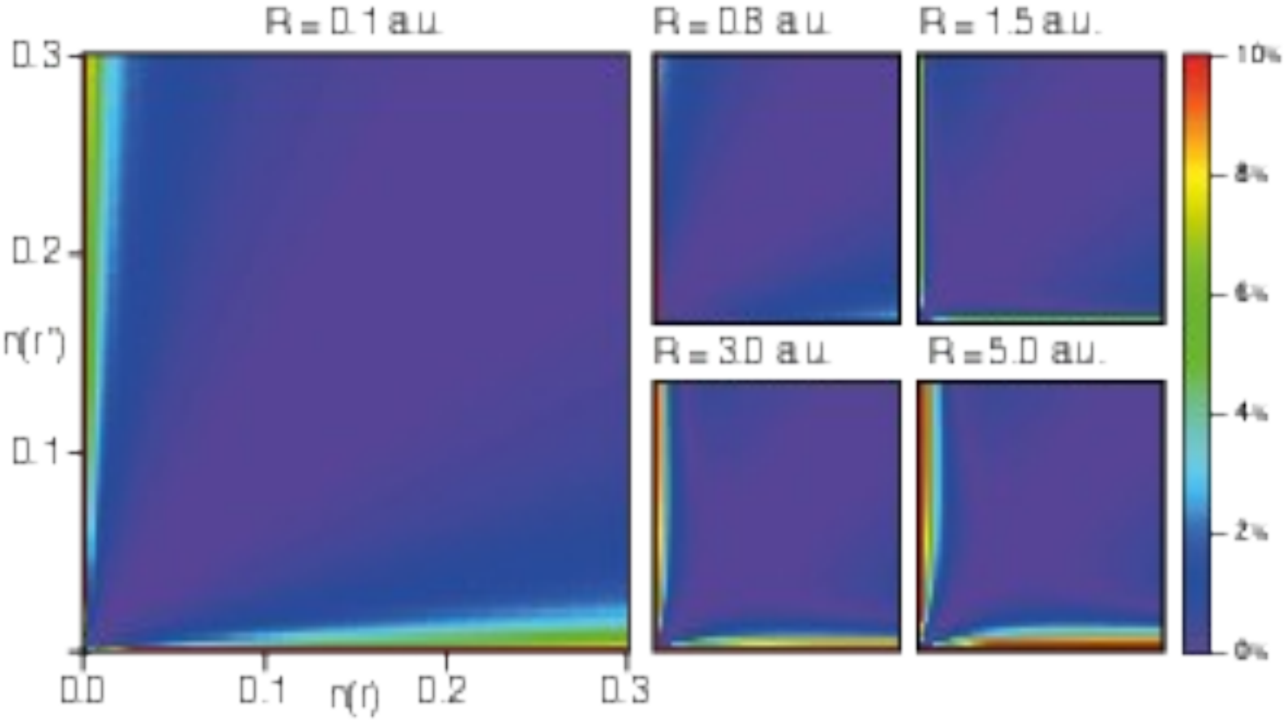


$$\Phi^{rVV10}(r,r') = -\frac{3e^4}{2m^2}\frac{1}{k^{3/2}k'^{3/2}}\frac{1}{(qR^2+1)(q'R^2+1)(qR^2+q'R^2+2)}$$

Separable !

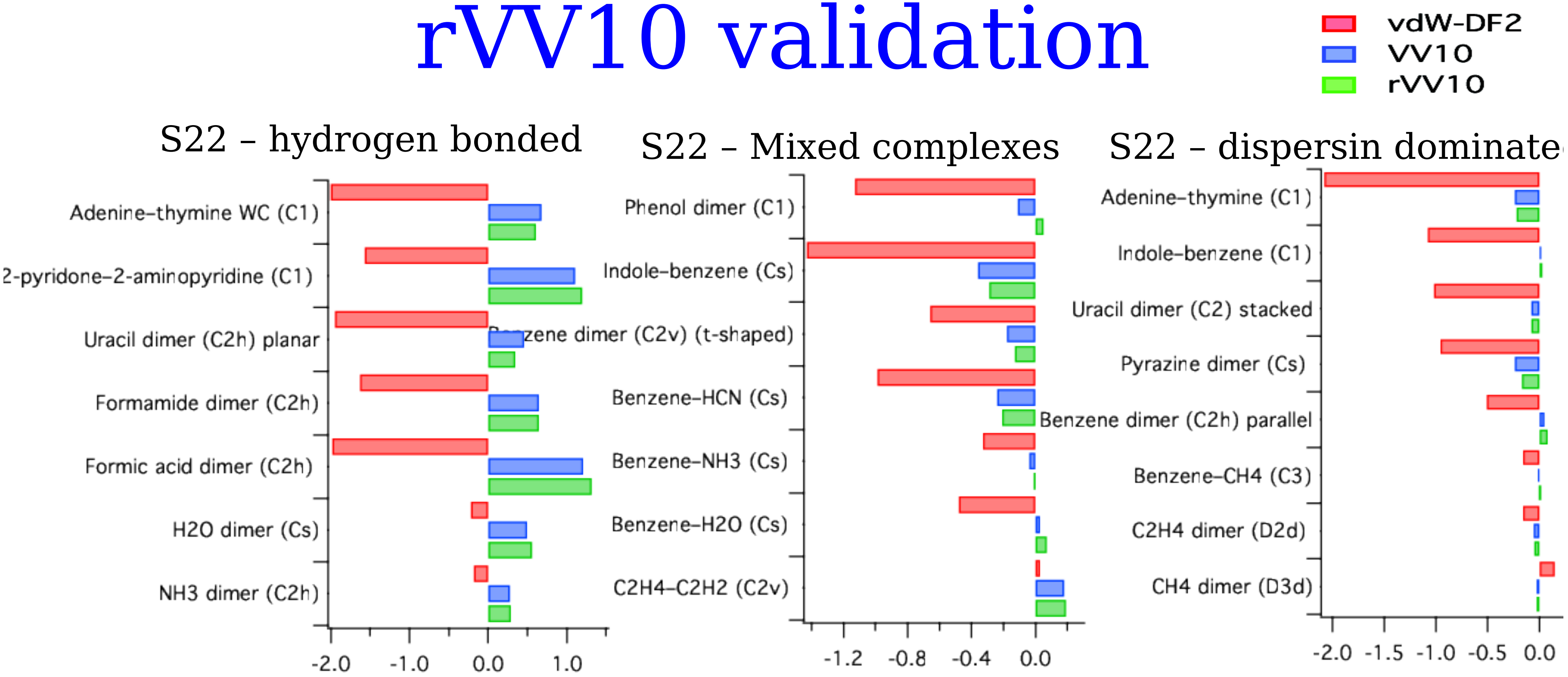
VV10 vs rVV10

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



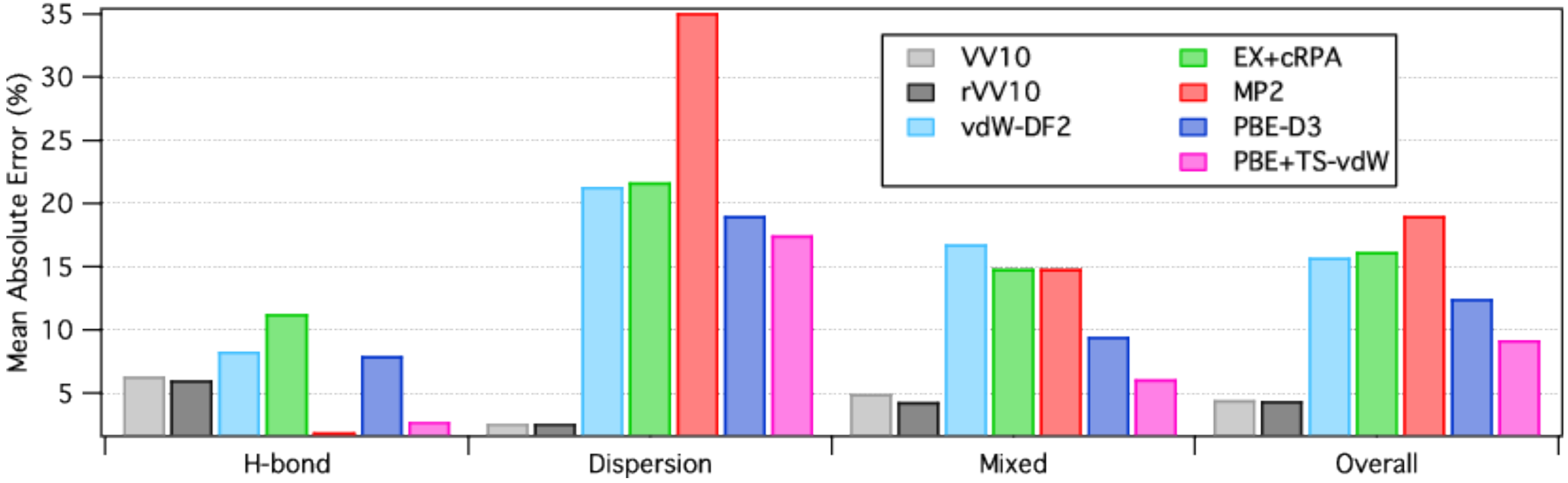
The error in the kernel is small except when the density itself is very small !

rVV10 validation


S22 – hydrogen bonded

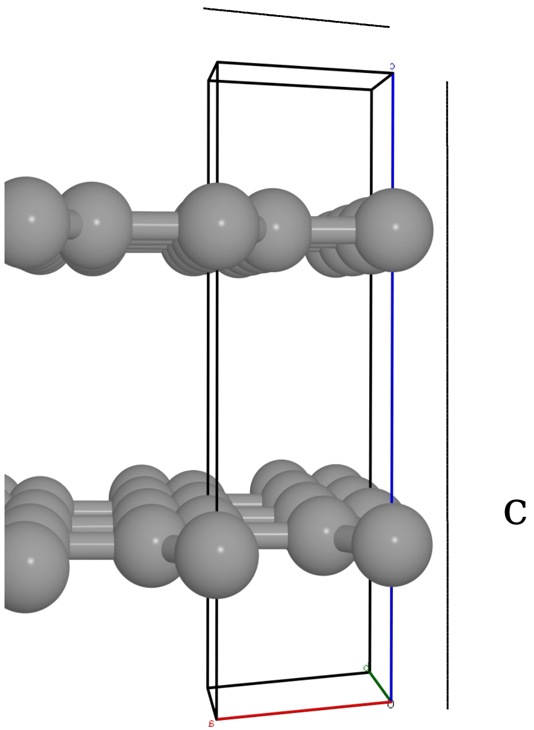
S22 – Mixed complexes

S22 – dispersin dominate

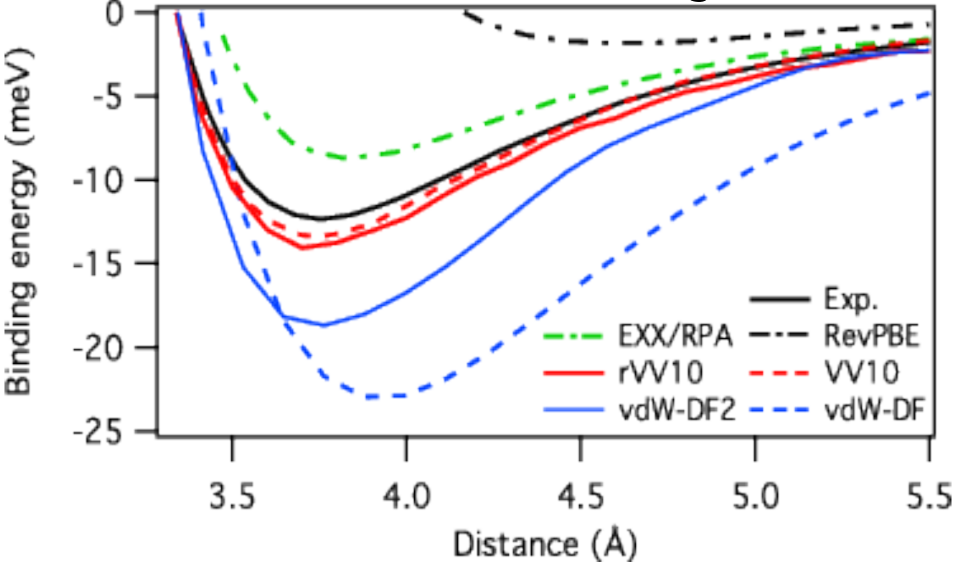


rVV10 applications

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



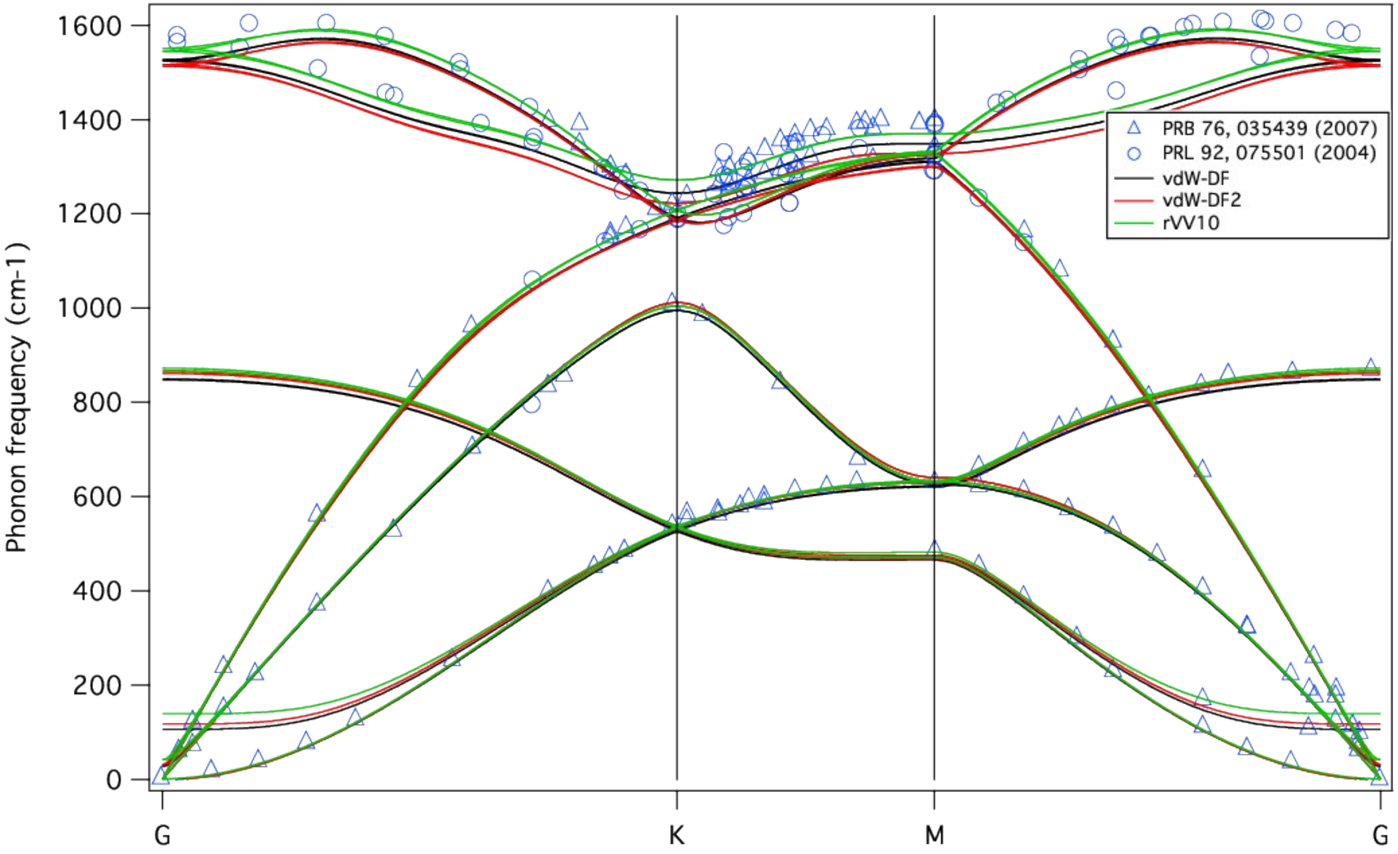
Argon dimer

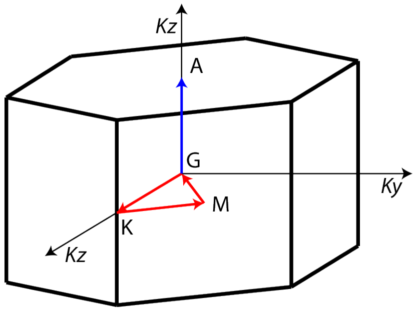


Graphite cel parameters (A)

	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



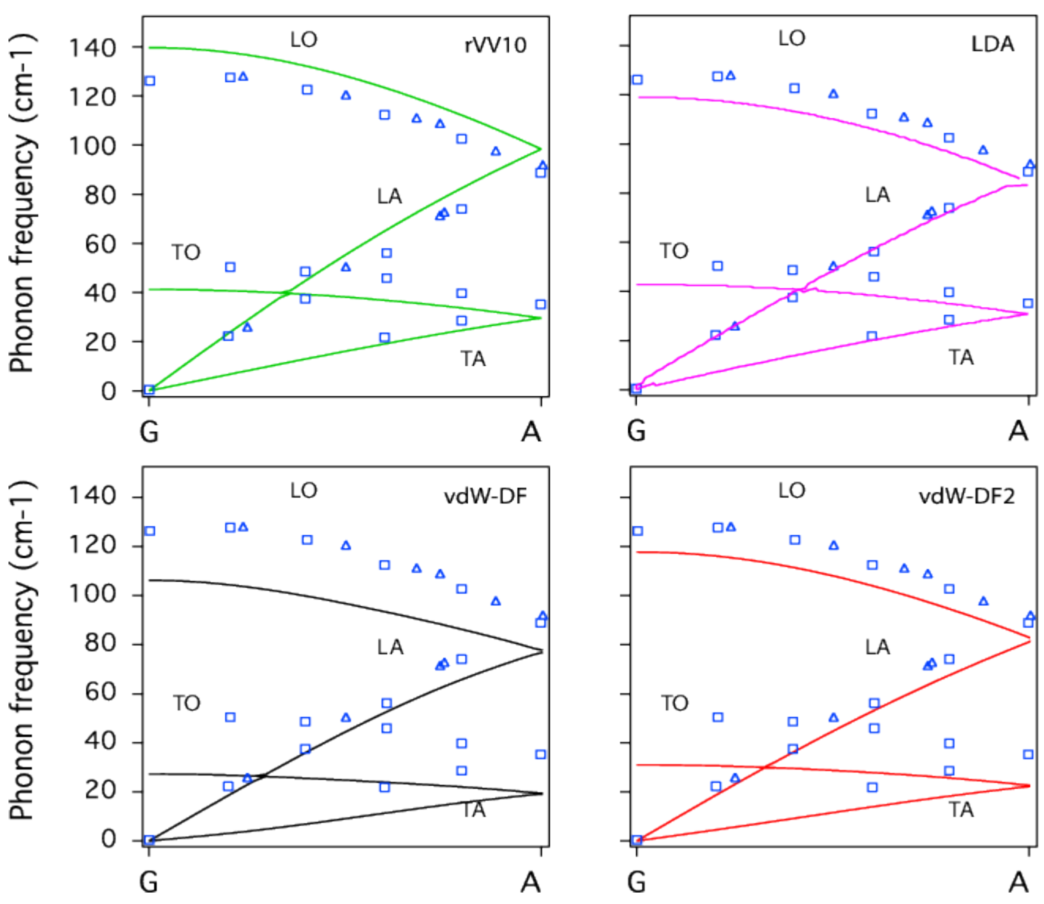


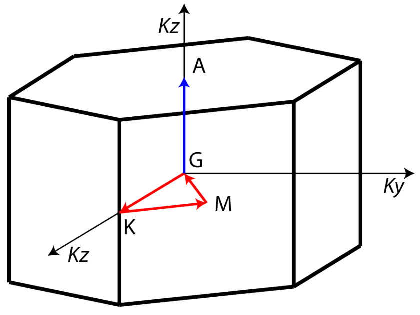
Stiff intralayer modes

	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

THE END