

Density-functional theory using finite uniform electron gases

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23rd March 2017

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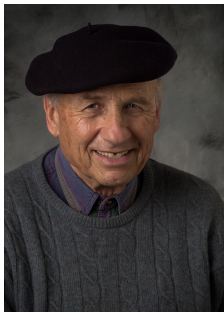
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(Received 18 December 2016; accepted 27 February 2017; published online 21 March 2017)

We show how one can construct a simple exchange functional by extending the well-known local-density approximation (LDA) to finite uniform electron gases. This new generalized local-density approximation functional uses only two quantities: the electron density ρ and the curvature of the Fermi hole α . This alternative “rung 2” functional can be easily coupled with generalized-gradient approximation (GGA) functionals to form a new family of “rung 3” *meta*-GGA (MGGA) functionals that we have named factorizable MGGAs. Comparisons are made with various LDA, GGA, and MGGA functionals for atoms and molecules. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4978409>]

Idea behind density-functional theory (DFT)

Walter Kohn (1923-2016)



Hohenberg-Kohn theorem

The ground state electronic energy is completely determined by the electron density ρ

There is a one-to-one correspondence between ρ and the energy E

Hohenberg-Kohn theorem shows that you can use the electron density $\rho(\mathbf{r})$ instead of the wave function $\Psi(\mathbf{r}_1, \dots, \mathbf{r}_n)$

The functional connecting ρ and E is unknown....

The goal is to design functionals connecting the electron density with the energy...

Hohenberg & Kohn, Phys Rev 136 (1964) B864

Kohn-Sham (KS) theory

In the **KS formalism**, one writes the total energy as

$$E_{\text{KS}}[\rho] = T_{\text{S}}[\rho] + E_{\text{ne}}[\rho] + J[\rho] + E_{\text{xc}}[\rho]$$

where

$$\rho(\mathbf{r}) = \sum_i^{\text{occ}} |\psi_i(\mathbf{r})|^2 \quad = \quad \text{electronic density}$$

$$T_{\text{S}}[\rho] = \sum_i^{\text{occ}} \langle \psi_i | -\frac{\nabla^2}{2} | \psi_i \rangle \quad = \quad \text{non-interacting kinetic energy}$$

$$E_{\text{ne}}[\rho] = - \sum_A^{\text{nuc}} \int \frac{Z_A \rho(\mathbf{r})}{|\mathbf{R}_A - \mathbf{r}|} d\mathbf{r} \quad = \quad \text{electron-nucleus attraction}$$

$$J[\rho] = \frac{1}{2} \iint \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 \quad = \quad \text{classical Coulomb repulsion}$$

$$E_{\text{xc}}[\rho] = (T[\rho] - T_{\text{S}}[\rho]) + (E_{\text{ee}}[\rho] - J[\rho]) \quad = \quad \text{exchange-correlation energy}$$

Kohn & Sham Phys Rev 140 (1965) A1133

Density, Exchange and Correlation

The **exchange-correlation** energy is defined as

$$\begin{aligned}
 E_{xc}[\rho, \zeta] &= E_x[\rho, \zeta] + E_c[\rho, \zeta] \\
 &= \int \rho(\mathbf{r}) e_x[\rho(\mathbf{r}), \zeta] d\mathbf{r} + \int \rho(\mathbf{r}) e_c[\rho(\mathbf{r}), \zeta] d\mathbf{r}
 \end{aligned}$$

The **total density** is

$$\rho = \rho_\alpha + \rho_\beta$$

The **spin polarization** is

$$\zeta = \frac{\rho_\alpha - \rho_\beta}{\rho} = \frac{n_\alpha - n_\beta}{n}$$

The **exchange energy** is given by

$$E_x[\rho, \zeta] = E_{x,\alpha}[\rho_\alpha] + E_{x,\beta}[\rho_\beta]$$

The **correlation energy** is given by

$$E_c[\rho, \zeta] = E_{c,\alpha\alpha}[\rho_\alpha] + E_{c,\beta\beta}[\rho_\beta] + E_{c,\alpha\beta}[\rho_\alpha, \rho_\beta]$$

Density-functional approximations for exchange

From a **practical point of view**, the exchange energy is given by

$$E_{x,\sigma} = \int e_x(\rho_\sigma, \nabla\rho_\sigma, \tau_\sigma, \dots) \rho_\sigma d\mathbf{r}$$

$$\approx \sum_i w_i e_x[\rho_\sigma(\mathbf{r}_i), \nabla\rho_\sigma(\mathbf{r}_i), \tau_\sigma(\mathbf{r}_i), \dots] \rho_\sigma(\mathbf{r}_i)$$

where

- $\rho(\mathbf{r}) = \sum_i^{\text{occ}} |\psi_i(\mathbf{r})|^2$ is the **one-electron density**
- $\nabla\rho(\mathbf{r})$ is the **gradient of the density**
- $\tau(\mathbf{r}) = \sum_i^{\text{occ}} |\nabla\psi_i(\mathbf{r})|^2$ is the **kinetic energy density**

Local density approximation (LDA) exchange

The LDA exchange energy (Dirac formula or D30) is

$$E_x^{\text{LDA}} = \int \rho(\mathbf{r}) e_x^{\text{LDA}}(\rho) d\mathbf{r} = C_x \int \rho(\mathbf{r})^{4/3} d\mathbf{r}$$

$$e_x^{\text{LDA}}(\rho) = C_x \rho^{1/3}$$

where

$$C_x = -\frac{3}{2} \left(\frac{3}{4\pi} \right)^{1/3} = -0.930526 \dots$$

has been obtained based on the infinite uniform electron gas (IUEG) or jellium

Dirac, Proc Cam Phil Soc 26 (1930) 376

Loos & Gill, WIREs Comput Mol Sci 6 (2016) 410

How good is LDA?

Table: Reduced (i.e. per electron) mean error (ME) and mean absolute error (MAE) (in kcal/mol) of the error (compared to UHF) in the exchange energy

		hydrogen-like ions		helium-like ions		neutral atoms	
		ME	MAE	ME	MAE	ME	MAE
LDA	D30	153.5	69.7	150.6	69.5	70.3	9.1

Computational details

- Implemented in a development version of Q-Chem4.4 (will be available in Q-Chem5!!)
- Self-consistent KS calculations
- Dunning's aug-cc-pVTZ basis set
- Quadrature grid: 100 radial points (Euler-MacLaurin) and 590 angular points (Lebedev)

Rule of thumb: LDA underestimates the exchange by 10%

Generalized gradient approximation (GGA) exchange

Sham has shown that, for an “almost” uniform electron gas,

$$E_x^{\text{GGA}} \approx E_x^{\text{LDA}} - \frac{5}{(36\pi)^{5/3}} \int \rho(\mathbf{r})^{4/3} x^2 d\mathbf{r}$$

where

$$x = \frac{|\nabla\rho|}{\rho^{4/3}} \text{ is the reduced gradient.}$$

The GGA exchange energy is

$$E_x^{\text{GGA}} = \int F_x^{\text{GGA}}(x) e_x^{\text{LDA}}(\rho) \rho(\mathbf{r}) d\mathbf{r} = C_x \int F_x^{\text{GGA}}(x) \rho(\mathbf{r})^{4/3} d\mathbf{r}$$

$F_x^{\text{GGA}}(x)$ is usually called the GGA enhancement factor and “smart” GGAs have

$$\lim_{x \rightarrow 0} F_x^{\text{GGA}}(x) = 1$$

Sham, in Computational Methods in Band Theory, edited by P. M. Marcus, J. F. Janak, and A. R. Williams (Plenum, New York, 1971)

Fashionable GGAs

B88 [PRA 38 (1988) 3098]

$$F_x^{\text{B88}}(x) = 1 - \frac{0.0042 x^2}{1 + 0.0252 x \sinh^{-1} x}$$

PW91 [PRB 46 (1992) 6671]

$$F_x^{\text{PW91}}(x) = \text{ugly}$$

G96 [Mol Phys 89 (1996) 433]

$$F_x^{\text{G96}}(x) = 1 - \frac{x^{3/2}}{137}$$

PBE [PRL 77 (1996) 3865]

$$F_x^{\text{PBE}}(x) = 1.804 - \frac{0.804}{1 + 0.0071x^2}$$

Are GGAs better than LDA?

Table: Reduced (i.e. per electron) mean error (ME) and mean absolute error (MAE) (in kcal/mol) of the error (compared to UHF) in the exchange energy

		hydrogen-like ions		helium-like ions		neutral atoms	
		ME	MAE	ME	MAE	ME	MAE
LDA	D30	153.5	69.7	150.6	69.5	70.3	9.1
GGA	B88	9.5	4.3	9.3	4.7	2.8	0.5
	G96	4.4	2.0	4.4	2.2	2.1	0.5
	PW91	19.4	8.8	19.1	9.3	4.5	0.8
	PBE	22.6	10.3	22.3	10.7	7.4	0.6

Rule of thumb: GGAs are really good...

Meta-generalized gradient approximation (MGGA) exchange

Because it wasn't enough, people have introduced τ in functionals

$$e_x^{\text{MGGA}}(\rho, x, \tau) = e_x^{\text{LDA}}(\rho) F_x^{\text{MGGA}}(x, \tau)$$

or

$$e_x^{\text{MGGA}}(\rho, x, \alpha) = e_x^{\text{LDA}}(\rho) F_x^{\text{MGGA}}(x, \alpha)$$

where $0 \leq \alpha < \infty$ is the **curvature of the Fermi hole***:

$$\alpha = \frac{\tau - \tau_W}{\tau_{\text{UEG}}} = \frac{\tau}{\tau_{\text{UEG}}} - \frac{x^2}{4C_F} \quad C_F = \frac{3}{5}(6\pi^2)^{2/3}$$

$$\tau_W = \frac{|\nabla\rho|^2}{4\rho} \quad \text{is the von Weizsäcker kinetic energy density}$$

$$\tau_{\text{UEG}} = C_F \rho^{5/3} \quad \text{is the kinetic energy density of the IUEG}$$

Well thought-out MGGA's ensure that

$$\lim_{x \rightarrow 0} \lim_{\alpha \rightarrow 1} F_x^{\text{MGGA}}(x, \alpha) = 1$$

***Remember ELF!?** $\text{ELF} = (1 + \alpha^2)^{-1}$

Fashionable MGGAs

M06-L [JCP 125 (2006) 194101]

$$F_x^{\text{M06-L}}(x) = \text{awful (17 parameters)}$$

TPSS [PRL 91 (2003) 146401]

$$F_x^{\text{TPSS}}(x) = \text{not pretty}$$

mBEEF [JCP 140 (2014) 144107]

$$F_x^{\text{mBEEF}}(x) = \text{very ugly (64 parameters)*}$$

SCAN [PRL 115 (2015) 036402]

$$F_x^{\text{SCAN}}(x) = \text{long (constraint with "model" systems)}$$

*spits you out a Bayesian error estimate for the same price

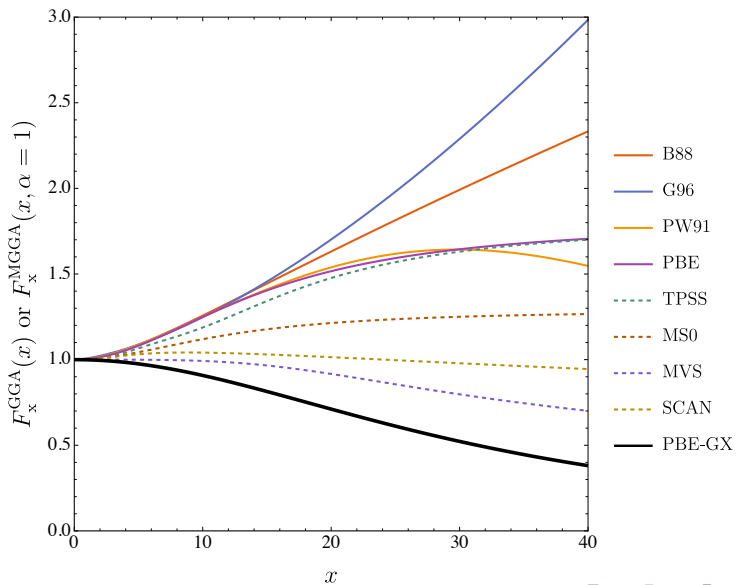
Are MGGAs better than GGAs?

Table: Reduced (i.e. per electron) mean error (ME) and mean absolute error (MAE) (in kcal/mol) of the error (compared to UHF) in the exchange energy

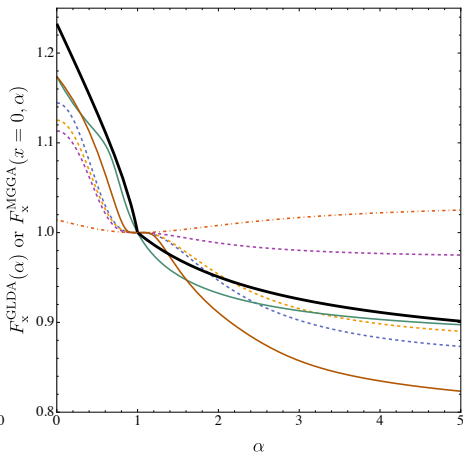
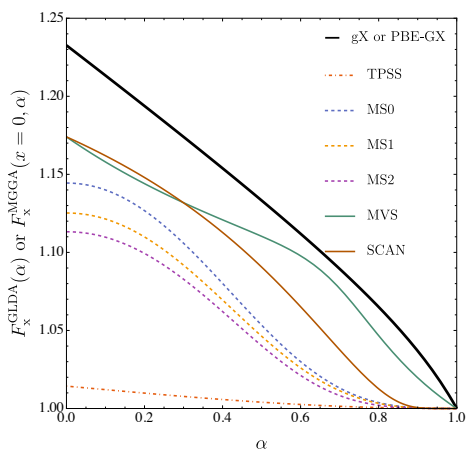
		hydrogen-like ions		helium-like ions		neutral atoms	
		ME	MAE	ME	MAE	ME	MAE
LDA	D30	153.5	69.7	150.6	69.5	70.3	9.1
GGA	B88	9.5	4.3	9.3	4.7	2.8	0.5
	G96	4.4	2.0	4.4	2.2	2.1	0.5
	PW91	19.4	8.8	19.1	9.3	4.5	0.8
	PBE	22.6	10.3	22.3	10.7	7.4	0.6
MGGA	M06-L	44.4	88.8	12.0	24.0	4.2	2.9
	TPSS	0.0	0.0	0.7	0.4	0.7	1.1
	revTPSS	0.0	0.0	0.5	0.3	3.5	2.5
	MS0	0.0	0.0	0.4	0.2	1.3	2.4
	MVS	0.0	0.0	0.3	0.2	2.7	0.9
	SCAN	0.0	0.0	0.3	0.2	1.2	1.6

Rule of thumb: MGGAs are slightly better than GGAs...

GGAs vs MGGAs: round 1

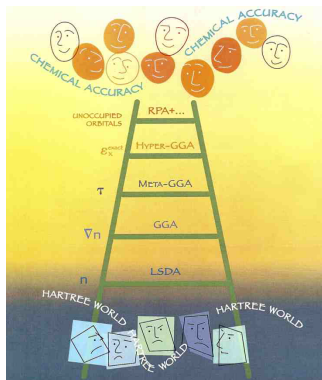


GGAs vs MGGAs: round 2



Jacob's ladder of DFT

Level	Name	Variables	Examples
1	LDA	ρ	VWN,PZ81, X_{α}
2	GGA	$\rho, \nabla\rho$	BLYP,OLYP,PW86,PW91,PBE,PBEsol
3	meta-GGA	$\rho, \nabla\rho, \nabla^2\rho, \tau$	BR,B95,TPSS,SCAN
4	hyper-GGA	+ HF exchange	BH&H, B3LYP,B3PW91,O3LYP,PBE0
5	generalized-RPA	+ HF virtual orbitals	OEP2



The good, the bad and the ugly...

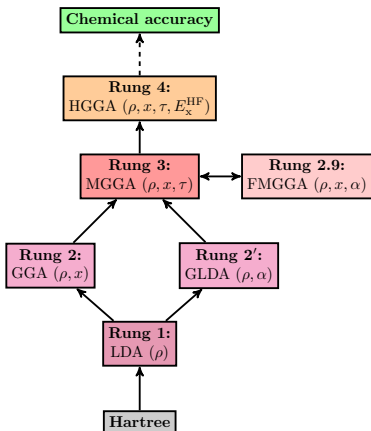
DFT successes

- Sometimes predicts **reaction energetics** with amazing accuracy
- Often predicts **molecular structures** of high quality
- Often predicts **vibrational frequencies** that agree well with experiment
- **Vertical transition energies** to low-lying excited states very good
- and many others...

DFT failures

- H_2^+ , He_2^+ and other odd-electron bonds: **self-interaction error**
- Relative alkane energies, large extended π systems, Diels-Alder reaction, etc.
- **Weak interactions due to dispersion forces** (van der Waals)
- **Charge-transfer excited**, **core-excited** and **Rydberg** states
- Strongly-correlated systems
- and many others...

Jacob's ladder of DFT revisited



Loos, JCP 146 (2017) 114108

Rung 2': Generalized LDAs (GLDA)

$$e_x^{\text{GLDA}}(\rho, \alpha) = e_x^{\text{LDA}}(\rho) F_x^{\text{GLDA}}(\alpha)$$

with

$$\lim_{\alpha \rightarrow 1} F_x^{\text{GLDA}}(\alpha) = 1$$

Rung 2.9: Factorizable MGGAs (FMGGa)

$$e_x^{\text{FMGGa}}(\rho, x, \alpha) = e_x^{\text{LDA}}(\rho) F_x^{\text{FMGGa}}(x, \alpha)$$

$$F_x^{\text{FMGGa}}(x, \alpha) = F_x^{\text{GGA}}(x) F_x^{\text{GLDA}}(\alpha)$$

with

$$\lim_{x \rightarrow 0} F_x^{\text{FMGGa}}(x, \alpha) = F_x^{\text{GLDA}}(\alpha)$$

$$\lim_{\alpha \rightarrow 1} F_x^{\text{FMGGa}}(x, \alpha) = F_x^{\text{GGA}}(x)$$

How to create FUEGs? [Loos & Gill, JCP 135 (2011) 214111]

- We confine n electrons on the surface of a 3-sphere (or a glome)

$$n = \frac{1}{3}(L+1)(L+3/2)(L+2) \quad \text{with } L \in \mathbb{N}$$

- For magic numbers of electrons (full shell), the density is uniform over the sphere

$$\rho = \frac{n}{V} = \frac{(L+2)(L+3/2)(L+1)}{6\pi^2 R^3}$$

- The curvature of the Fermi hole is

$$\alpha = \frac{L(L+3)}{[(L+1)(L+3/2)(L+2)]^{2/3}} \quad \text{which yields}$$

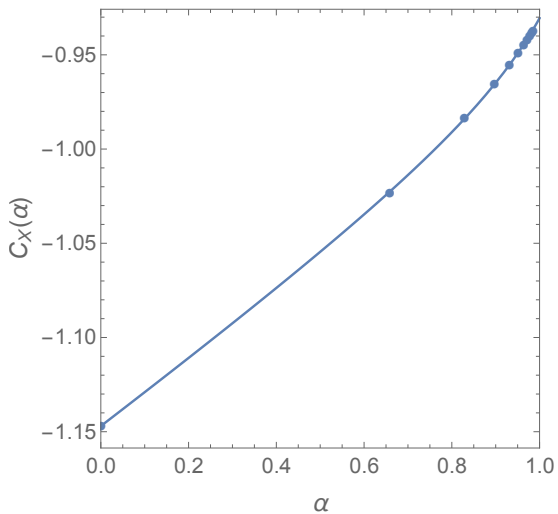
$$\lim_{n \rightarrow 1} \alpha = 0$$

$$\lim_{n \rightarrow \infty} \alpha = 1$$

- The exchange energy is

$$E_x(L) = C_x(L) \int \rho^{4/3} dr$$

$$C_x(L) = C_x^{\text{LDA}} \frac{\frac{1}{2}(L+\frac{5}{4})(L+\frac{7}{4}) \left[\frac{1}{2} H_{2L+\frac{5}{2}} + \ln 2 \right] + (L+\frac{3}{2})^2 (L^2 + 3L + \frac{13}{8})}{[(L+1)(L+\frac{3}{2})(L+2)]^{4/3}}$$

$C_x(\alpha)$ in FUEGs for $0 \leq \alpha \leq 1$ 

How to use FUEGs in DFT?

The **GX functional** (which is a **GLDA**) is defined as

$$F_x^{\text{GX}}(\alpha) = \begin{cases} F_x^{\text{GX}}(\alpha), & 0 \leq \alpha \leq 1 \\ 1 + (1 - \alpha_\infty) \frac{1-\alpha}{1+\alpha}, & \alpha > 1 \end{cases}$$

with

$$F_x^{\text{GX}}(\alpha) = \frac{C_x^{\text{GLDA}}(0)}{C_x^{\text{GLDA}}(1)} + \alpha \frac{c_0 + c_1 \alpha}{1 + (c_0 + c_1 - 1)\alpha} \left[1 - \frac{C_x^{\text{GLDA}}(0)}{C_x^{\text{GLDA}}(1)} \right]$$

where $c_0 = +0.827411$, $c_1 = -0.643560$ are fitted on the exchange energy of FUEGs.

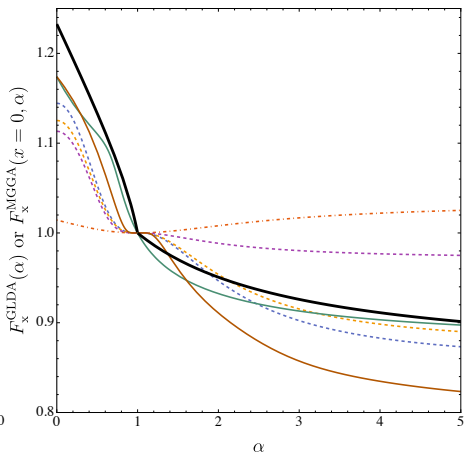
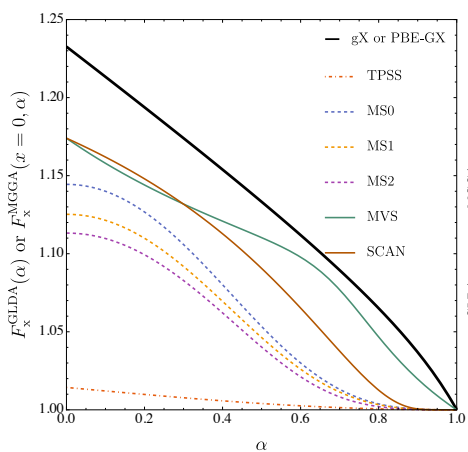
- For $\alpha = 1$, we recover the **LDA**:

$$C_x^{\text{GLDA}}(1) = C_x^{\text{LDA}} = -\frac{3}{2} \left(\frac{3}{4\pi} \right)^{1/3}$$

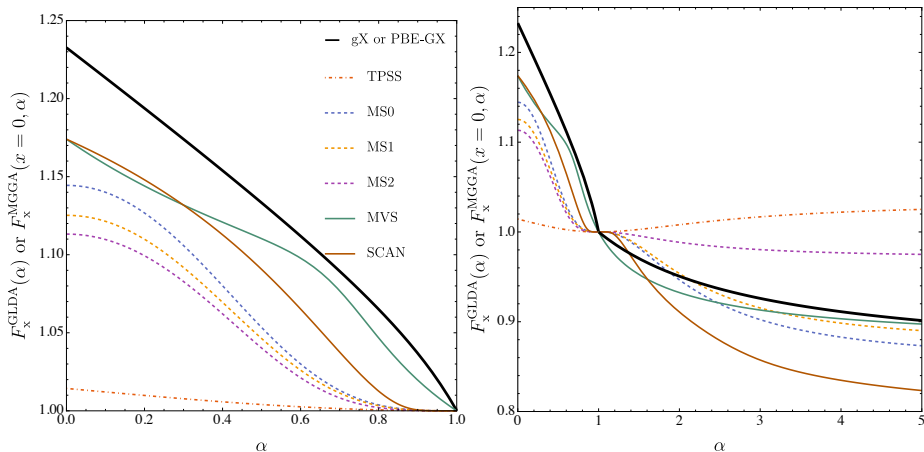
- For $\alpha = 0$, we get:

$$C_x^{\text{GLDA}}(0) = -\frac{4}{3} \left(\frac{2}{\pi} \right)^{1/3}$$

Plots of the GX functional



Plots of the GX functional



Problem of GLDAs: cannot discriminate between homogeneous and inhomogeneous one-electron systems ($\alpha = 0$)

The PBE-GX functional

The **PBE-GX functional** (which is a **FMGGA**) is defined as

$$F_x^{\text{PBE-GX}}(x, \alpha) = F_x^{\text{PBE}}(x) F_x^{\text{GX}}(\alpha)$$

where

$$F_x^{\text{PBE}}(x) = \frac{1}{1 + \mu x^2}$$

is a PBE-like GGA enhancement factor

How do we set the “free” parameters?

- $\mu = +0.001015549$ to get the **exact exchange energy** of the hydrogen atom
- $\alpha_\infty = +0.852$ to obtain **good exchange energies** for neutral atoms

Unlike GX, PBE-GX is accurate for both the (inhomogeneous) hydrogen-like ions and the (homogeneous) one-electron FUEGs

Are FMGGAs as good as MGGAs?

Table: Reduced (i.e. per electron) mean error (ME) and mean absolute error (MAE) (in kcal/mol) of the error (compared to UHF) in the exchange energy

		hydrogen-like ions		helium-like ions		neutral atoms	
		ME	MAE	ME	MAE	ME	MAE
LDA	D30	153.5	69.7	150.6	69.5	70.3	9.1
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	MS0	0.0	0.0	0.4	0.2	1.3	2.4
	SCAN	0.0	0.0	0.3	0.2	1.2	1.6
FMGGA	MVS	0.0	0.0	0.3	0.2	2.7	0.9
	PBE-GX	0.0	0.0	0.7	0.4	1.0	1.1

Rule of thumb: FMGGAs are as good as MGGAs...

MGGAs for molecules

Table: Reduced (i.e. per electron) mean error (ME) and mean absolute error (MAE) (in kcal/mol) of the error (compared to the experimental value) in the atomization energy of diatomic molecules at experimental geometry.

	functional		diatomics	
	exchange	correlation	ME	MAE
LDA	D30	VWN5	1.8	3.7
GGA	B88	LYP	0.6	1.2
	PBE	PBE	0.7	1.2
MGGA	M06-L	M06-L	0.4	0.7
	TPSS	TPSS	0.6	1.1
	revTPSS	revTPSS	0.6	1.2
	MVS	regTPSS	0.5	0.9
	SCAN	SCAN	0.4	0.7
	PBE-GX	PBE	0.6	1.2
	PBE-GX	regTPSS	0.6	1.1
	PBE-GX	LYP	0.6	1.1
	PBE-GX	TPSS	0.7	1.3
	PBE-GX	revTPSS	0.8	1.5
PBE-GX	SCAN	0.6	1.0	

What's the purpose of this project?

My goal is to find new paradigms to guide each part of the functional

GLDA part

- What's the exact functional form of F_x^{GLDA} for $\alpha > 1$
- How does F_x^{GLDA} decay for large α ?
- What is the limiting value for large α ?

$$\lim_{\alpha \rightarrow \infty} F_x^{\text{GLDA}} = \text{I have no idea}$$

- Is it possible to design a paradigm to parametrize F_x^{GLDA} for $\alpha > 1$?

GGA part

- Shall F_x^{GGA} decay to zero? (the functional overbinds when coupled with conventional correlation functional)
- What should be the decay of F_x^{GGA} for large x ?
- Is it possible to design a paradigm to parametrize F_x^{GGA} ?

Students, Postdocs, Collaborators and Funding

- **Honours students:** Anneke Knol & Fergus Rogers
 - **PhD students:** Caleb Ball & Giuseppe Barca
 - **Postdocs:** Davids Agboola, Jia Deng & Marat Sibaeov
 - **Collaborator:** Peter Gill
-
- Research School of Chemistry & Australian National University
 - Australian Research Council:
Discovery Early Career Researcher Award 2013 & Discovery Project 2014



Australian Government

Australian Research Council