Density-functional theory using finite uniform electron gases

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The local density approximation (LDA)

- ☺ Treat a molecular density as a collection of tiny bits of uniform electron gases (UEGs)
- ☺ The LDA is an *ab initio* model with no adjustable parameters
- ☺ This is an attractive approach to molecular electronic structure
- ☺ It also forms a foundation for more accurate approximations
- ☹ Not very accurate for molecules:
  - underestimate the exchange by roughly 10%
  - overestimate the correlation by roughly 100%

LDA exchange

The LDA exchange energy (Dirac formula) is

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

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

where

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

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

Dirac, Proc Cam Phil Soc 26 (1930) 376

The uniform electron gas in Flatland

The infinite uniform electron gas (IUEG)

- ☺ One of the most popular models in condensed matter physics
- ☺ Characterized by one parameter: Seitz radius $r_s \propto \rho^{-1/D}$
- ☹ Clearly suitable for metals. Less clearly suitable for molecules

The "jellium" recipe

1. Put n electrons into a D-dimensional cube of volume V
2. Add a background of positive "jelly" to achieve neutrality
3. Increase both n and V so that $\rho = n/V$ remains constant
4. In the limit as $n \to \infty$ and $V \to \infty$, one obtains an infinite UEG

Parr & Yang, *DFT for atoms and molecules* (1989)
Loos & Gill, WIREs Comput Mol Sci 6 (2016) 410

The uniform electron gas in Sphereland

Finite UEGs (FUEGs)

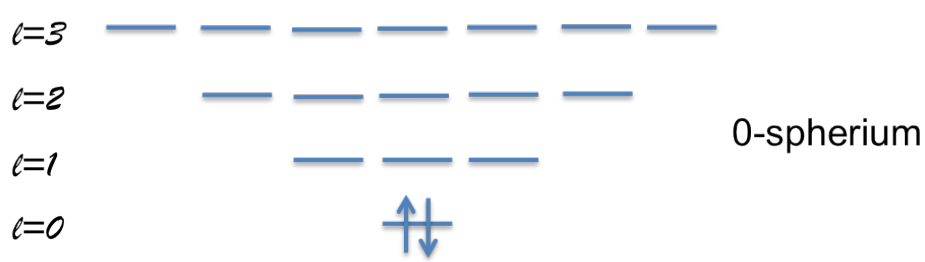
- One can also construct UEGs using a finite number of electrons
- The recipe:
  1. Put n electrons onto a D-dimensional sphere
  2. Add a background positive charge to achieve neutrality
  3. That's all

☺ For $n \to \infty$, we get the infinite UEG!!

Loos & Gill, JCP 135 (2011) 214111
Gill & Loos, TCA 131 (2012) 1069

Uniform electron gases in Sphereland

We fill each (hyper)spherical harmonic $Y_{\ell m(n)}$ up to $\ell = L$ with one spin-up and one spin-down electron



L-Spherium

$$\boxed{\sum_{m=-\ell}^{\ell} |Y_{\ell m}(\theta,\phi)|^2 = \frac{2\ell+1}{4\pi}}$$

$$\rho = \frac{2(L+1)^2}{4\pi R^2} = \frac{1}{\pi r_s^2}$$

L-Glomium

$$\boxed{\sum_{m=0}^{\ell} \sum_{n=-m}^{m} |Y_{\ell mn}(\chi,\theta,\phi)|^2 = \frac{(\ell+1)^2}{2\pi^2}}$$

$$\rho = \frac{2(L+1)(L+2)(2L+3)/3}{4\pi^2 R^3} = \frac{3}{4\pi r_s^3}$$

Loos & Gill, JCP 135 (2011) 214111

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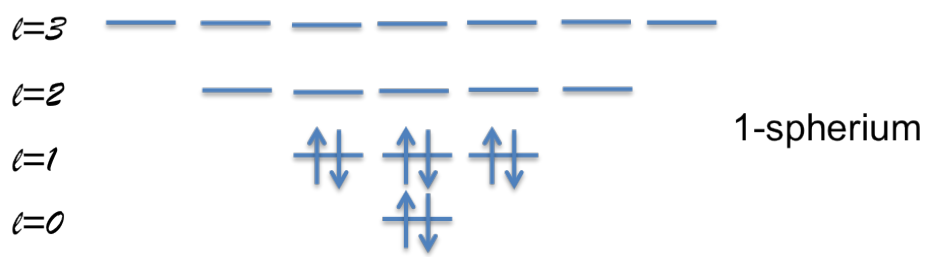

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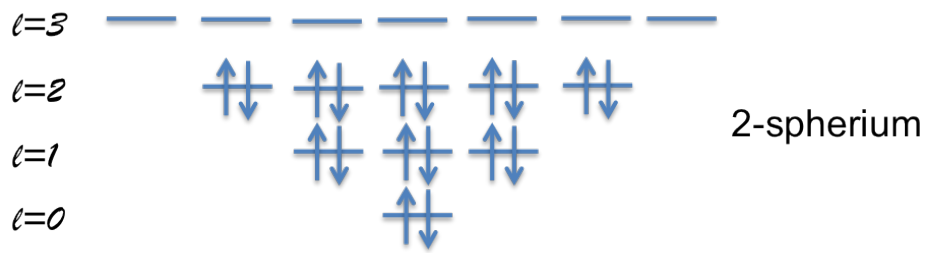

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Loos & Gill, JCP 135 (2011) 214111

Non-uniqueness of the uniform electron gas

Are jellium-based functionals accurate for finite UEGs?

		Exact			Jellium-based Kohn-Sham DFT						Error
	$2R$	E_T	E_{ee}	E	T_S	E_V	E_J	$-E_X$	$-E_c^{jell}$	E_{KS}	$E_{KS} - E$
0-sph.	$\sqrt{3}$	0.0520	0.4480	1/2	0	0	1.1547	0.4901	0.1028	0.562	0.062
	$\sqrt{28}$	0.0186	0.1243	1/7	0	0	0.3780	0.1604	0.0593	0.158	0.015
0-glo.	$\sqrt{10}$	0.0142	0.2358	1/4	0	0	0.5368	0.2178	0.0437	0.275	0.025
	$\sqrt{66}$	0.0078	0.0831	1/11	0	0	0.2090	0.0848	0.0270	0.097	0.006

Why? We are missing some two-electron information

Loos & Gill, PRL 103 (2009) 123008
Gill & Loos, TCA 131 (2012) 1069

Curvature of the Fermi hole

The curvature of the Fermi hole* is ($0 \leq \alpha < \infty$):

$$\boxed{\alpha = \frac{\tau - \tau_W}{\tau_{IUEG}} = \frac{\tau}{\tau_{IUEG}} - \frac{x^2}{4 C_F}} \qquad C_F = \frac{3}{5}(6\pi^2)^{2/3}$$

$\tau = \sum_i^{occ} |\nabla \psi_i|^2$ is the kinetic energy density

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

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

Becke & Edgecombe, JCP 92 (1990) 5397
Loos, Ball & Gill, JCP 140 (2014) 18A524

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

High-density ($r_s \to 0$) limit: *L*-spherium vs 2D jellium

$$\boxed{e_{\text{jellium}}^{\text{2D}}(r_s) = \frac{\varepsilon_{-2}}{r_s^2} + \frac{\varepsilon_{-1}}{r_s} + (\varepsilon_{0,\text{J}} + \varepsilon_{0,\text{K}}) + \lambda_1 r_s \ln r_s + O(r_s)}$$

$\varepsilon_{-2} =$

$\varepsilon_{-1} =$

$\varepsilon_{0,\text{J}} =$

$\varepsilon_{0,\text{K}} =$

$\lambda_1 =$

Loos & Gill, PRB 83 (2011) 233102; ibid 84 (2011) 033103

High-density ($r_s \to 0$) limit: L-spherium vs 2D jellium

$$\boxed{e_{\text{jellium}}^{\text{2D}}(r_s) = \frac{\varepsilon_{-2}}{r_s^2} + \frac{\varepsilon_{-1}}{r_s} + (\varepsilon_{0,\text{J}} + \varepsilon_{0,\text{K}}) + \lambda_1 r_s \ln r_s + O(r_s)}$$

$$\varepsilon_{-2} = + \frac{L(L+2)}{2(L+1)^2}$$

$$\varepsilon_{-1} = - \frac{1}{\sqrt{2}} F \left[\begin{matrix} -L, & L+2, & \frac{1}{2}, & -\frac{1}{2} \\ -L-\frac{1}{2}, & L+\frac{3}{2}, & 2 & \end{matrix} \right]$$

$$\varepsilon_{0,\text{J}} = - \frac{2}{n} \sum_{ij}^{\text{occ}} \sum_{ab}^{\text{virt}} \frac{\langle ij|ab\rangle^2}{\kappa_a + \kappa_b - \kappa_i - \kappa_j}$$

$$\varepsilon_{0,\text{K}} = \frac{1}{n} \sum_{ij}^{\text{occ}} \sum_{ab}^{\text{virt}} \frac{\langle ij|ab\rangle\langle ba|ij\rangle}{\kappa_a + \kappa_b - \kappa_i - \kappa_j}$$

$$\lambda_1 = \text{(resummation)}$$

Loos & Gill, PRB 83 (2011) 233102; ibid 84 (2011) 033103

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$$\boxed{e_{\text{jellium}}^{\text{2D}}(r_s) = \frac{\varepsilon_{-2}}{r_s^2} + \frac{\varepsilon_{-1}}{r_s} + (\varepsilon_{0,\text{J}} + \varepsilon_{0,\text{K}}) + \lambda_1 r_s \ln r_s + O(r_s)}$$

$$\varepsilon_{-2} = + \frac{L(L+2)}{2(L+1)^2} \qquad \xrightarrow[L\to\infty]{} + \frac{1}{2}$$

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$$\varepsilon_{0,\text{K}} = \frac{1}{n} \sum_{ij}^{\text{occ}} \sum_{ab}^{\text{virt}} \frac{\langle ij|ab\rangle\langle ba|ij\rangle}{\kappa_a + \kappa_b - \kappa_i - \kappa_j} \qquad \xrightarrow[L\to\infty]{} G - \frac{8}{\pi^2}\beta(4)$$

$$\lambda_1 = (\text{resummation}) \qquad \xrightarrow[L\to\infty]{} - \sqrt{2}\left(\frac{10}{3\pi} - 1\right)$$

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$$\boxed{e_{\text{jellium}}^{\text{2D}}(r_s) = \frac{\varepsilon_{-2}}{r_s^2} + \frac{\varepsilon_{-1}}{r_s} + (\varepsilon_{0,\text{J}} + \varepsilon_{0,\text{K}}) + \lambda_1 r_s \ln r_s + O(r_s)}$$

$$\varepsilon_{-2} = + \frac{L(L+2)}{2(L+1)^2} \xrightarrow[L\to\infty]{} + \frac{1}{2} \quad \checkmark$$

$$\varepsilon_{-1} = - \frac{1}{\sqrt{2}} F \left[\begin{matrix} -L, & L+2, & \frac{1}{2}, & -\frac{1}{2} \\ -L-\frac{1}{2}, & L+\frac{3}{2}, & 2 & \end{matrix} \right] \xrightarrow[L\to\infty]{} - \frac{4\sqrt{2}}{3\pi} \quad \checkmark$$

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Loos & Gill, PRB 83 (2011) 233102; ibid 84 (2011) 033103

High-density ($r_s \to 0$) limit: *L*-glomium vs 3D jellium

$$\boxed{e_{\text{jellium}}^{\text{3D}}(r_s) = \frac{\varepsilon_{-2}}{r_s^2} + \frac{\varepsilon_{-1}}{r_s} + \lambda_0 \ln r_s + (\varepsilon_{0,\text{J}} + \varepsilon_{0,\text{K}}) + O(r_s \ln r_s)}$$

ε_{-2}

ε_{-1}

λ_0

$\varepsilon_{0,\text{J}}$

$\varepsilon_{0,\text{K}}$

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$$\varepsilon_{-2} \xrightarrow[L\to\infty]{} +\frac{3}{10}\left(\frac{9\pi}{4}\right)^{2/3}$$

$$\varepsilon_{-1} \xrightarrow[L\to\infty]{} -\frac{3}{4\pi}\left(\frac{9\pi}{4}\right)^{1/3}$$

$$\lambda_0 \xrightarrow[L\to\infty]{\text{resum.}} \frac{1-\ln 2}{\pi^2}$$

$$\varepsilon_{0,\text{J}} \xrightarrow[L\to\infty]{\text{resum.}} -0.071099$$

$$\varepsilon_{0,\text{K}} \xrightarrow[L\to\infty]{} \frac{\ln 2}{6} - \frac{3}{4\pi^2}\zeta(3)$$

High-density ($r_s \to 0$) limit: *L*-glomium vs 3D jellium

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$$\varepsilon_{0,\text{K}} \xrightarrow[L\to\infty]{} \frac{\ln 2}{6} - \frac{3}{4\pi^2}\zeta(3) \quad \checkmark$$

Our conjecture

$$e(r_s) = \frac{\varepsilon_{-2}}{r_s^2} + \frac{\varepsilon_{-1}}{r_s} + \sum_{\ell=0}^{\infty} [\lambda_\ell \ln r_s + \varepsilon_\ell] r_s^\ell$$

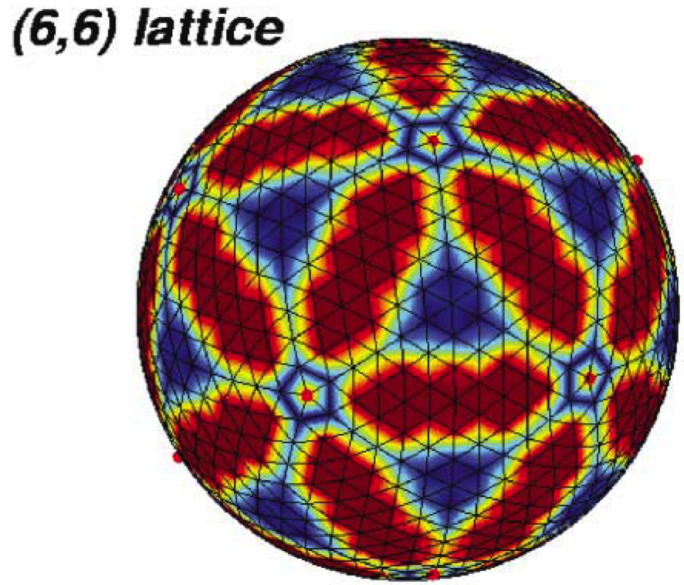
"[...] the high-density expansions are identical to all order"

$\Leftrightarrow$ "short-sightedness" of electronic matter
Kohn PRL 76 (1996) 3168

Loos & Gill, JCP 135 (2011) 214111

Low-density ($r_s \to \infty$) limit of L-spherium

$$\boxed{e_{\text{jellium}}^{\text{2D}}(r_s) = \frac{\eta_1}{r_s} + \frac{\eta_{3/2}}{r_s^{3/2}} + \frac{\eta_2}{r_s^2} + \ldots}$$



Thomson problem

"determine the minimum energy configuration of n electrons on the surface of a sphere that repel each other with a force given by Coulomb's law"

$$e_{\text{sph.}}(r_s) \sim -\frac{1.10494}{r_s} \quad \text{(large-}n\text{ limit)}$$

Note: identical to the Wigner crystal phase of 2D jellium (hexagonal lattice)

Bowick et al. PRL 89 (2002) 185502
Agboola, Knol, Gill & Loos, JCP 143 (2015) 084114

DFT with finite UEGs

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Exchange functionals based on finite uniform electron gases

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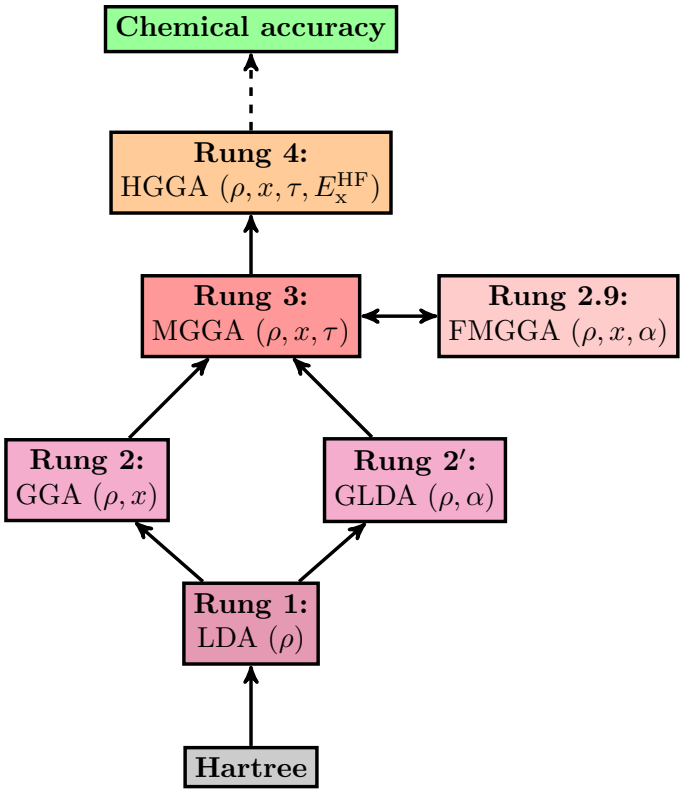
We show how one can construct a simple exchange functional by extending the well-know local-density approximation (LDA) to finite uniform electron gases. This new generalized local-density approximation functional uses only two quantities: the electron density ρ and the curvature of the Fermi hole α. 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]

Jacob's ladder of DFT revisited



Loos, JCP 146 (2017) 114108

Rung 2′: Generalized LDAs (GLDA)

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

with

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

Rung 2.9: Factorizable MGGAs (FMGGA)

$$\boxed{e_x^{FMGGA}(\rho, x, \alpha) = e_x^{LDA}(\rho) F_x^{FMGGA}(x, \alpha)}$$

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

with

$$\lim_{x \to 0} F_x^{FMGGA}(x, \alpha) = F_x^{GLDA}(\alpha)$$

$$\lim_{\alpha \to 1} F_x^{FMGGA}(x, \alpha) = F_x^{GGA}(x)$$

How to create finite UEGs (FUEGs)?

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

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

$$\lim_{n\to 1} \alpha = 0 \qquad \lim_{n\to\infty} \alpha = 1$$

- The exchange energy is

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

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

How to use FUEGs in DFT?

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

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

with

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

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

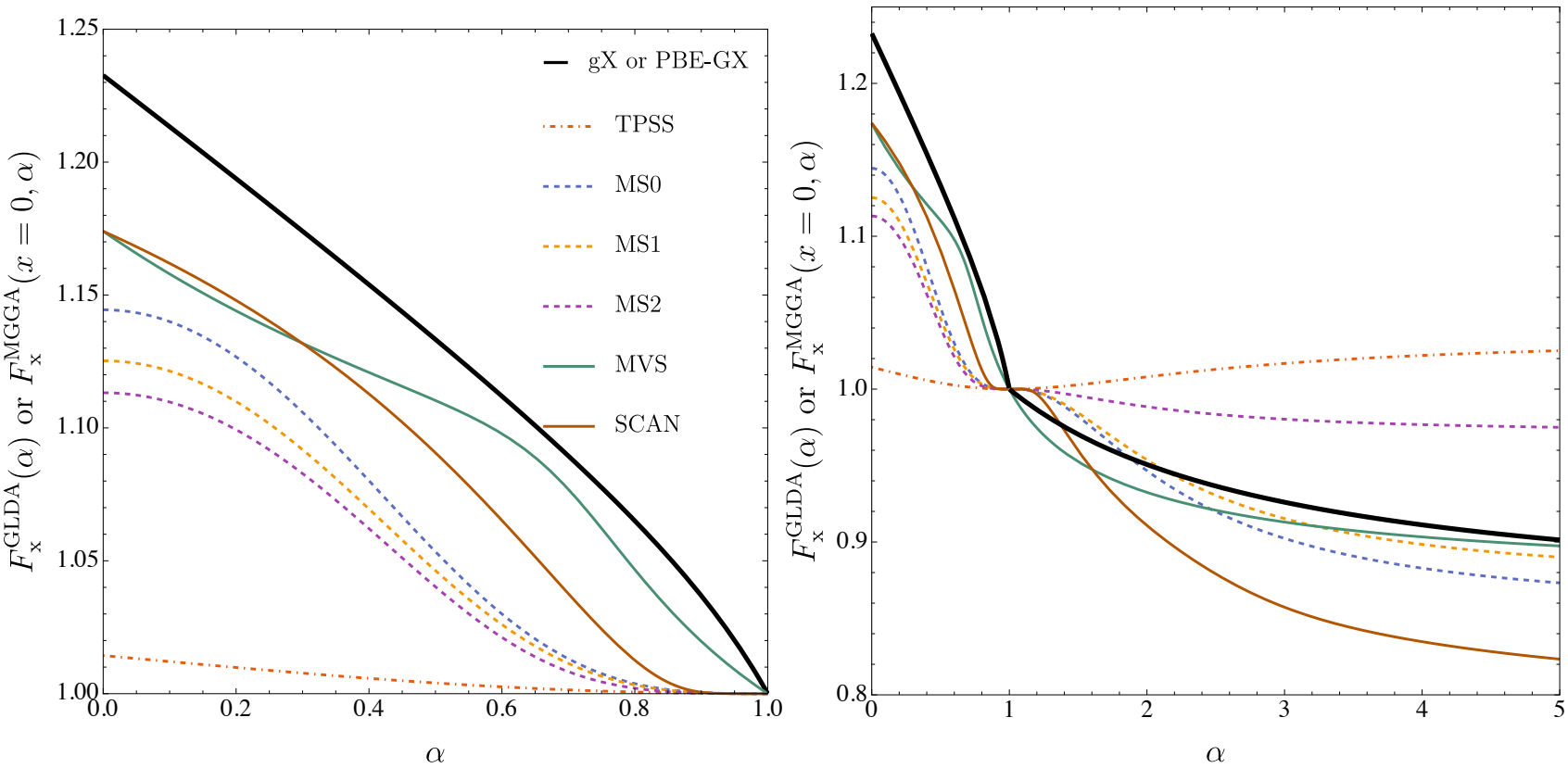
- For $\alpha = 1$, we recover the LDA:

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

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

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

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

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

where

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

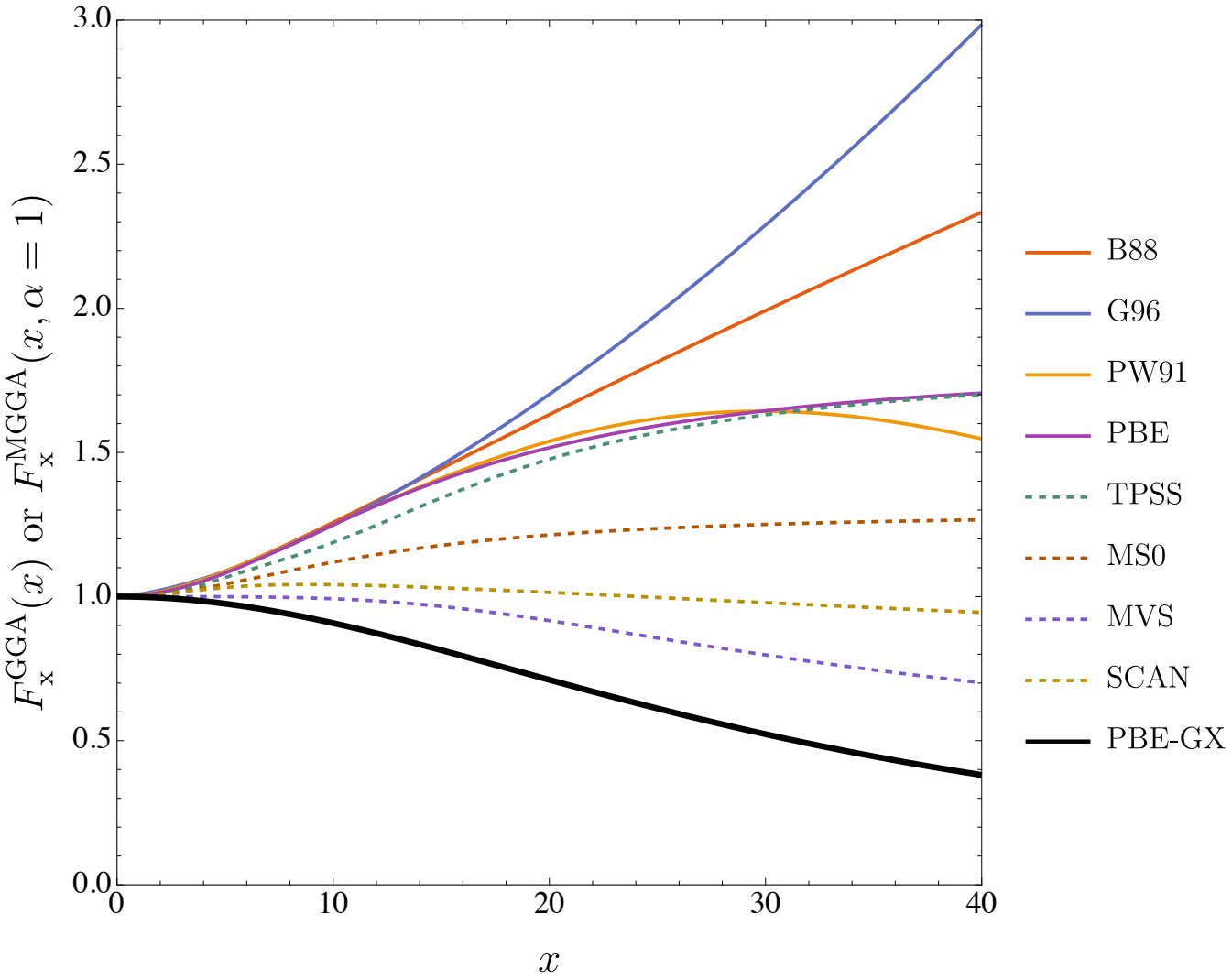
is a PBE-like GGA enhancement factor

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

Plot of the PBE-GX functional



Students, Postdocs, Collaborators and Funding

- Collaborator: Peter Gill
- Honours students: Anneke Knol & Fergus Rogers
- PhD students: Caleb Ball
- Postdocs: Davids Agboola

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Australian Government
Australian Research Council