

XC-Functionals

Dr. Ricardo Faccio
Centro NanoMat
Facultad de Química
Universidad de la República

Kohn-Sham Equations(DFT)

$$E[\rho] = T_0[\rho] + V_H[\rho] + V_{xc}[\rho] + V_{ext}[\rho]$$

$$\hat{H}_{KS} = \hat{T}_0 + \hat{V}_H + \hat{V}_{xc} + \hat{V}_{ext}$$

$$\hat{H}_{KS} = \underbrace{-\frac{\hbar^2}{2m_e} \nabla^2 + \frac{e^2}{4\pi\epsilon_0} \int \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' + V_{xc} + V_{ext}}_{Universal!}$$

$$\hat{V}_{xc} = \frac{\delta V_{xc}[\rho]}{\delta \rho}$$

$$\rho(\vec{r}) = \sum_{i=1}^N \phi_i^*(\vec{r}) \phi_i(\vec{r})$$

All the unknown terms below a carpet: the exchange-correlation functional

Local Density Approximation (LDA)

$$V_{xc}^{\sigma}(\vec{r}) \equiv \frac{\delta E_{xc}}{\delta n(\vec{r}, \sigma)}$$

Solids can be often considered as close to the limit of the homogeneous electron gas
In this limit, effects of exchange and correlation are local in character

$$V_{xc}[n] \approx V_{xc}[n(\vec{r})]$$

Exchange-correlation energy of the homogeneous electron gas a function of
density

Exchange:
analytic
form

Correlation:
calculated to great accuracy
with Monte Carlo methods

Generalized Gradient Approximation (GGA)

$$V_{xc}[n] \approx V_{xc}[n(\vec{r}), \nabla n(\vec{r})]$$

Provide required accuracy for DFT to be adopted by the Chemistry Community

Problem: does not lead to consistent improvement over the LSDA

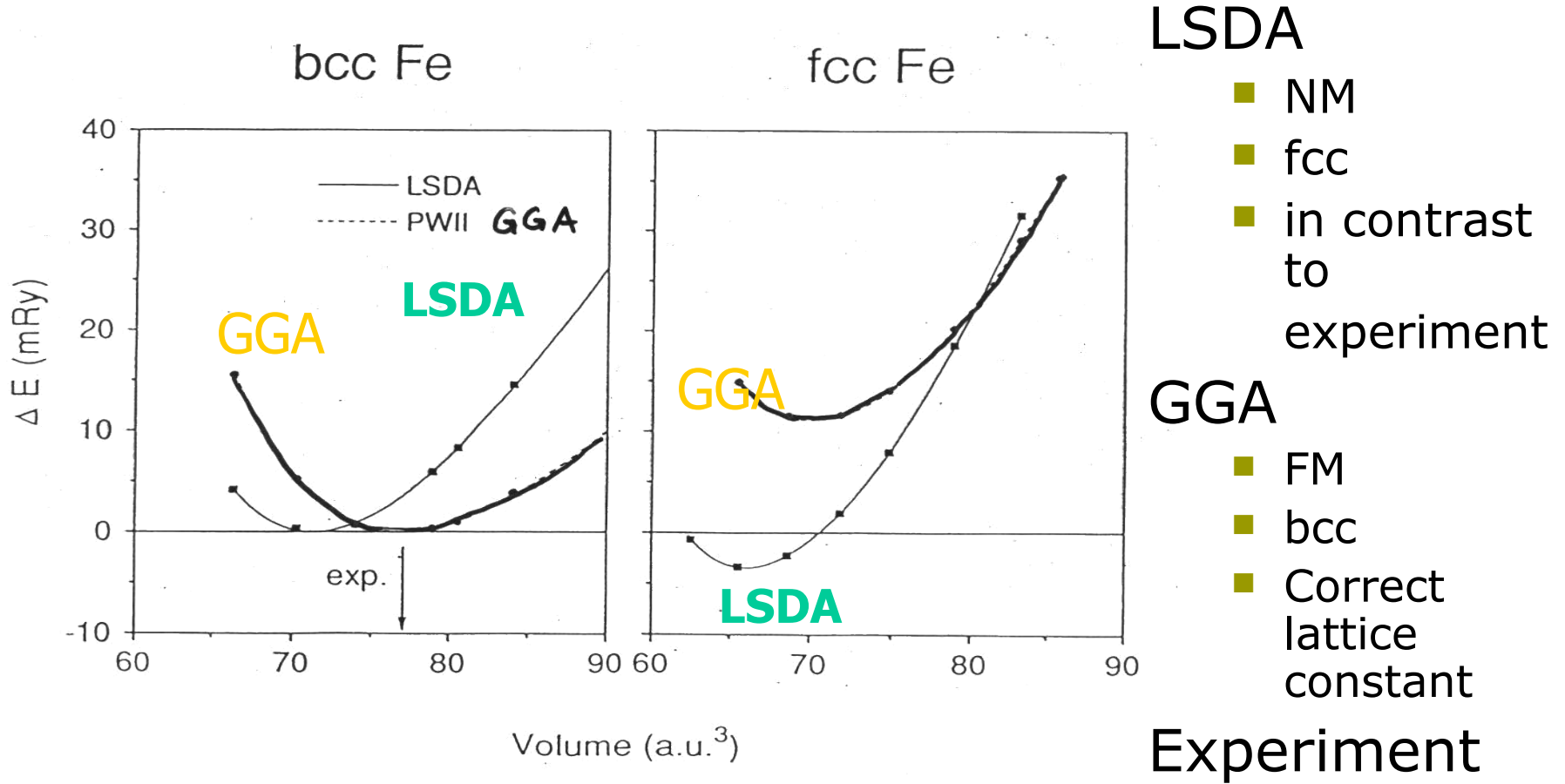
Accuracy of the xc functionals

	LDA	GGA
a	-1% , -3%	+1%
B	+10, +40%	-20%, +10%
E_c	+15%	-5%
E_{gap}	-50%	-50%

LDA: crude approximation but sometimes is accurate enough (structural properties, ...)

GGA: usually tends to overcompensate LDA results, not always better than LDA.

In some cases, GGA is a must: DFT ground state of iron



Results obtained with Wien2k.

by Karl H. Schwartz

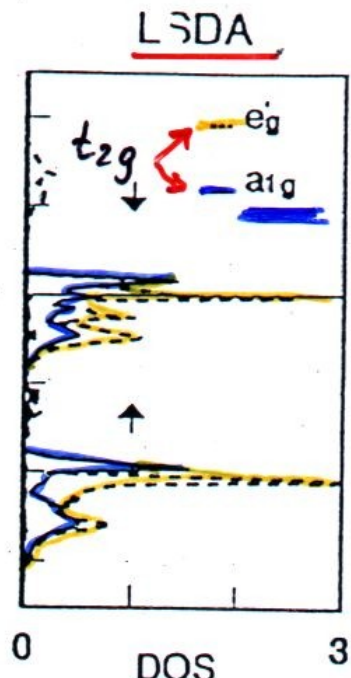
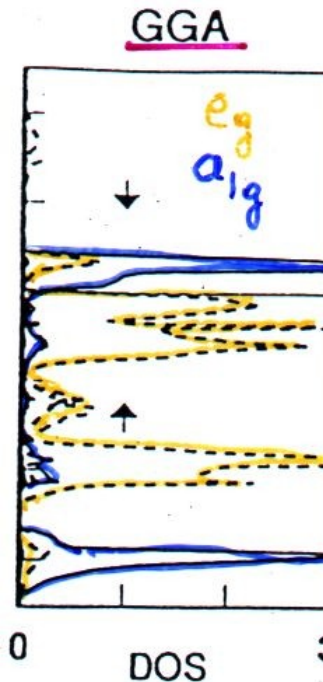
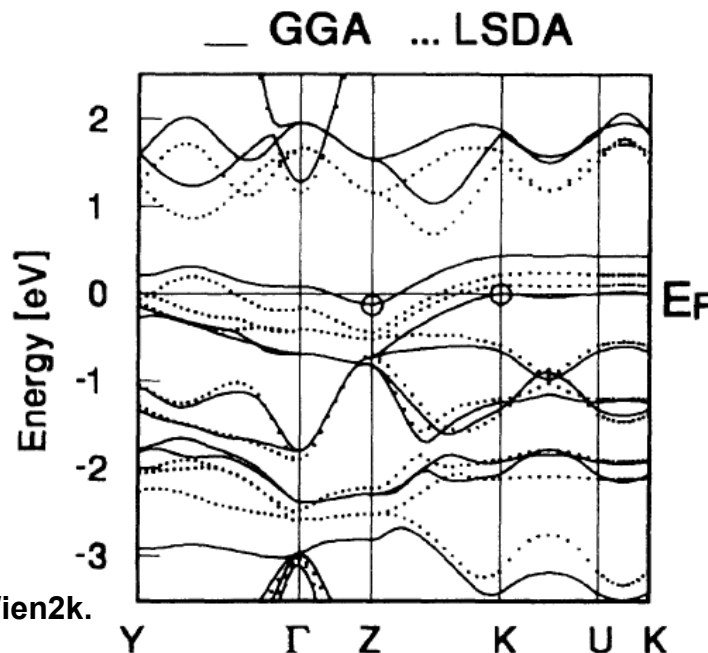
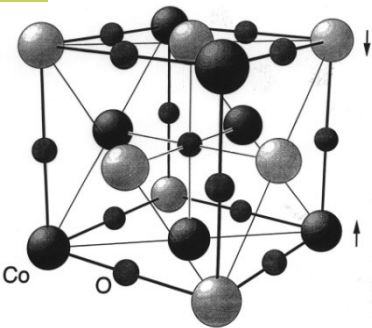
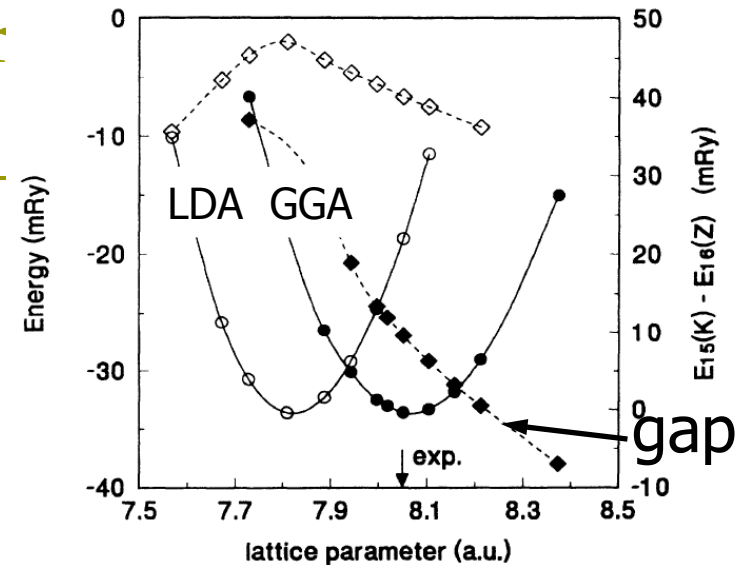
XC.Authors SIESTA

- **CA (Ceperley-Alder)** equivalent to PZ (Perdew-Zunger). Local density approximation. Ref: Perdew and Zunger, PRB 23, 5075 (1981)
- **PW92** (Perdew-Wang-92). Local density approximation. Ref: Perdew and Wang, PRB, 45, 13244 (1992)
- **PBE** (Perdew-Burke-Ernzerhof). Generalized gradients approximation. Ref: Perdew, Burke and Ernzerhof, PRL 77, 3865 (1996)
- **revPBE** (Revised Perdew-Burke-Ernzerhof). Generalized gradients approximation. Ref: Y. Zhang and W. Yang, PRL 80, 890 (1998)
- **RPBE** (Revised Perdew-Burke-Ernzerhof). Generalized gradients approximation. Ref: Hammer, Hansen and Norskov PRB 59, 7413 (1999)
- **WC** (Wu-Cohen modification of PBE functional). Generalized gradients approximation. Ref: Z. Wu and R.E. Cohen, PRB 73, 235116 (2006)
- **PBEsol** (Perdew-Burke-Ernzerhof for solids). Generalized gradients approximation. Ref: Perdew et al, PRL 100, 136406 (2008)
- **LYP** Generalized gradients approximation that implements Becke gradient exchange functional (A. D. Becke, Phys. Rev. A 38, 3098 (1988)) and Lee, Yang, Parr correlation functional (C. Lee, W. Yang, R. G. Parr, Phys. Rev. B 37, 785 (1988)), as modified by Miehlich, Savin, Stoll and Preuss, Chem. Phys. Lett. 157, 200 (1989). See also Johnson, Gill and Pople, J. Chem. Phys. 98, 5612 (1993).

Kohn-Sham fails in strongly cor

CoO

- in NaCl structure
- antiferromagnetic: AF II
- insulator
- t_{2g} splits into a_{1g} and e_g
- Both LDA and GGA find them to be metals (although GGA almost splits the bands)



Results obtained with Wien2k.

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Accuracy of DFT for TM

Lattice parameters (Å)

	Exp.	LDA	PBE	WC
Co	2.51	2.42	2.49	2.45
Ni	3.52	3.42	3.52	3.47
Cu	3.61	3.52	3.63	3.57
Ru	2.71	2.69	2.71	2.73
Rh	3.80	3.76	3.83	3.80
Pd	3.88	3.85	3.95	3.89
Ag	4.07	4.01	4.15	4.07
Ir	3.84	3.84	3.90	3.86
Pt	3.92	3.92	4.00	3.96
Au	4.08	4.07	4.18	4.11

■ 3d elements:

- *PBE superior, LDA much too small*

■ 4d elements:

LDA too small, PBE too large

- *New functional Wu-Cohen (WC)*

Z.Wu, R.E.Cohen,
PRB 73, 235116 (2006)

■ 5d elements:

- *LDA superior, PBE too large*

Treatment of Exchange Correlation

Approximations for E_{xc}

- ▶ LDA: $E_{xc}^{LDA} = \int f(\rho(\mathbf{r})) d^3r$
- ▶ GGA: $E_{xc}^{GGA} = \int f(\rho(\mathbf{r}), |\nabla \rho(\mathbf{r})|) d^3r$
- ▶ MGGA: $E_{xc}^{MGGA} = \int f(\rho(\mathbf{r}), |\nabla \rho(\mathbf{r})|, \nabla^2 \rho(\mathbf{r}), t(\mathbf{r})) d^3r$
- ▶ LDA+U: $E_{xc}^{LDA+U} = E_{xc}^{LDA} + E_{ee} - E_{dc}$
- ▶ GGA+U: $E_{xc}^{GGA+U} = E_{xc}^{GGA} + E_{ee} - E_{dc}$
- ▶ hybrid: $E_{xc}^{hybrid} = E_{xc}^{DFT} + \alpha (E_x^{HF} - E_x^{DFT})$
where

$$E_x^{HF} = -\frac{1}{2} \sum_{\sigma} \sum_{\substack{n, \mathbf{k} \\ n', \mathbf{k}'}} w_{\mathbf{k}} w_{\mathbf{k}'} \int \int \frac{\psi_{n\mathbf{k}}^{\sigma*}(\mathbf{r}) \psi_{n'\mathbf{k}'}^{\sigma*}(\mathbf{r}') \psi_{n'\mathbf{k}'}^{\sigma}(\mathbf{r}) \psi_{n\mathbf{k}}^{\sigma}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3r d^3r'$$

Modified Becke-Johnson Potential

- Becke-Johnson potential (J. Chem. Phys. 124, 221101 (2006))
 - *designed to reproduce OEP potentials in atoms*
 - *tests for bandgaps in solids* (Tran, Blaha, Schwarz, J. Phys. CM. 19, 196208 (2007))
give only minor improvements over LDA/GGA gaps
- modified Becke-Johnson potential (F. Tran and PB, PRL 102, 226401 (2009))

$$v_{x,\sigma}^{\text{MBJ}}(\mathbf{r}) = c v_{x,\sigma}^{\text{BR}}(\mathbf{r}) + (3c - 2) \frac{1}{\pi} \sqrt{\frac{5}{12}} \sqrt{\frac{2t_{\sigma}(\mathbf{r})}{\rho_{\sigma}(\mathbf{r})}},$$

$$t_{\sigma} = (1/2) \sum_{i=1}^{N_{\sigma}} \nabla \psi_{i,\sigma}^* \cdot \nabla \psi_{i,\sigma}$$

kinetic energy density

$$v_{x,\sigma}^{\text{BR}}(\mathbf{r}) = -\frac{1}{b_{\sigma}(\mathbf{r})} \left(1 - e^{-x_{\sigma}(\mathbf{r})} - \frac{1}{2} x_{\sigma}(\mathbf{r}) e^{-x_{\sigma}(\mathbf{r})} \right)$$

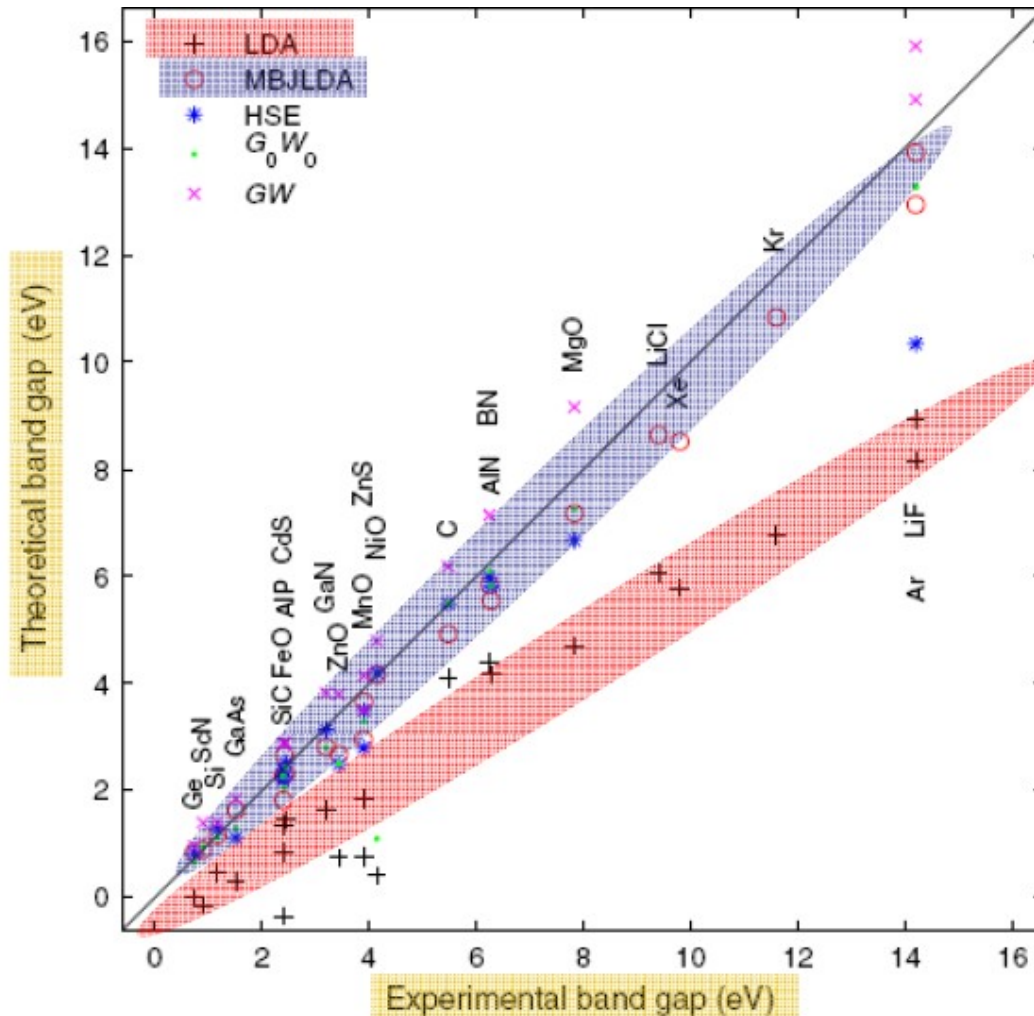
Becke-Roussel potential
(approximate Slater-pot.)

$$c = \alpha + \beta \left(\frac{1}{V_{\text{cell}}} \int_{\text{cell}} \frac{|\nabla \rho(\mathbf{r}')|}{\rho(\mathbf{r}')} d^3 r' \right)^{1/2}$$

c depends on the density
properties of a material

Comparative Study

- LDA strongly underestimates gaps
- mBJ gives gaps of „GW quality“



mBJ Gaps!

- accuracy of a few tenth of an eV
- works for small gap semiconductors to large gap insulators (Ne!!!)
- works for TM-oxides (in contrast to G_0W_0)
- improves unoccupied bands
- nearly unchanged occupied bands

Solid	LDA	MBJLDA	HSE	G_0W_0	GW	Expt.
Ne (A1)	11.42	22.72		19.59 ^e	22.1 ^g	21.70
Ar (A1)	8.16	13.91	10.34 ^a	13.28 ^e	14.9 ^g	14.20
Kr (A1)	6.76	10.83				11.6
Xe (A1)	5.78	8.52				9.8
C (A4)	4.11	4.93	5.49 ^b	5.50 ^e	6.18 ^g	5.48
Si (A4)	0.47	1.17	1.28 ^b	1.12 ^e	1.41 ^g	1.17
Ge (A4)	0.00	0.85	0.83 ^b	0.66 ^f	0.95 ^g	0.74
LiF (B1)	8.94	12.94		13.27 ^e	15.9 ^g	14.20
LiCl (B1)	6.06	8.64				9.4
MgO (B1)	4.70	7.17	6.67 ^b	7.25 ^e	9.16 ^g	7.83
ScN (B1)	-0.14	0.90		0.95 ^f	1.4 ^h	~0.9
MnO (B1)	0.76	2.95	2.8 ^c		3.5 ⁱ	3.9 ± 0.4
FeO (B1)	-0.35	1.82	2.2 ^c			2.4
NiO (B1)	0.42	4.16	4.2 ^c	1.1 ^f	4.8 ⁱ	4.0, 4.3
SiC (B3)	1.35	2.28	2.40 ^b	2.27 ^e	2.88 ^g	2.40
BN (B3)	4.39	5.85	5.99 ^b	6.10 ^e	7.14 ^g	~6.25
GaN (B3)	1.63	2.81	3.14 ^b	2.80 ^e	3.82 ^g	3.20
GaAs (B3)	0.30	1.64	1.12 ^b	1.30 ^e	1.85 ^g	1.52
AlP (B3)	1.46	2.32	2.51 ^b	2.44 ^e	2.90 ^g	2.45
ZnS (B3)	1.84	3.66	3.49 ^b	3.29 ^e	4.15 ^g	3.91
CdS (B3)	0.86	2.66	2.25 ^b	2.06 ^e	2.87 ^g	2.42
AlN (B4)	4.17	5.55	5.81 ^b	5.83 ^f		6.28
ZnO (B4)	0.75	2.68	2.49 ^d	2.51 ^f	3.8 ^g	3.44