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

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SISSA and INFM DEMOCRITOS

Scuola Internazionale Superiore di Studi Avanzati

...ma per seguir virtute e conoscenza...

DEMOCRITOS

DEmocritos MOdeling Center for Research In aTOmistic Simulation INFM

Density Functional Theory

$$[T_e + W_{eI} + W_{ee} + W_{II}]\,\Phi_\nu(\mathbf{r};\mathbf{R}) = E_\nu(\mathbf{R})\Phi_\nu(\mathbf{r};\mathbf{R})$$

$E_{GS}(\mathbf{R})$ depends only on the GS density $n(\vec{r})$ (3D function) and satisfies a variational principle [Hohenberg and Kohn, 1964]

$$\begin{aligned} E_{GS}(\mathbf{R}) \quad &= \mathtt{min} \quad \Big\{ T_0[n(\vec{r})] + \int V_{ext}(\vec{r},\mathbf{R})\, n(\vec{r})\, d\vec{r} \\ &\quad + \frac{e^2}{2}\int \frac{n(\vec{r})n(\vec{r}')}{|\vec{r}-\vec{r}'|}\, d\vec{r}d\vec{r}' + E_{xc}[n(\vec{r})] \Big\} \\ &\quad + W_{II}(\mathbf{R}) \end{aligned}$$

Self-consistent equations [Kohn and Sham, 1965]:

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

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

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

- It is as simple as a MF approx. but it is exact !
- $E_{xc}[n]$ is not known exactly → approximations

n(r) is a smooth and simple function of r

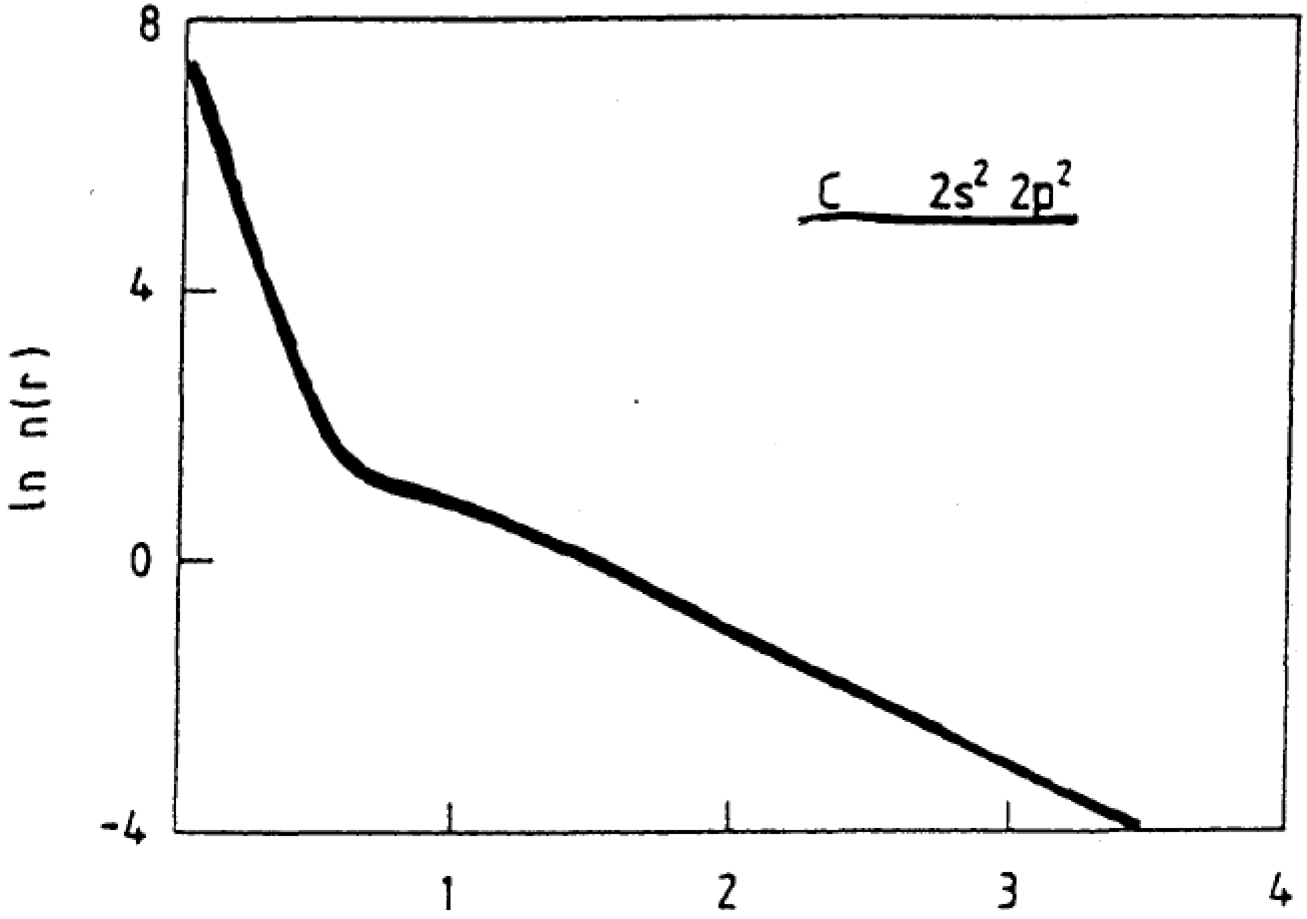
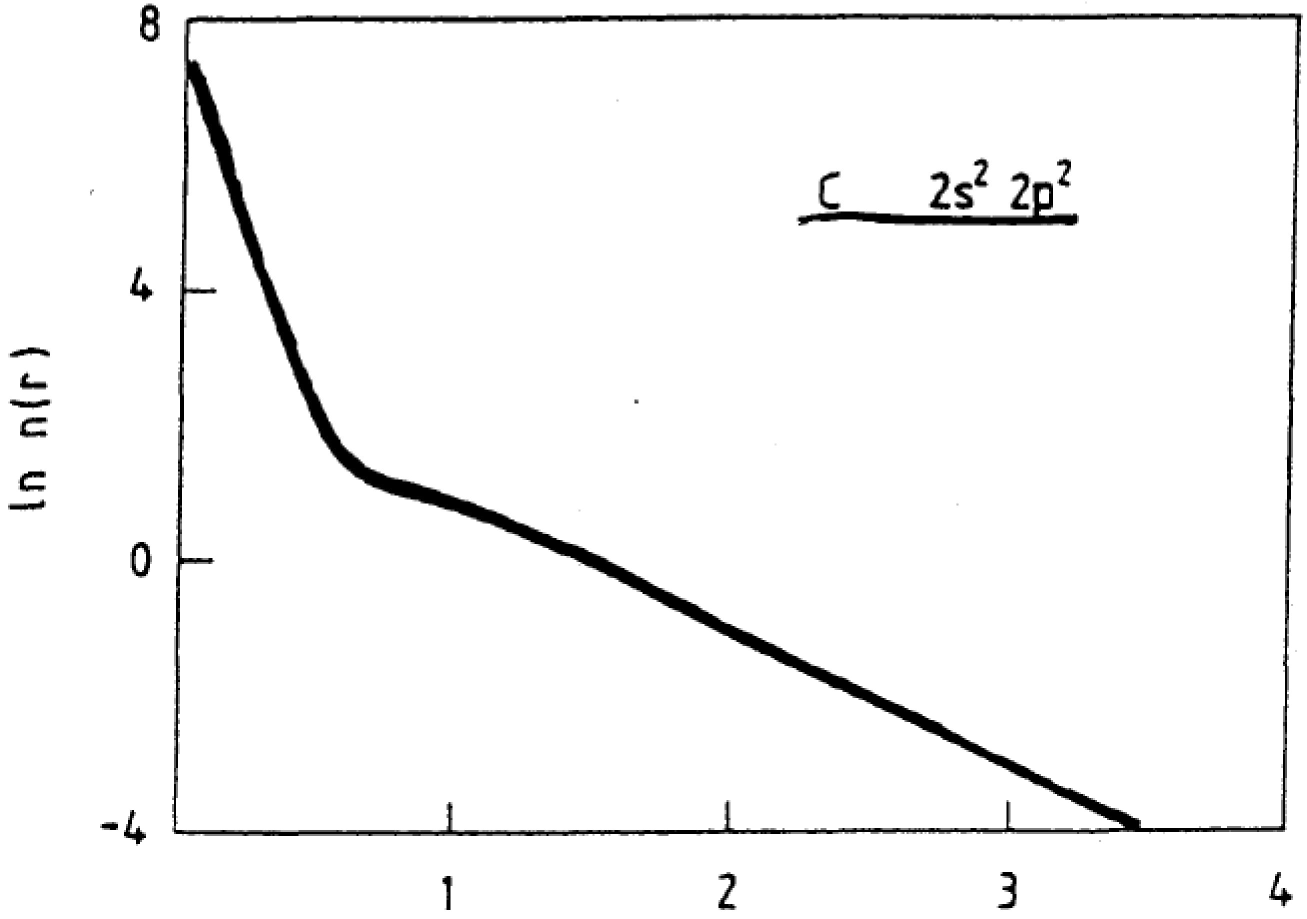


FIG. 1. Spherically averaged density $n(r)$ in ground state of carbon atom as a function of distance r from nucleus.

F[n] is a very non trivial functional of n(r)



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Jacob's laddder of Density Functional Theory

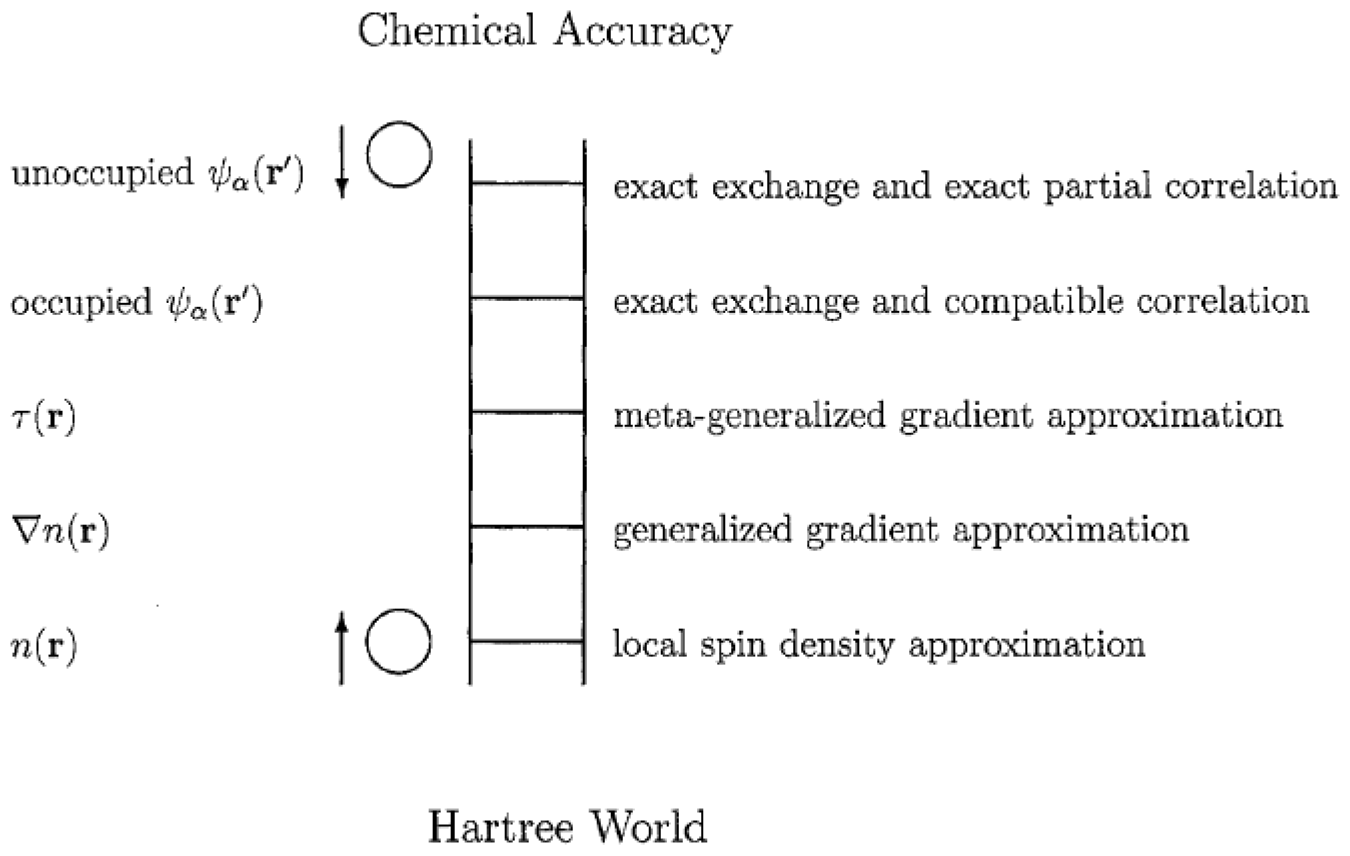


FIGURE 1. Jacob's ladder of density functional approximations. Any resemblance to the Tower of Babel is purely coincidental. Also shown are angels in the spherical approximation, ascending and descending. Users are free to choose the rungs appropriate to their accuracy requirements and computational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

LDA and LSDA

GGA : PW91, PBE, revPBE, RPBE, BLYP

META-GGA: PKZB, TPSS,

SIC, DFT+U, hybrids

Van der Waals functionals

Still simple approximations can work reasonably

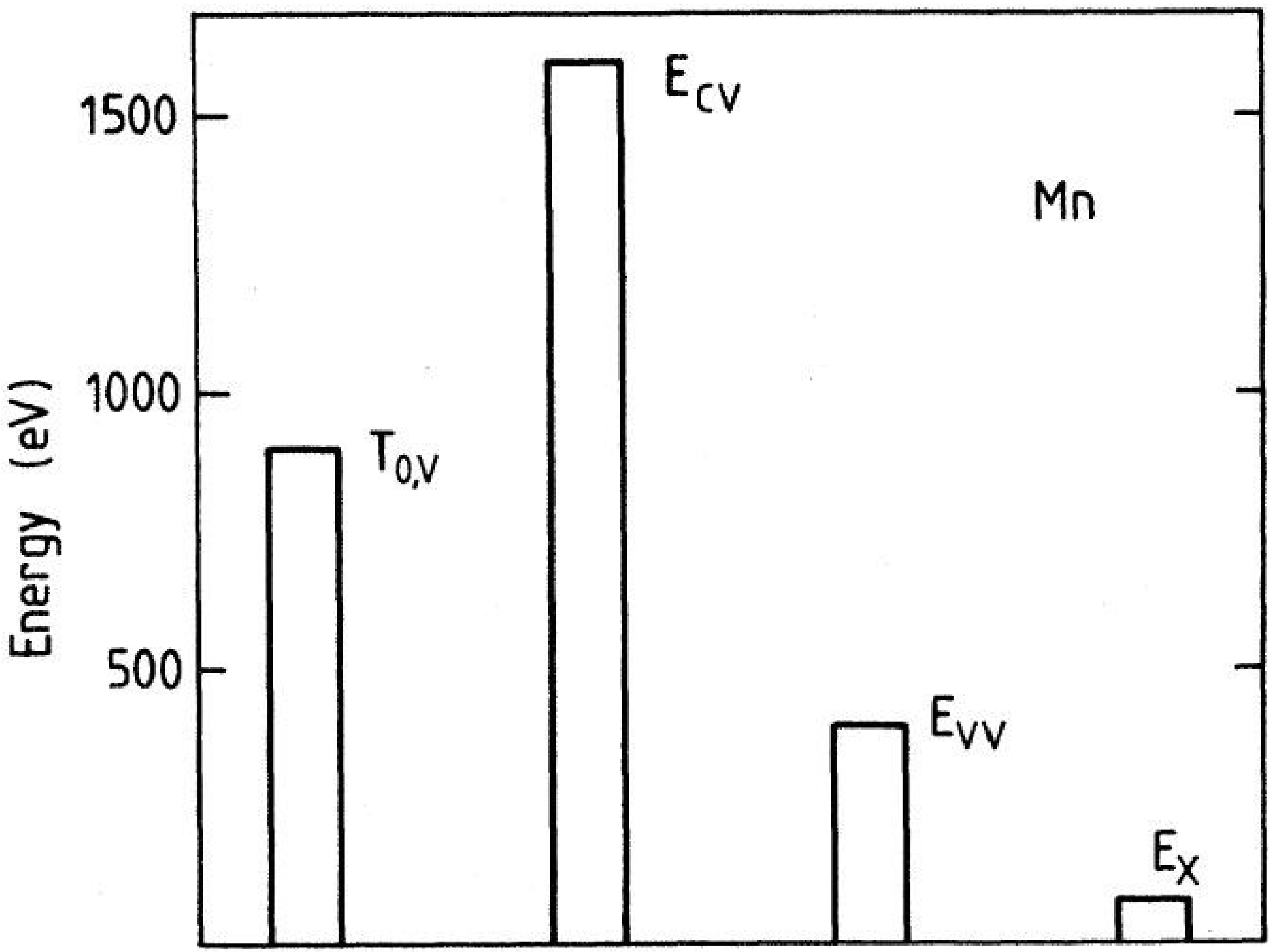


FIG. 4. Relative magnitudes of contributions to total valence energy of Mn atom (in eV).

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

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

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

- 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

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

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

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

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

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

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

Random Phase Approximation (RPA)

Random Phase Approximation: $f_{xc}^{\lambda} = 0$

$$\chi_{\lambda}^{RPA} = \chi_0 + \chi_0[\lambda v_c]\chi_{\lambda}^{RPA}$$

- The Kohn-Sham (non-interacting) response function

$$\chi_0(\mathbf{r}, \mathbf{r}'; iu) = \sum_{i,j} (f_i - f_j) \frac{\phi_i^*(\mathbf{r})\phi_j(\mathbf{r})\phi_j^*(\mathbf{r}')\phi_i(\mathbf{r}')}{\epsilon_i - \epsilon_j + iu}$$

  determines the(λ-)interacting response

$g(r,r',\lambda) \to 1$ for $|r-r'| \to \infty$ $\forall \lambda$

$(g(r,r',\lambda) - 1) \to 0$

$$F[n] = T_s[n] + \frac{e^2}{2} d^3r\, d^3r' \frac{n(r)\, n(r')}{|r-r'|} +$$

$$\underbrace{\frac{e^2}{2}\int d^3r\, d^3r' \frac{n(r)\, n(r')}{|r-r'|} \int_0^1 d\lambda \left[g(r,r',\lambda) - 1\right]}_{E_{xc}}$$

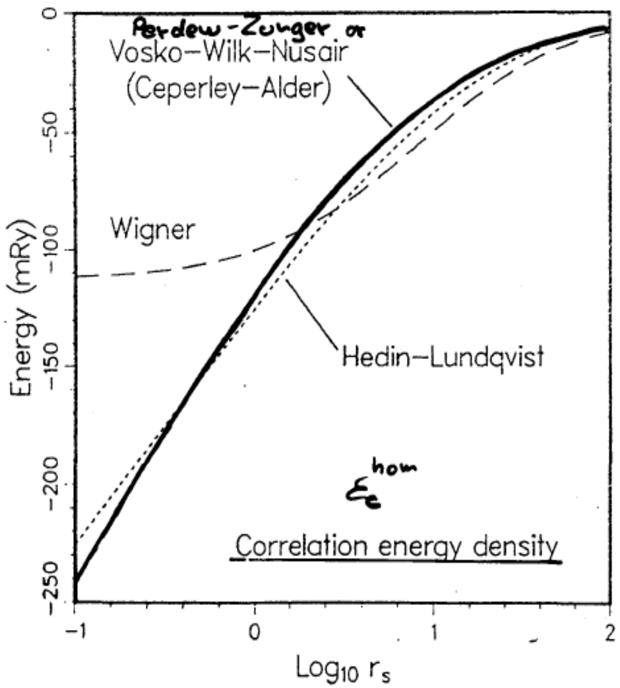
$$n_{xc}(r, r'-r) = n(r') \int_0^1 d\lambda \left[g(r,r',\lambda) - 1\right]$$ exchange-correlatio hole

LOCAL DENSITY APPROXIMATION (LDA)

since $g(r,r',\lambda)-1$ is "short ranged"

$$n_{xc}(r,s) \cong n_{xc}^{hom}(r,s;n=n(r))$$

$$E_{xc}^{LDA} = \int d^3r \; n(r)\; \varepsilon_{xc}^{hom}(n(r))$$



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

$$\varepsilon_{xc}^{hom}(n) = \varepsilon_x^{hom}(n) + \varepsilon_c^{hom}(n)$$

$$\varepsilon_x^{hom}(n) = -\frac{3}{4\pi} e^2 (3\pi^2 n)^{1/3}$$

$\varepsilon_c^{hom}(n)$ from accurate DMC data

Ceperley and Alder

Phys. Rev. Lett. 45, 566 - 569 (1980)

From L(S)DA

$$E_{\mathrm{XC}}^{\mathrm{LSD}}[n_\uparrow, n_\downarrow] = \int d^3r\, n\, \epsilon_{\mathrm{XC}}^{\mathrm{unif}}(n_\uparrow, n_\downarrow)$$

to GGA

$$E_{\mathrm{XC}}^{\mathrm{GGA}}[n_\uparrow, n_\downarrow] = \int d^3r\, f(n_\uparrow, n_\downarrow, \nabla n_\uparrow, \nabla n_\downarrow)$$

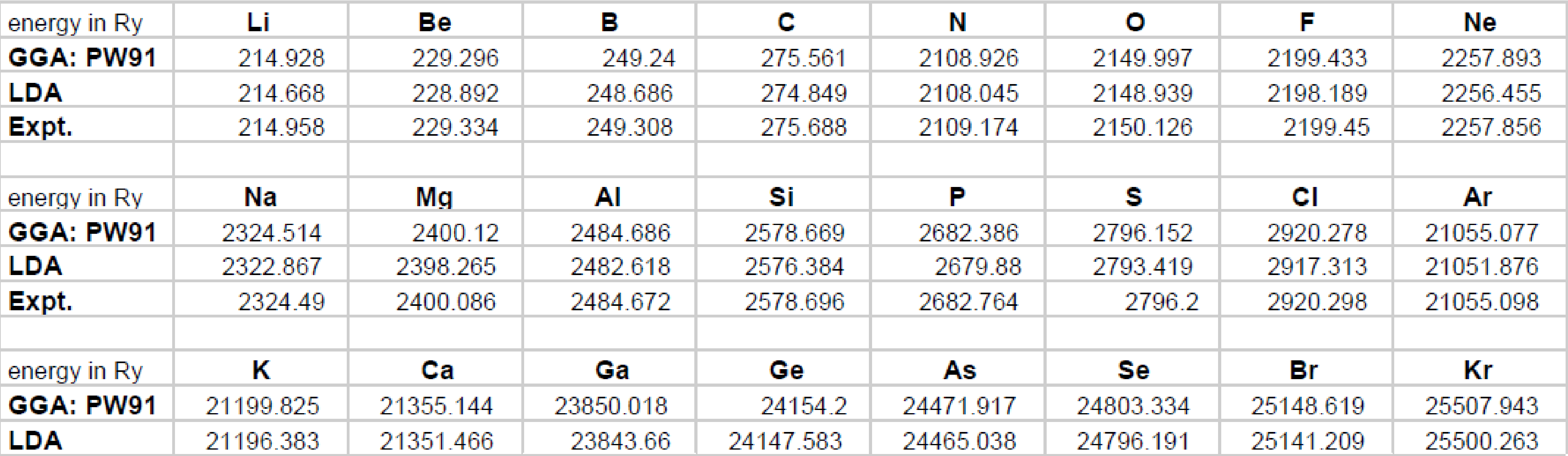
… not a unique recipe

A lot of work is gone in proposing and comparing new functionals

A few functional are widely used today

PW91, PBE, revPBE, RPBE …
BLYP

Energies of Atoms



energy in Ry	Li	Be	B	C	N	O	F	Ne
GGA: PW91	214.928	229.296	249.24	275.561	2108.926	2149.997	2199.433	2257.893
LDA	214.668	228.892	248.686	274.849	2108.045	2148.939	2198.189	2256.455
Expt.	214.958	229.334	249.308	275.688	2109.174	2150.126	2199.45	2257.856
energy in Ry	**Na**	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**	**Ar**
GGA: PW91	2324.514	2400.12	2484.686	2578.669	2682.386	2796.152	2920.278	21055.077
LDA	2322.867	2398.265	2482.618	2576.384	2679.88	2793.419	2917.313	21051.876
Expt.	2324.49	2400.086	2484.672	2578.696	2682.764	2796.2	2920.298	21055.098
energy in Ry	**K**	**Ca**	**Ga**	**Ge**	**As**	**Se**	**Br**	**Kr**
GGA: PW91	21199.825	21355.144	23850.018	24154.2	24471.917	24803.334	25148.619	25507.943
LDA	21196.383	21351.466	23843.66	24147.583	24465.038	24796.191	25141.209	25500.263

LDA underestimates stability of atom, GGA is closer

Small Molecules

Binding Energy

	exp (ev)	LDA	GGA	HF
H2	-4.753	-4.913	-4.540	-3.64
LiH	-2.509	-2.648	-2.322	
O2	-5.230	-7.595	-6.237	-1.28
H20	-10.078	-11.567	-10.165	
F2	-1.66	-3.32		1.37

Binding energy too high in LDA, GGA is closer but sometimes bound to weak. Pure Hartree Fock without corrections is terrible.

Lattice Parameters in Solids

	exp	LDA	Δ	GGA	Δ
Si	5.427	5.4	-0.50%	5.49	1.16%
Ge	5.65	5.62	-0.53%	5.74	1.59%
GaAs	5.65	5.62	-0.53%	5.73	1.42%
Al	4.03	3.98	-1.31%	4.09	1.57%
Cu	3.60	3.52	-2.35%	3.62	0.44%
Ag	4.07	4.00	-1.69%	4.17	2.47%
Ta	3.30	3.26	-1.12%	3.32	0.80%
W	3.16	3.14	-0.67%	3.18	0.67%
Pt	3.91	3.90	-0.41%	3.97	1.49%
Au	4.06	4.05	-0.13%	4.16	2.48%

LDA tends to “overbind”, GGA “underbinds” GGA error more variable

Bulk Modulus in Solids (in GPA)

	exp	LDA	Δ	GGA	Δ
Si	99	96	-3.03%	83	-16.16%
Ge	77	78	1.30%	61	-20.78%
GaAs	76	74	-2.63%	65	-14.47%
Al	77	84	9.09%	73	-5.19%
Cu	138	192	39.13%	151	9.42%
Ag	102	139	36.27%	85	-16.67%
Ta	193	224	16.06%	197	2.07%
W	310	337	8.71%	307	-0.97%
Pt	283	307	8.48%	246	-13.07%
Au	172	198	15.12%	142	-17.44%

LDA tends to be too stiff. GGA too soft

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 of Geometry Prediction

LDA under-predicts bond lengths (always ?)

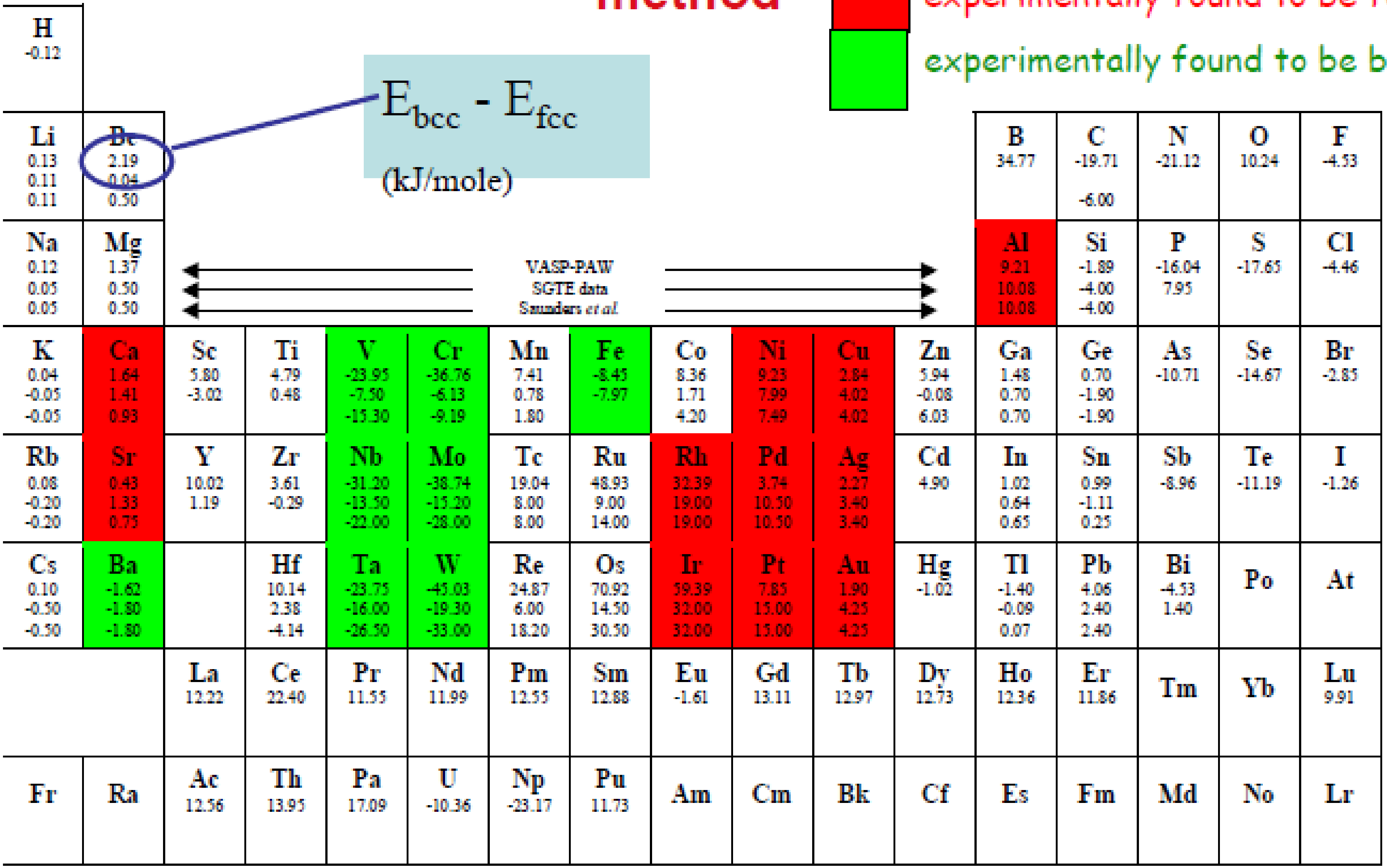
GGA error is less systematic though over-prediction is common.

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)

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					← VASP-PAW → ← SGTE data → ← Saunders *et al* →						🟥 **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 Thermochemistry (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)

Reaction Energies

Reaction	**Exp (eV)**	**LDA (eV)**	Δ
Li (bcc) + Al (fcc) -> LiAl (compound)	-0.2457	-0.2234	9.08%
0.5 Cu(fcc) + 0.5 Au(fcc) -> CuAu	-0.053	-0.0193	63.58%
Li(bcc) + CoO2 -> LiCoO2	-4.25	-3.75	11.76%

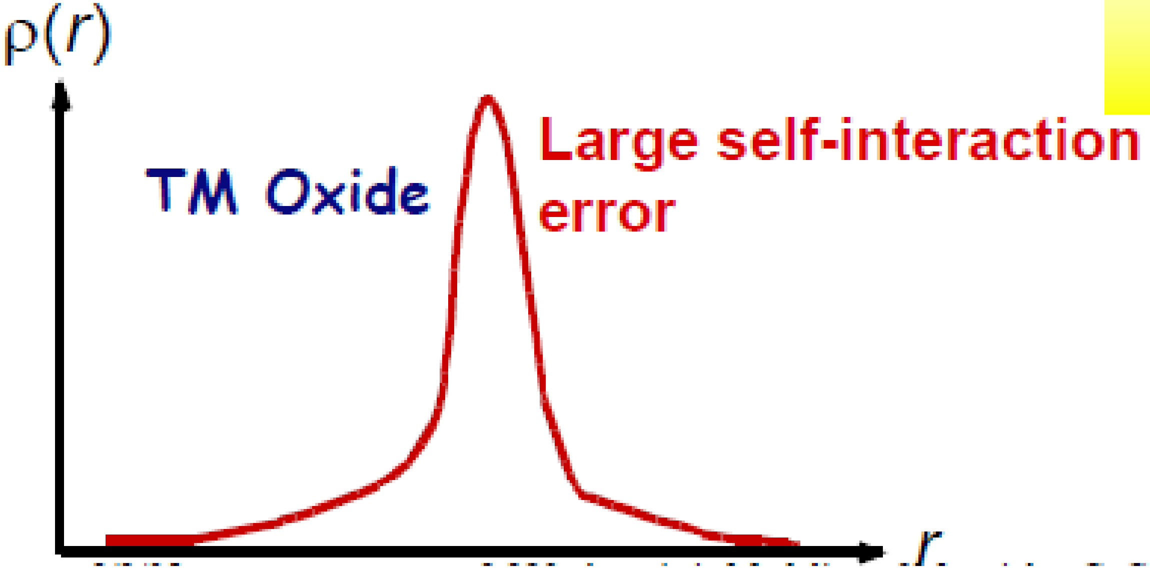
Redox Reactions can be more Problematic

	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)

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

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

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

From GGA

$$E_{\mathrm{XC}}^{\mathrm{GGA}}[n_\uparrow, n_\downarrow] = \int d^3r\, f(n_\uparrow, n_\downarrow, \nabla n_\uparrow, \nabla n_\downarrow)$$

to Meta-GGA

$$E_{\mathrm{xc}}[n_\uparrow, n_\downarrow] = \int d^3r\, n\,\epsilon_{\mathrm{xc}}(n_\uparrow, n_\downarrow, \nabla n_\uparrow, \nabla n_\downarrow, \tau_\uparrow, \tau_\downarrow),$$

where $n(\mathbf{r}) = n_\uparrow(\mathbf{r}) + n_\downarrow(\mathbf{r})$ is the total density, and

$$\tau_\sigma(\mathbf{r}) = \sum_i^{\mathrm{occup}} \frac{1}{2} |\nabla \psi_{i\sigma}(\mathbf{r})|^2$$

Formulation is significantly more complicated and it is not widely used.
Still …

Electron Localization Function

$$C(\vec{r}) = \frac{1}{2}\sum_i n_i |\nabla \varphi_i|^2 - \frac{1}{8}\frac{|\nabla \rho|^2}{\rho}$$

$$\rho = \sum_i n_i |\varphi_i|^2 \qquad C_h(\vec{r}) \sim \rho^{5/3}$$

$$\mathrm{ELF} = \left\{1 + \left[\frac{C(\vec{r})}{C_h(\rho(\vec{r}))}\right]^2\right\}^{-1}$$

ELF can distinguish metallic (ELF=~0.5) from covalent (ELF=~1.0) regions of the electron density

Meta-GGA has the potential to treat in a different way correlation in electronically different materials.

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.

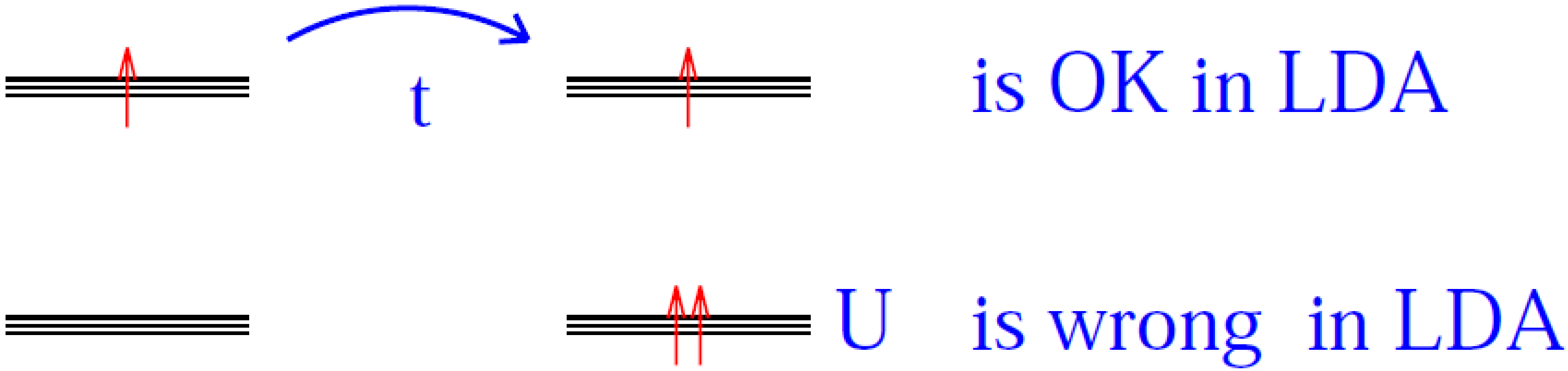
  - molecular dissociation limit, TMO & RE and other atom-in-solid system.

- Van der Waals interactions are not taken into account
  - occasional agreement with exp. from compensation of errors

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 ?

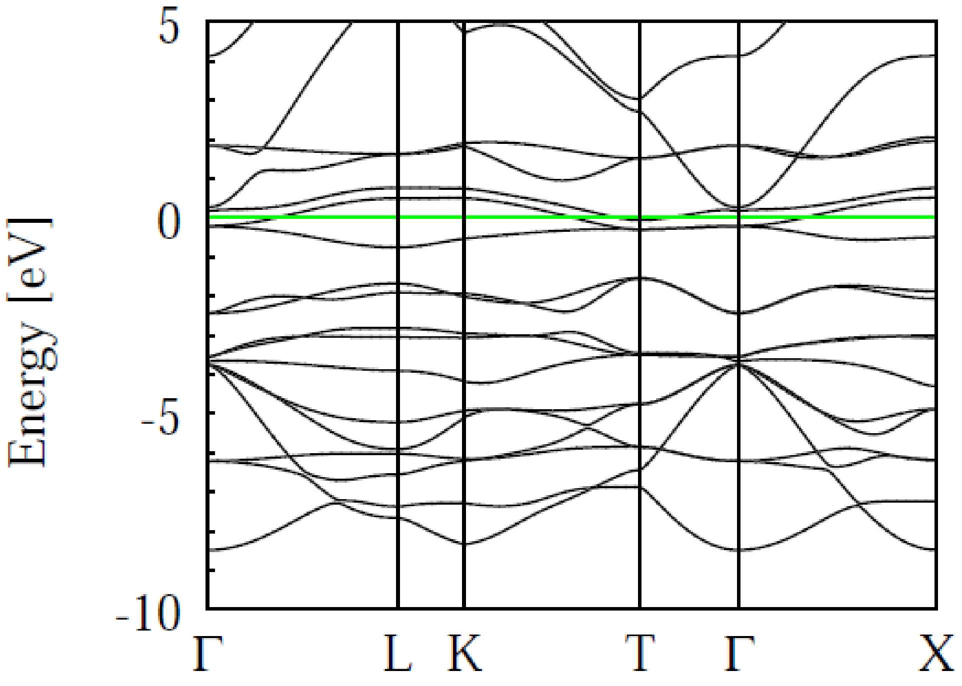


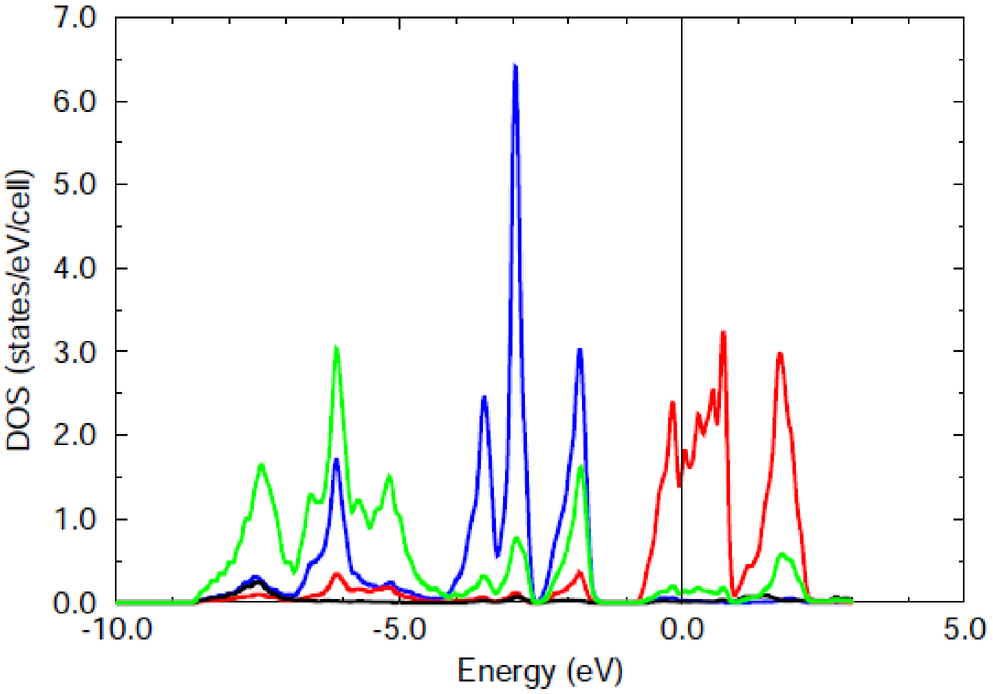
is OK in LDA

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.

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.

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.

The LDA+U energy functional

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

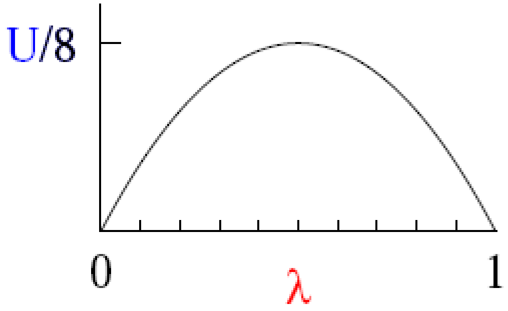
[Anisimov, Zaanen and Andersen, *PRB* **44**, 943 (1991).]

A simplified LDA+U model:

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

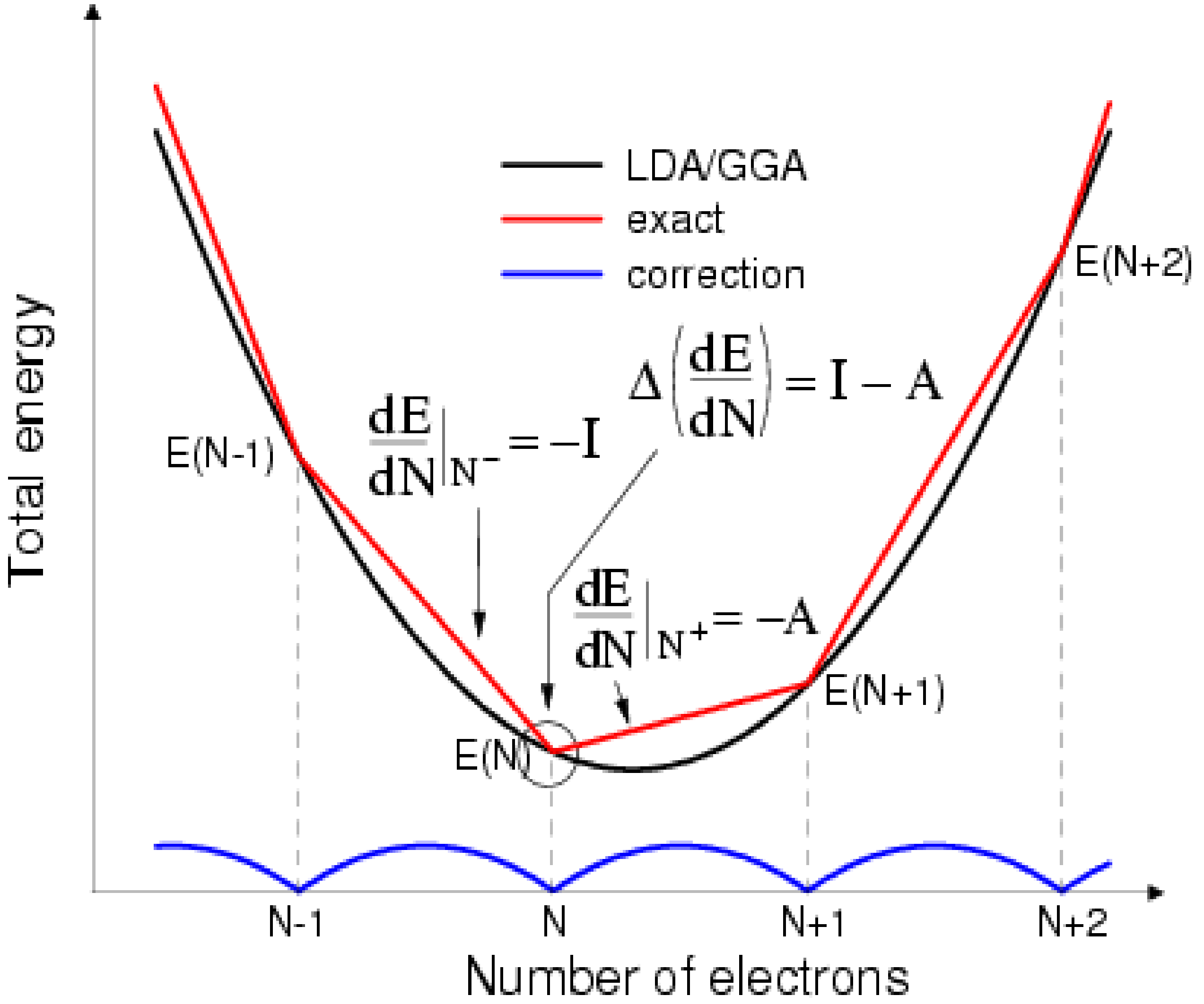
In the diagonal basis, where $\mathbf{n}^{I\sigma}\cdot\vec{v}^{I\sigma}_{\alpha} = \lambda^{I\sigma}_{\alpha}\vec{v}^{I\sigma}_{\alpha}$, the LDA+U correction is simply

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



Fractional occupation are strongly discouraged for large U.

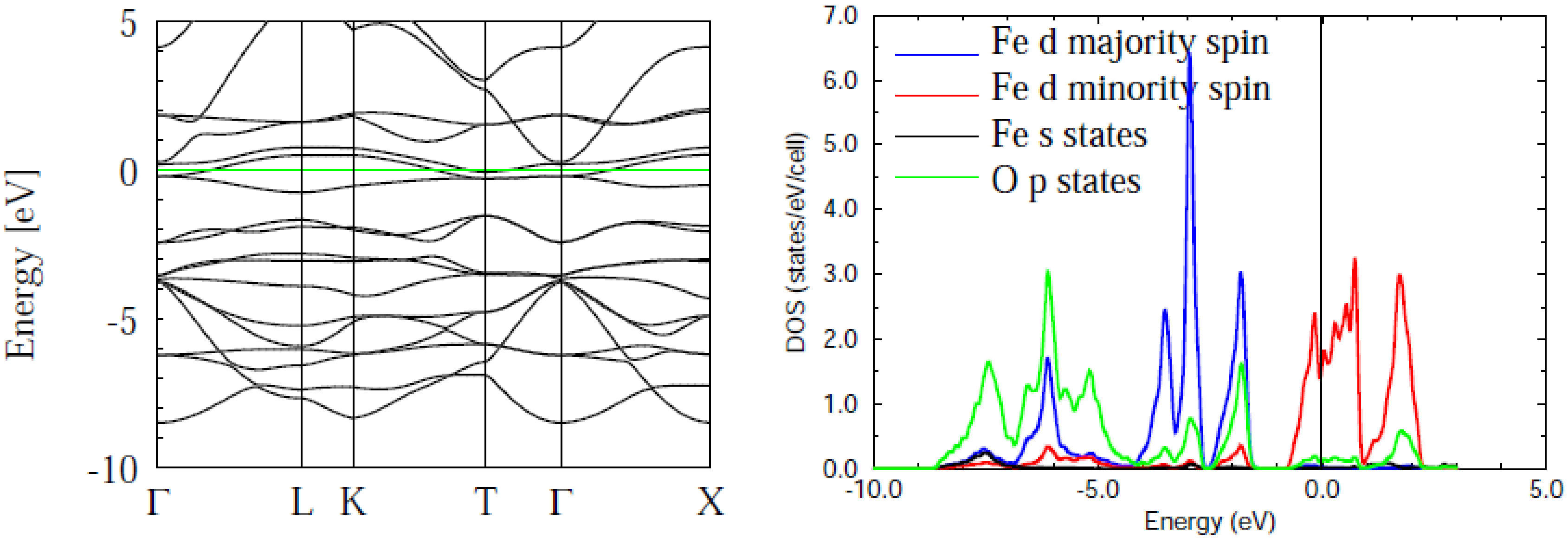
LDA/GGA failure in the atomic limit



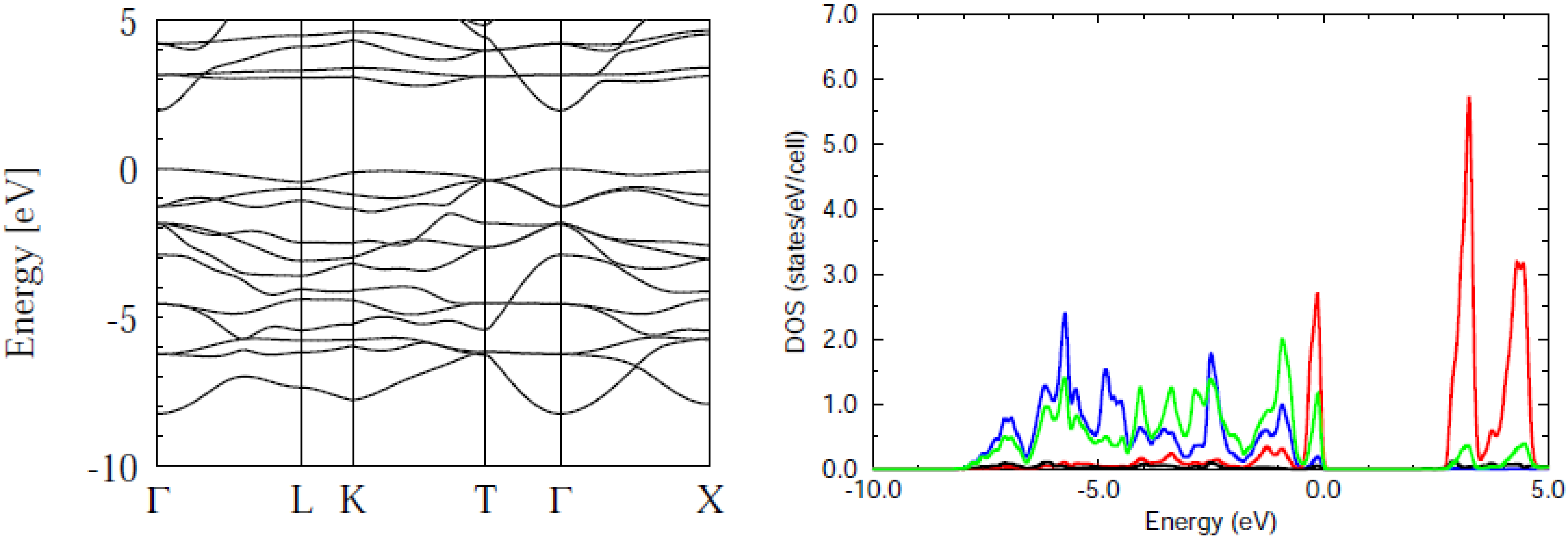
A correction is needed to remove spurious self-interaction

Electronic Structure of FeO

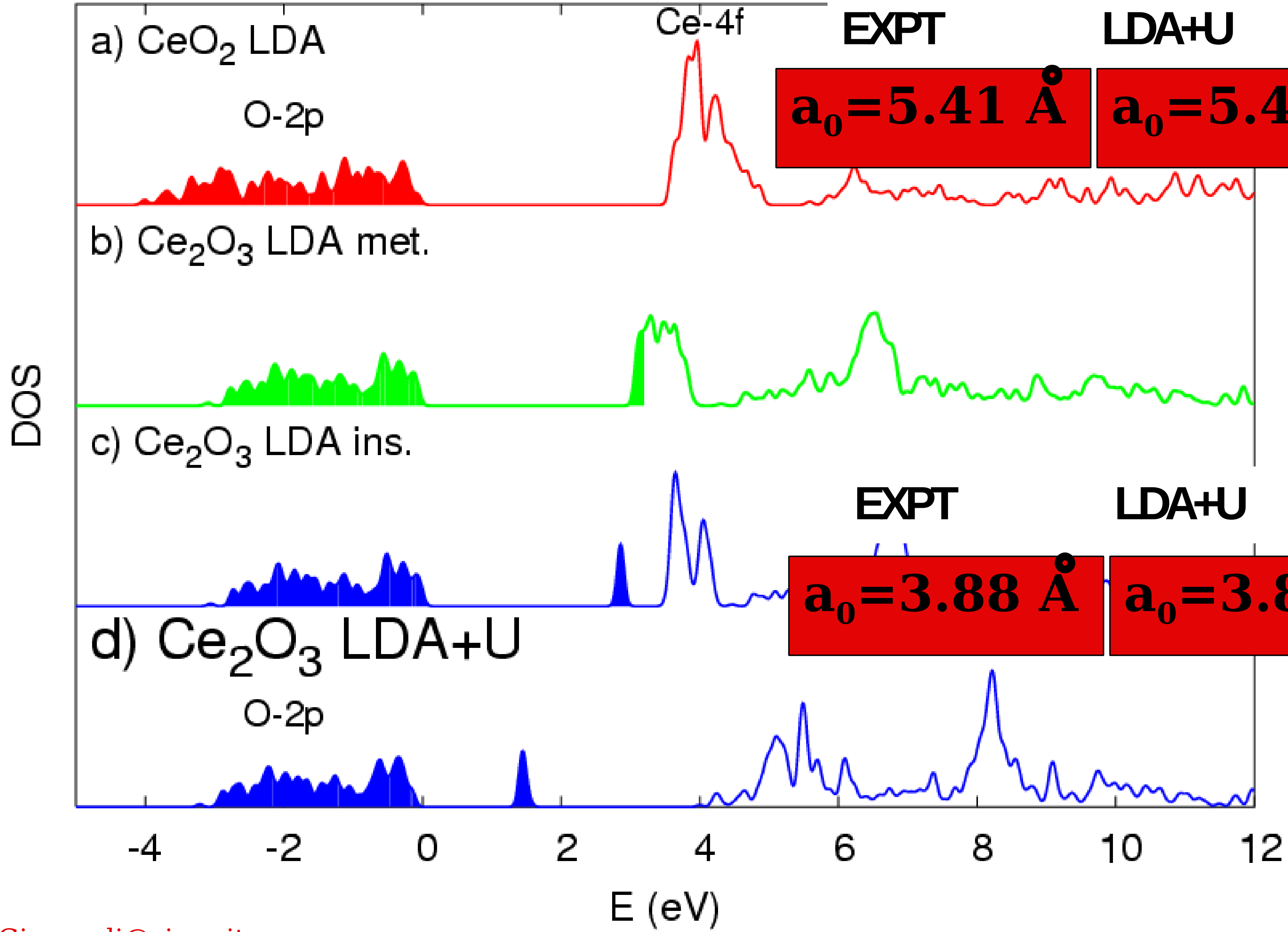
GGA



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 :

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

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)

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

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

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

The q+G=0 divergence

- Gygi-Baldereschi PRB 34, 4405 (1986)

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

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

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

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

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

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

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

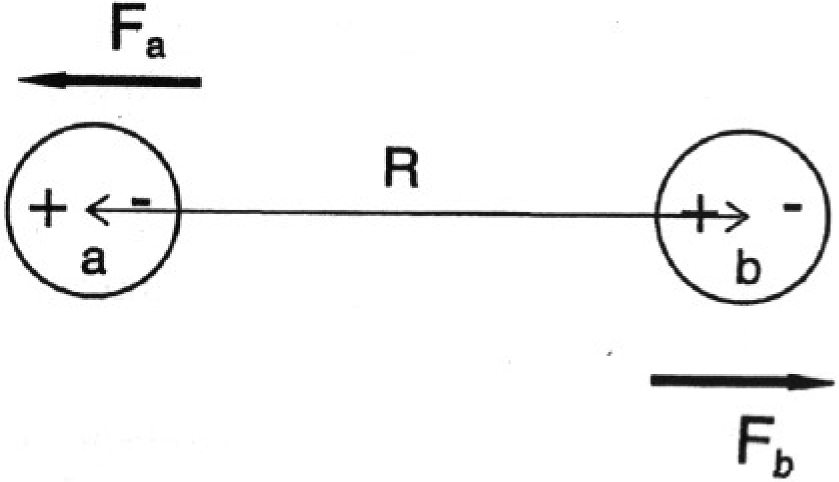
From 10 to 100 times slower than standard case

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

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.



How to deal with van der Waals ?

- neglect it

- add an empirical damped dispersion correction
  Grimme, Tatckenko

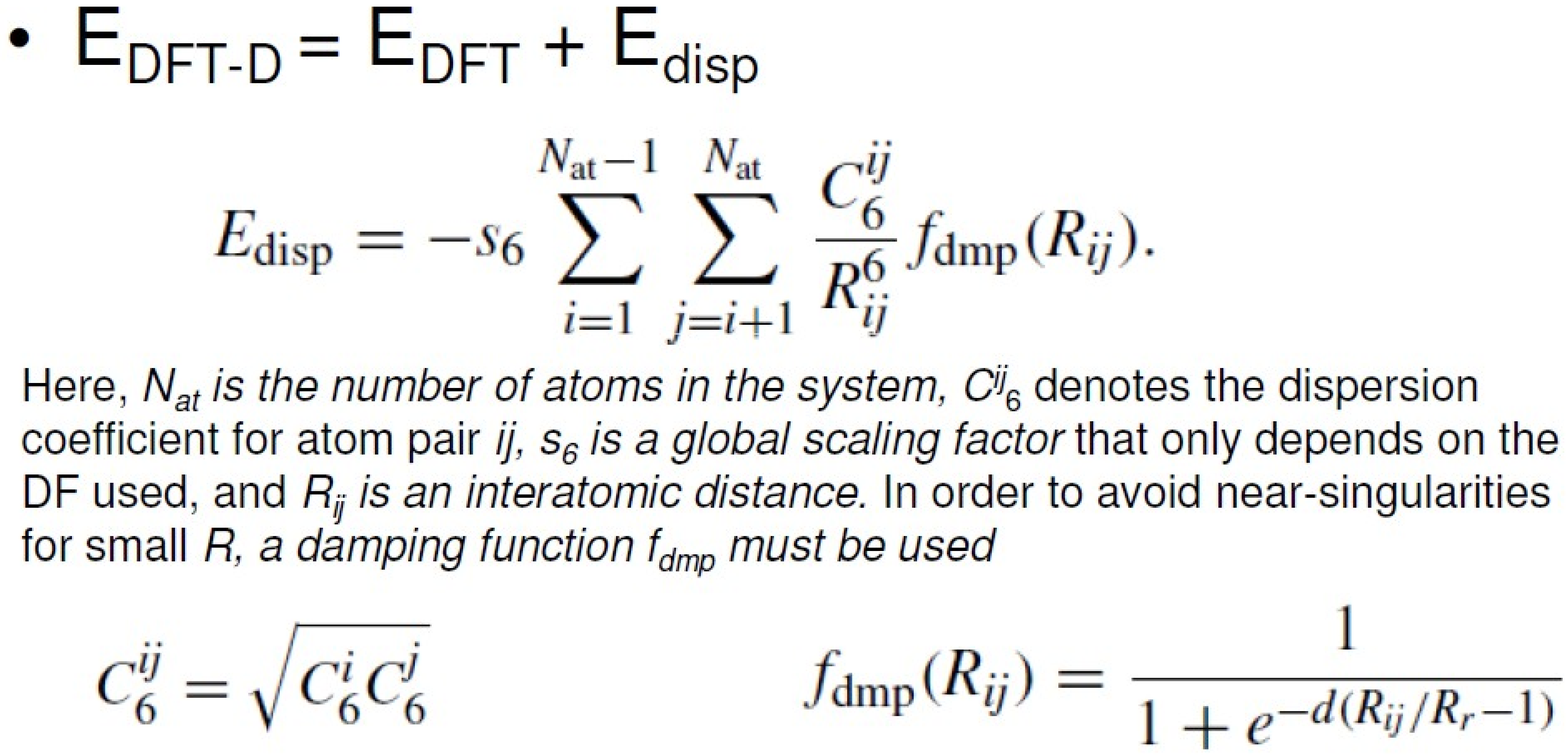
- develop a truly non local XC functional
  Vdw-DF, vdw-DF2, VV09, VV10

- RPA and beyond RPA

How to deal with van der Waals ?

- add an empirical damped dispersion correction

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

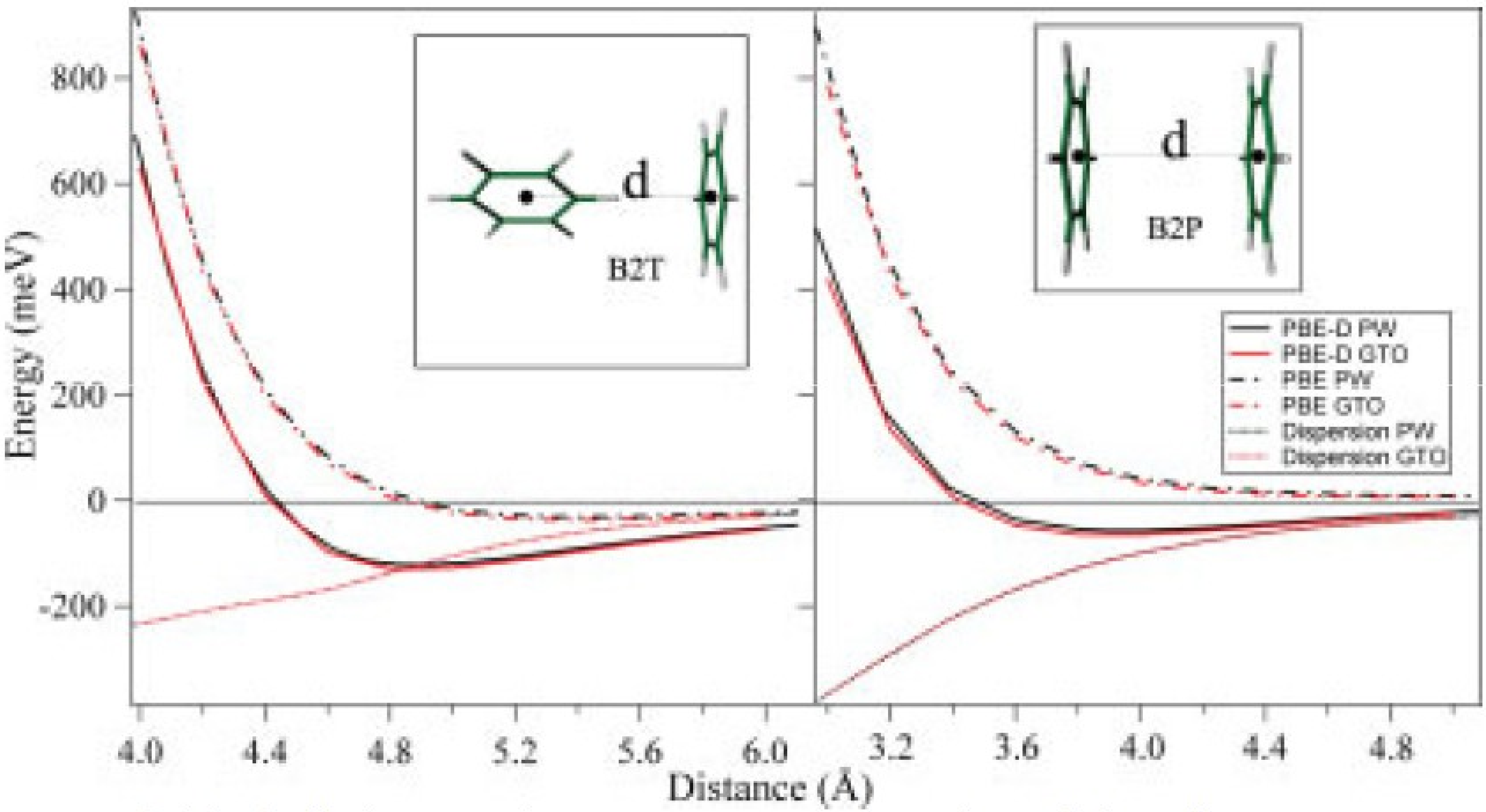


- $E_{\text{DFT-D}} = E_{\text{DFT}} + E_{\text{disp}}$

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

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)

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

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

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

-vdw-DF : Dion et al, PRL **92**, 246401 (2006)
-vdW-DF2 : Lee et al, PRB **82**, 081101 (2010)

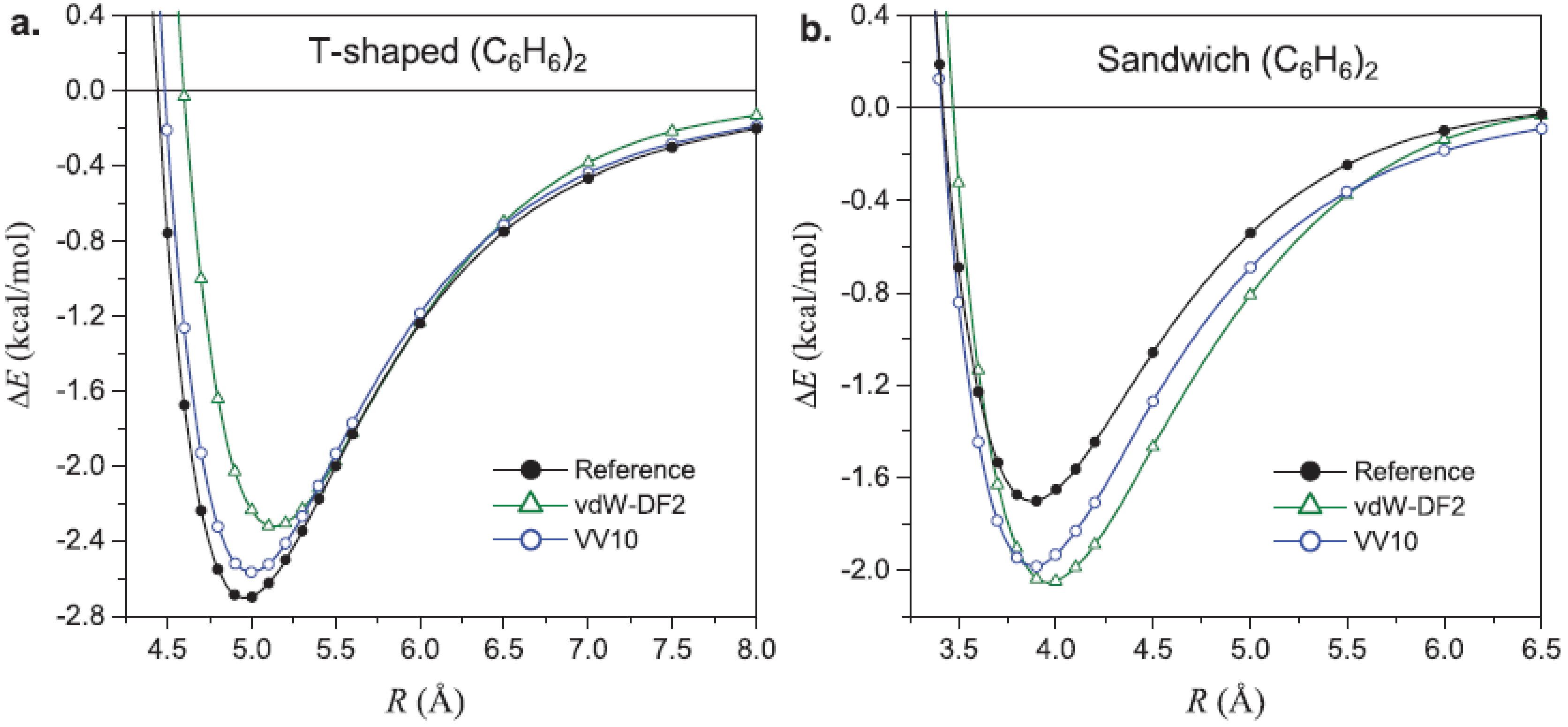
-VV09 : Vydrov and Van Voorhis, PRL **103**, 063004 (2009)
-VV10 : Vydrov and Van Voorhis, JCP **133**, 244103 (2010)

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'|)



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

THE END

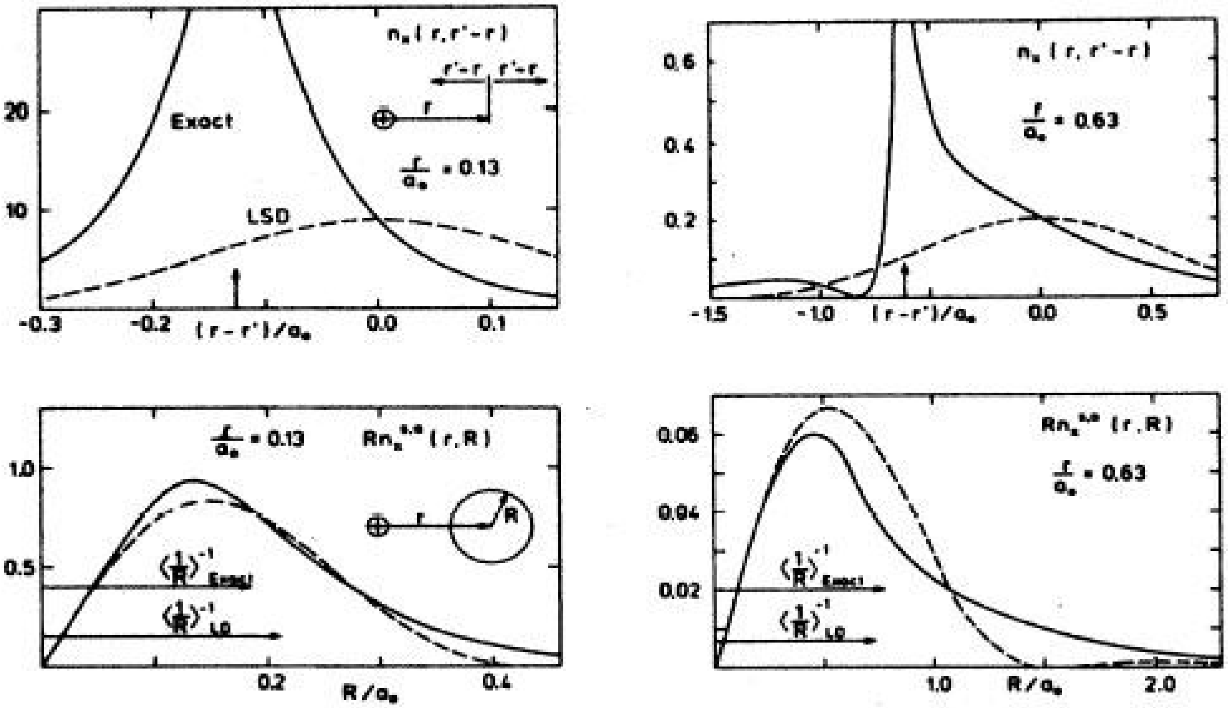


FIG. 7. Exact (solid line) and approximate (dashed line) exchange hole $n_x(\mathbf{r},\mathbf{r}'-\mathbf{r})$ [Eq. (3.10)] for a spin-up electron in a nitrogen atom for $r=0.13$ and 0.63 a.u. The top figure shows the hole along a line through the nucleus and the electron. The arrow indicates the nuclear position and $\mathbf{r}-\mathbf{r}'=0$ gives the electron position. The exact hole has a large weight at the nucleus, while the approximate hole is centered at the electron. The lower figure shows the spherical average of the hole around the electron. The area under the curve is proportional to the exchange energy. The figure also shows the value of $\langle 1/\mathbf{R}\rangle_r$ defined in Eq. (3.13).

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	···