



*The Abdus Salam
International Centre for Theoretical Physics*



1929-8

**Advanced School on Quantum Monte Carlo Methods in Physics and
Chemistry**

21 January - 1 February, 2008

Solids 1.

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Diffusion Quantum Monte Carlo for Solids

ICTP Advanced School on Quantum Monte Carlo
Methods in Physics and Chemistry

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Wednesday 23rd January 2008

Outline

- 1 Introduction
- 2 Periodic Boundary Conditions
- 3 Trial Wave Functions for Periodic Systems
- 4 Finite-Size Errors
- 5 Summary

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Introduction

- DMC simulations for solids work almost exactly as for atoms and molecules.
- So why a special lecture on solids?
 - ▶ Periodic boundary conditions
 - ▶ Coulomb interactions in periodic systems
 - ▶ Construction of trial functions for periodic systems
 - ▶ Finite-size errors
 - ▶ Interesting applications

Large Many-Particle Systems

Tight-binding model

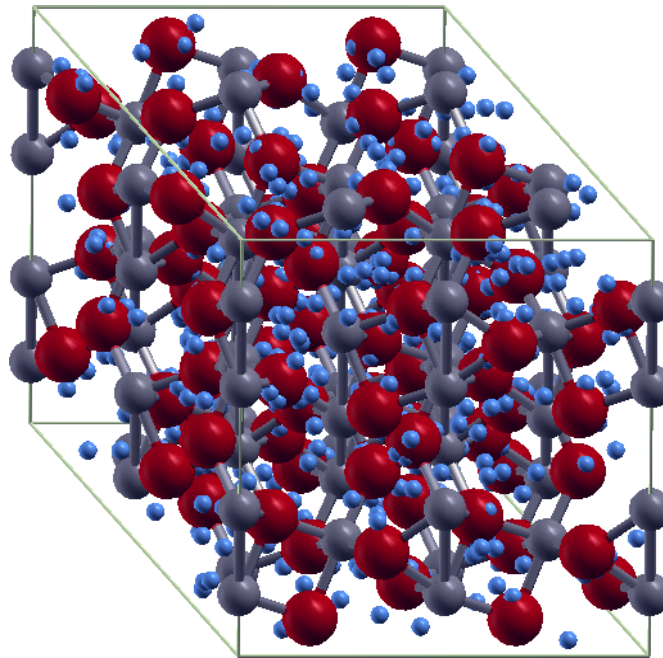
2 orbitals and 1 electron per site
N sites/electrons altogether

$$\text{Hilbert space dimension} = \frac{(2N)!}{N!N!} \approx e^{2N \ln 2}$$

using Stirling's approximation.

- The exponential increase in the number of relevant configurations makes quantum chemistry hard.
- But MC methods were invented for high-dimensional problems ...

QMC for Large Systems



- No serious competition except DFT.
- Lower standards expected than in molecules.
- Scales well with system size.

Scaling with System Size

$$\begin{aligned} \text{Work to move } N \text{ electrons } M \text{ times} &\propto M(N^2 + \epsilon N^3) \\ \text{Error } \Delta E \text{ in mean energy} &\propto \frac{\sigma_N}{\sqrt{M}} \end{aligned}$$

Hence, number of moves M required to achieve a given error ΔE scales as

$$M \propto \frac{\sigma_N^2}{(\Delta E)^2} \propto \frac{N}{(\Delta E)^2}$$

and total run time T_{run} scales as

$$T_{\text{run}} \propto \frac{N^3 + \epsilon N^4}{(\Delta E)^2}$$

(If you are only interested in achieving a given relative error $f = \Delta E/E$, then $\Delta E = fE \propto N$ and $T_{\text{run}} \propto N + \epsilon N^2$.)

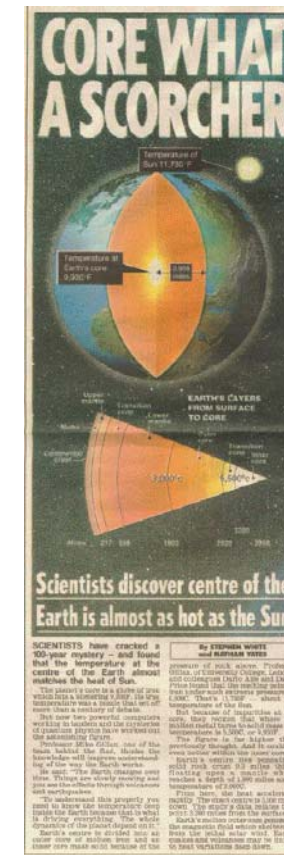
The Earth's Core

- What is it?
- How hot is it?

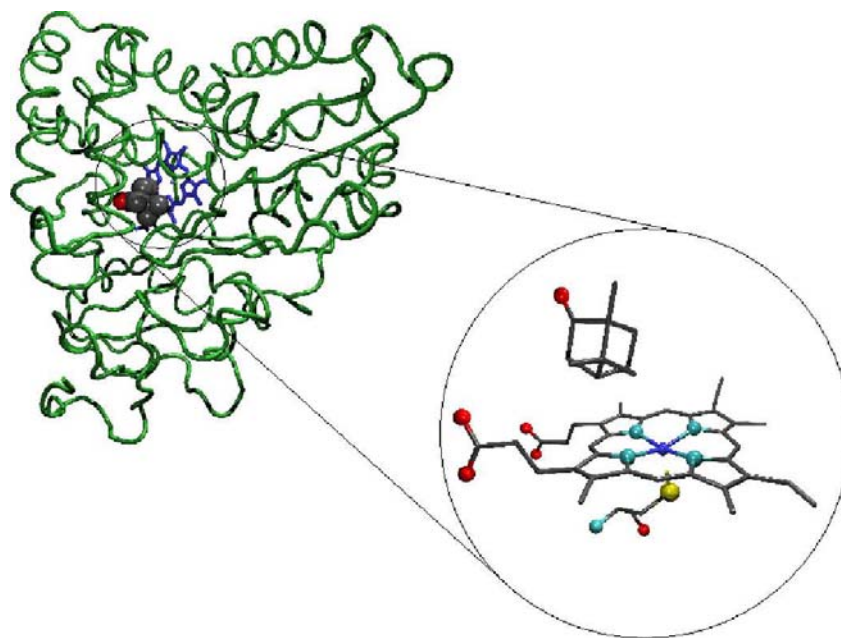
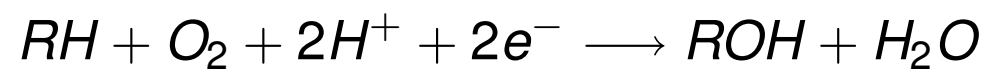
About 5500K at inner/outer core boundary

- How viscous it is?

Estimates span 12 orders of magnitude



Cytochrome P450 Family of Enzymes



Energy Scales I

Total electronic	$> 10^2 \text{ eV}$	$(> 10^3 \text{ eV})$
Chemical bond	few eV	
Chemical reaction	$< 10^{-1} \text{ eV}$	
Room temperature	$2.5 \times 10^{-2} \text{ eV}$	
High T_c superconductivity	$< 10^{-2} \text{ eV}$	

Energy Scales II

C atom

$$\begin{aligned}
 E_{\text{total}} &= -1075 \text{ eV} \\
 E_{\text{HF}} &= 99.6\% E_{\text{total}} = -1070.7 \text{ eV} \\
 E_{\text{corr}} &= 0.4\% E_{\text{total}} = -4.3 \text{ eV}
 \end{aligned}$$

C pseudo-atom

$$\begin{aligned}
 E_{\text{total}} &= -150 \text{ eV} \\
 E_{\text{HF}} &= 98.2\% E_{\text{total}} = -147.3 \text{ eV} \\
 E_{\text{corr}} &= 1.8\% E_{\text{total}} = -2.7 \text{ eV}
 \end{aligned}$$

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 - Periodic Boundary Conditions
 - The Ewald Interaction
- 3 Trial Wave Functions for Periodic Systems
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Periodic Boundary Conditions in One-Electron Theory

$$\hat{H} = -\frac{1}{2}\nabla^2 + V_{\text{eff}}(\mathbf{r})$$

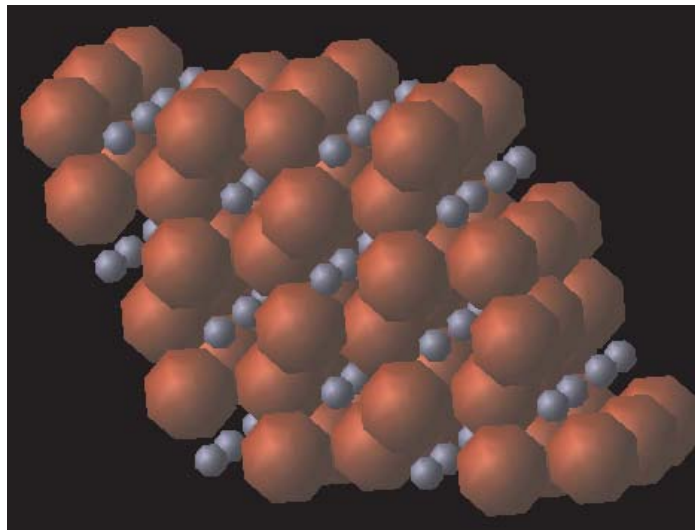
- Translating the electron by a primitive lattice vector leaves \hat{H} unchanged:

$$\hat{H}(\mathbf{r} + \mathbf{R}_p) = \hat{H}(\mathbf{r})$$

- No need to replace infinite system by a finite simulation cell.

Periodic Boundary Conditions in Many-Electron Theory

- Cannot even *write down* the Schrödinger equation for an infinite many-electron system (periodic or not).
- Instead, consider a **simulation cell** of $L \times L \times L$ unit cells



subject to periodic boundary conditions.

Periodic Hamiltonian

Insist that

$$\begin{aligned}\hat{H}(\mathbf{r}_1 + \mathbf{R}_p, \dots, \mathbf{r}_i + \mathbf{R}_p, \dots, \mathbf{r}_N + \mathbf{R}_p) &= \hat{H}(\mathbf{r}_1, \dots, \mathbf{r}_i, \dots, \mathbf{r}_N) \\ \hat{H}(\mathbf{r}_1, \dots, \mathbf{r}_i + \mathbf{R}_s, \dots, \mathbf{r}_N) &= \hat{H}(\mathbf{r}_1, \dots, \mathbf{r}_i, \dots, \mathbf{r}_N)\end{aligned}$$

- The first invariance (on translation of **all** electrons by a primitive lattice vector) seems "natural". Corresponds to conservation of centre-of-mass crystal momentum.
- The second invariance (on translation of any **one** electron by a simulation-cell lattice vector) follows if
 - ▶ We assume that the simulation cell is subject to strict periodic (toroidal) boundary conditions, or
 - ▶ The potential energy appearing in \hat{H} is the energy per cell of an infinite periodic lattice of identical copies of the simulation cell.

The Ewald Interaction

The cluster Hamiltonian

$$\hat{H} = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 + \frac{1}{2} \sum_{\alpha \neq \beta}^{N_q} \frac{q_\alpha q_\beta}{|\mathbf{r}_\alpha - \mathbf{r}_\beta|}$$

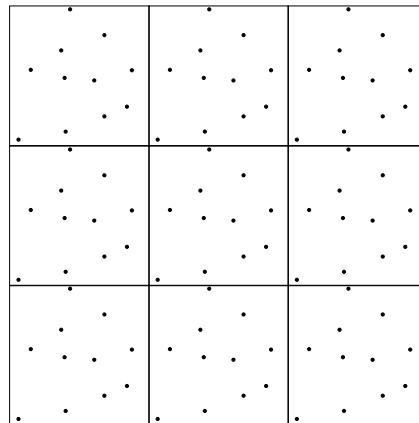
does not have the right symmetries. For example,

$$\hat{H}(\mathbf{r}_1, \dots, \mathbf{r}_i + \mathbf{R}_s, \dots, \mathbf{r}_N) \neq \hat{H}(\mathbf{r}_1, \dots, \mathbf{r}_i, \dots, \mathbf{r}_N)$$

To fix the problem, we replace $1/|\mathbf{r}_\alpha - \mathbf{r}_\beta|$ by the [Ewald interaction](#), $v_{\text{Ew}}(\mathbf{r}_\alpha - \mathbf{r}_\beta)$, which has the periodicity of the simulation cell by construction.

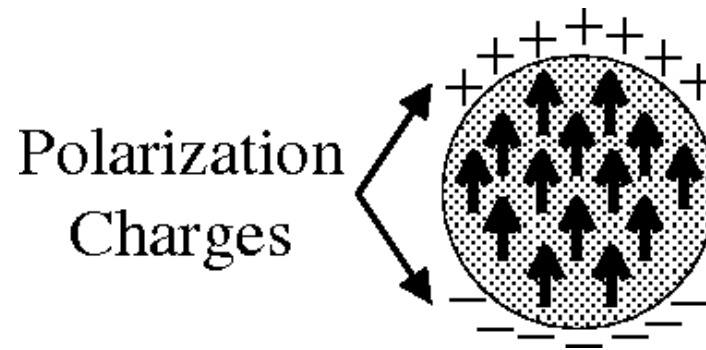
Coulomb Interactions in Periodic Systems

- Start with a simulation cell containing charges (electrons + ions) q_α at positions \mathbf{r}_α . The cell is neutral overall: $\sum_{\alpha=1}^{N_q} q_\alpha = 0$.
- Embed the simulation cell in a *finite* lattice of identical copies of itself.



- Calculate the Coulomb energy per cell as a function of lattice size and let the lattice size tend to infinity to get a result for the solid.

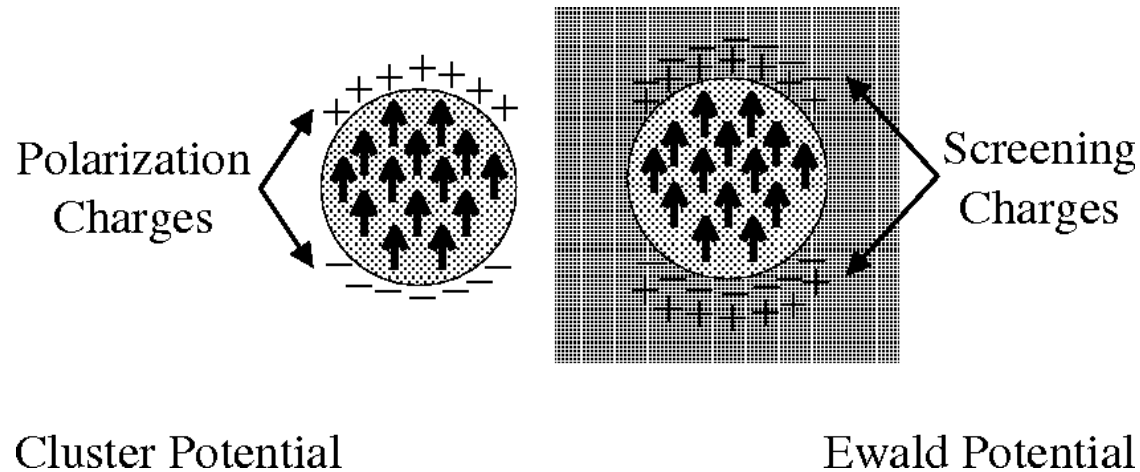
But which answer do you want?



Because of the long range of the Coulomb interaction, result depends on cluster shape even in the limit as the cluster size $\rightarrow \infty$!

The Periodic Limit

To obtain a periodic result, we adopt “tin-foil” boundary conditions,



The Coulomb potential deep within the cluster is then periodic and takes the form

$$\phi(\mathbf{r}) = \sum_{\alpha=1}^{N_q} q_{\alpha} v_{\text{Ew}}(\mathbf{r} - \mathbf{r}_{\alpha})$$

Reciprocal-Space Representation

To within an (irrelevant) arbitrary constant, the Ewald potential due to a point charge $\delta(\mathbf{r})$, a neutralising uniform background, and all its images, may also be obtained by solving Poisson's equation

$$\nabla^2 v_{\text{Ew}}(\mathbf{r}) = -4\pi \left(\delta(\mathbf{r}) - \frac{1}{\Omega_s} \right) ,$$

within one simulation cell subject to periodic boundary conditions.

Evaluating the reciprocal lattice vector Fourier components gives:

$$\begin{aligned} \int_{\Omega_s} e^{-i\mathbf{G}_s \cdot \mathbf{r}} \nabla^2 v_{\text{Ew}}(\mathbf{r}) d\mathbf{r} &= -4\pi \int_{\Omega_s} e^{-i\mathbf{G}_s \cdot \mathbf{r}} \left(\delta(\mathbf{r}) - \frac{1}{\Omega_s} \right) d\mathbf{r} \\ -G_s^2 \tilde{v}_{\text{Ew}}(\mathbf{G}_s) &= \begin{cases} -4\pi & \mathbf{G}_s \neq 0 , \\ 0 & \mathbf{G}_s = 0 . \end{cases} \end{aligned}$$

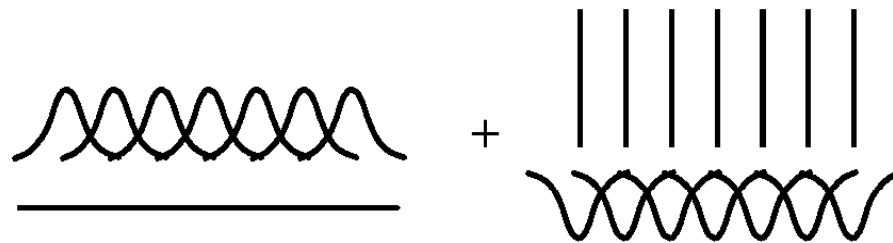
Although the Fourier components $\tilde{v}_{\text{Ew}}(\mathbf{G}_s)$ are well defined, the corresponding Fourier series

$$v_{\text{Ew}}(\mathbf{r}) = \frac{1}{\Omega_s} \sum_{\mathbf{G}_s \neq 0} \tilde{v}_{\text{Ew}}(\mathbf{G}_s) e^{i\mathbf{G}_s \cdot \mathbf{r}} = \frac{1}{\Omega_s} \sum_{\mathbf{G}_s \neq 0} \frac{4\pi}{G_s^2} e^{i\mathbf{G}_s \cdot \mathbf{r}}$$

does not converge absolutely and is useless in practice.

The Ewald Formula

A practical method for evaluating the Ewald interaction is obtained by splitting up the charges as follows:



- The periodic potential corresponding to the first, smooth, distribution may be expressed as a rapidly convergent Fourier series.
- The short-range potential from a delta function plus its neutralising Gaussian may be evaluated in real space.

The resulting Ewald formula is

$$v_{\text{Ew}}(\mathbf{r}) = \frac{1}{\Omega_s} \sum_{\mathbf{G}_s (\neq \mathbf{0})} \frac{4\pi \exp\left(-\frac{\kappa^2 G_s^2}{2} + i\mathbf{G}_s \cdot \mathbf{r}\right)}{G_s^2} - \frac{2\pi\kappa^2}{\Omega_s} + \sum_{\mathbf{R}_s} \frac{\text{erfc}\left(\frac{|\mathbf{r}-\mathbf{R}_s|}{\sqrt{2}\kappa}\right)}{|\mathbf{r}-\mathbf{R}_s|}$$

where κ is the width of the auxiliary Gaussian charges.

The Coulomb Energy

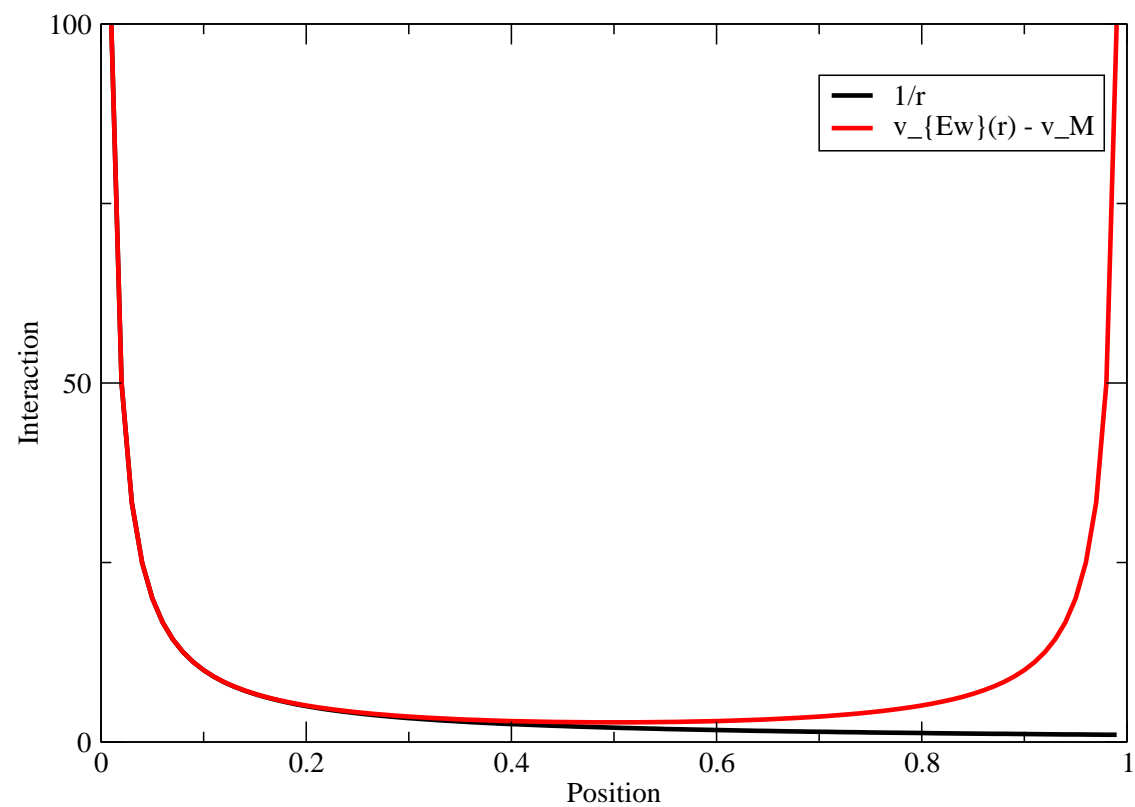
The total Coulomb energy per simulation cell takes the form

$$E_{\text{Coulomb}} = \frac{1}{2} \sum_{\alpha \neq \beta}^{N_q} q_{\alpha} q_{\beta} v_{\text{Ew}}(\mathbf{r}_{\alpha} - \mathbf{r}_{\beta}) + \frac{1}{2} \sum_{\alpha}^{N_q} q_{\alpha}^2 v_M$$

where

$$v_M = \lim_{|\mathbf{r}| \rightarrow 0} \left(v_{\text{Ew}}(\mathbf{r}) - \frac{1}{r} \right)$$

is called the **Madelung potential**. It is the potential at a unit point charge due to the cancelling background and all the images of that charge.

Comparison of Ewald and $1/r$ Interactions

"Dodgy" Fourier Representations

$$v_{\text{Ew}}(\mathbf{r}) = \frac{1}{\Omega_s} \sum_{\mathbf{G}_s(\neq 0)} \frac{4\pi \exp\left(-\frac{\kappa^2 G_s^2}{2} + i\mathbf{G}_s \cdot \mathbf{r}\right)}{G_s^2} - \frac{2\pi\kappa^2}{\Omega_s} + \sum_{\mathbf{R}_s} \frac{\text{erfc}\left(\frac{|\mathbf{r}-\mathbf{R}_s|}{\sqrt{2}\kappa}\right)}{|\mathbf{r}-\mathbf{R}_s|}$$

Although numerically efficient, the Ewald formula is analytically awkward.

If we choose $\epsilon = \kappa/\sqrt{2}$ very small and assume that $|\mathbf{r} - \mathbf{R}_s| \gg \epsilon$, then

$$v_{\text{Ew}}(\mathbf{r}) \approx \frac{1}{\Omega_s} \sum_{\mathbf{G}_s(\neq 0)} \frac{4\pi e^{-\epsilon^2 G_s^2} e^{i\mathbf{G}_s \cdot \mathbf{r}}}{G_s^2}.$$

This convenient Fourier representation is far wrong in tiny regions of radius ϵ about each lattice point, but very accurate elsewhere. Similarly

$$v_M = \lim_{r \rightarrow 0} \left(v_{\text{Ew}}(\mathbf{r}) - \frac{1}{r} \right) \approx \frac{1}{\Omega_s} \sum_{\mathbf{G}_s(\neq 0)} \frac{4\pi e^{-\epsilon^2 G_s^2}}{G_s^2} - \int_{\text{all space}} \frac{4\pi e^{-\epsilon^2 G^2}}{G^2} \frac{d\mathbf{G}}{(2\pi)^3}$$

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Bloch's Theorem in One-Electron Theory

- Hamiltonian is periodic: $\hat{H}(\mathbf{r} + \mathbf{R}_p) = \hat{H}(\mathbf{r})$
- Bloch's theorem enables you to study the infinite system by solving the Schrödinger equation within a *single* primitive cell subject to twisted (Bloch) boundary conditions:

$$\psi(\mathbf{r} + \mathbf{R}_p) = e^{i\mathbf{k} \cdot \mathbf{R}_p} \psi(\mathbf{r}), \quad \mathbf{k} \in \text{primitive BZ},$$

and integrating over twists (the BZ).

- Any eigenfunction can be written in the form

$$\psi(\mathbf{r}) = e^{i\mathbf{k} \cdot \mathbf{r}} u(\mathbf{r}) \quad \text{where} \quad u(\mathbf{r} + \mathbf{R}_p) = u(\mathbf{r})$$

Bloch's Theorem(s) in Many-Electron Theory

In many-electron theory, we have two translational symmetries

$$\begin{aligned}\hat{H}(\mathbf{r}_1 + \mathbf{R}_p, \dots, \mathbf{r}_i + \mathbf{R}_p, \dots, \mathbf{r}_N + \mathbf{R}_p) &= \hat{H}(\mathbf{r}_1, \dots, \mathbf{r}_i, \dots, \mathbf{r}_N) \\ \hat{H}(\mathbf{r}_1, \dots, \mathbf{r}_i + \mathbf{R}_s, \dots, \mathbf{r}_N) &= \hat{H}(\mathbf{r}_1, \dots, \mathbf{r}_i, \dots, \mathbf{r}_N)\end{aligned}$$

These lead to

Two different versions of Bloch's theorem

The Primitive-Cell Bloch Theorem

$$\Psi(\mathbf{r}_1 + \mathbf{R}_p, \dots, \mathbf{r}_i + \mathbf{R}_p, \dots, \mathbf{r}_N + \mathbf{R}_p) = e^{i\mathbf{k}_p \cdot \mathbf{R}_p} \Psi(\mathbf{r}_1, \dots, \mathbf{r}_i, \dots, \mathbf{r}_N)$$

- \mathbf{k}_p may be reduced into the primitive BZ.
- Not very useful because it only fixes the boundary conditions in 3 of the $3N$ configuration-space directions.

The Simulation-Cell Bloch Theorem

$$\Psi(\mathbf{r}_1, \dots, \mathbf{r}_i + \mathbf{R}_s, \dots, \mathbf{r}_N) = e^{i\mathbf{k}_s \cdot \mathbf{R}_s} \Psi(\mathbf{r}_1, \dots, \mathbf{r}_i, \dots, \mathbf{r}_N)$$

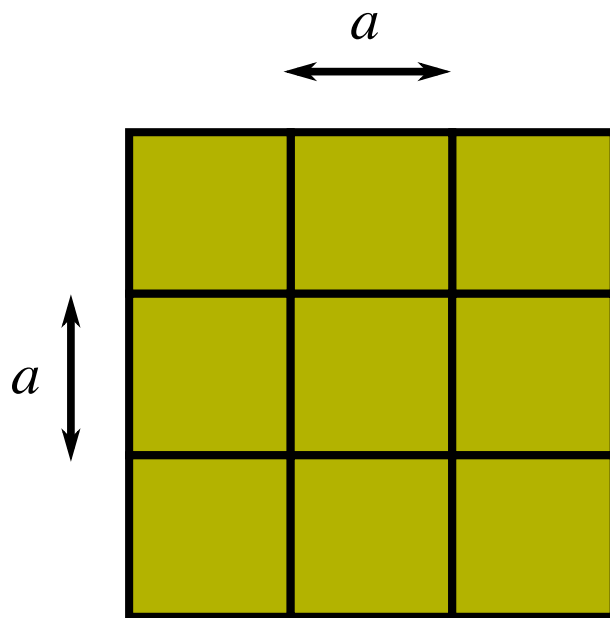
- \mathbf{k}_s may be reduced into the simulation-cell BZ.
- Antisymmetry implies that all electrons have the same \mathbf{k}_s .
- If you regard the simulation cell as a torus

$$\mathbf{r}_i + \mathbf{R}_s \equiv \mathbf{r}_i$$

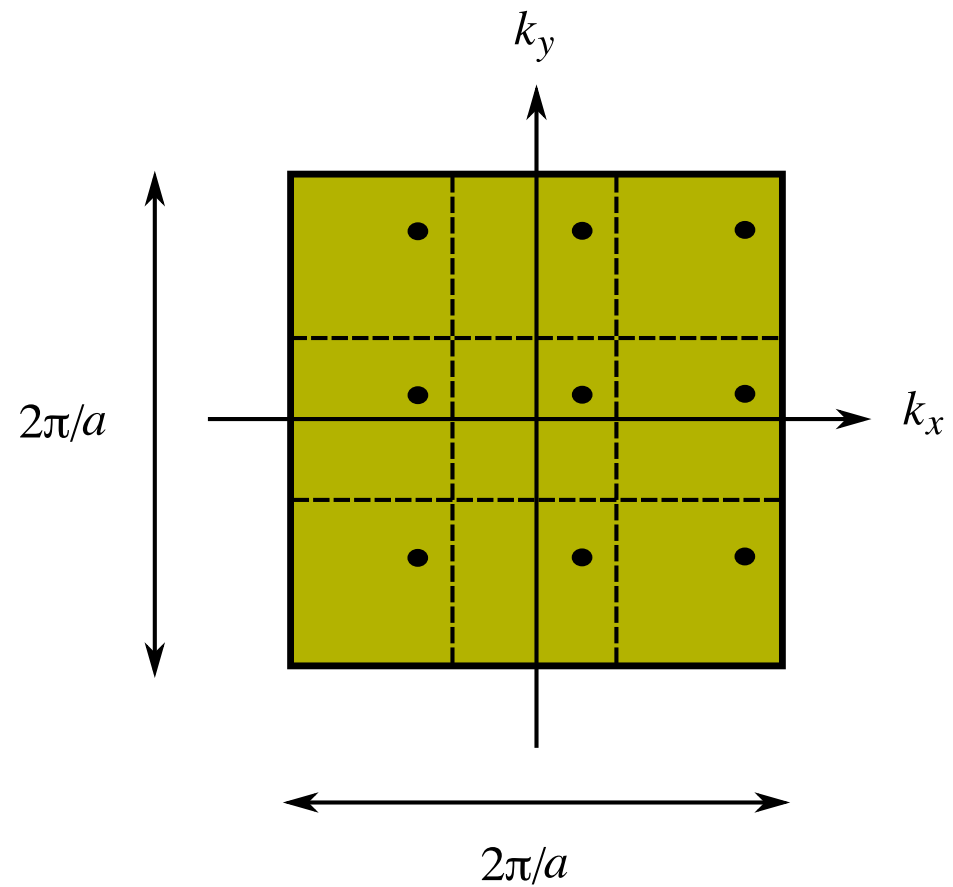
then \mathbf{k}_s must be zero (and $\mathbf{k}_p \in \{\mathbf{G}_s\}$).

- Fixes the boundary conditions in all 3N configuration-space directions.

3×3 simulation cell



Primitive and simulation-cell
Brillouin zones



Bloch's Theorem and Slater Determinants

Any point \mathbf{k}_s in the simulation-cell BZ of an $L \times L$ simulation cell lies on an $L \times L$ grid of points of the form $\mathbf{k} = \mathbf{k}_s + \mathbf{G}_s$ in the primitive BZ. All grid points are equivalent modulo \mathbf{G}_s .

Consider a Slater determinant constructed using any set of N one-electron orbitals with Bloch wavevectors \mathbf{k} on the grid:

$$D_{\mathbf{k}_s} = \begin{vmatrix} \psi_{\mathbf{k}_1}(\mathbf{r}_1) & \psi_{\mathbf{k}_1}(\mathbf{r}_2) & \cdot & \cdot & \psi_{\mathbf{k}_1}(\mathbf{r}_N) \\ \psi_{\mathbf{k}_2}(\mathbf{r}_1) & \psi_{\mathbf{k}_2}(\mathbf{r}_2) & \cdot & \cdot & \psi_{\mathbf{k}_2}(\mathbf{r}_N) \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \psi_{\mathbf{k}_N}(\mathbf{r}_1) & \psi_{\mathbf{k}_N}(\mathbf{r}_2) & \cdot & \cdot & \psi_{\mathbf{k}_N}(\mathbf{r}_N) \end{vmatrix}$$

- Since, for any $\mathbf{k}_i = \mathbf{k}_s + \mathbf{G}_s$ on the grid,

$$\psi_{\mathbf{k}_i}(\mathbf{r} + \mathbf{R}_s) = e^{i(\mathbf{k}_s + \mathbf{G}_s) \cdot \mathbf{R}_s} \psi_{\mathbf{k}_i}(\mathbf{r}) = e^{i\mathbf{k}_s \cdot \mathbf{R}_s} \psi_{\mathbf{k}_i}(\mathbf{r})$$

it is easy to see that $D_{\mathbf{k}_s}$ satisfies the simulation-cell Bloch theorem,

$$D_{\mathbf{k}_s}(\mathbf{r}_1, \dots, \mathbf{r}_i + \mathbf{R}_s, \dots, \mathbf{r}_N) = e^{i\mathbf{k}_s \cdot \mathbf{R}_s} D_{\mathbf{k}_s}(\mathbf{r}_1, \dots, \mathbf{r}_i, \dots, \mathbf{r}_N)$$

- Moreover, since

$$D(\mathbf{r}_1 + \mathbf{R}_p, \dots, \mathbf{r}_N + \mathbf{R}_p) = e^{i(\sum_i \mathbf{k}_i) \cdot \mathbf{R}_p} D(\mathbf{r}_1, \dots, \mathbf{r}_N)$$

it also satisfies the primitive-cell Bloch theorem with

$$\mathbf{k}_p = \sum_i \mathbf{k}_i \quad (\text{modulo } \mathbf{G}_p)$$

Procedure for Constructing Bloch Slater Determinants

- 1 Choose grid offset $\mathbf{k}_s \in$ simulation-cell BZ.
- 2 Construct the grid of $L \times L \times L$ \mathbf{k} points of form $\mathbf{k}_s + \mathbf{G}_s$ in the primitive BZ.
- 3 Solve non-interacting (DFT or HF) problem to obtain the one-electron orbitals at every point on grid.
- 4 Occupy the N lowest orbitals in the set.
 - If $\mathbf{k}_s = \mathbf{0}$ or $\mathbf{k}_s = \mathbf{G}_s/2$ and \hat{H} is real, the one-electron orbitals can be chosen to be real.
 - For other values of \mathbf{k}_s , need complex wavefunctions and hence fixed-phase DMC.

Orbital Representation

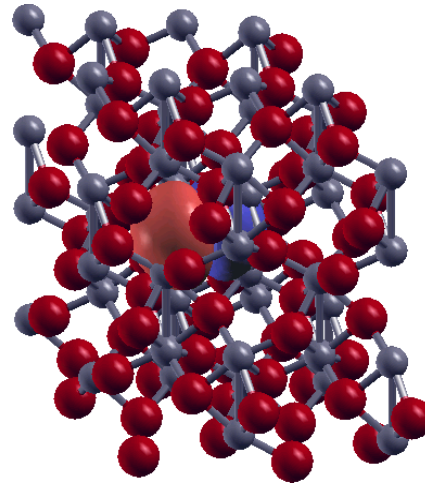
- The most time-consuming part of calculation is repeated evaluation of $\psi_{\mathbf{k}_i}(\mathbf{r}_j)$.
 - ▶ For one move of all N electrons, need to evaluate N^2 orbitals.
- If each orbital is expanded in plane waves
 - ▶
$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}_p} c_{\mathbf{k}}(\mathbf{G}_p) e^{i(\mathbf{k} + \mathbf{G}_p) \cdot \mathbf{r}}$$

this is very time consuming, especially when the primitive unit cell is large.

- Better to use a basis of localised functions
 - ▶ Blips (splines)
 - ▶ Gaussians
 - ▶ ...

Wannier Functions

In insulators, one can find exponentially localised linear combinations of the occupied one-electron orbitals.



But taking linear combinations of rows has no effect on the value of a determinant.

When D is expressed in terms of Wannier functions,
many elements are nearly zero

(Very useful at LLNL!)

Bloch Slater-Jastrow Functions

Multiply a Bloch Slater Determinant by a Jastrow factor:

$$\psi = e^{J(\{\mathbf{r}_i\}, \{\mathbf{r}_l\})} D$$

where

$$J = \sum_{i>j} u(r_{ij}) + \sum_i \sum_l \chi_l(r_{il}) + \sum_l \sum_{i>j} f_l(r_{il}, r_{jl}, r_{ij}) \\ + \sum_{i>j} p(r_{ij}) + \sum_i q(r_i)$$

- u , χ_l , f_l are polynomials chosen to approach zero smoothly at cut-off distances (which \leq the simulation-cell Wigner-Seitz radius).
- Cusp conditions satisfied.
- p and q are plane wave terms useful in the "corners" of the WS cell.

- Optimize parameters (in our case in Jastrow factor only) using energy or variance minimisation.
- Multiple determinants are rarely used in solids.
 - ▶ Which (of the millions) to choose?
 - ▶ Some evidence that they don't help much.
 - ▶ Would certainly be necessary, e.g., to describe localised states on defects.

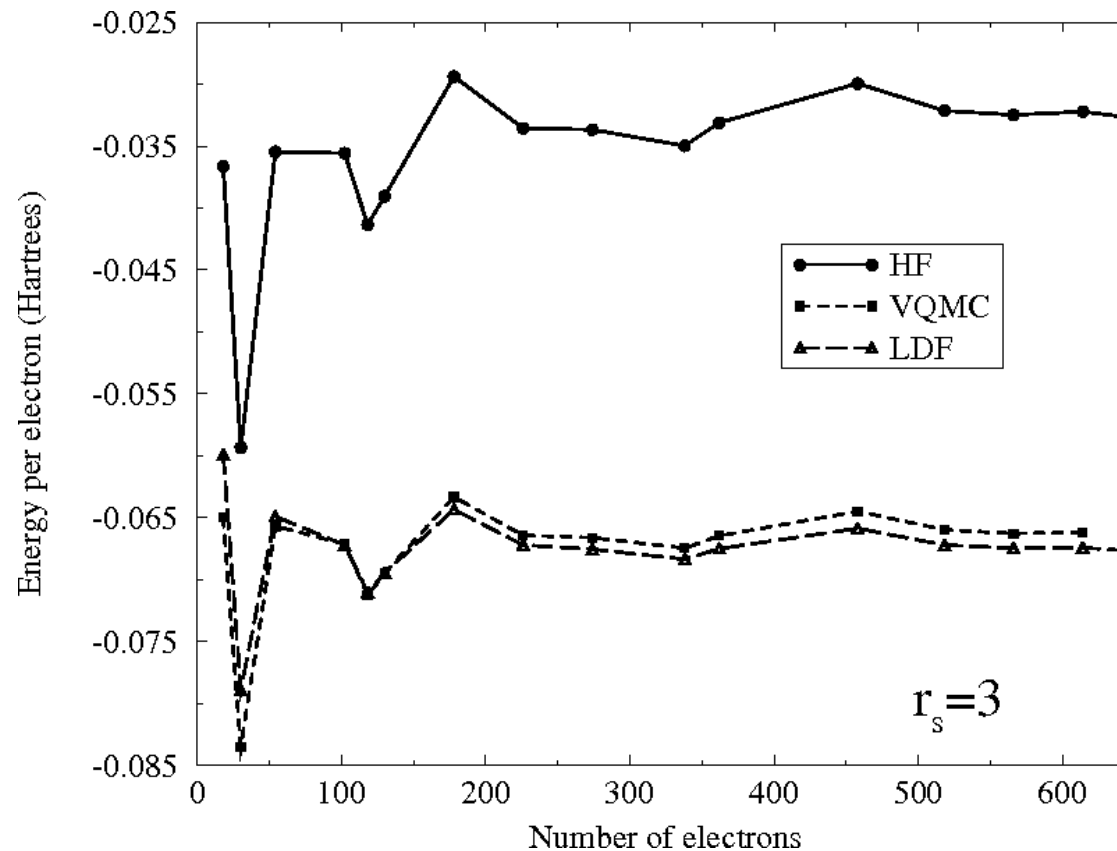
Off you go!

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 - Introduction to Finite-Size Errors
 - Independent-Particle Errors
 - Coulomb Errors
 - Kinetic Energy Errors
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Introduction to Finite-Size Errors

The small simulation cell size leads to finite-size errors.



Finite-size errors (and pseudopotentials ...) are the *main* problem in solid-state simulations. Normally **much** larger than fixed-node errors.

To help understand them, it helps to consider the constituent terms in the expression for the total energy.

$$\begin{aligned}
 E &= \langle \Psi | \hat{T} + \sum_i V_{\text{nuc}}(\mathbf{r}_i) + \frac{1}{2} \sum_{i \neq j} v_{\text{Ew}}(\mathbf{r}_{ij}) + \frac{1}{2} N v_M | \Psi \rangle + E_{nn} \\
 &= T + \int_{\Omega_s} V_{\text{nuc}}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} + E_{\text{ee}} + E_{\text{nn}}
 \end{aligned}$$

$$E = T + \int_{\Omega_s} V_{\text{nuc}}(\mathbf{r})n(\mathbf{r})d\mathbf{r} + E_{\text{ee}} + E_{\text{nn}}$$

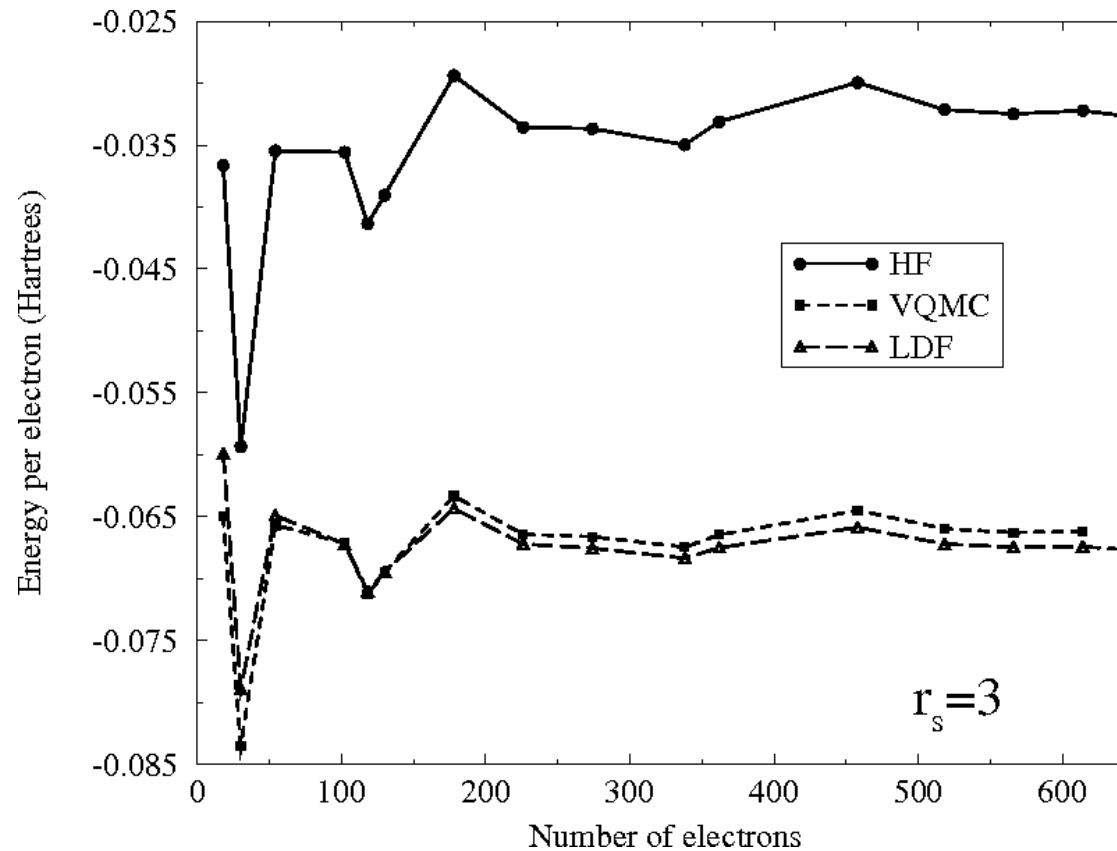
- E_{nn}/N and $V_{\text{nuc}}(\mathbf{r})$ are independent of simulation-cell size.
- $n(\mathbf{r})$ has the periodicity of the primitive cell and so (normally) settles down quickly as the simulation-cell size increases.
- The main finite-size errors are in the T and E_{ee} terms.
- If we write

$$E_{\text{ee}} = E_{\text{Hartree}} + E_{\text{xc}}$$

we find that the errors in E_{ee} are actually in the exchange-correlation energy.

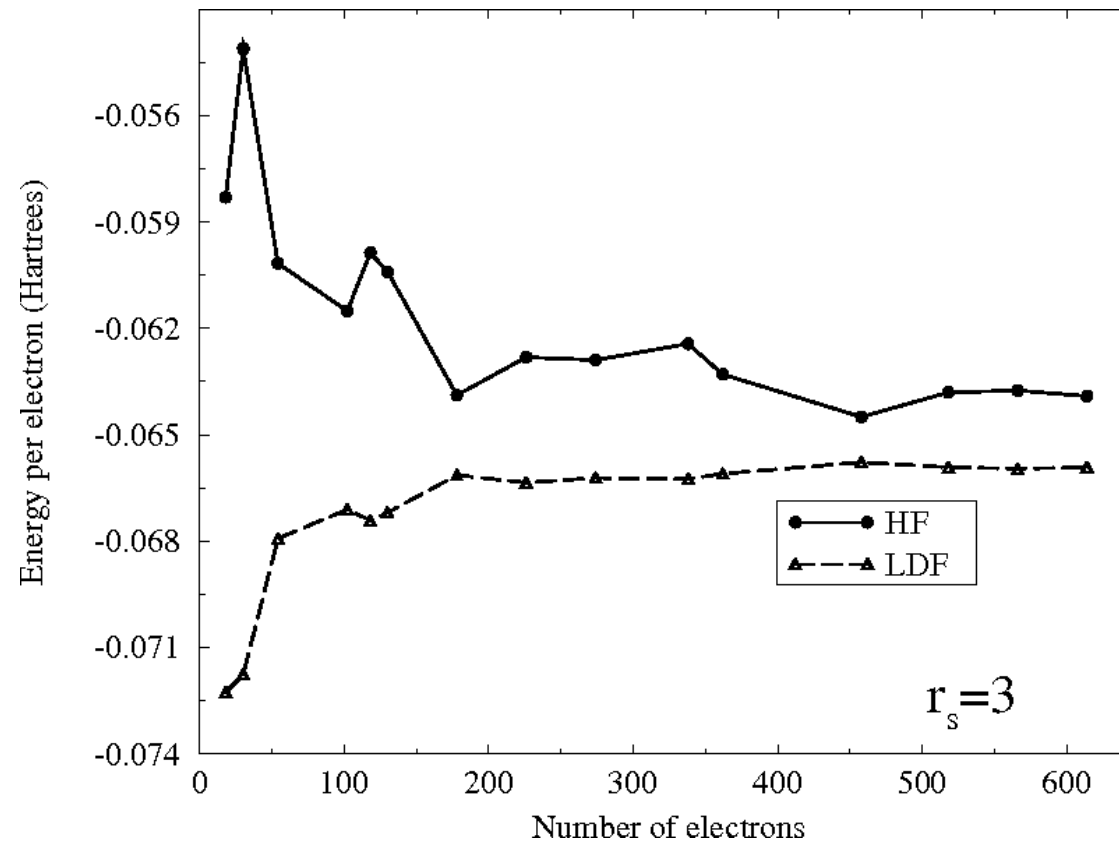
Independent-Particle Errors

Most of the finite-size error is also present in independent-particle (DFT/HF) calculations:



LDA Finite-Size Corrections

... so apply LDA (or HF) corrections:

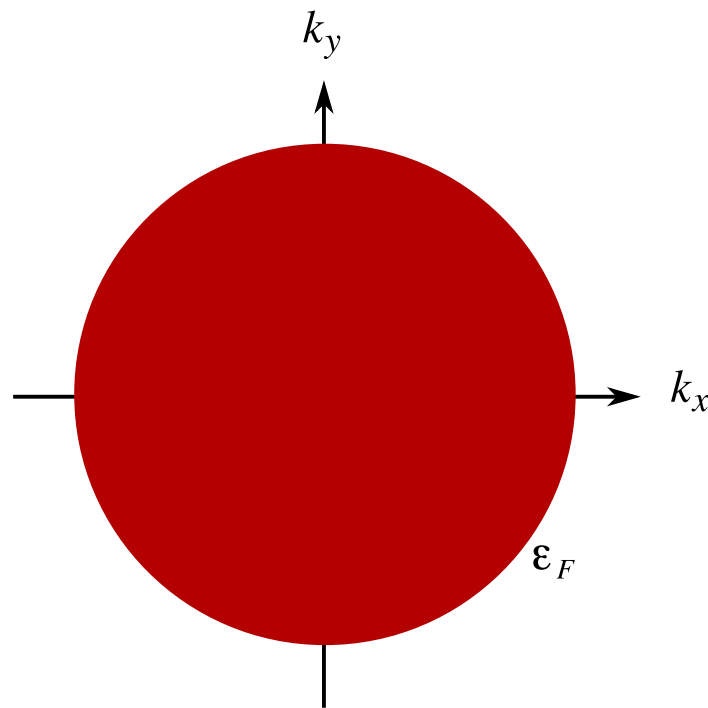


- LDA corrections fix most of the error in T .
- The residual finite-size errors arise from E_{xc} and the many-body parts of T .
- They are negative and decay very slowly — roughly like $1/N$.
- They can be very problematic.

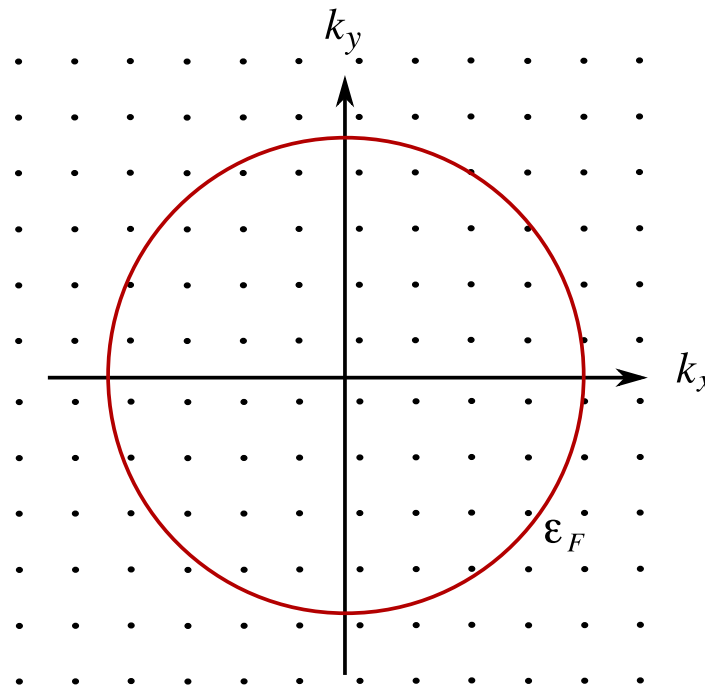
Twist Averaging

- DFT-based independent particle corrections are straightforward and easy to apply, but ugly.
- Twist averaging is an alternative method for taking care of the independent-particle errors in T .

Consider a non-interacting electron gas with $E = \int_{k < k_F} \frac{1}{2} k^2 d^3 k$.



Consider a non-interacting electron gas with $E = \int_{k < k_F} \frac{1}{2} k^2 d^3 k$.
What happens if we use a simulation cell with some given \mathbf{k}_s ?

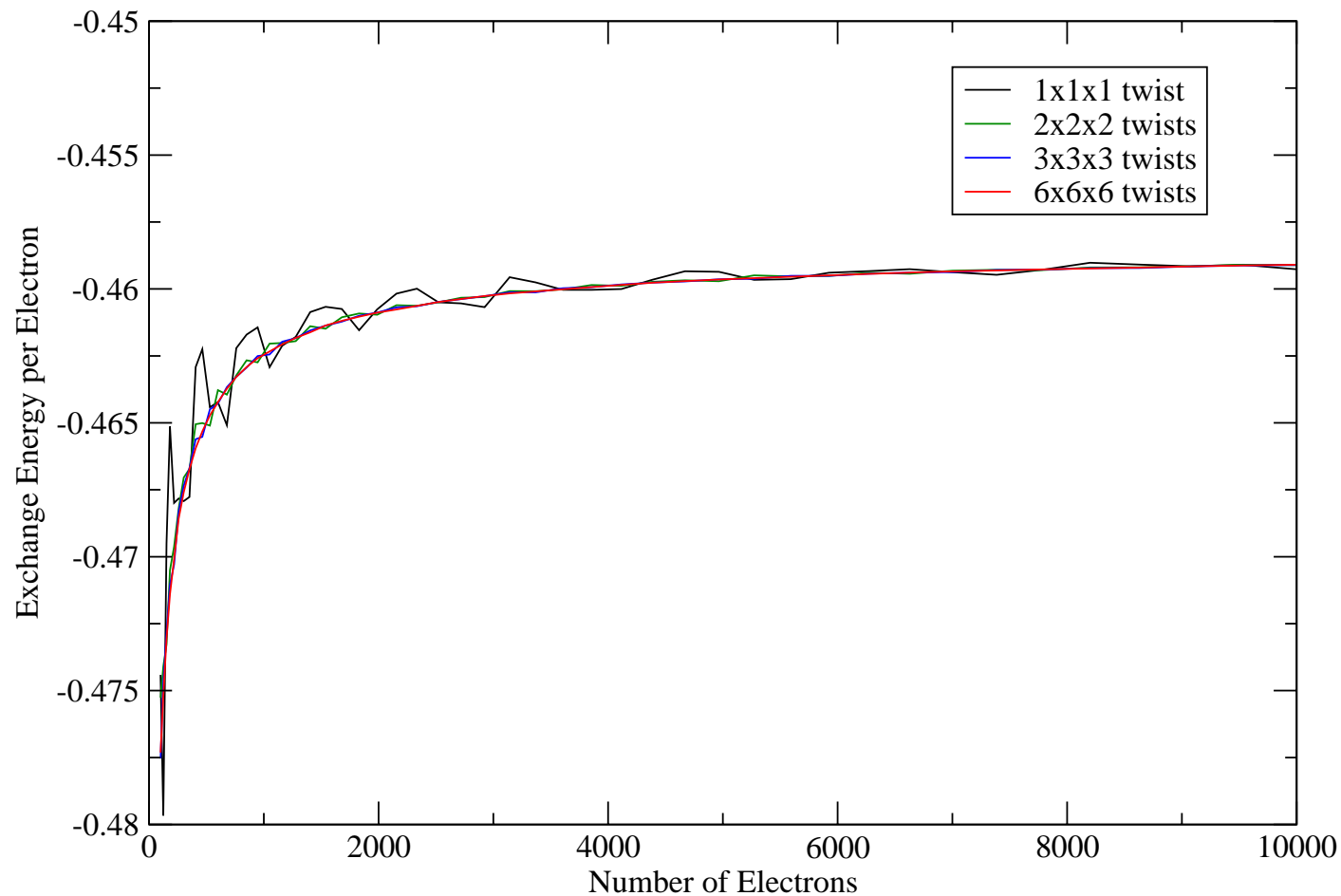


The integral is replaced by a summation

- One way to get closer to the right answer is to average the simulation cell energies over twist vectors \mathbf{k}_s :
 - ▶ **Grand canonical averaging:** For each twist \mathbf{k}_s , occupy all grid point with $k < k_F$. (The number of electrons depends on \mathbf{k}_s .)
 - ▶ **Canonical averaging:** Occupy the lowest N grid points at each twist \mathbf{k}_s . (Equivalent to integrating over the first N simulation-cell BZs — almost, but not quite, the same as the Fermi sphere).
- Some single twists (e.g. the Baldereschi point) give better results than others. One of the worst is $\mathbf{k}_s = \mathbf{0}$.
- Averaging over surprisingly small numbers of twists dramatically decreases the independent particle error.

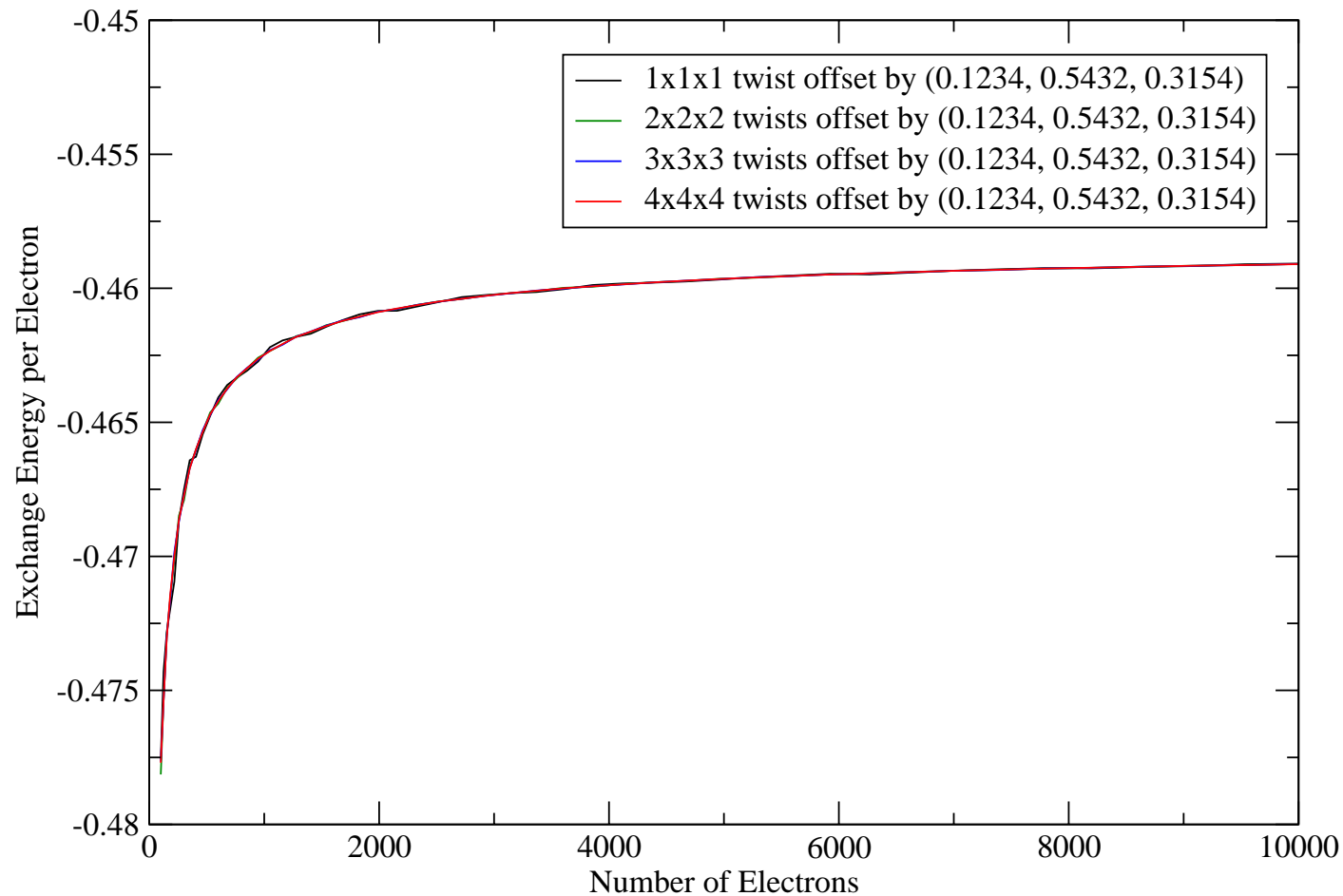
Exchange Energy of the $r_s=1$ Electron Gas

Convergence with number of twists in the canonical ensemble



Exchange Energy of $r_s=1$ Electron Gas

Convergence with number of offset twists in the canonical ensemble



The Good and the Bad

The Good: No increase in number of QMC steps.

The Bad: Need separate trial functions and (parallel) QMC runs for each twist. Most of these trial functions are likely to be complex (\Rightarrow fixed-phase approximation).

Everything I said about LDA corrections

- LDA corrections fix most of the error in T .
- The residual finite-size errors arise from E_{xc} and the many-body parts of T .
- They are negative and decay very slowly — roughly like $1/N$.
- They can be very problematic.

applies to twist averaging too. The two methods fix the same problem.
(Don't do both at once.)

Coulomb Errors

- The twist-averaging results above showed a long-ranged finite-size error in the exchange energy.
- In QMC simulations, analogous **Coulomb errors** appear in the exchange-correlation energy.
- These errors converge like $1/N$.

Questions

- 1 Why $1/N$?
- 2 Can we do anything to alleviate the problem?

Before we can make progress, we need to understand a little about exchange and correlation.

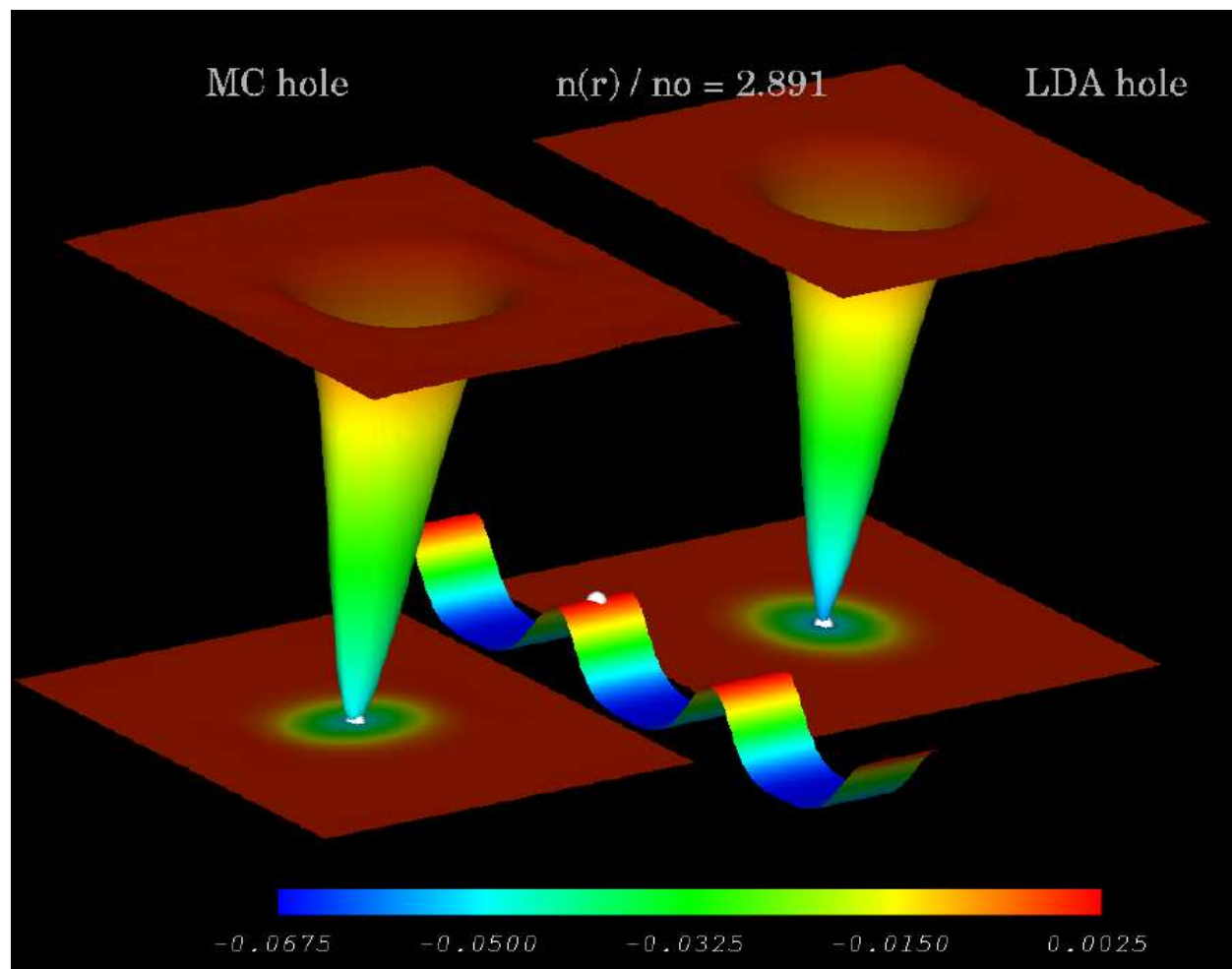
The Exchange-Correlation Hole

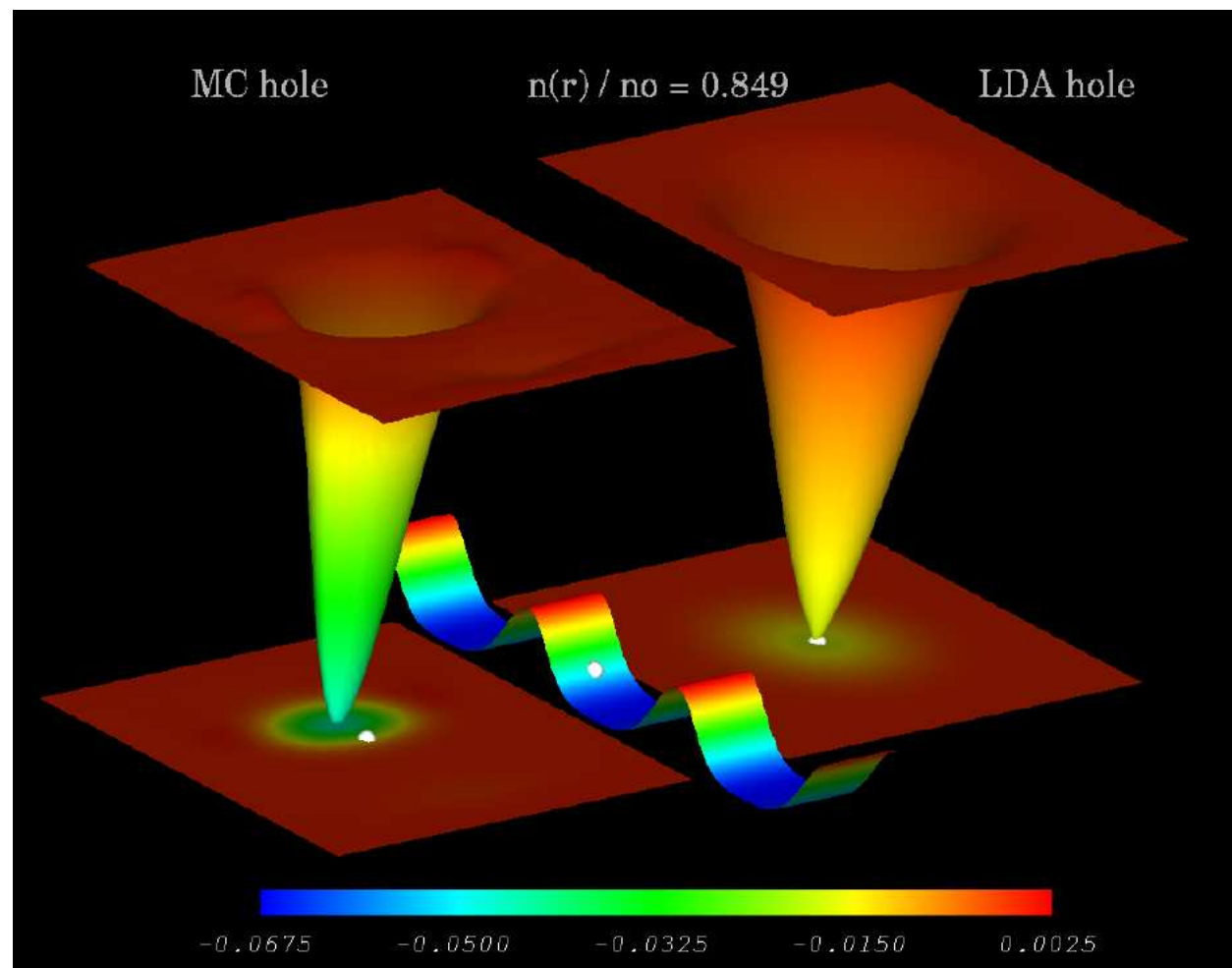
The exchange-correlation hole $n_{xc}(\mathbf{r}, \mathbf{r}')$ is defined by

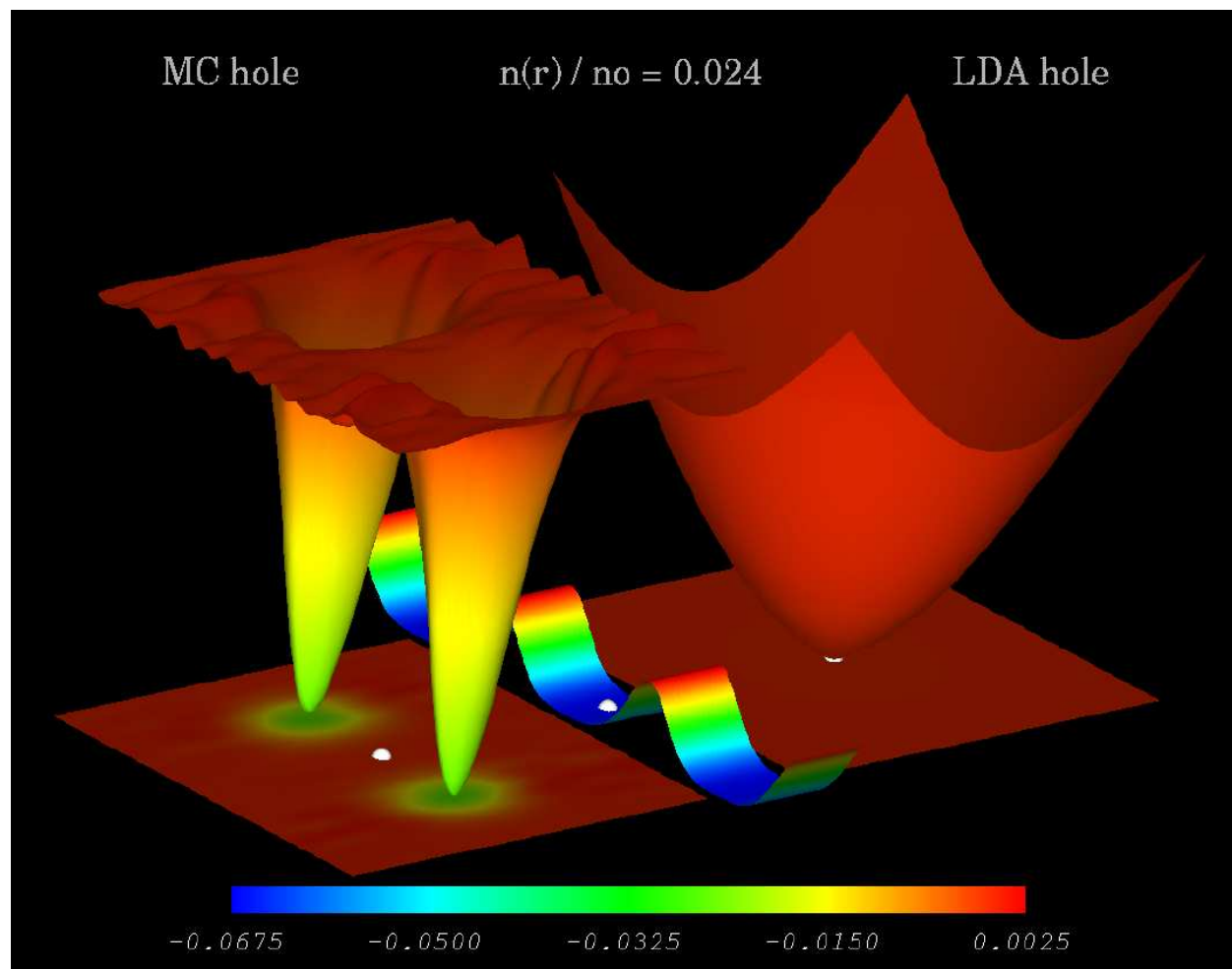
$$n(\mathbf{r}'|\mathbf{r}) = n(\mathbf{r}') + n_{xc}(\mathbf{r}', \mathbf{r})$$

The sum rule

$$\int_{\Omega_s} n(\mathbf{r}'|\mathbf{r}) d\mathbf{r}' = N - 1 \quad \Rightarrow \quad \int_{\Omega_s} n_{xc}(\mathbf{r}', \mathbf{r}) d\mathbf{r}' = -1$$







The Exchange-Correlation Energy

By definition, the XC energy per electron, $\bar{\epsilon}_{\text{xc}} = E_{\text{xc}}/N$, is the mean energy of interaction between an electron and its XC hole

$$\begin{aligned}\bar{\epsilon}_{\text{xc}} &= \frac{1}{2} \int_{\Omega_s} n_{\text{xc}}^{\text{Av}}(\mathbf{r}) (v_{\text{Ew}}(\mathbf{r}) - v_M) d\mathbf{r} \\ &= \frac{1}{2} \int_{\Omega_s} n_{\text{xc}}^{\text{Av}}(\mathbf{r}) v_{\text{Ew}}(\mathbf{r}) d\mathbf{r} + \frac{v_M}{2}\end{aligned}$$

where v_M is the Madelung potential and $n_{\text{xc}}^{\text{Av}}(\mathbf{r})$ is the system-averaged XC hole:

$$n_{\text{xc}}^{\text{Av}}(\mathbf{r}) = \frac{\int_{\Omega_s} n(\mathbf{r}') n_{\text{xc}}(\mathbf{r}', \mathbf{r}' + \mathbf{r}) d\mathbf{r}'}{\int_{\Omega_s} n(\mathbf{r}') d\mathbf{r}'}$$

Why $v_{\text{Ew}}(\mathbf{r}) - v_M$?

- The Ewald potential $v_{\text{Ew}}(\mathbf{r})$ includes contributions from
 - ▶ the electron at the origin,
 - ▶ its background,
 - ▶ all its images.
- Only the first of these ought to contribute to the XC energy.

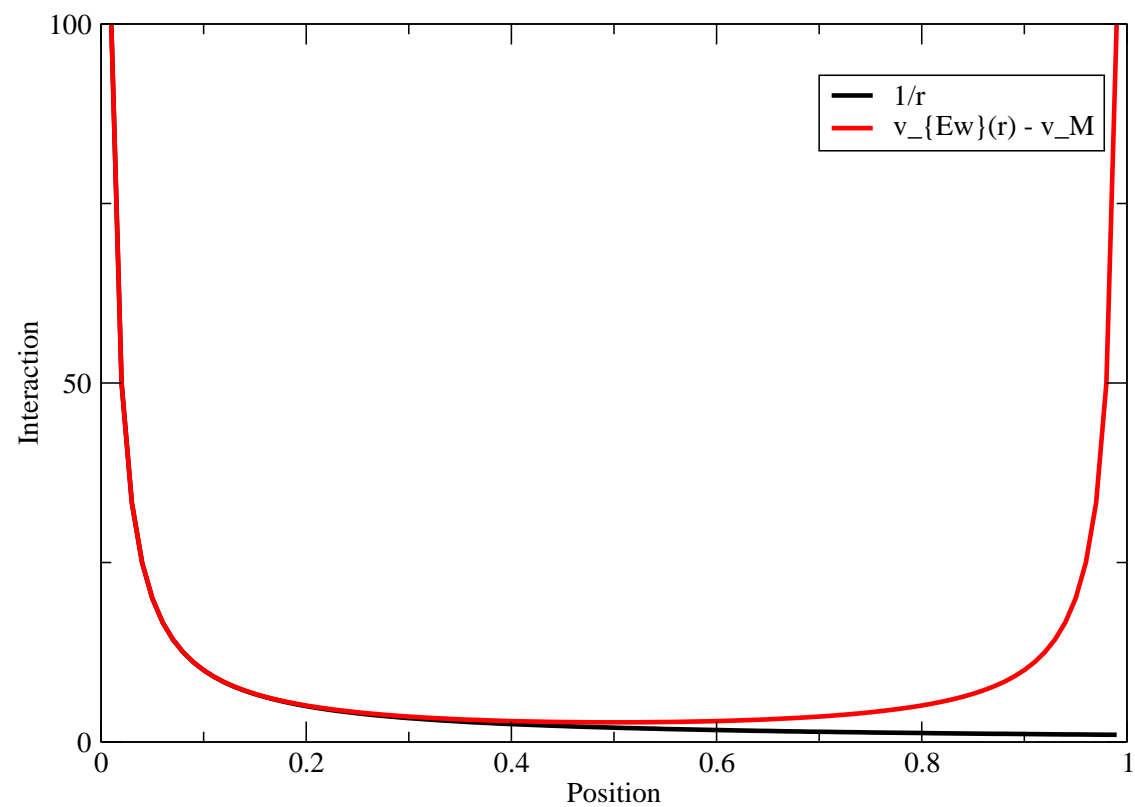
Real-Space Approach to Coulomb Errors

$$\bar{\epsilon}_{\text{xc}} = \frac{1}{2} \int_{\Omega_s} n_{\text{xc}}^{\text{Av}}(\mathbf{r}) (v_{\text{Ew}}(\mathbf{r}) - v_M) d\mathbf{r}$$

- Since $n_{\text{xc}}^{\text{Av}}(\mathbf{r})$ converges quite rapidly to the infinite system-size limit, the error must be in the interaction.
- Expanding $v_{\text{Ew}}(\mathbf{r}) - v_M$ about $\mathbf{r} = 0$ gives

$$v_{\text{Ew}}(\mathbf{r}) - v_M = \frac{1}{r} + \frac{2\pi r^2}{3\Omega_s} + \mathcal{O}(r^4) .$$

- In an infinite system, this reduces to $1/r$ as expected; in a finite system, the quadratic term gives a $1/\Omega_s \sim 1/N$ error.

Comparison of Ewald and $1/r$ Interactions

The Modified Periodic Coulomb Interaction

Replace

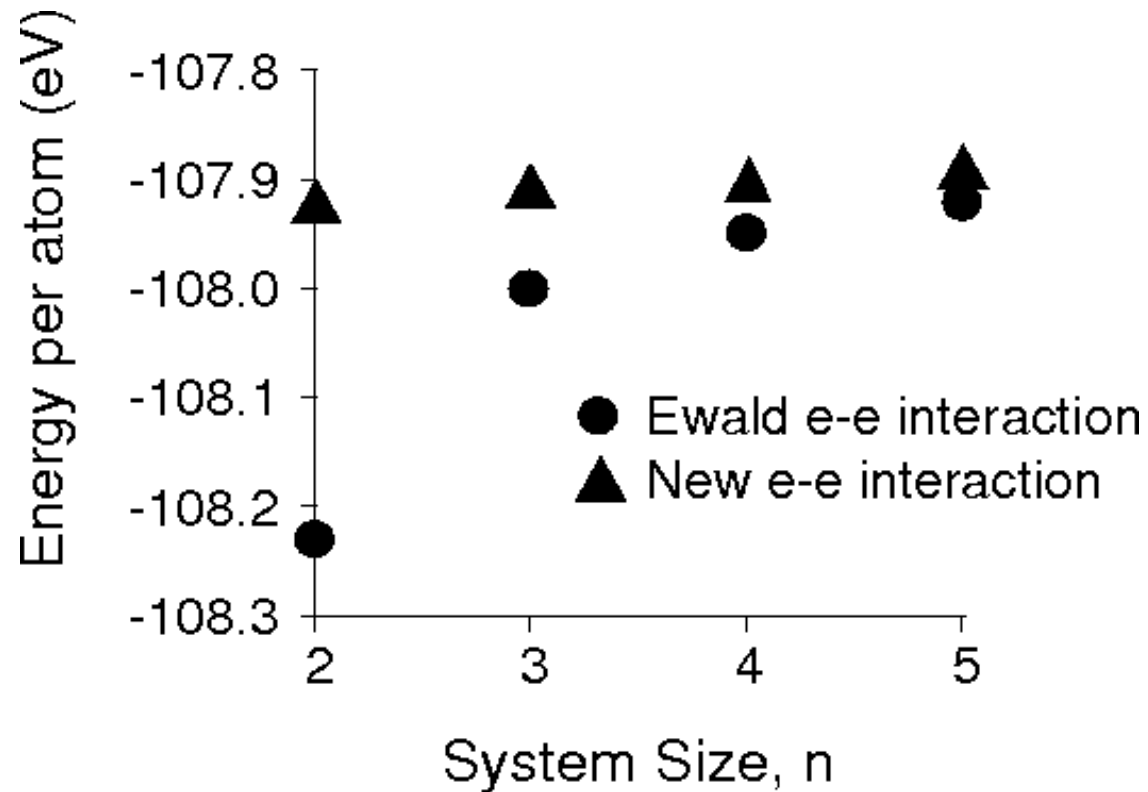
$$\bar{\epsilon}_{xc} = \frac{1}{2} \int_{\Omega_s} n_{xc}^{Av}(\mathbf{r}) (v_{Ew}(\mathbf{r}) - v_M) d\mathbf{r}$$

by

$$\bar{\epsilon}_{xc} = \frac{1}{2} \int_{\Omega_s} \frac{n_{xc}^{Av}(\mathbf{r})}{r} d\mathbf{r}$$

- Use minimum image convention to extend $1/r$ periodically.
- Keep Ewald interaction for Hartree energy terms.

Fixes $1/N$ error. Works well for exchange-correlation energy.



Reciprocal-Space Approach to Coulomb Errors

Re-expressing $\bar{\epsilon}_{xc}$ in k -space using the "dodgy" Fourier representations of v_{Ew} and v_M gives

$$\bar{\epsilon}_{xc} = \frac{1}{2\Omega_s} \sum_{\mathbf{G}_s (\neq 0)} \frac{4\pi(\tilde{n}_{xc}^{Av}(\mathbf{G}_s) + 1)e^{-\epsilon^2 G_s^2}}{G_s^2} - \frac{1}{2} \int \frac{4\pi e^{-\epsilon^2 G^2}}{G^2} \frac{d\mathbf{G}}{(2\pi)^3}$$

- $\tilde{S}(\mathbf{G}_s) = \tilde{n}_{xc}^{Av}(\mathbf{G}_s) + 1$ is called the *static structure factor*.
- Since $\tilde{S}(\mathbf{G}_s)$ is (normally) proportional to G_s^2 at small G_s , the summand does not diverge as $G_s \rightarrow 0$.

In the $\Omega_s \rightarrow \infty$ limit, the sum becomes an integral and we obtain the standard result

$$\bar{\epsilon}_{\text{xc}} \rightarrow \frac{1}{2} \int \frac{4\pi(\tilde{S}(\mathbf{G}) - 1)e^{-\epsilon^2 G^2}}{G^2} \frac{d\mathbf{G}}{(2\pi)^3} .$$

$$\bar{\epsilon}_{xc} = \frac{1}{2\Omega_s} \sum_{\mathbf{G}_s (\neq 0)} \frac{4\pi \tilde{S}(\mathbf{G}_s) e^{-\epsilon^2 G_s^2}}{G_s^2} - \frac{1}{2} \int \frac{4\pi e^{-\epsilon^2 G^2}}{G^2} \frac{d\mathbf{G}}{(2\pi)^3}$$

- Chiesa asserts that the leading contribution to the error arises from the omission of the $\mathbf{G}_s = 0$ term.
- Expanding $\tilde{n}_{xc}^{Av}(\mathbf{G}_s)$ and $\tilde{S}(\mathbf{G}_s)$ about $\mathbf{G}_s = 0$,

$$\tilde{n}_{xc}^{Av}(\mathbf{G}_s) = -1 + \alpha G_s^2 + \dots \quad \tilde{S}(\mathbf{G}_s) = \alpha G_s^2 + \dots ,$$

gives the finite-size correction

$$\Delta_{\text{Chiesa}} = \frac{2\pi\alpha}{\Omega_s} .$$

- The constant α can be obtained from RPA theory or by extrapolating the calculated $\tilde{S}(\mathbf{G}_s)$ towards $\mathbf{G}_s = 0$.

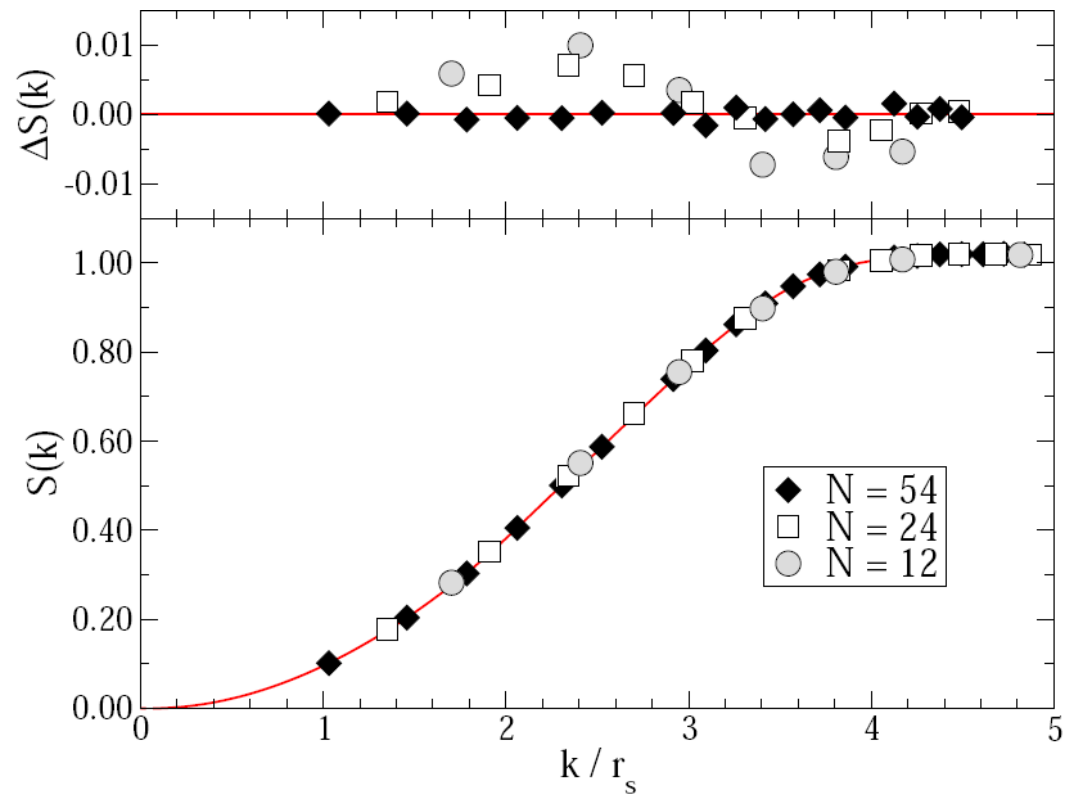


FIG. 1: Lower panel: Static structure factor for the electron gas at $r_s = 10$. Upper panel: $\Delta S = S_N(k) - S_{66}(k)$. The difference is computed using a spline function interpolation of S_{66} .

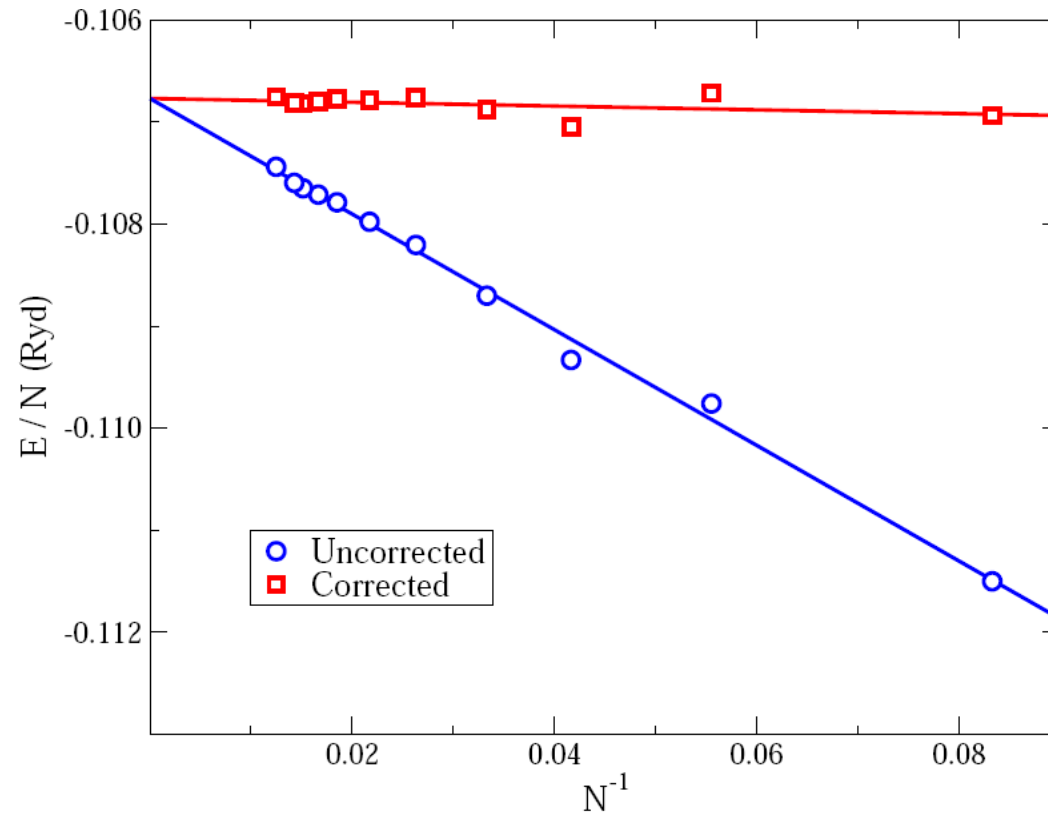


FIG. 2: Energies per particle of the electron gas at $r_s = 10$ in Rydberg as a function of the inverse particle number. Circles are the Monte Carlo energies averaged over twist angles. Squares are the energies after the additional $\hbar\omega_p/2N$ correction (see text).

Link between the two approaches

According to Chiesa,

$$\bar{\epsilon}_{\text{xc}} = \bar{\epsilon}_{\text{xc}}^{\text{Ew}} + \frac{2\pi\alpha}{\Omega_s}, \quad \text{where} \quad \tilde{n}_{\text{xc}}^{\text{Av}}(\mathbf{G}_s) = -1 + \alpha G_s^2 + \dots$$

$$\begin{aligned} \text{Since } \tilde{n}_{\text{xc}}^{\text{Av}}(\mathbf{G}_s) &= \int_{\Omega_s} n_{\text{xc}}^{\text{Av}}(\mathbf{r}) e^{-i\mathbf{G}_s \cdot \mathbf{r}} d\mathbf{r} \\ &= -1 - \frac{1}{6} G_s^2 \int_{\Omega_s} n_{\text{xc}}^{\text{Av}}(\mathbf{r}) r^2 d\mathbf{r} + \dots, \end{aligned}$$

it follows that

$$\alpha = -\frac{1}{6} \int_{\Omega_s} n_{\text{xc}}^{\text{Av}}(\mathbf{r}) r^2 d\mathbf{r}.$$

Hence, the reciprocal-space correction is equivalent to

$$\bar{\epsilon}_{\text{xc}} = \bar{\epsilon}_{\text{xc}}^{\text{Ew}} - \frac{\pi}{3\Omega_s} \int_{\Omega_s} n_{\text{xc}}^{\text{Av}}(\mathbf{r}) r^2 d\mathbf{r} .$$

According to the real-space MPC approach,

$$\begin{aligned} \bar{\epsilon}_{\text{xc}} &= \frac{1}{2} \int_{\Omega_s} \frac{n_{\text{xc}}^{\text{Av}}(\mathbf{r})}{r} d\mathbf{r} \\ &= \frac{1}{2} \int_{\Omega_s} n_{\text{xc}}^{\text{Av}}(\mathbf{r}) \left(v_{\text{Ew}}(\mathbf{r}) - v_M - \frac{2\pi r^2}{3\Omega_s} + \dots \right) d\mathbf{r} \\ &= \bar{\epsilon}_{\text{xc}}^{\text{Ew}} - \frac{\pi}{3\Omega_s} \int_{\Omega_s} n_{\text{xc}}^{\text{Av}}(\mathbf{r}) r^2 d\mathbf{r} + \dots . \end{aligned}$$

Conclusion

Reciprocal-space correction is more or less equivalent to the MPC

- Don't use both MPC *and* Chiesa Coulomb corrections.
- Choice is up to you: would you rather modify the Hamiltonian or apply a correction after the simulation?
- Reciprocal-space approach works better when the XC hole does not "fit in" to the simulation cell, as in Hartree-Fock theory.

Kinetic Energy Errors

Chiesa also points out that a Slater-Jastrow trial function of the form

$$\exp \left[- \sum_{i>j} u(\mathbf{r}_{ij}) + \sum_i \chi(\mathbf{r}_i) \right] D$$

with $u(r) \sim 1/r$ at large r (and hence $\tilde{u}(\mathbf{G}_s) \sim 1/G_s^2$ at small G_s) contributes a term of the form

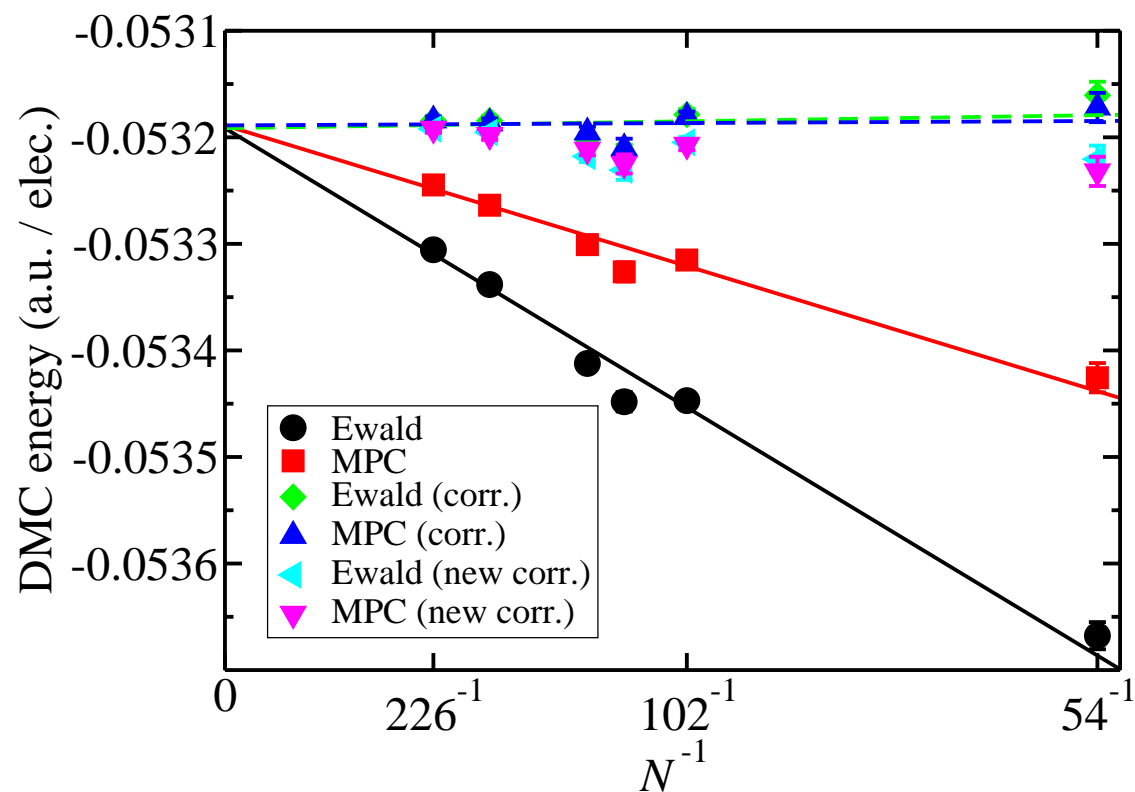
$$-\frac{1}{4\Omega_s} \sum_{\mathbf{G}_s(\neq 0)} G_s^2 \tilde{u}(\mathbf{G}_s)$$

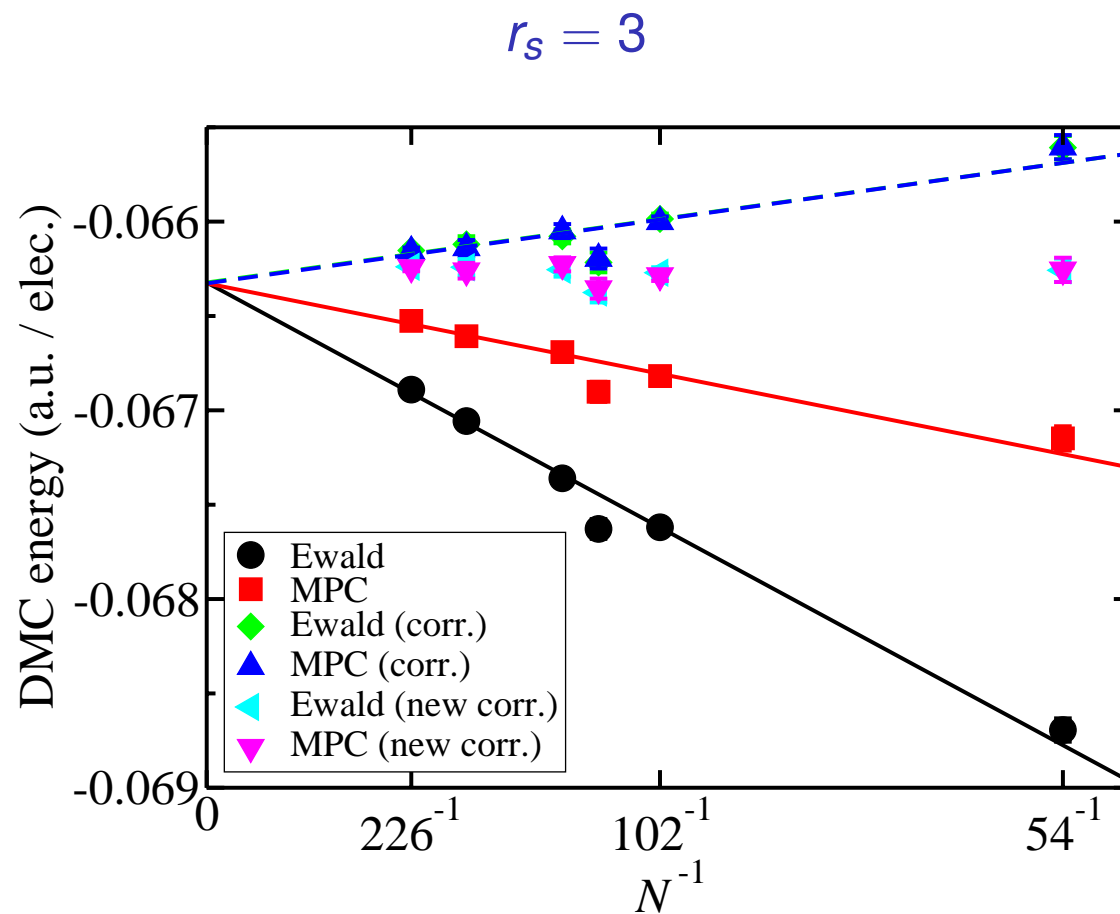
to the expected KE per electron.

$$-\frac{1}{4\Omega_s} \sum_{\mathbf{G}_s(\neq 0)} G_s^2 \tilde{u}(\mathbf{G}_s)$$

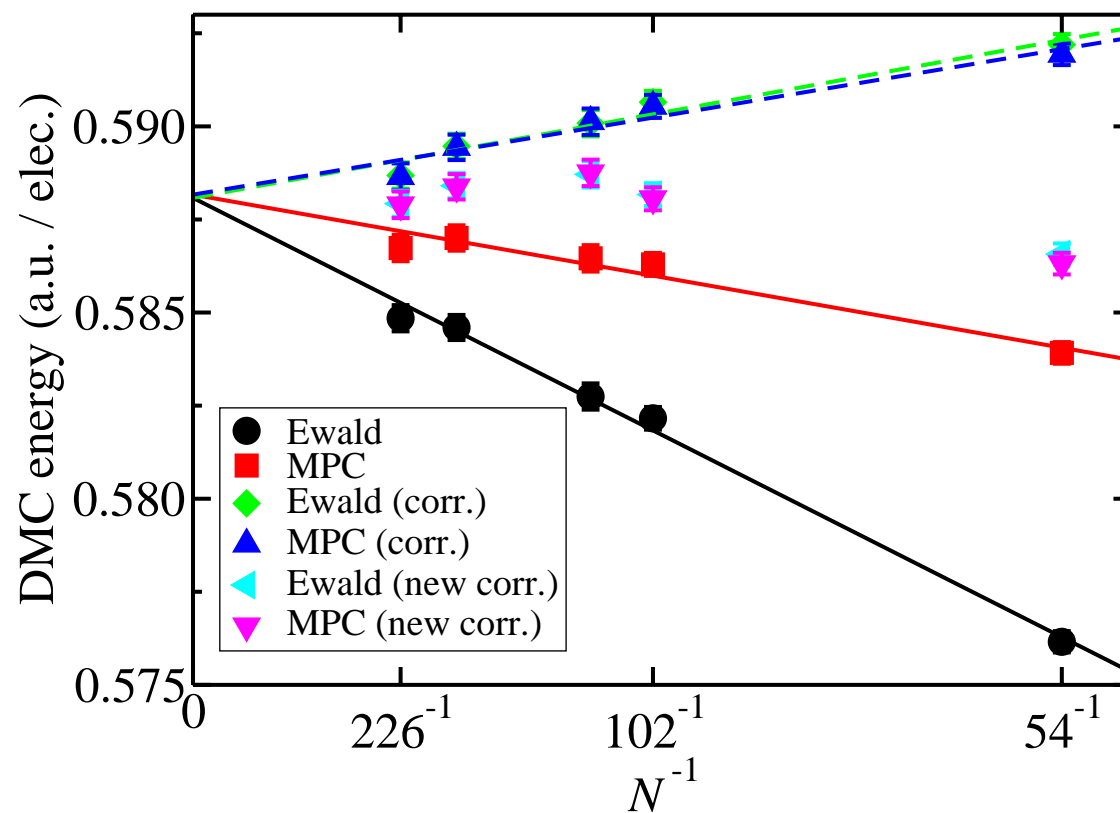
- Since $u(\mathbf{G}_s) \sim 1/G_s^2$ as $G_s \rightarrow 0$, the $G_s \rightarrow 0$ limit of the summand is finite.
- The omission of the $\mathbf{G}_s = 0$ term again looks fishy.
- Adding a contribution from the region near $\mathbf{G}_s = 0$ yields a second $1/N$ correction of the same sign and magnitude as the Coulomb correction.
- This many-body KE correction works well at very low density but not at more realistic densities.

$$r_s = 10$$





$$r_s = 1$$



Outline

- 1 Introduction
- 2 Periodic Boundary Conditions
- 3 Trial Wave Functions for Periodic Systems
- 4 Finite-Size Errors
- 5 Summary

Summary

- DMC has very favourable system-size scaling.
- DMC in solids works almost the same as in molecules.
- The only serious problem is the finite-size errors. My current recommendation is:
 - 1 Take care of the independent-particle errors by applying LDA corrections or twist averaging.
 - 2 (Use MPC or apply analytic $1/N$ Coulomb correction).
 - 3 (Apply analytic $1/N$ KE correction).
 - 4 Fit any residual error to c/N and extrapolate to infinite N .