# Exact constraint for exchange GGAs based on two term asymptotics of the free electron gas

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# Outline

# Introduction

# A few words on KS-DFT

Idea of DFT: Shift focus from the high dimensional wavefunction $\psi$ to the low dimensional one-body (electronic) density:

$$\rho(r) = N \sum_{\sigma \in \mathbb{Z}_2} \int_{\mathbb{R}^{3(N-1)}} |\psi(r, \sigma_1, r_2, \sigma_2 ..., r_N, \sigma_N)|^2 dr_2 ... dr_N$$

Hohenberg and Kohn 1964 : The ground state energy can be computed by minimizing a functional of the density

$$E_0 = \inf_{\rho} \{F_{HK}[\rho] + \int V\rho\}$$

$F_{HK}$ unknown $\Rightarrow$ approximate Functionals, Kohn and Sham 1965 :

$$F_{HK}(\rho) \approx T_{KS}[\rho] + J[\rho] + E_{xc}[\rho]$$

The exchange-correlation is usually split in $E_{xc}[\rho] = E_x[\rho] + E_c[\rho]$. We focus on the exchange part.

# Exchange Functionals

- Exact exchange (expensive):

$$E_x[\rho] = -\int_{\mathbb{R}^6} \frac{|\sum_{i=1}^{\frac{N}{2}} \phi_i(r)\bar{\phi}_i(\tilde{r})|^2}{|r-\tilde{r}|} \mathrm{d}r\mathrm{d}\tilde{r}, \quad \phi_1, ..\phi_N \text{ Kohn-Sham orbitals}$$

- LDA (local density approximation):

$$E_x^{LDA}[\rho] = \int e_x(\rho(r))\mathrm{d}r$$

where $e_x(\bar{\rho}) =$ (exact exchange energy per unit volume of free electron gas with density $\bar{\rho}$) $= -c_x\bar{\rho}^{\frac{4}{3}}$

- Milestone: GGAs (generalized gradient approximations):

$$E_x^{GGA}[\rho] = \int \Big( e_x(\rho(r)) + f^{GGA}(\rho(r), |\nabla\rho(r)|) \Big)\mathrm{d}r$$

Becke 1988, Perdew, Wang 1991, Perdew, Burke, Ernzerhof 1996. Improved accuracy of typical DFT energies from 1eV to 0.2 eV.

# Exchange functionals

Design of $f^{GGA}$: very low-dimensional ansatz, fit 1 parameter to wavefunction data for noble gas atoms (Becke) or 2 parameters to small-gradient expansion of electron gas and Lieb-Oxford ineq. (Perdew).

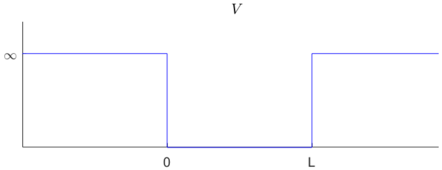
Criticism: design somewhat arbitrary (indeed, nowadays many approximations not of GGA form), relevance of small gradient expansion doubtful, low-dimensional ansatz partially falls out of thin air.

To our knowledge, no previous study of GGAs in the mathematical literature.

This work: careful asymptotic analysis of free electron gas with Dirichlet boundary conditions which reveals surface correction caused by a surface region where density gradient is $\mathcal{O}(1)$. Can be captured by the GGA ansatz, but gives exact constraint on $f^{GGA}$ not satisfied by current functionals.

# Free electron gas (in a box)

- The free electron gas is a 3 dimensional quantum systems that models N non-interacting electrons in a box $Q_L = [0, L]^3$. It can be seen as a high-density (or weakly interacting) limit of the uniform electron gas, where the interaction between electrons is neglected.
- Under periodic boundary conditions, one can see it as a gas of electrons in the Torus $T_3 = \mathbb{R}^3/(L\mathbb{Z})^3$.
- Under Dirichlet boundary conditions one could think of the potential $V$ being 0 inside the box $Q_L$ and $\infty$ outside.



# Free Electron Gas

Mathematically: Exact ground state $\psi_0 = \phi_{k_1,\uparrow} \wedge \phi_{k_1,\downarrow} ... \wedge \phi_{k_{\frac{N}{2}},\downarrow}$ where $k_j \in \mathbb{Z}^3$ (or $\mathbb{N}^3$ for Dirichlet) is the $j^{th}$ closest integer (or natural) valued vector to the origin.

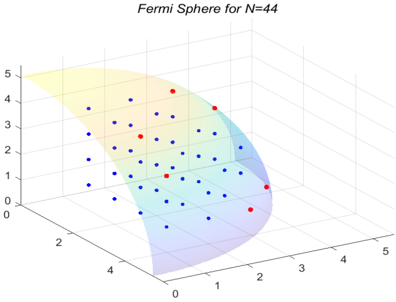
- Periodic b.c.:

$$\phi_k(r) = \frac{e^{i2\pi \frac{k \cdot r}{L}}}{L^{3/2}}, \quad \lambda_k = \frac{4\pi^2}{L^2}|k|^2$$

- Dirichlet b.c.:

$$\phi_k(r) = \left(\frac{2}{L}\right)^{3/2} \prod_{i=1}^{3} \sin\left(\frac{\pi}{L} k_i r_i\right)$$

$$\lambda_k = \frac{\pi^2}{L^2}|k|^2$$




The Fermi momentum is defined as $p_{N,L} = \frac{\pi R_N}{L}$ where $R_N$ is the radius of the Fermi sphere.

# Thermodynamic Limit

Fix $\bar{\rho} = N/L^3$ and take limit $N \to \infty, L \to \infty$. Our goal is to study the asymptotic limit of the exchange energy of the quantum ground state,

$$E_x[\psi_{N,L}] = V_{ee}[\psi_{N,L}] - J[\psi_{N,L}] = -\int_{Q_L^2} \frac{|\sum_{i=1}^{\frac{N}{2}} \phi_{k_i}(r)\bar{\phi_{k_i}}(\tilde{r})|^2}{|r-\tilde{r}|} \mathrm{d}r\mathrm{d}\tilde{r}$$

$$= E_x[\rho_{N,L}]$$

and compare to exchange functionals applied to the ground state one-body density:

$$E_x^{LDA}[\rho_{N,L}] = \int_{Q_L} e_x(\rho_{N,L}(r))\mathrm{d}r$$

$$(E_x^{LDA} + F^{GGA})[\rho_{N,L}] = \int_{Q_L} (e_x(\rho_{N,L}(r)) + f^{GGA}(\rho_{N,L}(r), |\nabla \rho_{N,L}(r)|))\mathrm{d}r$$

# Instructive example: derivation of Dirac exchange

Continuum approximation of ground state one-body density matrix:

$$\gamma_{N,L}(r,\tilde{r}) = \frac{1}{L^3} \sum_{k \in (\frac{2\pi\mathbb{Z}}{L})^3 \cap B_{p_{N,L}}} e^{ik\cdot(r-\tilde{r})} \approx \frac{1}{(2\pi)^3} \int_{B_{p_{N,L}}} e^{ik\cdot(r-\tilde{r})} dk$$

$$= \underbrace{\frac{p_{N,L}^3 |B_1|}{(2\pi)^3} h(p_{N,L}|(r-\tilde{r}) \mod L|)}_{:=\gamma_{N,L}^{ctm}}$$

where $h(s) = 3(\sin s - s\cos s)/s^3$. Moreover, since $p_{N,L} \to p_F := (3\pi^2\bar{\rho})^{\frac{1}{3}}$

$$E_x[\rho_{N,L}] = -\int_{Q_L^2} \frac{|\gamma_{N,L}^{ctm}|^2}{|r-\tilde{r}|} dr d\tilde{r} \approx -\left(\frac{p_{N,L}^3 |B_1|}{(2\pi)^3}\right)^2 L^3 \int_{Q_{L/2}} \frac{h(|p_{N,L}x|)^2}{|x|} dx$$

$$\approx -\bar{\rho}^{4/3} L^3 \underbrace{\frac{1}{(3\pi^2)^{\frac{2}{3}} 32} \int_{\mathbb{R}^3} \frac{h(|x|)^2}{|x|} dx}_{c_x}$$

Hence $E_x[\rho_{N,L}] = -c_x \bar{\rho}^{\frac{4}{3}} L^3 + \mathcal{O}(L^3)$. Moreover, since, $\rho_{N,L} = \bar{\rho}$ (homogeneous), one has $E_x^{LDA}[\rho_{N,L}] = e_x(\bar{\rho})L^3 + \mathcal{O}(L^3)$ and

$$\frac{E_x[\rho_{N,L}]}{E_x^{LDA}[\rho_{N,L}]} \to 1 \iff e_x(\rho) = -c_x \rho^{\frac{4}{3}}$$

.

Question (at least for mathematicians): Can one really replace the sum on $\mathbb{Z}^3 \cap B_R$ by an integral in $B_R$?? or how good is this approximation?

Friesecke 1997 [5]: Yes! It is this good:

$$\text{Lemma}: \left| \sum_{k \in B_R \cap \mathbb{Z}^3} e^{i2\pi k \cdot z} - \int_{B_R} e^{i2\pi k \cdot z} \right| \leq c(1 + R^{\frac{3}{2}}), \quad \forall |z|_{max} \leq 1/2$$

where $|z|_{max} = \max_{i \leq 3} |z_i|$.

So, $|\gamma_{N,L} - \gamma_{N,L}^{ctm}| \leq cL^{-\frac{3}{2}}$ and the derivation is good.

Question 2: But what about non homogeneous densities? For instance, energy asymptotics for the FEG under Dirichlet boundary conditions?

In this case, one-body density matrix:

$$\gamma_{N,L} = \frac{4}{L^3} \sum_{\sigma \in G} \det \sigma \sum_{k \in B_{R_N} \cap \mathbb{Z}^3} e^{i \frac{\pi}{L} k \cdot (r - \sigma \tilde{r})}$$

$$\rho_{N,L} = \frac{4}{L^3} \sum_{\sigma \in G} \det \sigma \sum_{k \in \mathbb{Z}^3 \cap B_{R_N}} e^{i \frac{\pi}{L} k \cdot (r - \sigma r)}$$

$$\gamma_{N,L}^{ctm} = \frac{p_{N,L}^3 |B_1|}{(2\pi)^3} \sum_{\sigma \in G} \det \sigma h(p_{N,L} | r - \sigma \tilde{r} \mod 2L|)$$

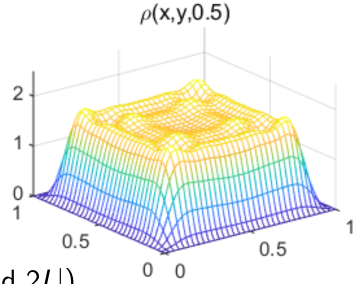



Figure: One-body density for $N = 240$.

# Review Friesecke 1997

## Theorem (Friesecke)

*Let $\bar{\rho} = N/L^3 =$ constant and $\rho_{N,L}$ be ground state density of any determinantal ground state of the FEG in the box $Q_L$. Then for $e^{LDA} \in C^1$, it holds:*

- *Under periodic boundary conditions:*

$$E_x[\rho_{N,L}^{Per}] = -c_x \bar{\rho}^{4/3} L^3 + \mathcal{O}(L^2)$$

$$E_x^{LDA}[\rho_{N,L}^{Per}] = -c_x \bar{\rho} L^3 + \mathcal{O}(L^{\frac{3}{2}})$$

- *Under Dirichlet boundary conditions:*

$$E_x[\rho_{N,L}^{Dir}] = -c_x \bar{\rho}^{4/3} L^3 + \mathcal{O}(L^2)$$

$$E_x^{LDA}[\rho_{N,L}^{Dir}] = -c_x \bar{\rho} L^3 + \mathcal{O}(L^2)$$

# Open questions:

1. What is the difference between them, i.e., $E_x[\rho^{Per}_{N,L}] - E_x[\rho^{Dir}_{N,L}] =??$ One would expect at least some difference of the order of surface area $L^2$, as the gradient is concentrated close to the boundary...

2. From previous theorem, the rest term is $\mathcal{O}(L^2)$ in Dirichlet, but only $\mathcal{O}(L^{\frac{3}{2}})$ in periodic case, so is the LDA so good that it already captures this boundary layer effect??

3. What about GGAs? Can GGAs capture this boundary layer effect, oor at least produce some meaningful correction to the LDA in this limit, i.e., $\frac{E_x[\rho^{Dir}_{N,L}] - E_x^{LDA}[\rho^{Dir}_{N,L}]}{F^{GGA}[\rho^{Dir}_{N,L}]} \to 1$ for some GGA?

# New result

# Answers

1. What is the difference between them, i.e., $E_x[\rho^{Per}_{N,L}] - E_x[\rho^{Dir}_{N,L}] =??$ One would expect at least some difference of the order of surface area $L^2$, as the gradient is concentrated close to the boundary...
   Yes, the difference is precisely of order of magnitude of the surface area $E_x[\rho^{Per}_{N,L}] - E_x[\rho^{Dir}_{N,L}] = cL^2 + \mathcal{O}(L^{45/23+\epsilon})$.
2. From previous theorem, the rest term is $\mathcal{O}(L^2)$ in Dirichlet, but only $\mathcal{O}(L^{\frac{3}{2}})$ in periodic case, so is the LDA so good that it already captures this boundary layer effect??
   Partially. The LDA does present some terms of the form $cL^2$ which are also present in the exact exchange, but not all.
3. What about GGAs? Can GGAs capture this boundary layer effect, oor at least produce some meaningful correction to the LDA in this limit, i.e., $\frac{E_x[\rho^{Dir}_{N,L}] - E_x^{LDA}[\rho^{Dir}_{N,L}]}{F^{GGA}[\rho^{Dir}_{N,L}]} \to 1$ for some GGA?
   Yes, GGAs do present a correction on the right order of magnitude $\mathcal{O}(L^2)$ and by properly choosing $f^{GGA}$ one can have $(E_x[\rho^{Dir}_{N,L}] - E_x^{LDA}[\rho^{Dir}_{N,L}])/F^{GGA}[\rho^{Dir}_{N,L}] \to 1$.

# Main Result:

## Theorem

- *Periodic b.c.*

$$E_x[\rho^{Per}_{N,L}] = -c_x \bar{\rho}^{4/3}|Q|L^3 + c_{FS}\bar{\rho}|\partial Q|L^2 + \mathcal{O}(L^{45/23+\epsilon})$$
$$E^{LDA}_x[\rho^{Per}_{N,L}] = -c_x \bar{\rho}^{4/3}|Q|L^3 + \mathcal{O}(L^{\frac{34}{23}+\epsilon})$$
$$F^{GGA}[\rho^{Per}_{N,L}] = \mathcal{O}(L^{\frac{34}{23}+\epsilon})$$

- *Dirichlet b.c.*

$$E_x[\rho^{Dir}_{N,L}] = -c_x \bar{\rho}^{4/3}|Q|L^3 + \overbrace{(c_{FS} + c^{x}_{BL} - c_{FM})}^{:=-c^{Dir}_{x,2}}\bar{\rho}|\partial Q|L^2 + \mathcal{O}(L^{\frac{45}{23}+\epsilon})$$

$$E^{LDA}_x[\rho^{Dir}_{N,L}] = -c_x \bar{\rho}^{4/3}|Q|L^3 + \overbrace{(c^{LDA}_{BL} - c_{FM})}^{:=c_{LDA}}\bar{\rho}|\partial Q|L^2 + \mathcal{O}(L^{\frac{34}{23}+\epsilon})$$

$$F^{GGA}[\rho^{Dir}_{N,L}] = c^{GGA}_{BL}|\partial Q|L^2 + o(L^2)$$

# Exact value of constants of surface term

QM:

$$c_{FS} = \frac{1}{8} \quad c_{FM} = \frac{3}{8} \quad c_{BL} = \frac{\log 2}{4} \quad \Rightarrow \quad c_{x,2}^{Dir} = \frac{1-\log 2}{4}$$

LDA:

$$c_{BL}^{LDA} = \frac{3}{8\pi} \int_0^\infty \left( (1-h(s))^{\frac{4}{3}} - 1 \right) \mathrm{d}s$$

GGA:

$$c_{BL}^{GGA} = \frac{1}{2p_F} \int_0^\infty f^{GGA}\left( \bar{\rho}(1-h(s), 2p_F|\dot{h}(s)|) \right) \mathrm{d}s$$

with $h(s) = 3(\sin s - s\cos s)/s^3$ and $p_F = (3\pi^2\bar{\rho})^{\frac{1}{3}}$

# Exact constraint on GGAs

## Corollary

*GGAs are exact to second order in the thermodynamic limit of the Dirichlet free electron gas iff the function $f^{GGA}$ satisfies an integral constraint:*

$$\lim_{L\to\infty} \frac{E_x[\rho_{N,L}] - (E^{LDA} + F^{GGA})[\rho_{N,L}]}{L^2} = 0$$

$$\iff -\frac{1}{2p_F} \int_0^\infty f^{GGA}\Big(\bar{\rho}(1 - h(s), 2p_F|\dot{h}(s)|)\Big)\mathrm{d}s = (c_{x,2}^{Dir} - c_{LDA})\bar{\rho}$$

*with* $h(s) = 3(\sin s - s\cos s)/s^3$ *and* $p_F = (3\pi^2\bar{\rho})^{\frac{1}{3}}$.

# Proof Sketch

Strategy: Continuum version of the density matrix seems pretty nice, let us try to use it!

Difficulties:

1. How to extract expressions for the second order terms ($\mathcal{O}(L^2)$) from the continuum density and density matrices?
2. Main lemma of Friesecke is not enough for terms of order $L^2$ for exact exchange? Roughly, an error of $L^{-\frac{3}{2}}$ squared integrated against coulomb potential $|r - \tilde{r}|^{-1}$ in the double box $Q_L$ yields precisely an error of order $L^2$.
3. For GGAs we need the gradients! Is it true that $\nabla \rho_L \approx \nabla \rho_L^{ctm}$ ?

1. How to extract expressions for the second order terms ($\mathcal{O}(L^2)$) from the continuum limit?

Strategy: use three ingredients:

1. $C^1$-regularity of functionals.
2. decay of $h$: $|h^{(k)}(s)| \leq c_k(1+|s|)^{-2}$
3. Asymptotic for the Fermi momentum $p_{N,L}$.

$$p_{N,L}^{Dir} = p_F + \frac{\pi|\partial Q|}{8|Q|}\frac{1}{L} + \mathcal{O}(L^{-\frac{35}{23}+\epsilon})$$

$$p_{N,L}^{Per} = p_F + \mathcal{O}(L^{-\frac{35}{23}+\epsilon})$$

with $p_F = (3\pi^2\bar{\rho})^{1/3}$.

Works for any semi-local like functional: $F[\rho] = \int f(\rho, \nabla\rho)$.

## Theorem (General Semi-Local Functional asymptotics)

*Let $f(s,p) \in C^1(\mathbb{R} \times \mathbb{R}^3)$ where $f$ depends on the norm of $p$. Let $\nu_{N,L} := (\rho_{N,L}, \nabla\rho_{N,L})$ be the combined variable of one-body density and gradient. Then, in the thermodynamic limit, it holds*

$$F[\rho_L^{Per}] = f(\nu_0)|Q|L^3 + \mathcal{O}(L^2)$$
$$F[\rho_L^{Dir}] = f(\nu_0)|Q|L^3 + (c_{BL}(f) + c_{FM}(f))|\partial Q|L^2 + \mathcal{O}(L^2)$$

*where the boundary layer and Fermi momentum corrections are given by*

$$c^{Dir}(f) = \frac{1}{2p_F}\int_0^\infty f(\nu_0 - \nu_1(s)) - f(\nu_0)\mathrm{d}s$$
$$c_{FM}(f) = \frac{3\pi\bar{\rho}}{8p_F}\partial_s f(\nu_0)$$

*with $\nu_0 = (\bar{\rho}, 0)$, $\nu_1(s) = \bar{\rho}(h(s), 2p_F\dot{h}(s))$.*

- Main lemma of Friesecke is not enough for terms of order $L^2$ for exact exchange. Roughly, an error of $L^{-\frac{3}{2}}$ squared integrated against coulomb potential $|r - \tilde{r}|^{-1}$ in the double box $Q_L$ yields precisely an error of order $L^2$.

- For GGAs we need the gradients! Is it true that $\nabla \rho \approx \nabla \rho_L^{ctm}$ ?

**Lemma (Improved version)**

*For any* $\alpha \in \mathbb{N}_0^3$ *(*$\mathbb{N}_0 = \mathbb{N} \cup \{0\}$*)and* $\epsilon > 0$*, there exists* $c_{\alpha,\epsilon}$ *such that:*

$$\left| \sum_{n \in \mathbb{Z}^3 \cap B_R} (i2\pi k)^\alpha e^{i2\pi k \cdot z} - \int_{B_R} (i2\pi k)^\alpha e^{i2\pi k \cdot z} dk \right| \leq c_{\alpha,\epsilon}(1 + R^{|\alpha| + \frac{34}{23} + \epsilon})$$

*for all* $|z|_{max} \leq 1/2$.

Note: $\frac{34}{23} - \frac{3}{2} = \frac{1}{46}$. Only slightly better, but enough! So, for $\alpha, \beta \in \mathbb{N}_0^3$:

$$|\partial_r^\alpha \partial_{\tilde{r}}^\beta \gamma_L - \partial_r^\alpha \partial_{\tilde{r}}^\beta \gamma_L^{ctm}| \leq c_{\alpha,\beta} L^{-\frac{35}{23} + \epsilon}$$

# Proof of Lemma

Idea: Use harmonic analysis and analytic number theory

Inspired by case $z = 0, \alpha = 0 \quad \Rightarrow \quad$ Sphere problem: find optimal $\theta$ such that

$$\#\{x \in \mathbb{Z}^3 : |x| \leq R\} = vol(B_R) + \mathcal{O}(R^\theta), \quad \theta \leq 2$$

Exponent $\theta = \frac{3}{2}$ from Friesecke 1997 already found with different proof by E. Landau in 1919.

Work on Sphere problem since Landau:

Vinogradov 1963 and Chen 1963 showed $\theta \leq 4/3$, Chamizo and Iwaniec 1995 improved to $\theta \leq 29/22$ and Heath-Brown 1999 with the best-to-date result $\theta \leq 21/16$.

Conclusion: Combining harmonic analysis (Poisson summation) and theory of exponential sums (book by Graham and Kolesnik 1991), gives the proof.

# Numerical results

- B88:

$$F^{B88}[\rho] = \int 2^{1/3}\beta \frac{|\nabla\rho|^2}{\rho^{4/3} + 6 * \beta * 2^{1/3} * |\nabla\rho| \sinh^{-1}(2^{1/3}\frac{|\nabla\rho|}{\rho^{4/3}})} dr$$

with $\beta = 0.0042$ and $\sinh^{-1}$ is the inverse of the hyperbolic sine.

- PBE:

$$F^{PBE}[\rho] = \int \frac{\mu|\nabla\rho|^2}{4(3\pi^2)^{2/3}\rho^{8/3} + \frac{\mu}{\kappa}|\nabla\rho|^2} dr$$

where $\mu = 0.21951$ and $\kappa = 0.804$.

Upon numerical integration:

$$c_{LDA}^{Dir} \approx 0.0673, \quad c_{PBE}^{Dir} \approx 0.0157, \quad c_{B88}^{Dir} \approx 0.0192, \quad c_{PBEsol}^{Dir} \approx 0.0105$$

$$c_{x,2}^{Dir} := \frac{1}{4}(1 - \log 2) \approx 0.0767$$

# Energy per unit volume

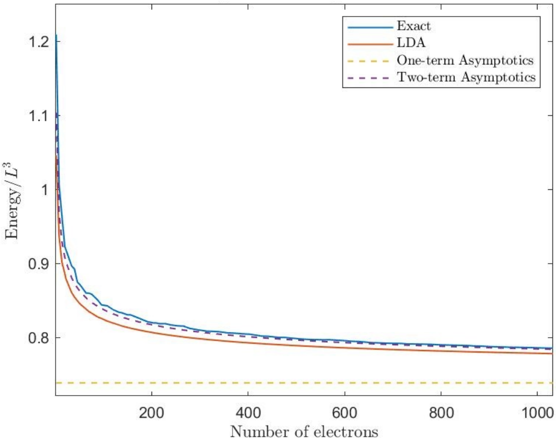



Figure: Comparison of exact exchange, LDA, one-term asymptotics (Dirac exchange constant) and two-term asymptotics (present work).

# Energy per unit volume

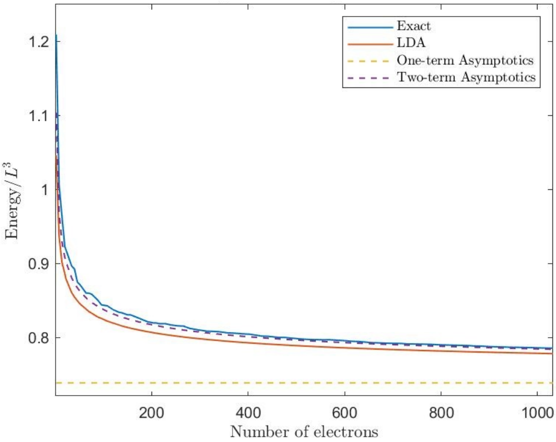
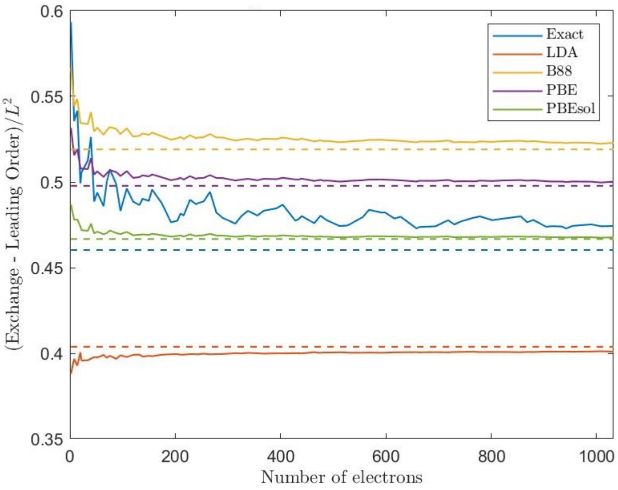


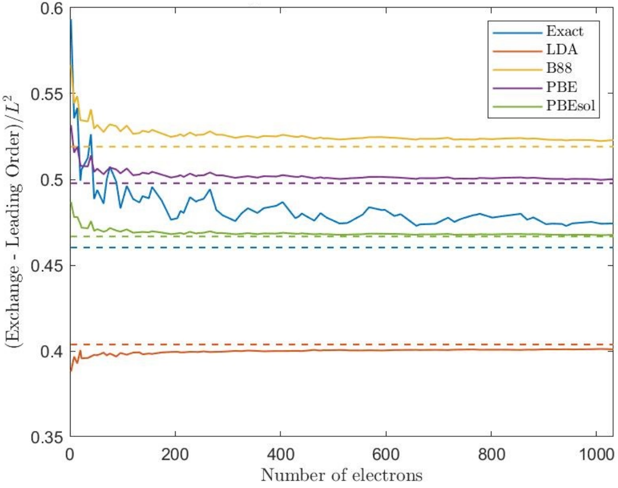

Figure: Comparison of exact exchange, LDA, one-term asymptotics (Dirac exchange constant) and two-term asymptotics (present work).

Surface correction huge. Two term asymptotics (our work) beats LDA.

# Surface correction (our work)



# Surface correction (our work)




- No current GGAs good for all $N$.
- B88 best for $N$ small, *PBEsol* best for $N$ large.

# Conclusions

# Conclusions

- GGAs are in principle capable of capturing surface corrections to the LDA, caused by density gradients of order 1 near the boundary of the region occupied by electrons.
- Current GGAs are not very good at capturing the correct size of these corrections for the free electron gas with Dirichlet boundary conditions.
- For capturing them exactly, the function $f^{GGA}$ must satisfy a simple explicit integral constraint.

Outlook

- Results can be extended to general domains via different methods (work in progress by T.C.).
- Results could in principle be extended to semi-local functionals depending on higher order derivatives of the density (meta-GGAs).

Main reference: T.C. and Gero Friesecke, on arxiv soon.

# Thank you!

# Questions??

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