The Surface Energy of the Electron Gas

A Battle with Error Bars

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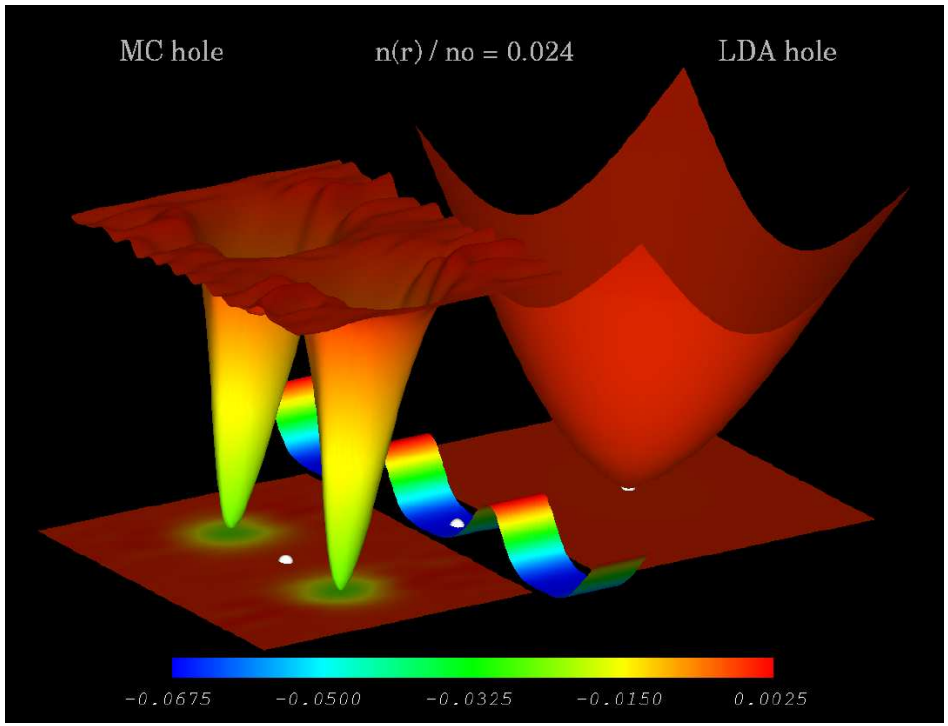
Outline

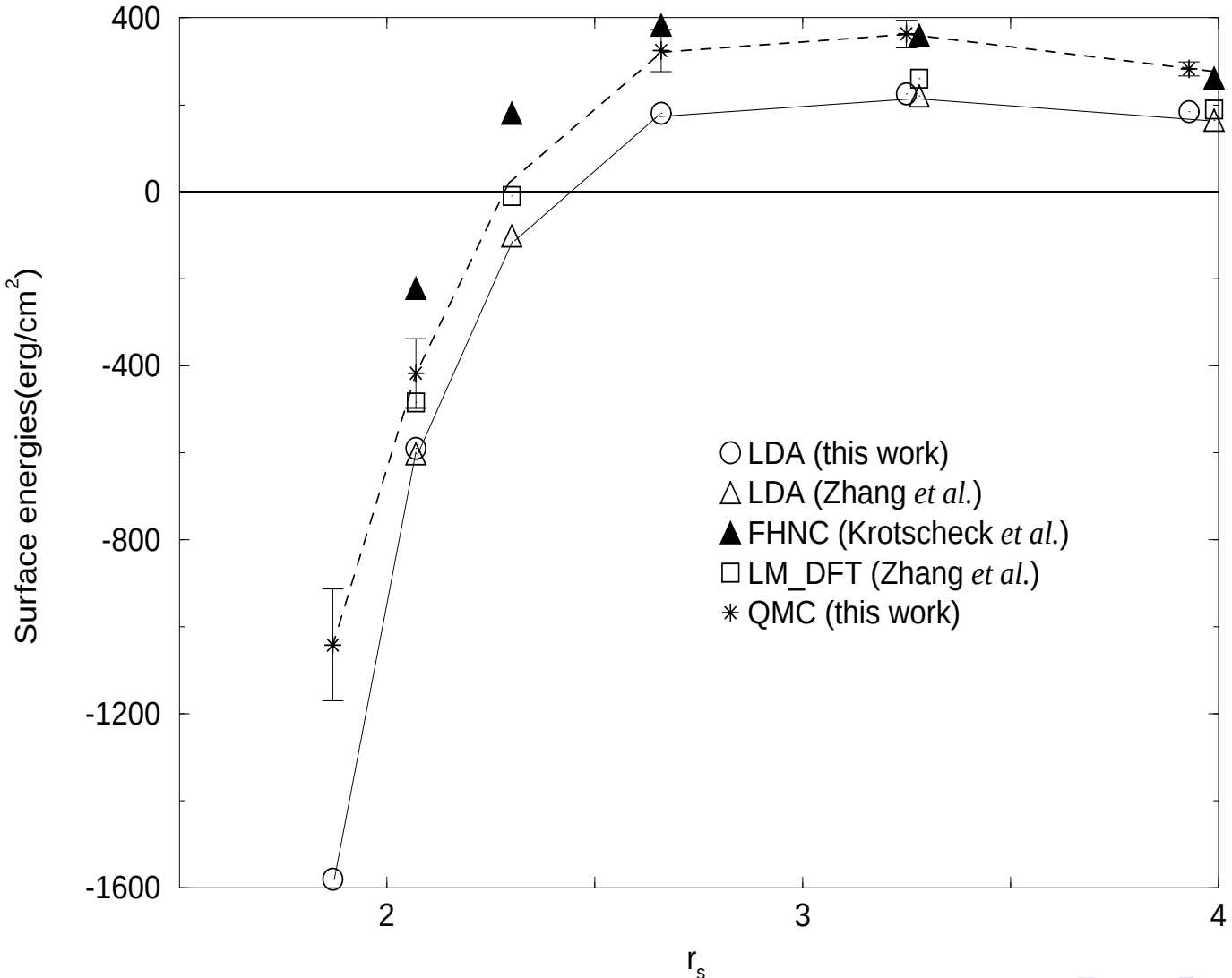
- Introduction
- QMC
- Possible Explanations
- Our Work
- Results and Summary

Who Cares?

- The surface of a semi-infinite electron gas is the simplest real test of most electronic structure methods.
- Exchange and correlation at surfaces is interesting.



The Controversy



- Surface energies extrapolated from DMC simulations of jellium spheres,

$$E = N\epsilon_{\text{bulk}} + 4\pi r^2\sigma + 2\pi r\gamma \ ,$$

  agree with DFT.
- RPA- and *GW*-based calculations agree with DFT.

For the surface energy of jellium at alkali-metal densities, the local-density approximation (LDA) and more advanced density-functional methods disagree strongly with the wave-function-based Fermi hypernetted-chain and diffusion Monte Carlo methods.

Z. Yan, J.P. Perdew, S. Kurth, C. Fiolhais and L. Almeida
Phys. Rev. B 61, 2595 (2000)

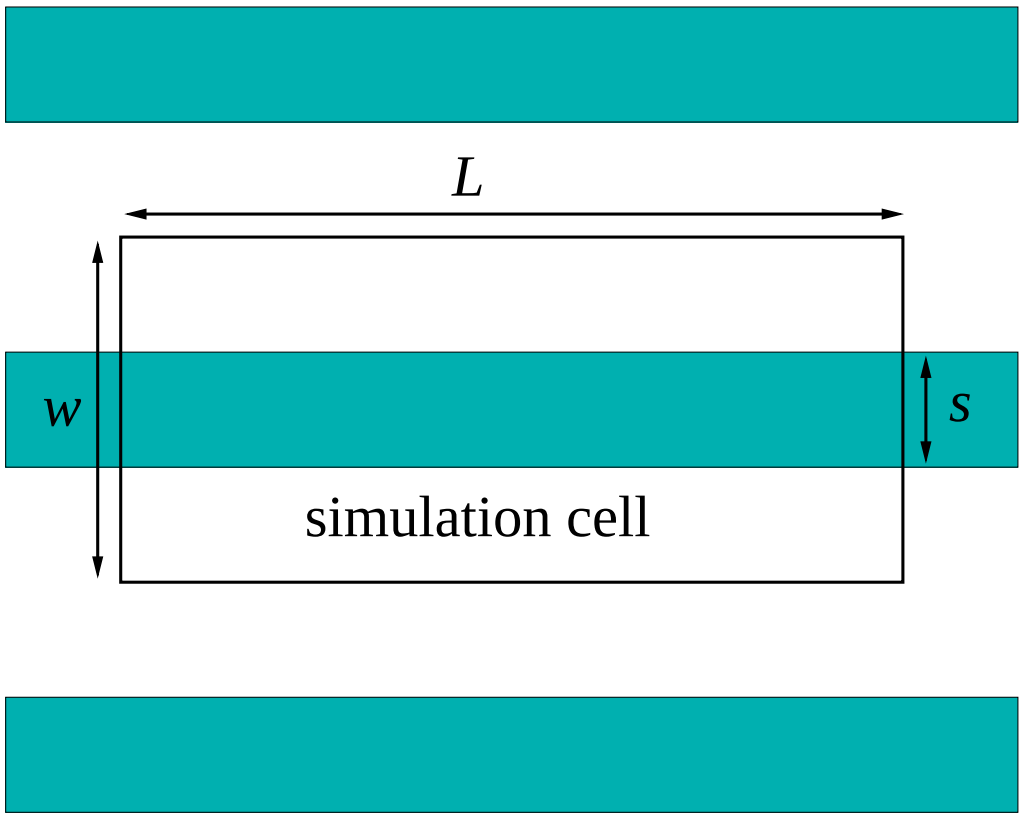
Are the slab DMC results wrong?

Surface Energies at (in erg cm^{-2}) when $r_s = 2.07$

Illinois (Li):	σ_{DMC}	$=$	-465 ± 50
Illinois (Acioli):	σ_{DMC}	$=$	-420 ± 80
Perdew *et al.*:	σ_{LDA}	$=$	-610
	σ_{GGA}	$=$	-690
	σ_{MGGA}	$=$	-567
	$\sigma_{\mathrm{LDA/RPA}}$	$=$	-553
	$\sigma_{\mathrm{GGA/RPA}}$	$=$	-587

$$1\ \mathrm{erg\,cm^{-2}} = 6.25 \times 10^{-5}\ \mathrm{eV\,\AA^{-2}}$$
$$= 6.42 \times 10^{-4}\ \mathrm{mHa\,Bohr^{-2}}$$

Accuracy



$$N\epsilon_{\text{slab}} = N\epsilon_{\text{bulk}} + 2L^2\sigma$$

$$\sigma = \frac{N}{2L^2}(\epsilon_{\text{slab}} - \epsilon_{\text{bulk}}) = \frac{N}{2L^2}\Delta\epsilon_{\text{slab}}$$

Assuming $r_s = 2.07$ and $s = 20$, require

$$\Delta\epsilon_{\text{slab}} \approx 0.1\ \text{mHa} \quad (3\ \text{meV})$$

for resolution $\Delta\sigma \approx 50\ \text{erg}\,\text{cm}^{-2}$.

Another problem:

$$\begin{aligned} \sigma &\approx -600 \quad \mathrm{erg\,cm^{-2}} \\ \sigma_s &\approx -4600 \quad \mathrm{erg\,cm^{-2}} \\ \sigma_{es} &\approx 1000 \quad \mathrm{erg\,cm^{-2}} \\ \sigma_{xc} &\approx 3000 \quad \mathrm{erg\,cm^{-2}} \end{aligned}$$

Because σ passes through zero near $r_s = 2.07$, σ is much smaller than its components.

Variational Quantum Monte Carlo

- Guess $\Psi_T(\mathbf{R}) = \Psi_T(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)$.
- Evaluate

$$E[\Psi_T] = \int \Psi_T^*(\mathbf{R}) \hat{H} \Psi_T(\mathbf{R}) d\mathbf{R} = \int \frac{\hat{H}\Psi_T(\mathbf{R})}{\Psi_T(\mathbf{R})} |\Psi_T(\mathbf{R})|^2 d\mathbf{R}$$

  using Monte Carlo integration.
- Adjust $\Psi_T(\mathbf{R})$ to minimise $E[\Psi_T]$.

$$\Psi_T(\mathbf{R}) = e^{J(\mathbf{R})} \begin{vmatrix} \psi_1(\mathbf{r}_1) & \psi_1(\mathbf{r}_2) & \dots & \dots & \psi_1(\mathbf{r}_N) \\ \psi_2(\mathbf{r}_1) & \psi_2(\mathbf{r}_2) & \dots & \dots & \psi_2(\mathbf{r}_N) \\ \dots & \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots \\ \psi_N(\mathbf{r}_1) & \psi_N(\mathbf{r}_2) & \dots & \dots & \psi_N(\mathbf{r}_N) \end{vmatrix}$$

where

$$J(\mathbf{R}) = -\frac{1}{2} \sum_i \sum_{j \neq i} u_{\sigma_i, \sigma_j}(\mathbf{r}_i, \mathbf{r}_j) + \sum_i \chi(\mathbf{r}_i) \, .$$

Diffusion Quantum Monte Carlo

$$\frac{\partial \Psi}{\partial \tau} = -\hat{H}\Psi \quad \Rightarrow$$

$$\Psi \longrightarrow c e^{-E_0 \tau} \Psi_0 \quad \text{as} \quad \tau \to \infty$$

Defining $f = \Psi_T \Psi$, the equation of motion becomes a drift/diffusion/branching equation:

$$\frac{\partial f}{\partial \tau} = \frac{1}{2}\nabla^2_{\mathbf{R}} f - \nabla_{\mathbf{R}} \cdot (\mathbf{v} f) - E_L f \ ,$$

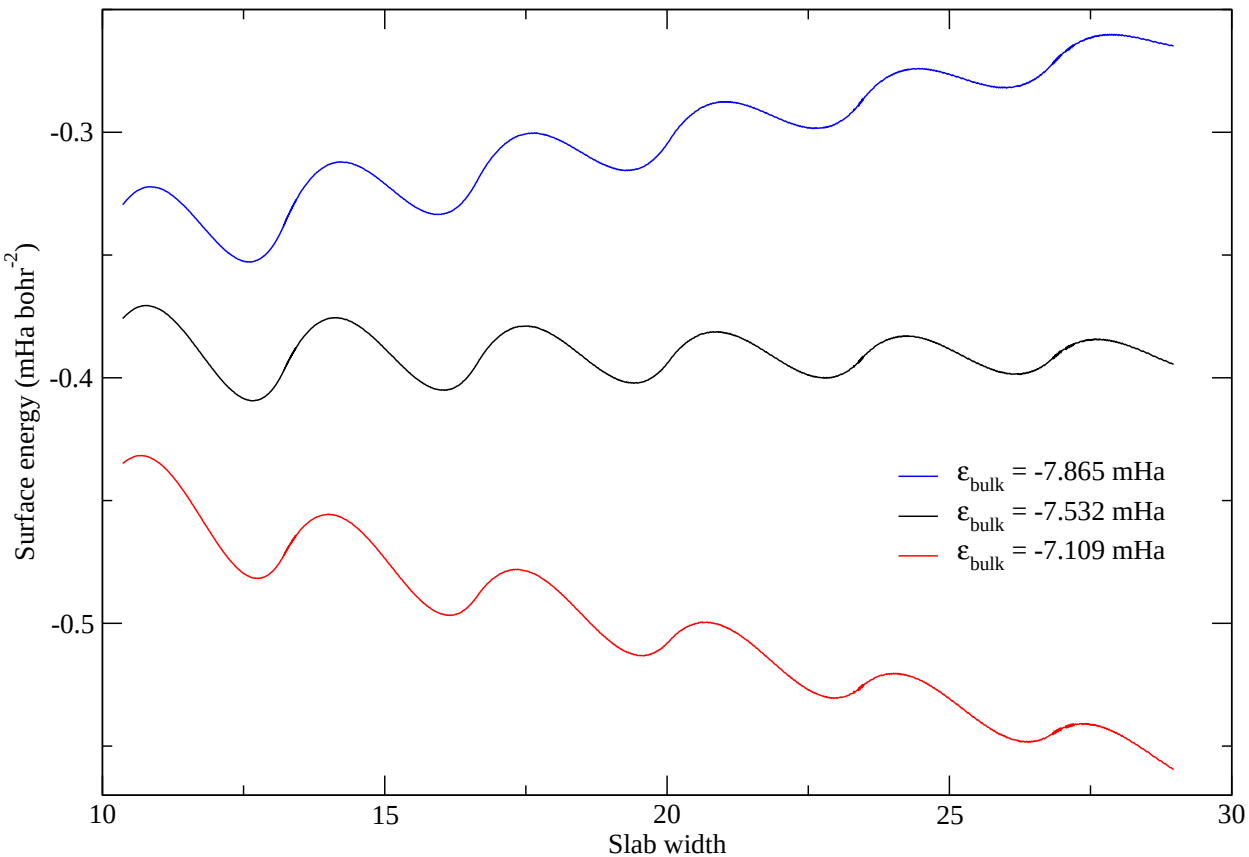
where

$$\mathbf{v} = \frac{1}{2}\nabla \ln(|\Psi_T|^2) \quad \text{and} \quad E_L = \frac{\hat{H}\Psi_T}{\Psi_T} \ .$$

Possible Explanations

- DMC is right and other methods fail.
- Fixed-node errors.
- Finite-size errors.
- Comparing apples and oranges (decreases likelihood of cancellation of errors).

Comparing Apples and Oranges



Effects of using different LDAs for the bulk calculation

Acioli's DMC result was

$$\sigma_{\mathrm{DMC}} = -420 \pm 80 \text{ erg cm}^{-2} .$$

Pitarke noticed that Acioli had compared *fixed-node* slab results with *release-node* bulk results. By comparing Acioli's fixed-node slab results with *fixed-node* bulk results, Pitarke obtained:

$$\sigma_{\mathrm{DMC}} = -554 \pm 80 \text{ erg cm}^{-2} .$$

(LDA result is -600 erg cm^{-2}.)

Li avoided this mistake, but did not account for Coulomb finite-size errors.

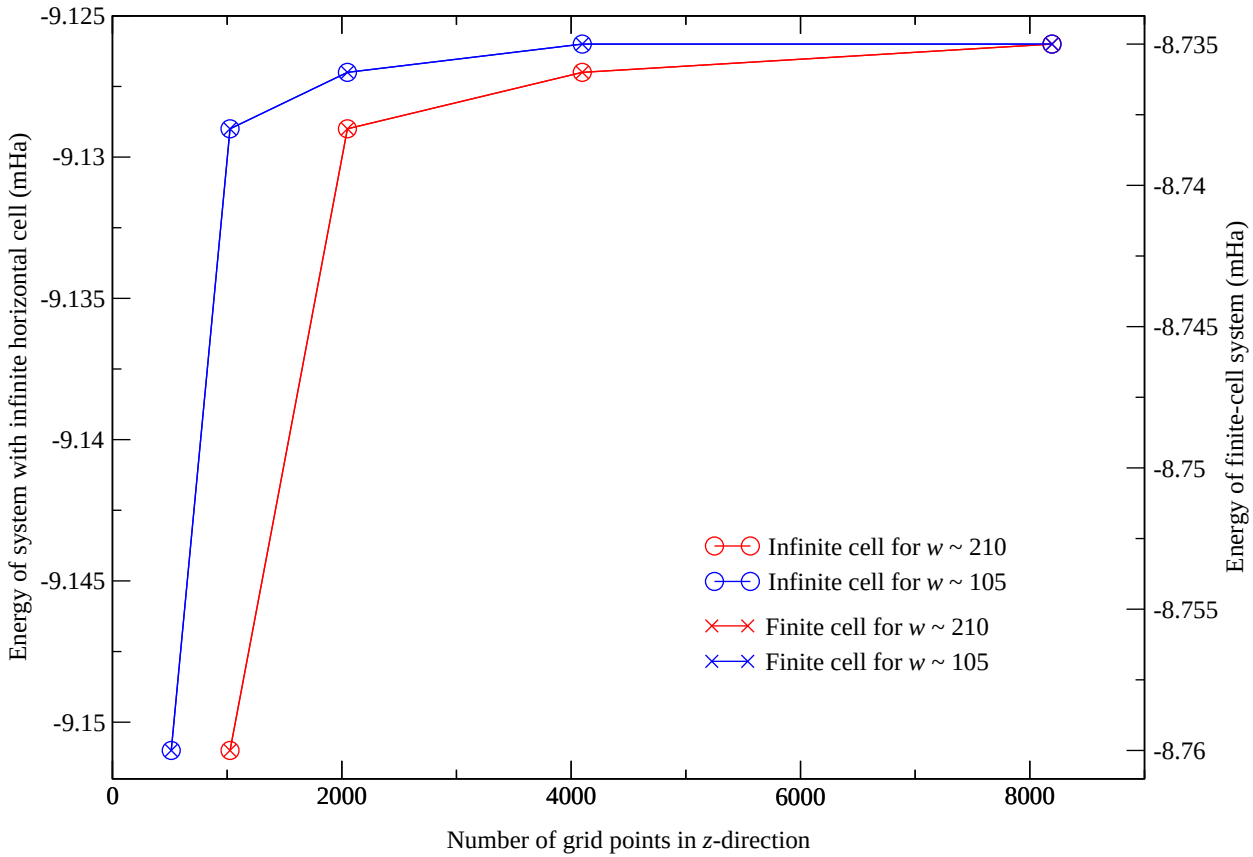
Here are surface energies calculated from our (uncorrected) fixed-node slab simulations and Ceperley and Alder's fixed-node bulk simulations.

Number of electrons	ϵ_{slab} (mHa)	σ (erg cm^{-2})
332	-9.18 ± 0.13	-440 ± 30
466	-8.901 ± 0.097	-370 ± 20
588	-8.818 ± 0.088	-350 ± 20

If Li had included Coulomb corrections, his surface energy would have been even worse! Looks as if the fixed-node error is larger in the slab than the bulk.

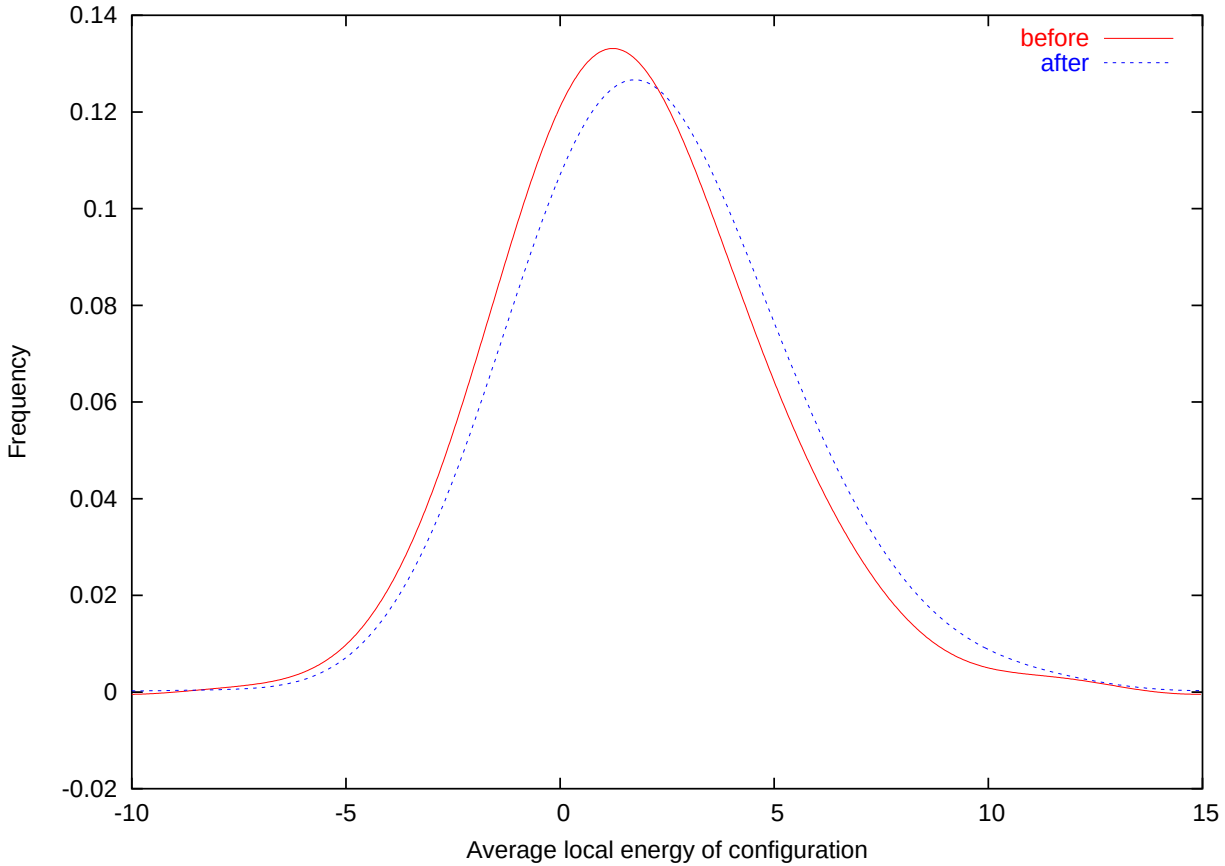
Trial Wave Functions

- Real-space grid in z direction.
- Plane waves in xy plane.



LDA energy as a function of the number of grid points

Variance Optimisation Problems



Distribution of energies before and after variance optimisation

- Variance and mean of initial configs reduced as expected, but variance and mean of new configs *increased*.
- New configs are more spread out: electron density outside slab increases. This decreases the KE, but increases the PE by a larger amount.

Speculative Explanation

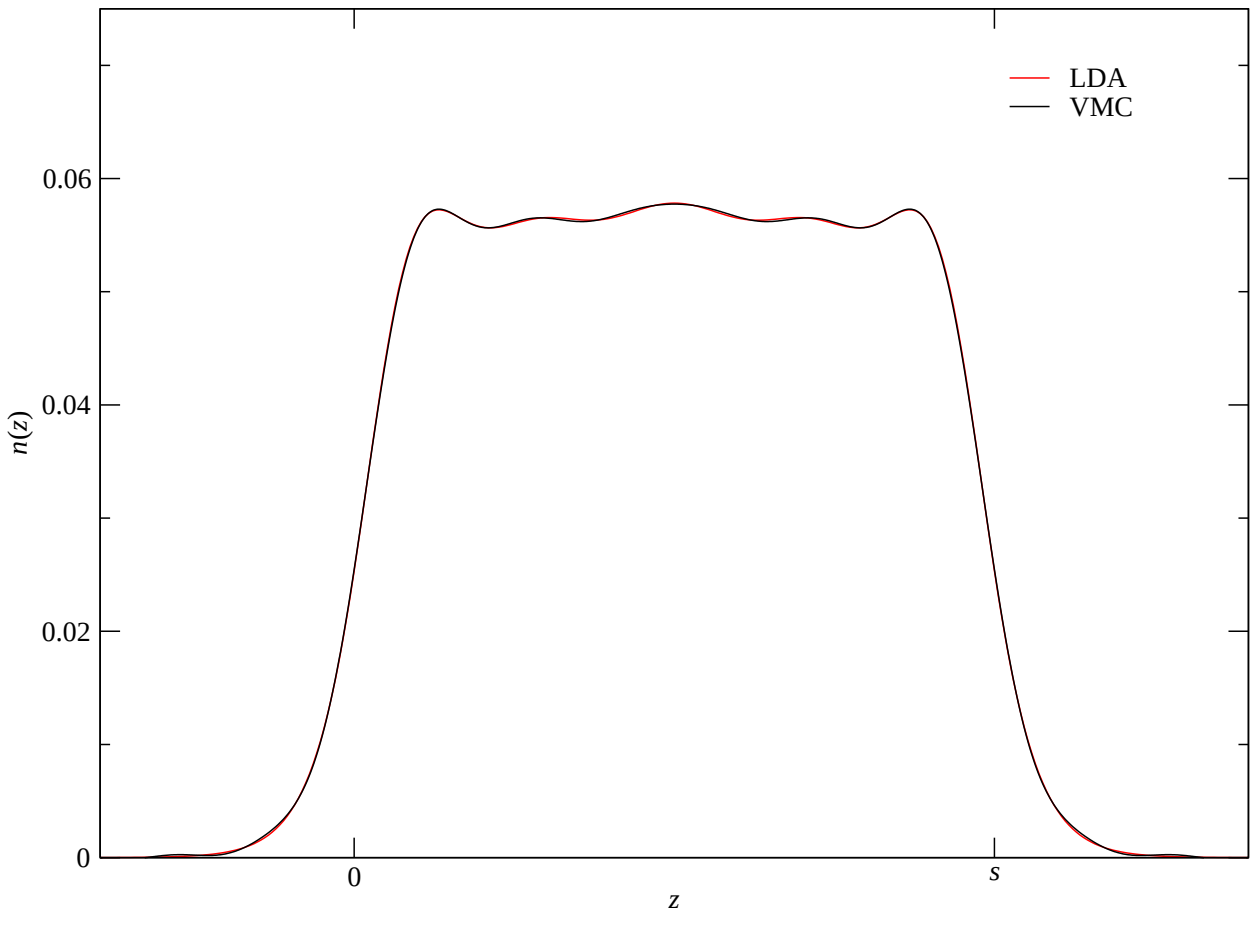
Since the initial configs do not venture outside the slab, the optimiser cannot “know” that going there is unfavourable.

But . . .

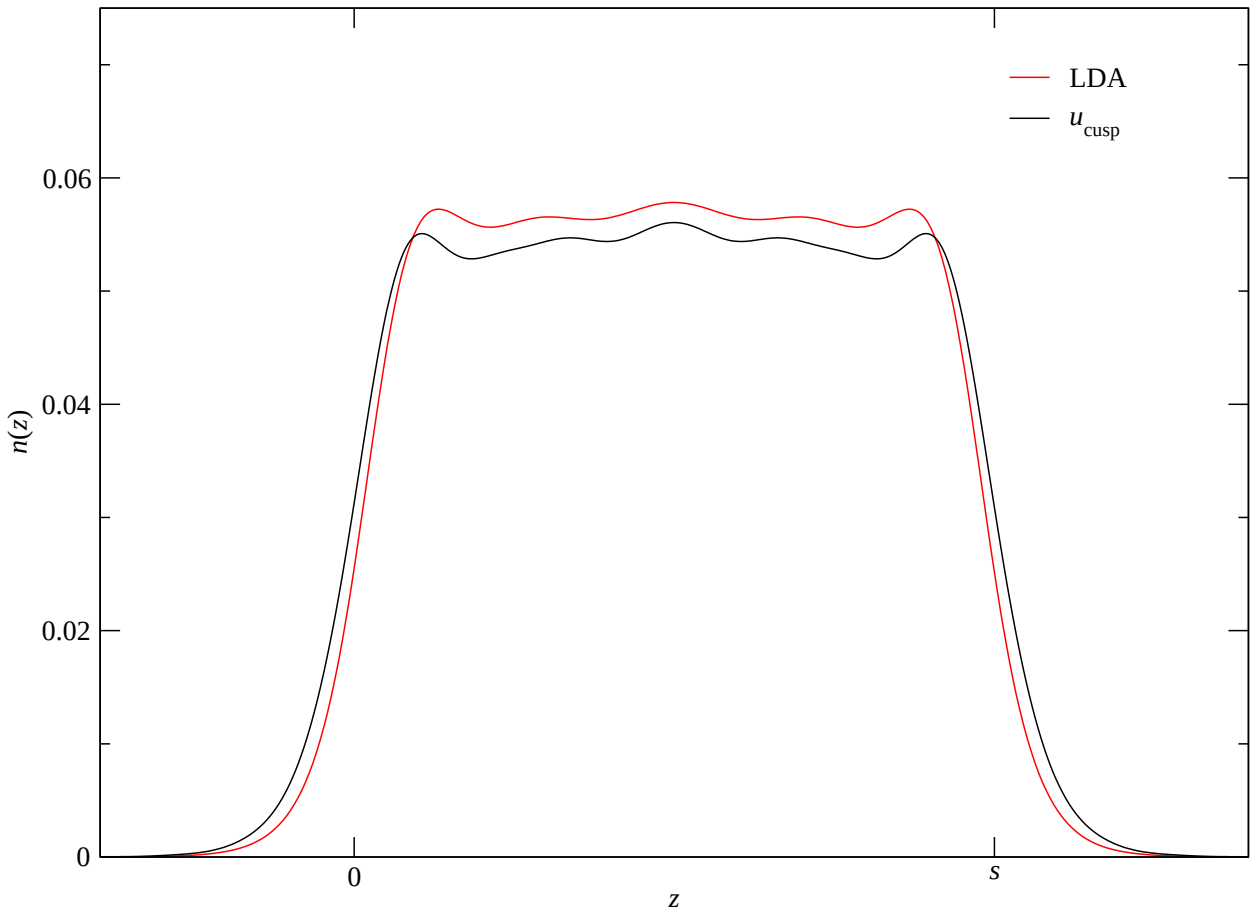
- Reweighting does not help.
- Changing the initial sampling to include more configs with electrons outside the slab does not help.

Another Speculative Explanation

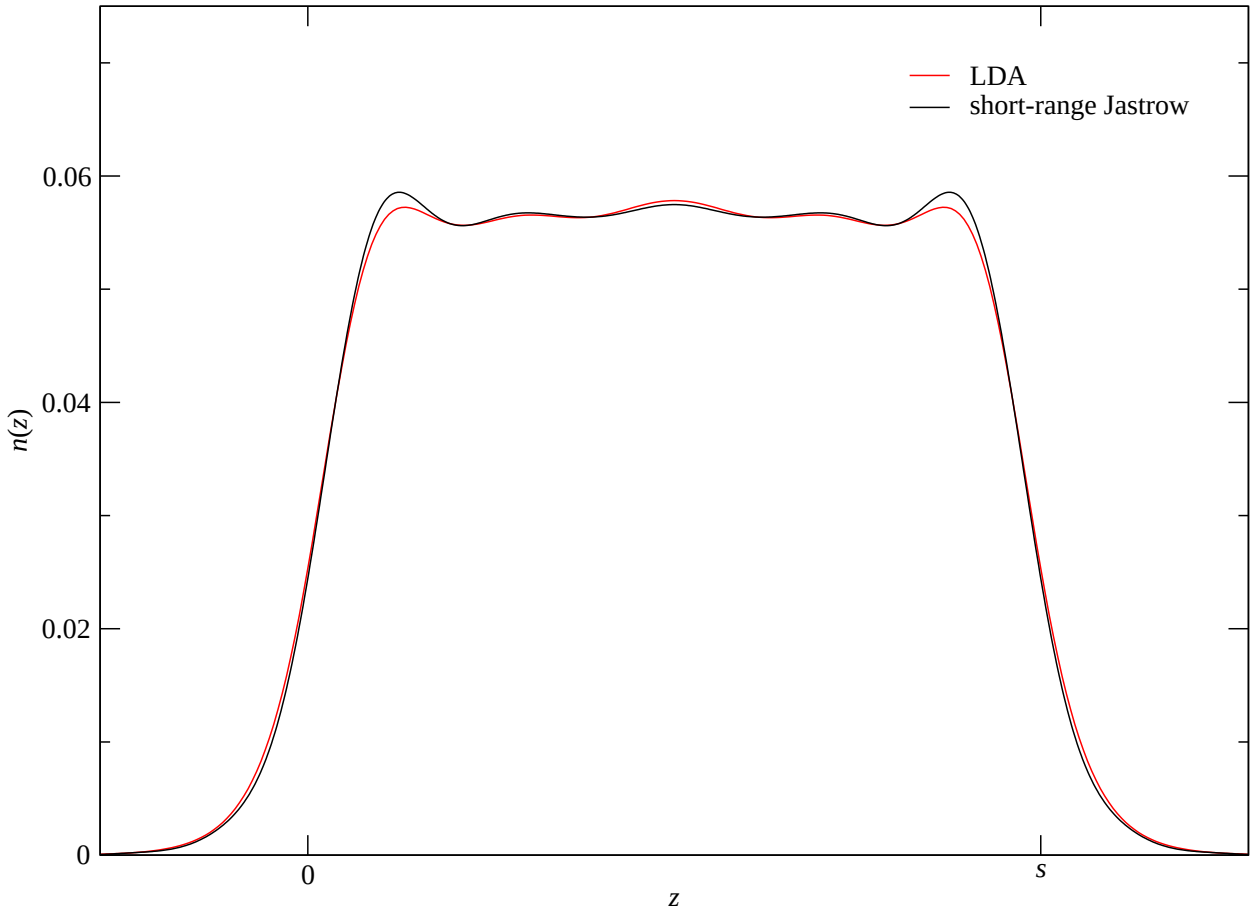
Long length scales cause optimisation problems.



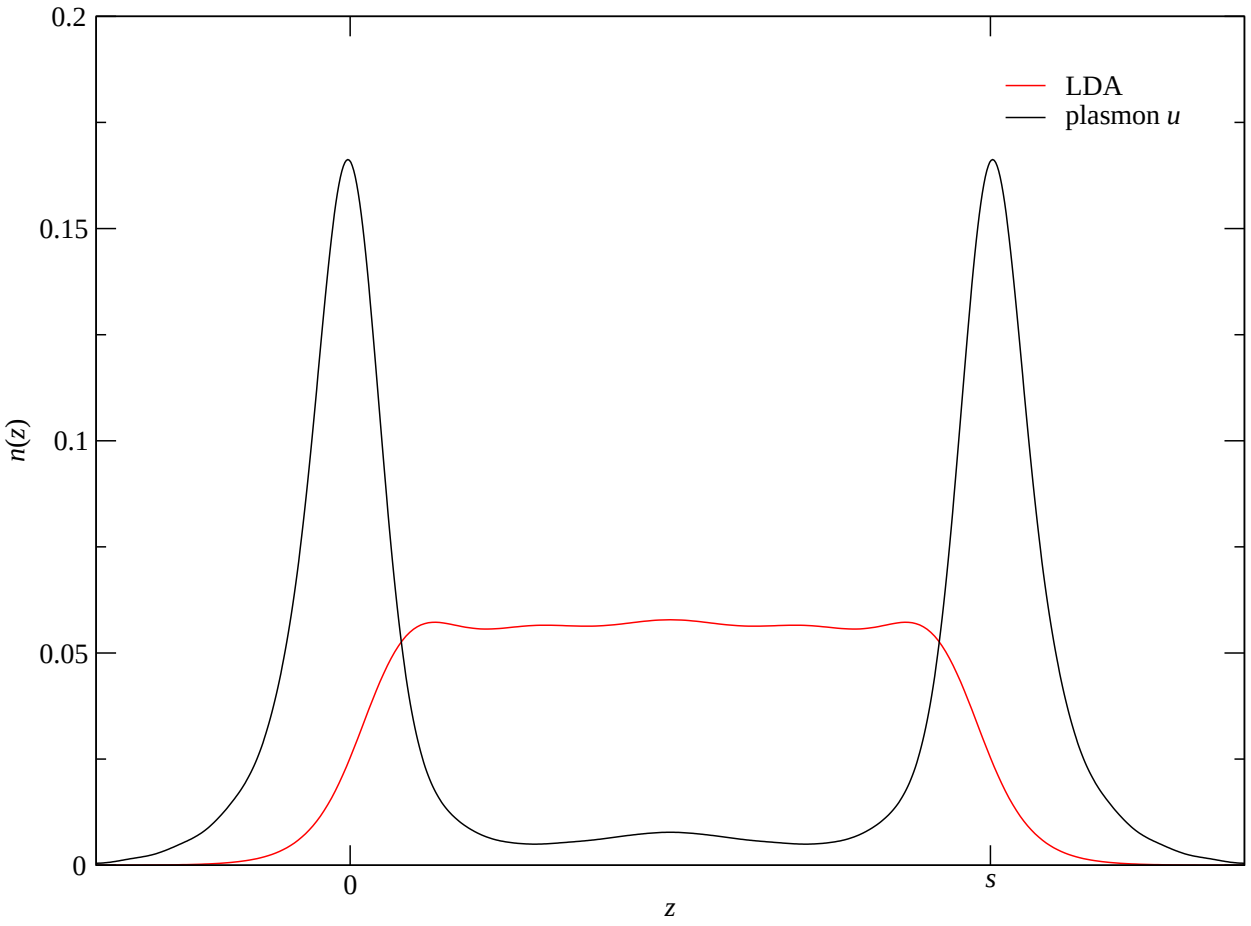
Electron densities in LDA and VMC with no Jastrow



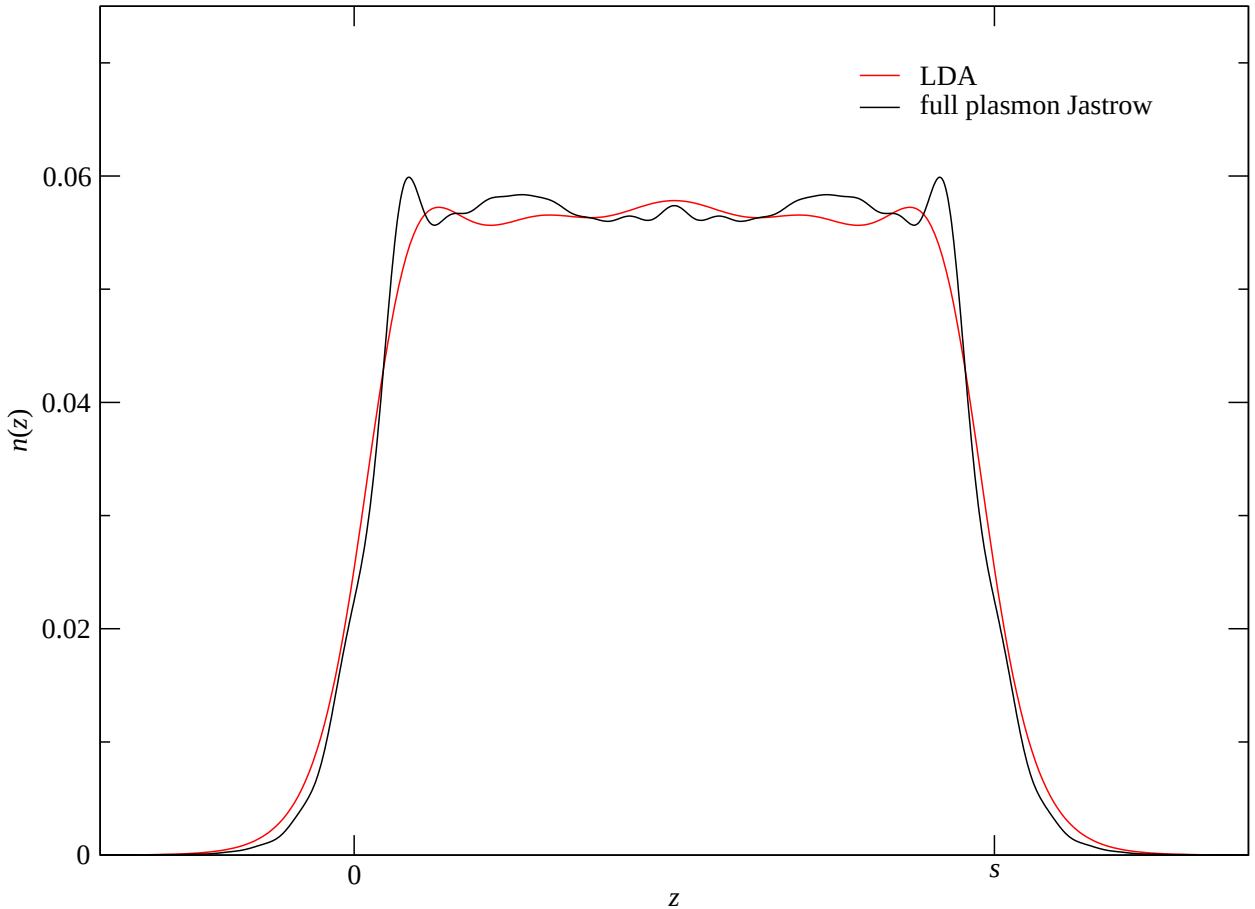
Electron densities in LDA and VMC with short-range u



Electron densities in LDA and VMC with full short-range Jastrow (short-range u plus corresponding χ)



Electron densities in LDA and VMC with long-range u



Electron densities in LDA and VMC with full plasmon Jastrow (long-range u plus corresponding χ)

Compromise Solution:

- LDA orbitals (with image-tail correction).
- Short-range u:

$$u(\mathbf{r}_i\sigma_i, \mathbf{r}_j\sigma_j) = \frac{\alpha}{2(1+\delta_{\sigma_i\sigma_j})} e^{-r_{ij}/\alpha - r_{ij}^2/L_c^2} .$$

- χ calculated analytically from u using Fahy prescription,

$$\chi(\mathbf{r}) = \frac{1}{2}\int \left[u(\mathbf{r}\uparrow, \mathbf{r}'\uparrow) + u(\mathbf{r}\uparrow, \mathbf{r}'\downarrow)\right] n(z')d^3r' ,$$

  and a model $n(z)$.
- Single parameter α optimised by hand.

Comparing Apples and Apples

Since

$$N = \frac{\text{Volume}}{\text{Volume per electron}} = \frac{L^2 s}{\frac{4}{3}\pi r_s^3} ,$$

the definition of σ,

$$N\epsilon_{\text{slab}} = N\epsilon_{\text{bulk}} + 2\sigma L^2 ,$$

may be rewritten as

$$\epsilon_{\text{slab}} = \epsilon_{\text{bulk}} + \frac{8\pi r_s^3 \sigma}{3s} .$$

Can obtain σ from dependence of ϵ_{slab} on thickness s.

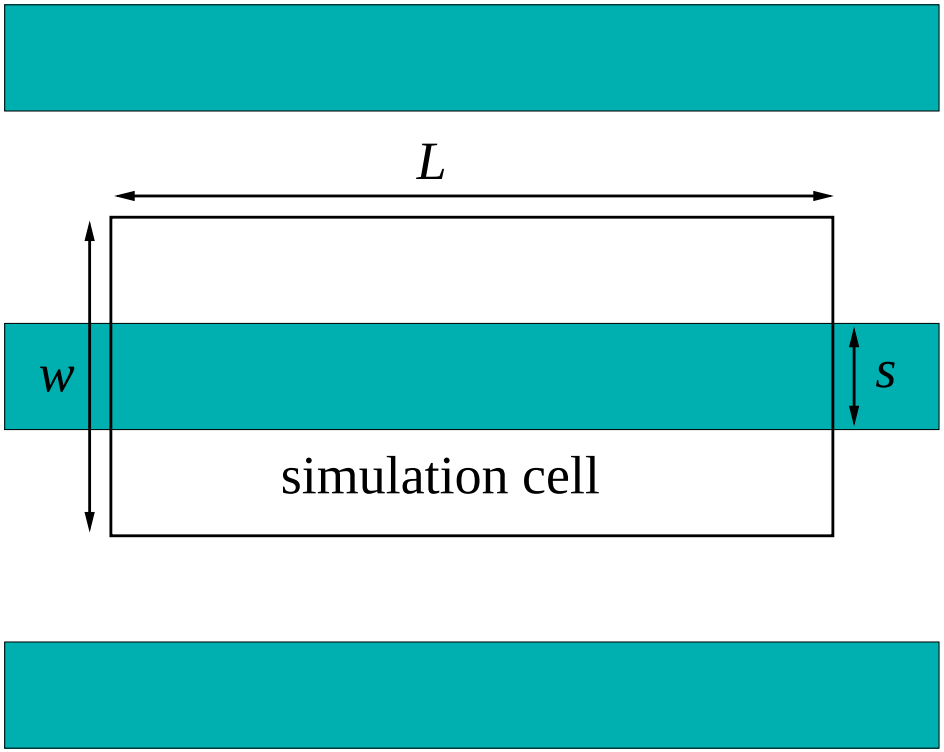
Ideally,

$$\epsilon_{\text{slab}} = \epsilon_{\text{bulk}} + \frac{8\pi r_s^3 \sigma}{3s},$$

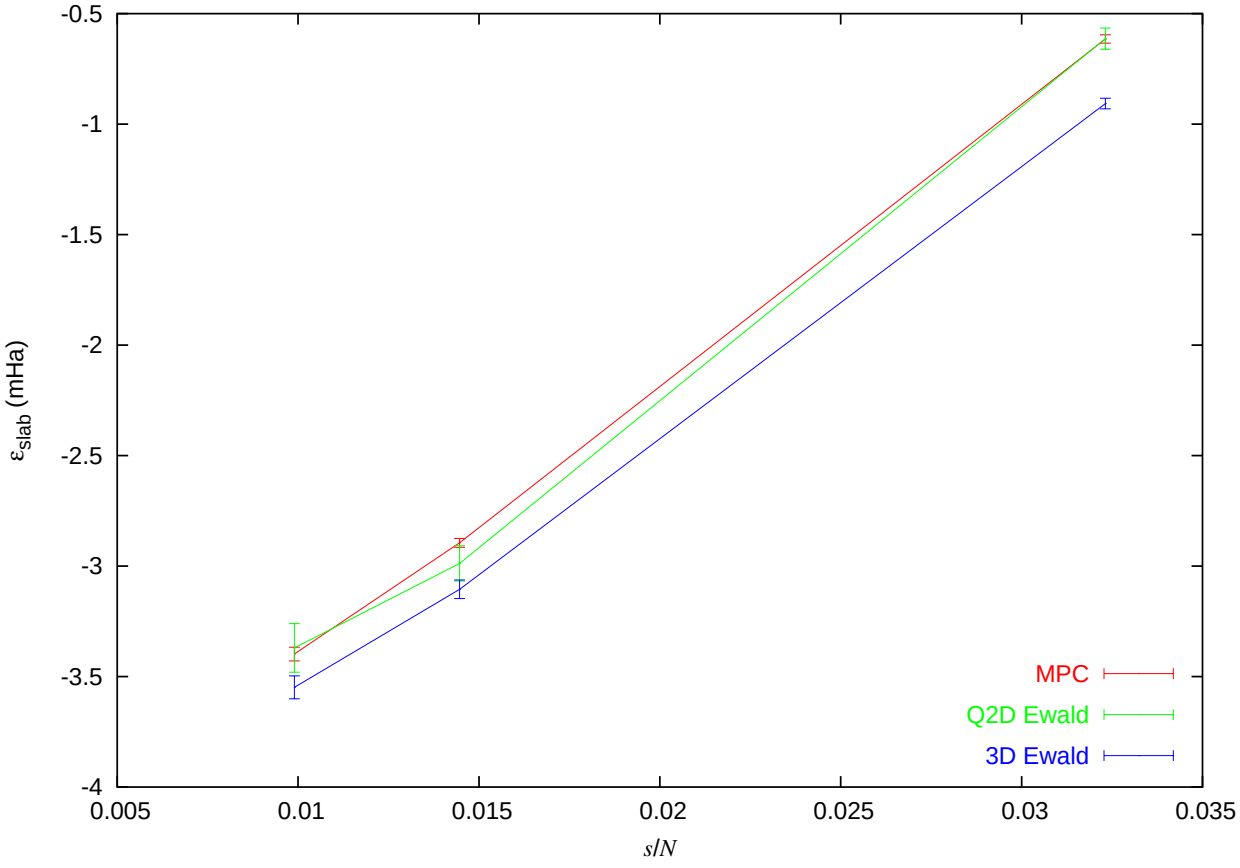
would be a function of s only. In practice, it also depends on L and w.

For accurate results, the L- and w-dependent contributions must be weak functions of s.

Finite-Size Errors



Ideally, ϵ_{slab} should depend on s only.

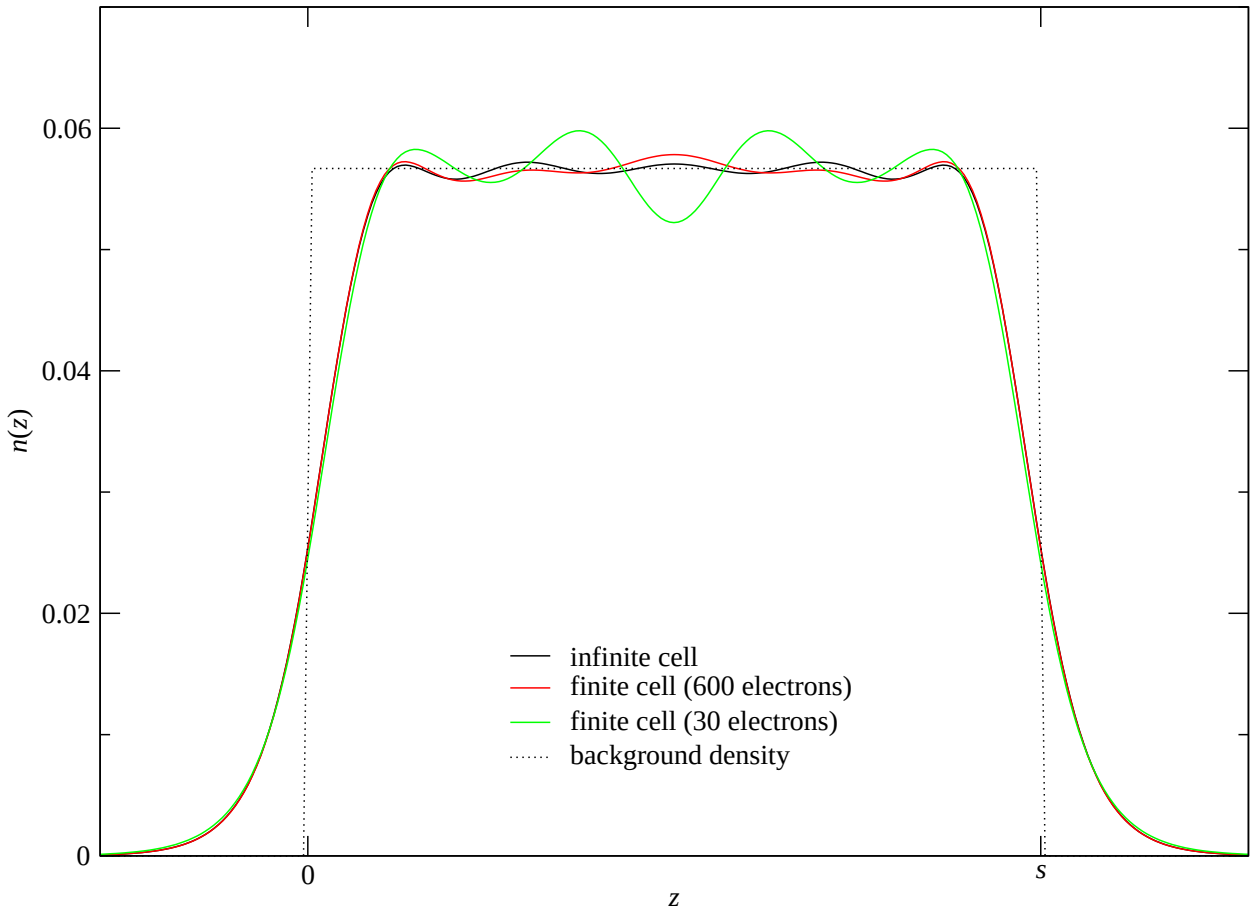


Energy per electron versus s/N when $s = 18.4851$

(s/N is proportional to $1/L^2$)

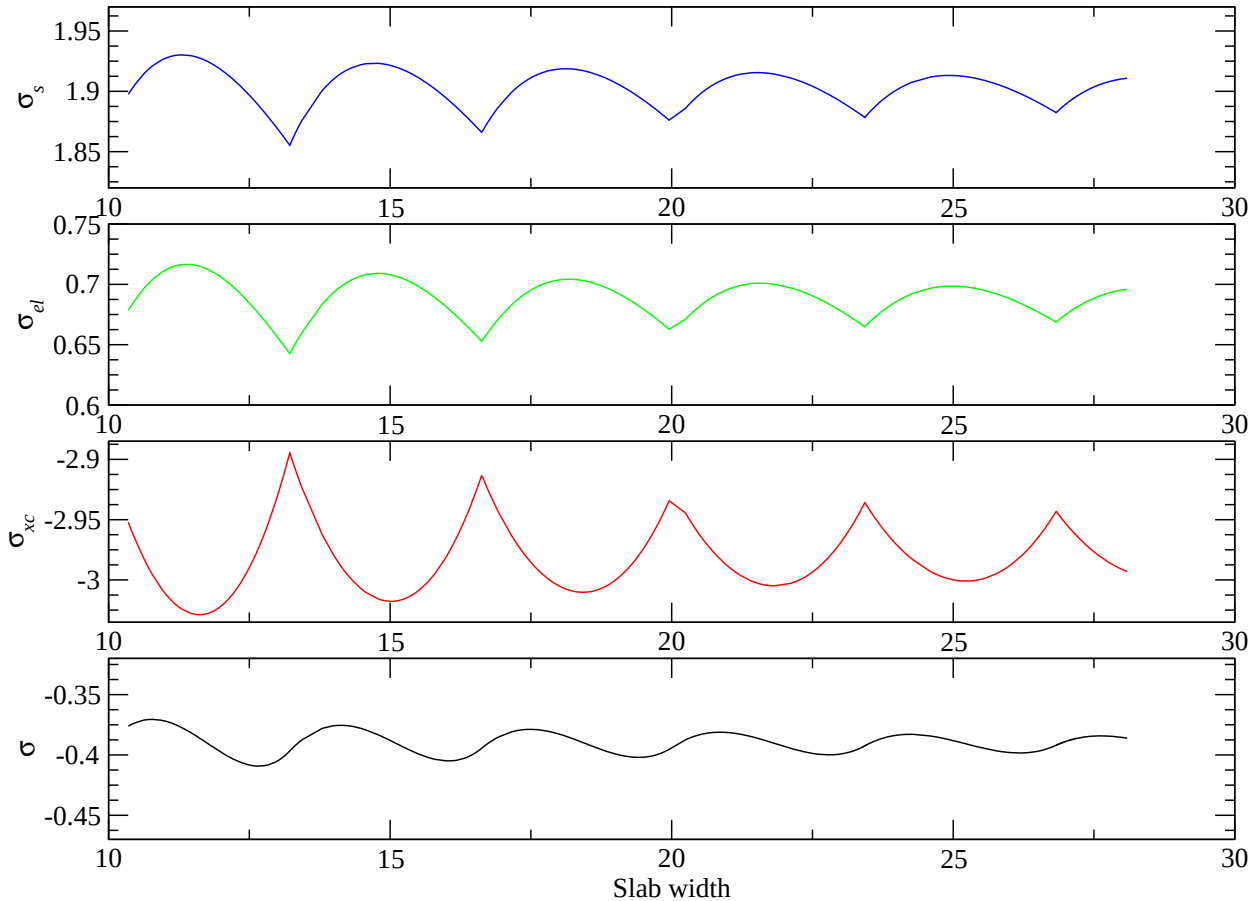
- VMC energy decreases as L^2 increases.
- Probable cause is the L_c cut-off in the Jastrow factor.
- Are we going to be able to reach 0.1 mHa accuracy?

In-Plane Finite-Size Errors



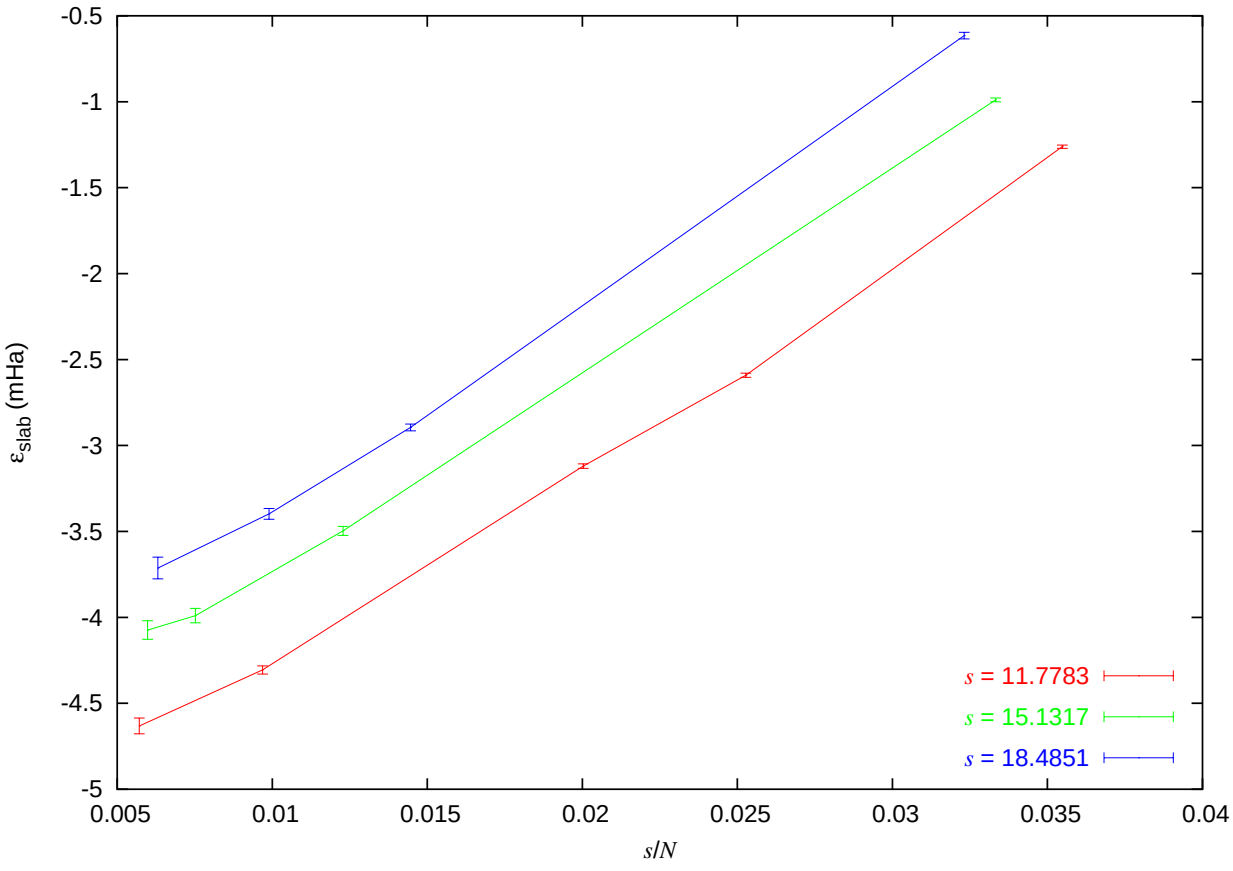
LDA electron density profiles for different values of L

Slab-Width Oscillations



LDA surface energy as a function of *s*

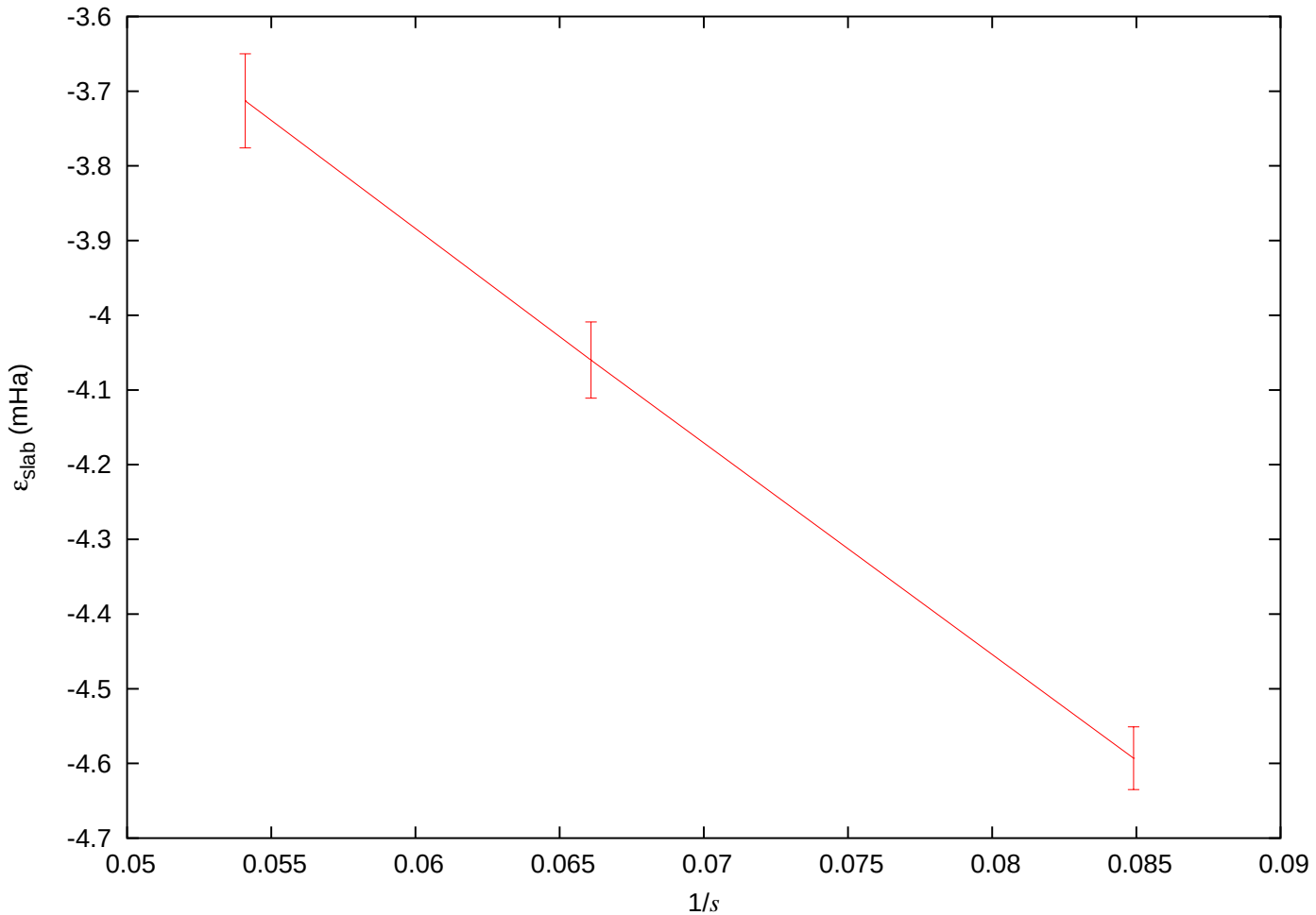
Results



Energy per electron versus s/N for three values of s

(s/N is proportional to $1/L^2$)

Linear Fit



The energy per electron (with $L^2 = 1150$) as a function of $1/s$

From

$$\epsilon_{\text{slab}} = \epsilon_{\text{bulk}} + \frac{8\pi r_s^3 \sigma}{3s}$$

and slope of straight line, find . . .

From

$$\epsilon_{\text{slab}} = \epsilon_{\text{bulk}} + \frac{8\pi r_s^3 \sigma}{3s}$$

and slope of straight line, find . . .

$$\sigma = -600 \pm 50 \text{ erg cm}^{-1} .$$

(Disappointingly?) consistent with other methods.

Summary

- Previous QMC calculations were inaccurate:
  - comparing apples with oranges.
  - poor treatment of finite-size errors.
- The surface energy is roughly as expected.
- More DMC results on the way.

(I hope . . .)