

Density-functional theory using finite and infinite uniform electron gases

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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

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

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

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

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

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

Kohn & Sham Phys Rev 140 (1965) A1133

Density, Exchange and Correlation

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

$$\begin{aligned}
 E_{\text{xc}}[\rho, \zeta] &= E_{\text{x}}[\rho, \zeta] + E_{\text{c}}[\rho, \zeta] \\
 &= \int \rho(\mathbf{r}) e_{\text{x}}[\rho(\mathbf{r}), \zeta] d\mathbf{r} + \int \rho(\mathbf{r}) e_{\text{c}}[\rho(\mathbf{r}), \zeta] d\mathbf{r}
 \end{aligned}$$

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

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

The **correlation energy** is given by

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

Local density approximation (LDA) exchange

The LDA exchange energy (Dirac formula) is

$$E_{x,\sigma}^{\text{LDA}} = \int \rho_{\sigma}(\mathbf{r}) e_x[\rho_{\sigma}(\mathbf{r})] d\mathbf{r} = C_x \int \rho_{\sigma}(\mathbf{r})^{4/3} d\mathbf{r} \quad \sigma = \alpha, \beta$$

$$e_x[\rho_{\sigma}] = C_x \rho_{\sigma}^{1/3}$$

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 or jellium

Dirac, Proc Cam Phil Soc 26 (1930) 376

Loos & Gill, WIREs Comput Mol Sci (2016) 10.1002/wcms.1257

How good is LDA?

System	Basis set	Exact UHF	Error LDA
H	exact	-0.3125	+0.0445
He (1S)	STO-6G	-1.0256	+0.1418
He (3S)	"	-0.8562	+0.1007
Li (2S)	"	-1.7808	+0.2433
Li (4S)	"	-1.2379	+0.1497
Be	"	-2.6675	+0.3546
B	"	-3.7656	+0.4703
C	"	-5.0733	+0.5872
N	"	-6.6119	+0.7073
O	"	-8.2223	+0.8331
F	"	-10.0587	+0.9572
Ne	"	-12.1448	+1.0838
H ₂ ⁺	6-31G** ($R = 2.0$)	-0.3257	+0.0446
H ₂	6-31G** ($R = 1.4$)	-0.6575	+0.09126

Rule of thumb: LDA underestimates the exchange by 10%

Generalized gradient approximation (GGA) exchange

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

$$E_{x,\sigma}^{\text{GGA}} \approx E_{x,\sigma}^{\text{LDA}} - \frac{5}{(36\pi)^{5/3}} \int \rho_{\sigma}(\mathbf{r})^{4/3} x_{\sigma}^2 d\mathbf{r}$$

where

$$x_{\sigma} = \frac{|\nabla\rho_{\sigma}|}{\rho_{\sigma}^{4/3}}$$

is the **reduced gradient**.

The **GGA exchange energy** is

$$E_{x,\sigma}^{\text{GGA}} = C_x \int F(x_{\sigma}) \rho_{\sigma}(\mathbf{r})^{4/3} d\mathbf{r}$$

$F(x_{\sigma})$ is usually called the **enhancement factor**

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]

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

PW91 [PRB 46 (1992) 6671]

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

G96 [Mol Phys 89 (1996) 433]

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

PBE [PRL 77 (1996) 3865]

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

Are GGAs better than LDA?

System	Basis set	Exact UHF	Error		
			LDA	B88	G96
H	exact	-0.3125	+0.0445	+0.0026	+0.0011
He (¹ S)	STO-6G	-1.0256	+0.1418	+0.0005	-0.0029
He (³ S)	STO-6G	-0.8562	+0.1007	-0.0051	-0.0085
Li (² S)	"	-1.7808	+0.2433	+0.0061	+0.0026
Li (⁴ S)	"	-1.2379	+0.1497	-0.0024	-0.0026
Be	"	-2.6675	+0.3546	+0.0094	+0.0092
B	"	-3.7656	+0.4703	+0.0079	+0.0082
C	"	-5.0733	+0.5872	+0.0078	+0.0078
N	"	-6.6119	+0.7073	+0.0125	+0.0103
O	"	-8.2223	+0.8331	-0.0038	-0.0054
F	"	-10.0587	+0.9572	-0.0158	-0.0191
Ne	"	-12.1448	+1.0838	-0.0197	-0.0278
H ₂ ⁺	6-31G** (<i>R</i> = 2.0)	-0.3257	+0.0446	-0.0003	-0.0025
H ₂	6-31G** (<i>R</i> = 1.4)	-0.6575	+0.0913	+0.0026	-0.0011

Rule of thumb: GGAs are really good...

LDA correlation

The VWN correlation functional is

$$e_c^{\text{LDA}}(r_s, \zeta) = e_c^{\text{LDA}}(r_s, 0) + e_a(r_s) \frac{\gamma_c(\zeta)}{\gamma_c''(0)} (1 - \zeta^4) + [e_c^{\text{LDA}}(r_s, 1) - e_c^{\text{LDA}}(r_s, 0)] \gamma_c(\zeta) \zeta^4$$

where

$$\frac{1}{\rho} = \frac{4\pi}{3} r_s^3 \quad \gamma_c(\zeta) = \frac{\gamma_x(\zeta) - 2}{2^{1/3} - 1} \quad \gamma_x(\zeta) = \frac{(1 - \zeta)^{4/3} + (1 + \zeta)^{4/3}}{2}$$

and

$$e_{c/a}(x) = A \left\{ \ln \frac{x^2}{X(x)} + \frac{2b}{Q} \tan^{-1} \left(\frac{Q}{2x + b} \right) - \frac{bx_0}{X(x_0)} \left[\ln \frac{(x - x_0)^2}{X(x)} + \frac{2(b + 2x_0)}{Q} \tan^{-1} \frac{Q}{2x + b} \right] \right\}$$

$$x = \sqrt{r_s} \quad X(x) = x^2 + bx + c \quad Q = \sqrt{4c - b^2}$$

It has been obtained based on the infinite uniform electron gas

Rule of thumb: VWN usually overestimates by 100%...

Ceperley & Alder, PRL 45 (1980) 566

Vosko, Wilk & Nusair, Can J Phys 58 (1980) 1200

GGA correlation

For example, the LYP correlation functional is [Lee, Yang & Parr, PRB 37 (1988) 785]

$$\epsilon_c^{\text{LYP}} = -4a \frac{\rho_\alpha \rho_\beta}{\rho^2 (1 + d\rho^{-1/3})} -$$

$$ab\omega \left\{ \frac{\rho_\alpha \rho_\beta}{18} \left[144(2^{2/3}) C_F (\rho_\alpha^{8/3} + \rho_\beta^{8/3}) + (47 - 7\delta) |\nabla \rho|^2 - \right. \right.$$

$$\left. \left. (45 - \delta) (|\nabla \rho_\sigma|^2 + |\nabla \rho_\beta|^2) + 2\rho^{-1} (11 - \delta) (\rho_\sigma |\nabla \rho_\sigma|^2 + \rho_\beta |\nabla \rho_\beta|^2) \right] \right\}$$

$$\left[+ \frac{2}{3} \rho^2 (|\nabla \rho_\sigma|^2 + |\nabla \rho_\beta|^2 - |\nabla \rho|^2) - (\rho_\alpha^2 |\nabla \rho_\beta|^2 + \rho_\beta^2 |\nabla \rho_\alpha|^2) \right]$$

$$\omega = \frac{e^{-c\rho^{-1/3}}}{\rho^{14/3} (1 + d\rho^{-1/3})}$$

$$\delta = c\rho^{-1/3} + \frac{d\rho^{-1/3}}{(1 + d\rho^{-1/3})}$$

- a , b , c and d are determined by fitting to data for He [Colle & Salvetti, TCA 37 (1975) 329]
- There is no same-spin correlation in LYP
- Perdew has also developed similar functionals called PW86, PW91 and PBE

The B3LYP functional

The widely-used B3LYP functional is an **hybrid functional** and is defined as [Becke, JCP 98 (1993) 5648]

$$E_{xc}^{\text{B3LYP}} = (1 - a)E_x^{\text{LDA}} + aE_x^{\text{HF}} + bE_x^{\text{B88}} + (1 - c)E_c^{\text{LDA}} + cE_c^{\text{LYP}}$$

where

$$a \approx 0.2$$

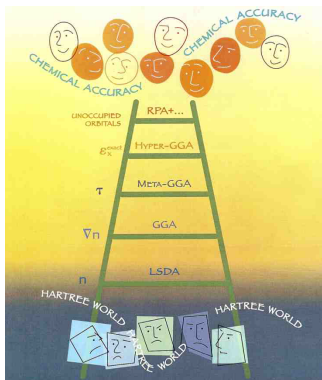
$$b \approx 0.7$$

$$c \approx 0.8$$

- B3LYP used VWN3 (not VWN5)!
- Subsequent versions denoted B97 and B98 employed **ten fitting parameters**...
- PBE with HF exchange gives **PBE0** (or sometimes calls PBE1PBE) with $a = 0.25$
- TPSS with HF exchange gives **TPSSh** with $a = 0.1$

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...

Back to basics: LDA in practice...

The local-density approximation (LDA)

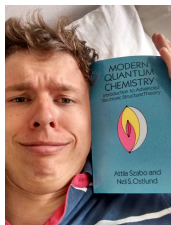
- Find the **exchange** and **correlation** energy of the **infinite uniform electron gas (UEG)** for all densities ρ
- Treat a molecular density as a **collection of tiny bits** of UEG

$$E_{x/c} = \int e_{x/c}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} \approx \sum_k w_k e_{x/c}(\mathbf{r}_k)\rho(\mathbf{r}_k)$$

- ☺ 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 **exchange** energy: **underestimate by roughly 10%**
- ☹☹ Not very accurate for **correlation** energy: **overestimate by roughly 100%**

What do we want to do?

- 1 e_x^{LDA} and e_c^{LDA} are based on **Fermi fluid (FF)** state of the UEG
- 2 However, since **Overhauser**, we know that the **FF** state is never the **HF** ground state of the UEG
- 3 Indeed, one can always find a lower, **symmetry-broken (SB)** state
- 4 The **Wigner crystal (WC)** state is an example of SB states
- 5 Using **SBHF** energies, we want to create new LDA-type xc functionals that we call **SBLDA** functionals
- 6 We ultimately want to do it for **three-dimensional systems** but we are lazy...
- 7 We will construct e_c^{SBLDA} for **ferromagnetic** ($\zeta = 1$) **1D** systems



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LDA for 1D systems [Loos, JCP 138 (2013) 064108]

The LDA correlation functional in 1D is

$$e_c^{\text{LDA}}(r_s) = t^2 \sum_{j=0}^3 c_j t^j (1-t)^{3-j}$$

$$t = \frac{\sqrt{1 + 4k r_s} - 1}{2k r_s} \quad r_s = \frac{1}{2\rho}$$

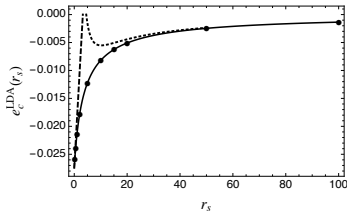
with $k = 0.418268$ and

$$c_0 = k \eta_0, \quad c_1 = 4k \eta_0 + k^{3/2} \eta_1, \quad c_2 = 5\varepsilon_0 + \varepsilon_1/k, \quad c_3 = \varepsilon_0,$$

and the high-density and low-density expansions

$$e_c(r_s) = \varepsilon_0 + \varepsilon_1 r_s + O(r_s^2), \quad r_s \ll 1$$

$$e_c(r_s) = \frac{\eta_0}{r_s} + \frac{\eta_1}{r_s^{3/2}} + O(r_s^{-2}), \quad r_s \gg 1$$



where

$$\varepsilon_0 = -\frac{\pi^2}{360}, \quad \varepsilon_1 = +0.00845, \quad \eta_0 = -\ln(\sqrt{2\pi}) + 3/4, \quad \eta_1 = +0.359933,$$

The LDA and DMC correlation energies agree to within 0.1 millihartree

Definition of the SBLDA correlation functional

[Rogers, Ball & Loos, PRB (in press) arXiv:1605.07602]

The “usual” definition of the correlation energy is (Löwdin equivalent)

$$e_c^{\text{FF}}(r_s) = e(r_s) - e_{\text{HF}}^{\text{FF}}(r_s)$$

We are going to use an alternative definition (Pople equivalent)

$$\begin{aligned} e_c^{\text{SB}}(r_s) &= e(r_s) - e_{\text{HF}}^{\text{SB}}(r_s) \\ &= e_c^{\text{FF}}(r_s) + \Delta e_{\text{HF}}^{\text{SB}}(r_s). \end{aligned}$$

Therefore, we define the SBLDA functional as

$$e_c^{\text{SBLDA}}(r_s) = e_c^{\text{LDA}}(r_s) + \Delta e_{\text{HF}}^{\text{SB}}(r_s)$$

We only need to calculate the SB stabilisation

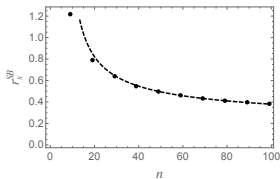
$$\Delta e_{\text{HF}}^{\text{SB}}(r_s) = \lim_{n \rightarrow \infty} \Delta e_{\text{HF}}^{\text{SB}}(r_s, n)$$

via extrapolation to the thermodynamic limit ($n \rightarrow \infty$)

SBHF calculations for the 1D UEG: $\Delta e_{\text{HF}}^{\text{SB}}$ (in millihartree)

n	r_s^{SB}	Wigner-Seitz radius r_s									
		0.5	1	2	5	10	15	20	50	75	100
9	1.22	0	0	2.685	6.852	6.226	5.187	4.392	2.267	1.628	1.273
19	0.79	0	0.666	5.042	7.695	6.621	5.445	4.583	2.346	1.678	1.311
29	0.64	0	1.576	5.525	7.860	6.698	5.496	4.621	2.361	1.688	1.319
39	0.55	0	1.985	5.700	7.920	6.727	5.515	4.635	2.366	1.692	1.321
49	0.50	0	2.188	5.784	7.949	6.741	5.524	4.642	2.369	1.694	1.323
59	0.46	0.000	2.302	5.830	7.965	6.749	5.529	4.646	2.370	1.695	1.324
69	0.43	0.008	2.371	5.859	7.975	6.754	5.532	4.648	2.371	1.695	1.324
79	0.41	0.143	2.418	5.878	7.982	6.757	5.534	4.650	2.372	1.695	—
89	0.40	0.198	2.450	5.891	7.986	6.759	5.535	4.651	2.372	—	—
99	0.38	0.244	2.473	5.901	7.989	6.760	5.536	4.652	—	—	—
109	0.36	0.281	2.490	—	—	—	—	—	—	—	—
119	0.35	0.312	2.503	—	—	—	—	—	—	—	—
129	0.35	0.337	—	—	—	—	—	—	—	—	—
⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮
∞	0	0.476	2.570	5.938	8.002	6.767	5.540	4.655	2.372	1.695	1.324

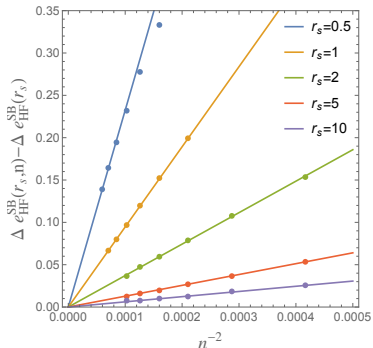
$$r_s^{\text{SB}}(n) = \frac{1.13535}{\ln n - 1.61346}$$



Extrapolation to the thermodynamic limit

$$\Delta e_{\text{HF}}^{\text{SB}}(r_s, n) = \Delta e_{\text{HF}}^{\text{SB}}(r_s) + A n^{-2}$$

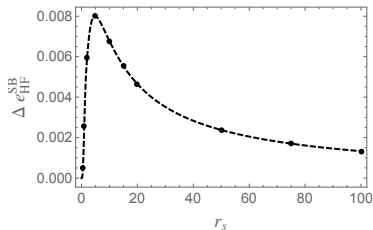
r_s	$-e_c^{\text{FF}}$	$-e_c^{\text{SB}}$	$1 - e_c^{\text{SB}}/e_c^{\text{FF}}$
0	27.416	27.416	0%
0.5	23.962	23.486	2%
1	21.444	18.874	12%
2	17.922	11.984	33%
5	12.318	4.316	65%
10	8.292	1.525	82%
15	6.319	0.779	88%
20	5.133	0.478	91%
50	2.476	0.104	96%
100	1.358	0.034	97%



Lee & Drummond, PRB 83 (2011) 245114

Fit of the SB stabilisation

$$\Delta e_{\text{HF}}^{\text{SB}}(r_s) = r_s^2 \frac{a_0 + a_1 r_s + a_2 r_s^2 - \eta_0 r_s^3}{b_0 + b_1 r_s^5 + b_2 r_s^{11/2} + r_s^6}$$



By construction, $\Delta e_{\text{HF}}^{\text{SB}}(r_s = 0) = 0$ and $\Delta e_{\text{HF}}^{\text{SB}}(r_s \rightarrow \infty) = -\frac{\eta_0}{r_s} + O(r_s^{-3/2})$

Maximum error of 7 microhartrees compared to data

Creation of a Wigner Crystal in 1D

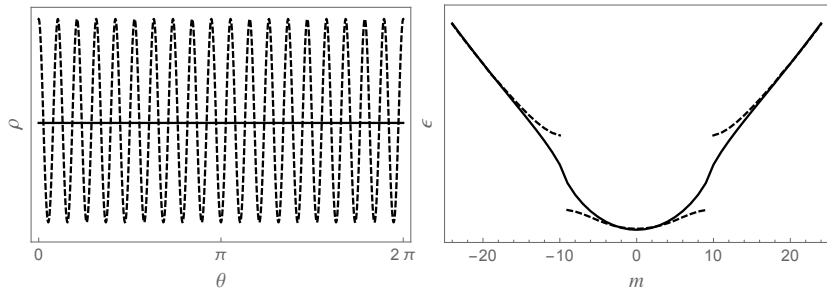


Figure: Electronic density ρ as a function of θ (left) and orbital energies ϵ as a function of m (right) for the HF (solid line) and SBHF (dashed line) solutions for $n = 19$ at $r_s = 5$.

Two electrons in a one-dimensional box

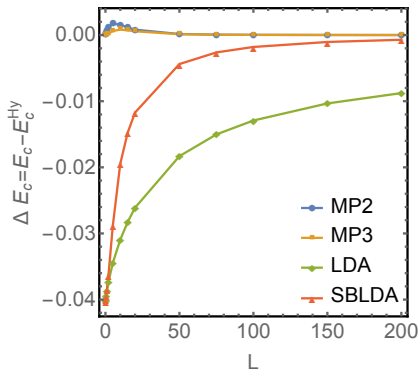


Figure: Error in correlation energy ΔE_c for two electrons in a box of length L with MP2, LDA and SBLDA.

Loos, Ball & Gill, JCP 140 (2014) 18A524;

Loos, PRA 89 (2014) 052523;

Rogers, Ball & Loos, PRB (in press) arXiv:1605.07602

Ionization energies and electron affinities in 1D atoms

Atom	Ionization energy $A \longrightarrow A^+ + e^-$			Electron affinity $A + e^- \longrightarrow A^-$		
	MP3	LDA	SBLDA	MP3	LDA	SBLDA
H	13.606	14.125	14.013	3.893	4.327	4.154
He	33.895	34.393	34.325	—	—	0
Li	4.522	4.895	4.712	1.395	1.717	1.512
Be	10.408	10.822	10.669	—	—	0
B	2.099	2.386	2.190	0.638	0.875	0.688
C	4.730	5.056	4.865	—	—	0
N	1.14	1.38	1.20	0.34	0.51	0.37
O	2.56	2.83	2.63	—	—	—
F	0.68	0.87	0.72	0.2	0.3	0.2
Ne	1.5	1.7	1.5	—	—	—

Loos, Ball & Gill, PCCP, 17 (2015) 3196;

Rogers, Ball & Loos, PRB (in press) arXiv:1605.07602

LDA and SBLDA for one- and two-electron diatomics

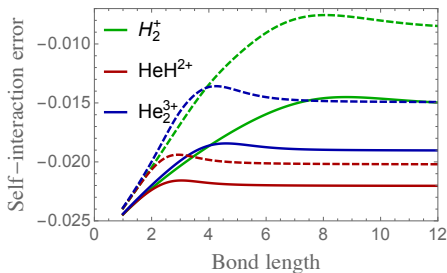


Figure: Self-interaction error in H_2^+ (green), HeH^{2+} (red) and He_2^{3+} (blue) calculated with LDA (solid) and SBLDA (dashed) as a function of the bond length.

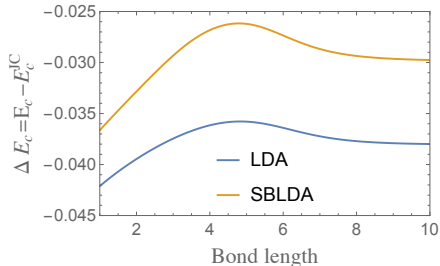


Figure: Error in correlation energy ΔE_c in H_2 calculated with LDA and SBLDA as a function of the bond length.

Loos, Ball & Gill, PCCP, 17 (2015) 3196;
 Rogers, Ball & Loos, PRB (in press) arXiv:1605.07602

What we are currently doing...

For three-dimensional systems,

- One has to consider **exchange and correlation**
- Are errors in exchange and correlation still cancelling nicely?
- One has to consider **spin polarization**
- How do we link properly the paramagnetic and ferromagnetic states?
- One has to consider **various symmetry-broken states**
- Are incommensurate crystals real?!

Trail, Towler & Needs, PRB 68 (2003) 045107;

Baguet, Delyon, Bernu & Holzmann, PRL 111 (2013) 166402; PRB 90 (2014) 165131

Students, Postdocs, Collaborators and Funding

- **Honours students:** Anneke Knol & Fergus Rogers
 - **PhD students:** Caleb Ball & Giuseppe Barca
 - **Postdocs:** Davids Agboola & Jia Deng
 - **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