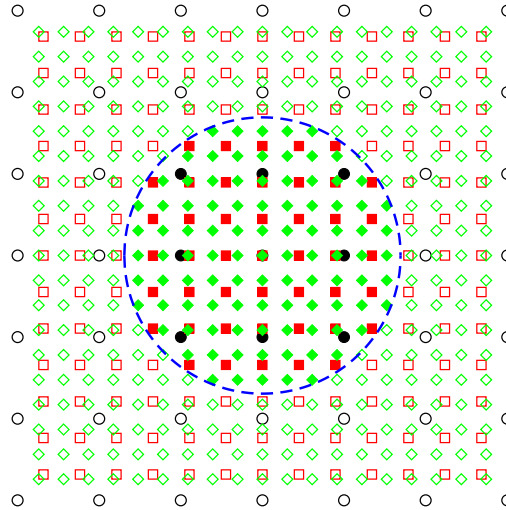


Quantum Monte Carlo Studies of Condensed Matter: Ewald Interactions and Finite-Size Effects



Neil D. Drummond

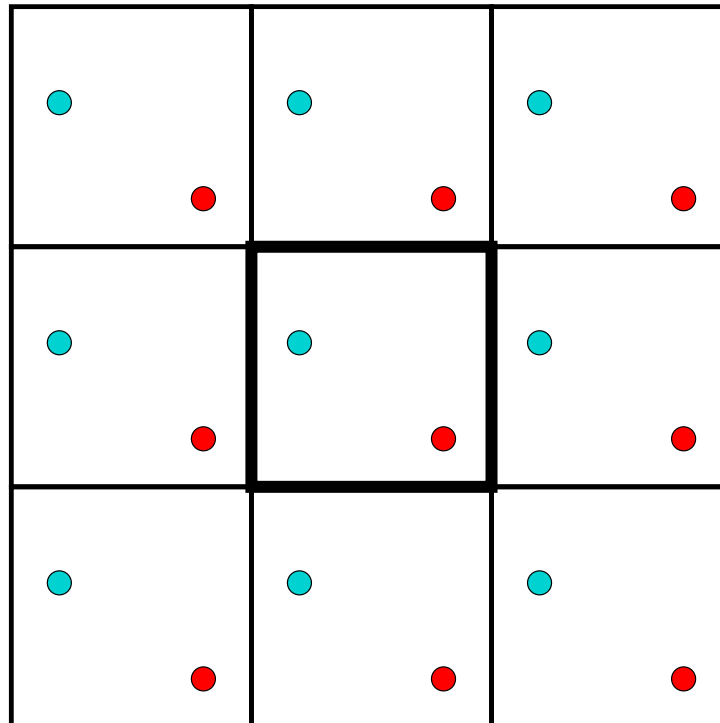
Department of Physics, Lancaster University

QMC and the CASINO program, TTI, Vallico Sotto, Italy

Wednesday 7th August, 2013

Periodic Boundary Conditions

- Suppose we are interested in the bulk properties of a material.
- Could in principle study a large finite system, but would have to simulate an infeasibly large number of particles to make surface effects negligible.
- Eliminate surfaces by using **periodic boundary conditions**.



The Ewald Interaction (I): the Problem

- Naïve expression for the electrostatic energy of a neutral, periodic cell:

$$\hat{V} = \frac{1}{2} \sum_{i \neq j} \frac{q_i q_j}{|\mathbf{r}_i - \mathbf{r}_j|} + \frac{1}{2} \sum_{\mathbf{R} \neq \mathbf{0}} \sum_{i,j} \frac{q_i q_j}{|\mathbf{r}_i - \mathbf{r}_j - \mathbf{R}|},$$

where q_i is the charge of particle i in the cell and $\{\mathbf{R}\}$ are the lattice vectors.

- Unfortunately this sum is **conditionally convergent**.
 - **Riemann series theorem**: can rearrange terms of a conditionally convergent sum to get any answer you like. . .
 - Physically, $\mathcal{O}(r^2)$ distant, neutral cells at distance r make dipole contributions [$\mathcal{O}(r^{-2})$] to the electrostatic potential at any given point.
- Practical solution: use **Ewald method** to calculate interaction energy.¹
 - Corresponds to a choice of boundary conditions on a macroscopic crystal.

¹ P. P. Ewald, Ann. Phys. **64**, 253 (1921).

The Ewald Interaction (II): Fourier Series

- Add uniform, neutralising background if nec. and write the charge density as

$$\rho(\mathbf{r}) = \sum_{\mathbf{R}} \sum_i q_i \delta(\mathbf{r} - \mathbf{r}_i - \mathbf{R}) - \frac{Q}{\Omega},$$

where $Q = \sum_i q_i$ is the total charge of the cell and Ω is the cell volume.

- Fourier representation of charge density:

$$\rho(\mathbf{r}) = \frac{1}{\Omega} \sum_{\mathbf{G} \neq \mathbf{0}} \rho(\mathbf{G}) \exp(-i\mathbf{G} \cdot \mathbf{r}),$$

where $\mathbf{G} = \mathbf{0}$ is excluded because the cell is electrically neutral.

- **Assume** the electrostatic potential is periodic. Choose it to be 0 on average. Then

$$\Phi(\mathbf{r}) = \frac{1}{\Omega} \sum_{\mathbf{G} \neq \mathbf{0}} \Phi(\mathbf{G}) \exp(-i\mathbf{G} \cdot \mathbf{r}).$$

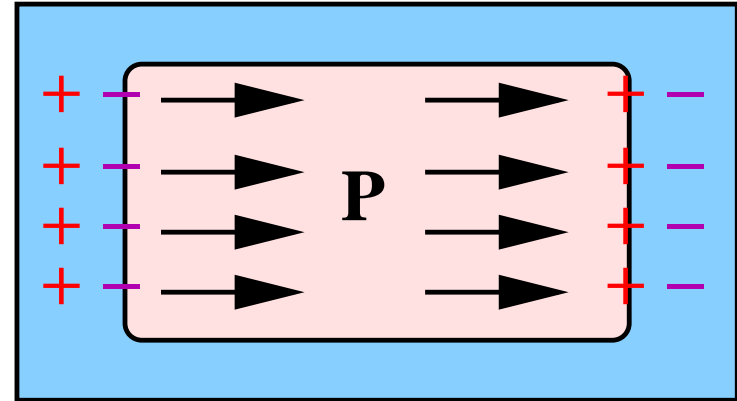
The Ewald Interaction (III): Poisson's Equation

- Periodic solution to Poisson's equation corresponds to adding a constant electric field to cancel that due to the nonzero dipole moment of the simulation cell.
- Ewald interaction corresponds to embedding the material in a perfect metal so that surface polarisation charges are screened. *Tin-foil boundary conditions*.
- Poisson's equation for the electrostatic potential:

$$\nabla^2 \Phi(\mathbf{r}) = -4\pi\rho(\mathbf{r}).$$

- Hence the Fourier components are related by

$$\Phi(\mathbf{G}) = \frac{4\pi\rho(\mathbf{G})}{G^2}.$$

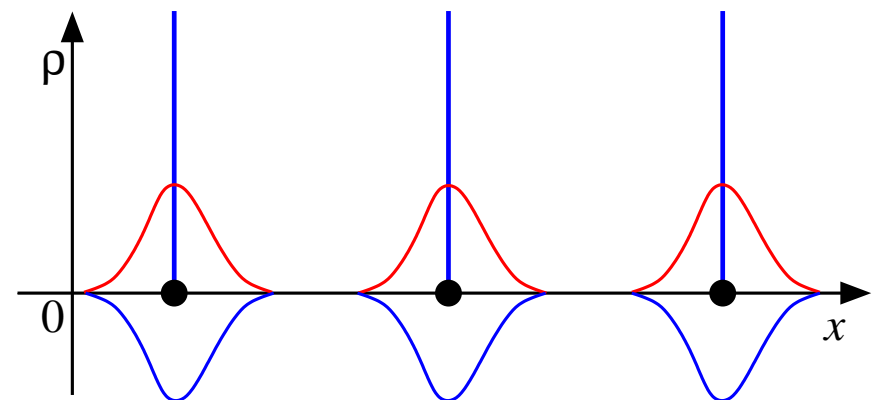


The Ewald Interaction (IV): the Charge Density

- The charge density due to a set of point charges can be written as

$$\rho(\mathbf{r}) = \rho_a(\mathbf{r}) + \rho_b(\mathbf{r}) = \left[\sum_i \sum_{\mathbf{R}} q_i \left(\frac{\gamma}{\pi} \right)^{3/2} \exp(-\gamma|\mathbf{r} - \mathbf{r}_i - \mathbf{R}|^2) - \frac{Q}{\Omega} \right] + \left[\sum_i \sum_{\mathbf{R}} q_i \left(\delta(\mathbf{r} - \mathbf{r}_i - \mathbf{R}) - \left(\frac{\gamma}{\pi} \right)^{3/2} \exp[-\gamma|\mathbf{r} - \mathbf{r}_i - \mathbf{R}|^2] \right) \right].$$

- The electrostatic energy of the **first term** will be evaluated as a sum in reciprocal space; that of the **second term** will be evaluated as a sum in real space.
- The electrostatic energy \hat{V}_{Ew} is independent of γ .
 - Smaller values make reciprocal-space sum more rapidly convergent.
 - Larger values of γ make real-space sum more rapidly convergent.



The Ewald Interaction (V): the Reciprocal-Space Sum

- The Fourier components of ρ_a are

$$\rho_a(\mathbf{G}) = \sum_i q_i \exp[-G^2/(4\gamma)] \exp(i\mathbf{G} \cdot \mathbf{r}_i).$$

- Hence the electrostatic potential due to ρ_a is

$$\Phi_a(\mathbf{r}) = \frac{4\pi}{\Omega} \sum_i \sum_{\mathbf{G} \neq \mathbf{0}} q_i \frac{\exp[-G^2/(4\gamma)]}{G^2} \exp[i\mathbf{G} \cdot (\mathbf{r} - \mathbf{r}_i)].$$

The Ewald Interaction (VI): the Real-Space Sum

- Consider a Gaussian charge distribution centred on the origin:

$$\rho_0(\mathbf{r}) = \left(\frac{\gamma}{\pi}\right)^{3/2} \exp(-\gamma r^2).$$

- The electrostatic potential is

$$\Phi_0(\mathbf{r}) = \left(\frac{\gamma}{\pi}\right)^{3/2} \int_{\text{All space}} \frac{\exp(-\gamma r'^2)}{|\mathbf{r}' - \mathbf{r}|} d\mathbf{r}' = \frac{\text{erf}(\sqrt{\gamma}r)}{r}$$

- The potential due to ρ_b is therefore

$$\Phi_b(\mathbf{r}) = \sum_i \sum_{\mathbf{R}} q_i \frac{1 - \text{erf}(\sqrt{\gamma}|\mathbf{r} - \mathbf{r}_i - \mathbf{R}|)}{|\mathbf{r} - \mathbf{r}_i - \mathbf{R}|} - \frac{\pi Q}{\Omega\gamma},$$

where we have added the constant term $-\pi Q/(\Omega\gamma)$ to ensure that $\int_{\Omega} \Phi_b(\mathbf{r}) d\mathbf{r} = 0$.

The Ewald Interaction (VII): the Ewald Energy

- The electrostatic energy of a set of point charges is

$$\hat{V} = \frac{1}{2} \sum_j q_j \Phi_j,$$

where Φ_j is the potential at \mathbf{r}_j due to the charges other than j .

- Noting that $\lim_{x \rightarrow 0} \operatorname{erf}(x)/x = 2/\sqrt{\pi}$, we find that

$$\begin{aligned} \Phi_j = \lim_{\mathbf{r} \rightarrow \mathbf{r}_j} \Phi(\mathbf{r}) - \frac{q_j}{|\mathbf{r} - \mathbf{r}_j|} &= \frac{4\pi}{\Omega} \sum_i \sum_{\mathbf{G} \neq \mathbf{0}} q_i \frac{\exp[-G^2/(4\gamma)] \exp[i\mathbf{G} \cdot (\mathbf{r}_j - \mathbf{r}_i)]}{G^2} \\ &+ \sum_{\mathbf{R}} \sum_i' q_i \frac{\operatorname{erfc}(\sqrt{\gamma}|\mathbf{r}_j - \mathbf{r}_i - \mathbf{R}|)}{|\mathbf{r}_j - \mathbf{r}_i - \mathbf{R}|} - 2\sqrt{\frac{\gamma}{\pi}} q_j - \frac{\pi Q}{\Omega\gamma}, \end{aligned}$$

where \sum_i' means that $i = j$ is excluded when $\mathbf{R} = \mathbf{0}$.

The Ewald Interaction (VIII)

- Can write Ewald energy in the form

$$\begin{aligned}\hat{V}_{\text{Ew}} &= \frac{1}{2} \sum_{i \neq j} q_i q_j v_E(\mathbf{r}_i - \mathbf{r}_j) + \frac{1}{2} \sum_j q_j^2 v_M \\ &= \frac{1}{2} \sum_{i \neq j} q_i q_j [v_E(\mathbf{r}_i - \mathbf{r}_j) - v_M] \quad \text{if } Q = 0,\end{aligned}$$

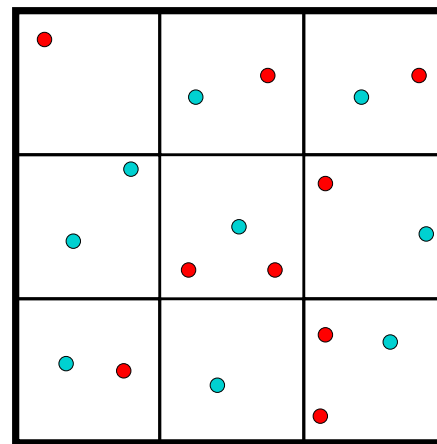
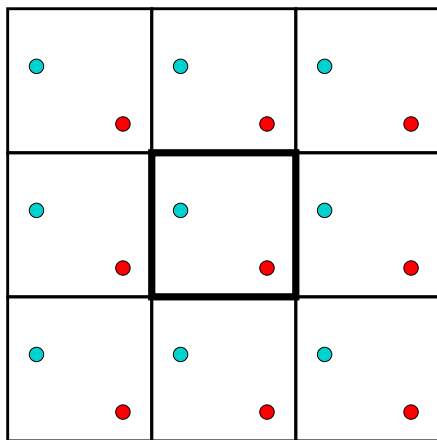
where

$$\begin{aligned}v_E(\mathbf{r}) &= \frac{4\pi}{\Omega} \sum_{\mathbf{G} \neq 0} \frac{\exp[-G^2/(4\gamma)] \exp(i\mathbf{G} \cdot \mathbf{r})}{G^2} + \sum_{\mathbf{R}} \frac{\text{erfc}(\sqrt{\gamma}|\mathbf{r} - \mathbf{R}|)}{|\mathbf{r} - \mathbf{R}|} - \frac{\pi}{\Omega\gamma} \\ v_M &= \frac{4\pi}{\Omega} \sum_{\mathbf{G} \neq 0} \frac{\exp[-G^2/(4\gamma)]}{G^2} + \sum_{\mathbf{R} \neq 0} \frac{\text{erfc}(\sqrt{\gamma}R)}{R} - 2\sqrt{\frac{\gamma}{\pi}} - \frac{\pi}{\Omega\gamma}.\end{aligned}$$

- Fourier transform (distribution) of $v_E(\mathbf{r})$ is $v_E(G) = 4\pi/G^2$.

Simulation and Primitive Unit Cells

- In one-electron theories (e.g. density-functional or Hartree–Fock theory) we can reduce the problem to the primitive unit cell and integrate over the first Brillouin zone.
- Reduction to the primitive unit cell is not possible in many-body calculations: correlation effects may be long-range.
 - Must use a simulation supercell consisting of several primitive cells in QMC.
 - When constructing the Slater wave function, single-particle Bloch orbitals on an $l \times m \times n$ \mathbf{k} -point mesh must be treated as Bloch orbitals at a single \mathbf{k} point for the supercell consisting of $l \times m \times n$ primitive cells.



Translational Symmetry

- Translational symmetries of the Hamiltonian:

1. $\hat{H}(\mathbf{r}_1, \dots, \mathbf{r}_i + \mathbf{R}_s, \dots, \mathbf{r}_N) = \hat{H}(\mathbf{r}_1, \dots, \mathbf{r}_i, \dots, \mathbf{r}_N) \quad \forall i \in \{1, \dots, N\},$
2. $\hat{H}(\mathbf{r}_1 + \mathbf{R}_p, \dots, \mathbf{r}_i + \mathbf{R}_p, \dots, \mathbf{r}_N + \mathbf{R}_p) = \hat{H}(\mathbf{r}_1, \dots, \mathbf{r}_i, \dots, \mathbf{r}_N)$

where \mathbf{R}_s and \mathbf{R}_p are the simulation-cell and primitive-cell lattice vectors.

- Lead to **many-body Bloch conditions**:

1. $\Psi_{\mathbf{k}_s}(\mathbf{r}_1, \dots, \mathbf{r}_N) = U_{\mathbf{k}_s}(\mathbf{r}_1, \dots, \mathbf{r}_N) \exp(i\mathbf{k}_s \cdot \sum_i \mathbf{r}_i)$
2. $\Psi_{\mathbf{k}_p}(\mathbf{r}_1, \dots, \mathbf{r}_N) = W_{\mathbf{k}_p}(\mathbf{r}_1, \dots, \mathbf{r}_N) \exp(i\mathbf{k}_p \cdot \frac{1}{N} \sum_i \mathbf{r}_i)$

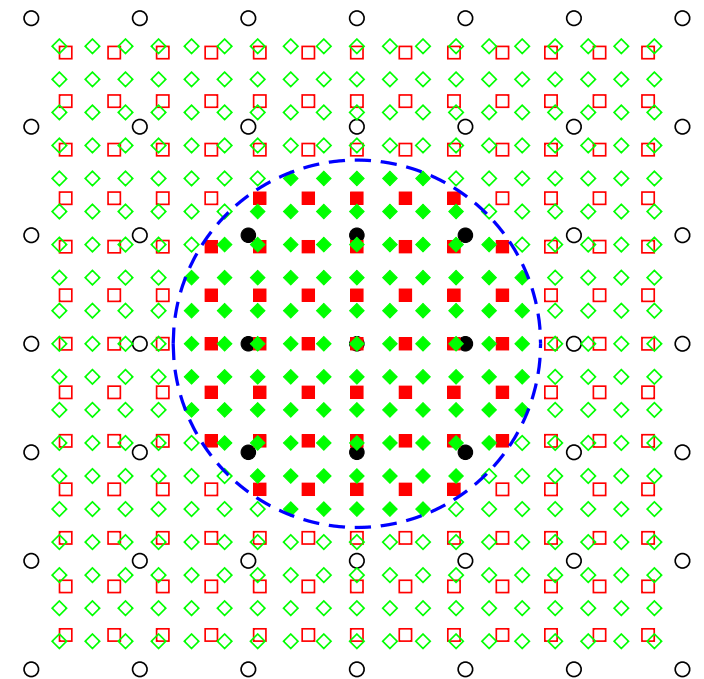
where U has periodicity of the simulation cell for all coordinates and W is invariant under simultaneous translation of all coordinates through \mathbf{R}_p .²

- Proof: similar to proof of single-electron Bloch theorem.
- Nonzero \mathbf{k}_s : **twisted boundary conditions** (see later).

² G. Rajagopal *et al.*, Phys. Rev. Lett. **73**, 1959 (1994); G. Rajagopal *et al.*, Phys. Rev. B **51**, 10591 (1995).

Single-Particle Finite-Size Errors

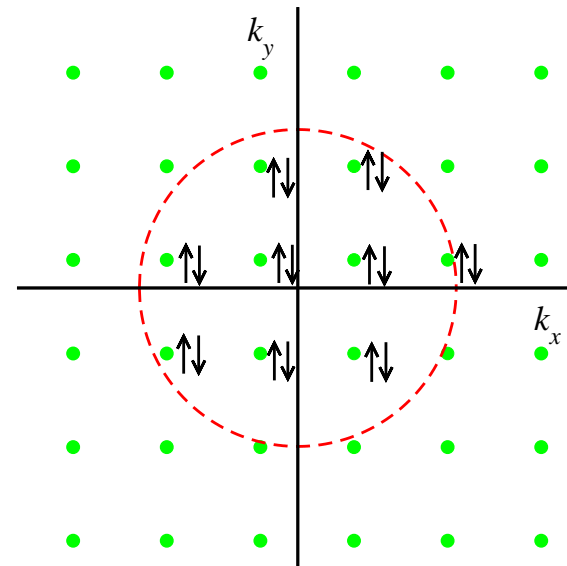
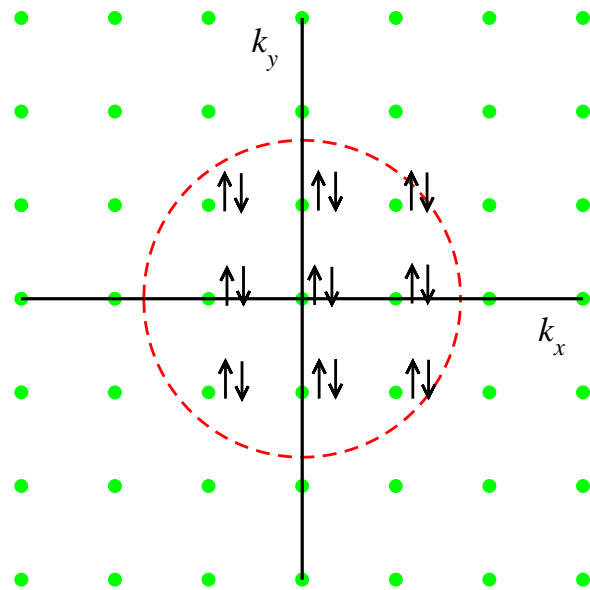
- **Momentum quantisation:** Bloch \mathbf{k} vectors must be integer multiples of simulation-cell reciprocal lattice vectors, so that orbitals are periodic.
 - Instead of integrating over orbitals inside the Fermi surface, one sums over the discrete set of \mathbf{k} vectors when a finite cell is used. (\mathbf{k} -point sampling.)
- Usually find that the fluctuations in the QMC energy as a function of system size are proportional to the corresponding \mathbf{k} -point sampling errors in the DFT energy.
- Hence can use DFT total energy (or Hartree–Fock kinetic energy) data to extrapolate to infinite system size.
- Large numbers of \mathbf{k} points are prohibitively expensive in QMC because an $n \times n \times n$ \mathbf{k} -point mesh must be unfolded into an $n \times n \times n$ simulation cell.



*Occ. \mathbf{k} for finite elec. gases.
Dashed line: Fermi circle.*

Twist Averaging (I)

- **Periodic boundary conditions:** $\Psi(\mathbf{r}_i + \mathbf{R}_s) = \Psi(\mathbf{r}_i)$. Single-particle orbitals are of the Bloch form $\psi_{\mathbf{k}}(\mathbf{r}) = \exp(i\mathbf{k} \cdot \mathbf{r})u_{\mathbf{k}}(\mathbf{r})$, where u has the periodicity of the primitive cell and $\mathbf{k} = \mathbf{G}_s$ is a reciprocal lattice vector of the simulation cell.
- **Twisted boundary conditions:** $\Psi(\mathbf{r}_i + \mathbf{R}_s) = \exp(i\mathbf{k}_s \cdot \mathbf{R}_s)\Psi(\mathbf{r}_i)$, where \mathbf{k}_s is in the first Brillouin zone of the simulation cell. Single-particle orbitals are of the form $\psi_{\mathbf{k}}(\mathbf{r}) = \exp(i\mathbf{k} \cdot \mathbf{r})u_{\mathbf{k}}(\mathbf{r})$, where $\mathbf{k} = \mathbf{k}_s + \mathbf{G}_s$, where \mathbf{G}_s is a reciprocal lattice point of the supercell.



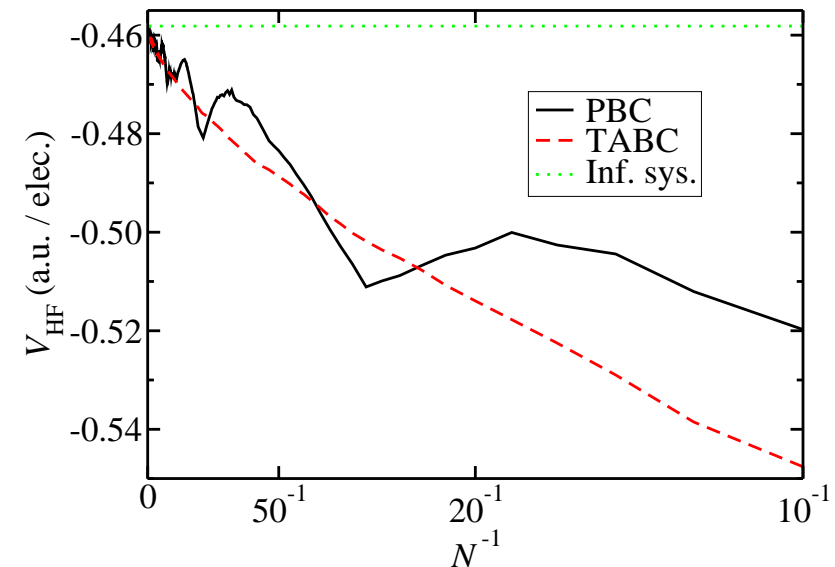
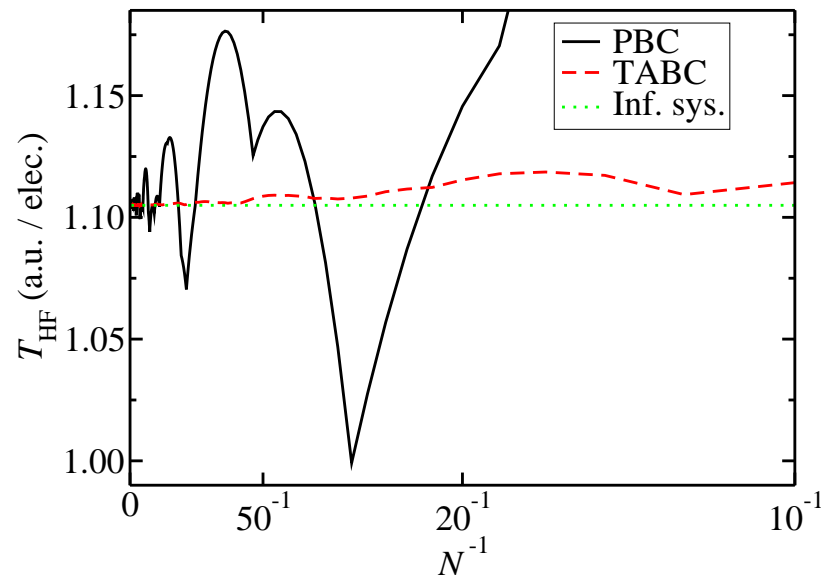
Twist Averaging (II)

- **Canonical-ensemble twist averaging**³: average over all \mathbf{k}_s , i.e. average over all offsets to the grid of \mathbf{k} vectors.
 - Greatly reduces single-particle finite-size errors.
 - Twist-averaged Fermi surface is not quite right. Gives small positive bias to Hartree–Fock kinetic energy because $k^2/2$ is concave.
- **Grand-canonical-ensemble twist averaging**: average over all \mathbf{k}_s , occupying only those states inside Fermi surface at each \mathbf{k}_s .
 - Particle number fluctuates.
 - Eliminates finite-size error in Hartree–Fock kinetic energy.
 - Better to average grand potential $\Phi = E - \mu N$, where $\mu = \mathcal{E}_F$ is the chemical potential, because Φ is stationary w.r.t. changes in N . Then evaluate $\langle E \rangle = \langle \Phi \rangle + \mu \langle N \rangle$.

³ C. Lin *et al.*, Phys. Rev. E **64**, 016702 (2001).

Twist Averaging (III)

- Effect of twist averaging on Hartree–Fock kinetic and exchange energies for a 3D paramagnetic electron gas of density parameter $r_s = 1$ a.u.:



- Replaces set of \mathbf{k} vectors with a Fermi volume.
 - *Shape of surface not quite right*: gives small, positive bias to kinetic energy.
- Twist averaging greatly dampens the energy fluctuations caused by shell filling.

Making Real Orbitals (I)

- QMC calculations run a bit faster if real arithmetic is used.
- Suppose Bloch orbitals at $\pm\mathbf{k}$ are occupied. Then

$$\psi_{\mathbf{k}}^*(\mathbf{r}) = \exp(-i\mathbf{k} \cdot \mathbf{r})u_{\mathbf{k}}^*(\mathbf{r}) = \psi_{-\mathbf{k}}(\mathbf{r}).$$

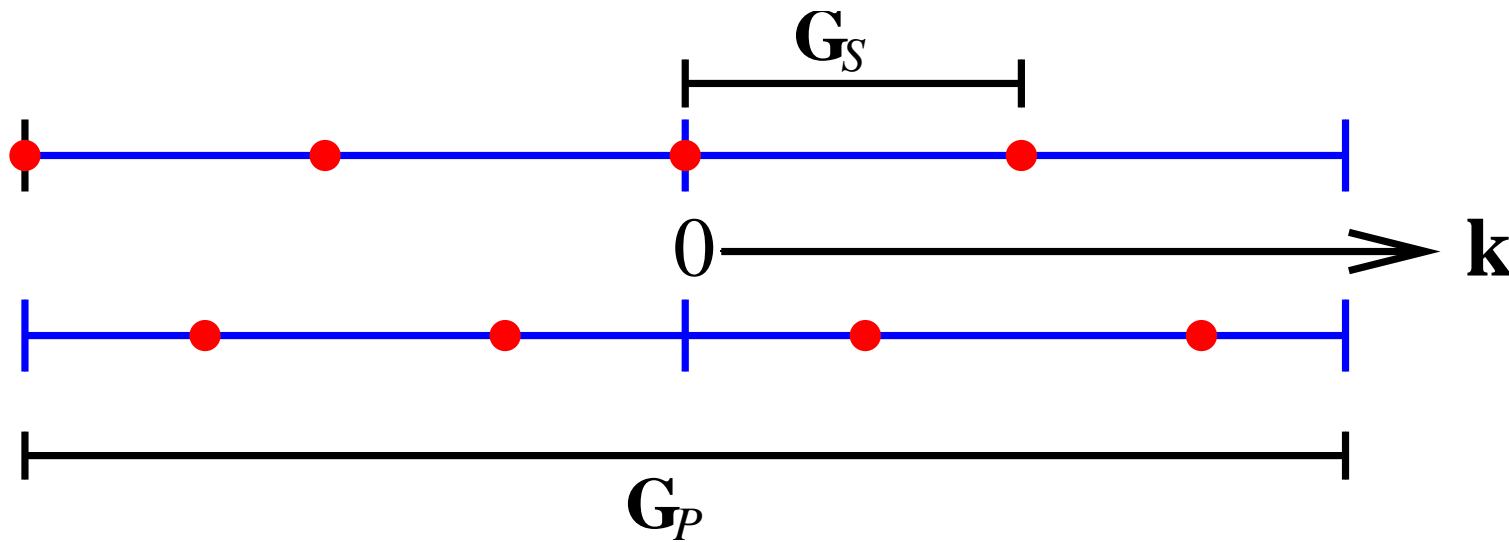
- Nonsingular linear transformations of the columns of the Slater determinant leave the wave function unchanged (up to normalisation).
- So can replace occupied orbitals $\psi_{\mathbf{k}}$ and $\psi_{-\mathbf{k}}$ by

$$\begin{aligned}\psi_{\mathbf{k}+} &= \frac{1}{\sqrt{2}} [\psi_{\mathbf{k}}(\mathbf{r}) + \psi_{-\mathbf{k}}(\mathbf{r})] = \sqrt{2}\text{Re} [\psi_{\mathbf{k}}(\mathbf{r})] \\ \psi_{\mathbf{k}-} &= \frac{1}{\sqrt{2}i} [\psi_{\mathbf{k}}(\mathbf{r}) - \psi_{-\mathbf{k}}(\mathbf{r})] = \sqrt{2}\text{Im} [\psi_{\mathbf{k}}(\mathbf{r})]\end{aligned}$$

without changing the Slater wave function.

Making Real Orbitals (II)

- The \mathbf{k} points are in $\pm\mathbf{k}$ pairs if the offset is $\mathbf{k}_s = \mathbf{0}$ or $\mathbf{k}_s = \mathbf{G}_s/2$, where \mathbf{G}_s and \mathbf{G}_p are simulation-cell and primitive-cell \mathbf{G} vectors.



Finite-Size Extrapolation of the Total Energy Per Particle

- Fit QMC data $\{E_N\}$ to

$$E_N = E_\infty + a \left(E_N^{\text{DFT}} - E_\infty^{\text{DFT}} \right) - \frac{b}{N},$$

where a , b and E_∞ are fitting parameters and E_N^{DFT} is the DFT energy of an N -particle system.

- E_N^{DFT} is the DFT energy with the \mathbf{k} -point mesh corresponding to the N -electron simulation cell. E_∞^{DFT} is the DFT energy in the limit of perfect \mathbf{k} -point sampling.
- E_N and E_N^{DFT} can be replaced by their twist-averaged versions.
 - To maximise the cancellation of errors, exactly the same twists should be used in DFT and QMC.
- For real systems, obtaining E_N at several different cell sizes can be time-consuming.
- There are several variants of this fitting formula in the literature; e.g. use Hartree–Fock kinetic energy instead of DFT energy.

Density and Static Structure Factor

- Charge density operator:

$$\hat{\rho}(\mathbf{r}) = \sum_i \delta(\mathbf{r} - \mathbf{r}_i).$$

- Charge density: $\rho(\mathbf{r}) = \langle \hat{\rho}(\mathbf{r}) \rangle$.

- Fourier transform of the density operator:

$$\hat{\rho}(\mathbf{G}) = \sum_i \exp(-i\mathbf{G} \cdot \mathbf{r}_i).$$

- Fourier transform of the density: $\rho(\mathbf{G}) = \langle \hat{\rho}(\mathbf{G}) \rangle$.

- Static structure factor:

$$S(\mathbf{G}) = \frac{1}{N} (\langle \hat{\rho}(\mathbf{G}) \hat{\rho}^*(\mathbf{G}) \rangle - \rho(\mathbf{G}) \rho^*(\mathbf{G})).$$

Exchange–Correlation Hole

- Pair density:

$$\rho_2(\mathbf{r}, \mathbf{r}') = \left\langle \sum_{i \neq j} \delta(\mathbf{r} - \mathbf{r}_i) \delta(\mathbf{r}' - \mathbf{r}_j) \right\rangle.$$

- Exchange–correlation hole:

$$\rho_{xc}(\mathbf{r}, \mathbf{r}') \rho(\mathbf{r}') = \rho_2(\mathbf{r}, \mathbf{r}') - \rho(\mathbf{r}) \rho(\mathbf{r}').$$

- System-averaged exchange–correlation hole:

$$\rho_{xc}(\mathbf{r}) = \frac{1}{N} \int \rho_{xc}(\mathbf{r}' + \mathbf{r}, \mathbf{r}') \rho(\mathbf{r}') d\mathbf{r}'.$$

Hartree and Exchange–Correlation Energies

- Ewald energy:

$$\begin{aligned}\langle \hat{V}_{\text{Ew}} \rangle &= \frac{Nv_M}{2} + \frac{\int |\Psi(\mathbf{R})|^2 \frac{1}{2} \sum_{i \neq j} v_E(\mathbf{r}_i - \mathbf{r}_j) d\mathbf{R}}{\int |\Psi|^2 d\mathbf{R}} \\ &= \frac{N}{2} \int [v_E(\mathbf{r}) - v_M] \rho_{\text{xc}}(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \int \int v_E(\mathbf{r} - \mathbf{r}') \rho(\mathbf{r}) \rho(\mathbf{r}') d\mathbf{r} d\mathbf{r}' \\ &= \frac{N}{2} \left(\sum_{\mathbf{G} \neq 0} \frac{4\pi}{\Omega G^2} [S(\mathbf{G}) - 1] + v_M \right) + \sum_{\mathbf{G} \neq 0} \frac{2\pi}{\Omega G^2} \rho(\mathbf{G}) \rho^*(\mathbf{G}).\end{aligned}$$

- First term: **exchange–correlation energy** (interaction of electrons with their exchange–correlation holes).
- Second term: **Hartree energy** (interaction of charge densities).

Coulomb Finite Size Errors

- Charge density and structure factor converge rapidly with system size; suggests that finite-size errors are due to slow convergence of Ewald interaction.
- Taylor expansion of Ewald interaction:

$$v_E(\mathbf{r}) - v_M = \frac{1}{r} + \frac{2\pi}{3\Omega} \mathbf{r}^T W \mathbf{r} + \mathcal{O}\left(\frac{r^4}{\Omega^{5/3}}\right),$$

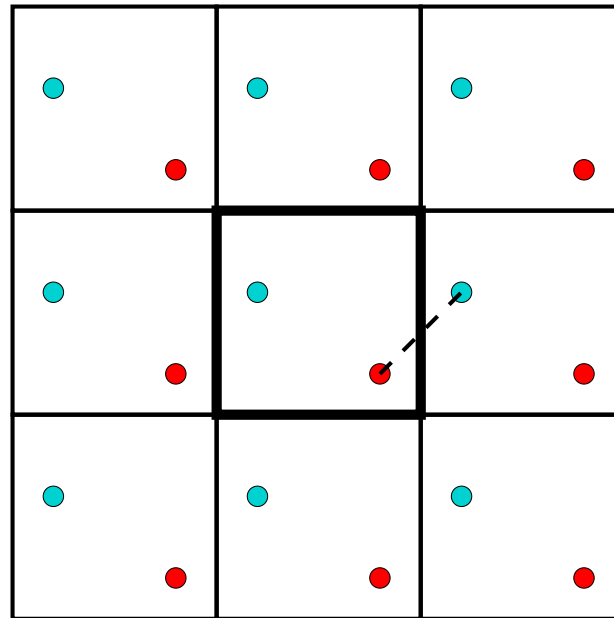
where tensor W depends on the symmetry of the lattice.

- For large simulation cells first term dominates, but for typical cell sizes second term is significant.
- Interaction between each electron and its exchange–correlation hole should be $1/r$.
- This is enforced in the **model periodic Coulomb** interaction.⁴

⁴ L. M. Fraser *et al.*, Phys. Rev. B **53**, 1814 (1996); A. J. Williamson *et al.*, Phys. Rev. B **55**, R4851 (1997).

Aside: Minimum Images

- **Minimum image** distance between particles A and B : distance from A to closest periodic image of B .



- Minimum image of \mathbf{r} is $\mathbf{r} - \mathbf{R}_C$, where \mathbf{R}_C is closest sim.-cell lattice point to \mathbf{r} .

Model Periodic Coulomb Interaction (I)

- MPC interaction operator:

$$\hat{V}_{\text{MPC}} = \frac{1}{2} \sum_{i \neq j} f(\mathbf{r}_i - \mathbf{r}_j) + \sum_i \int \rho(\mathbf{r}) [v_E(\mathbf{r}_i - \mathbf{r}) - f(\mathbf{r}_i - \mathbf{r})] d\mathbf{r} \\ - \frac{1}{2} \int \rho(\mathbf{r}) \rho(\mathbf{r}') [v_E(\mathbf{r} - \mathbf{r}') - f(\mathbf{r} - \mathbf{r}')] d\mathbf{r} d\mathbf{r}',$$

where $f(\mathbf{r})$ is $1/r$ treated within the minimum-image convention.

- Electron-electron interaction energy:

$$\langle \hat{V}_{\text{MPC}} \rangle = \frac{1}{2} \int \rho(\mathbf{r}) \rho(\mathbf{r}') v_E(\mathbf{r} - \mathbf{r}') d\mathbf{r} d\mathbf{r}' \\ + \int \int \rho_{\text{xc}}(\mathbf{r}, \mathbf{r}') \rho(\mathbf{r}') f(\mathbf{r} - \mathbf{r}') d\mathbf{r} d\mathbf{r}',$$

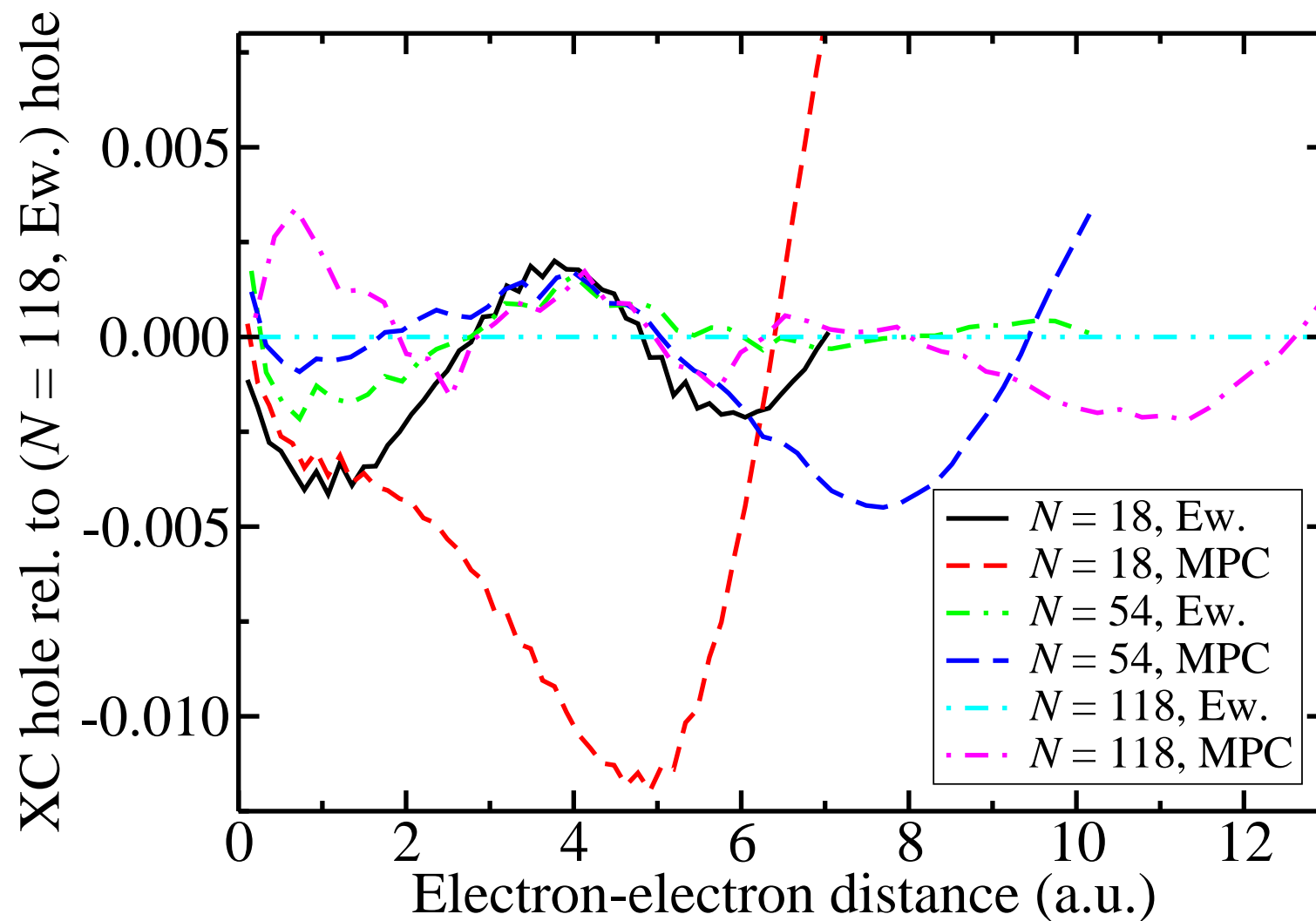
i.e. Hartree energy + exchange–correlation energy.

Model Periodic Coulomb Interaction (II)

- The Hartree energy is calculated using the Ewald interaction while the exchange–correlation energy is calculated using $1/r$ (within minimum-image convention).
- Can avoid the need to know ρ exactly by replacing it with the approximate charge density ρ_A from a DFT or Hartree–Fock calculation.
 - The error due to this approximation is $\mathcal{O}(\rho - \rho_A)^2$.
 - Furthermore the operator $(v_E - v_M - f)$ vanishes as the size of the simulation cell goes to infinity.
- Ewald and MPC energies per particle are the same in the limit of large system size, even if approximate charge density is used.
- MPC interaction is quicker to evaluate than the Ewald interaction; however MPC interaction distorts the XC hole, so Ewald interaction must be used in propagation.⁵
 - Probable reason for behaviour: MPC Hamiltonian does not include equivalent terms to deal with the error in the kinetic energy.

⁵ N. D. Drummond *et al.*, Phys. Rev. B **78**, 125106 (2008).

Model Periodic Coulomb Interaction (III)



Finite-Size Correction to the Exchange–Correlation Energy (I)

- Charge density and hence Hartree energy converge rapidly with system size.
- Form of structure factor converges rapidly with system size. It goes as k^2 at small k .
- So the finite-size correction to the Ewald interaction energy is⁶:

$$\begin{aligned}\Delta V &= \frac{N}{4\pi^2} \int \frac{S(\mathbf{k}) - 1}{k^2} d\mathbf{k} - \frac{2\pi N}{\Omega} \sum_{\mathbf{G} \neq 0} \frac{S(\mathbf{G}) - 1}{G^2} - \frac{Nv_M}{2} \\ &= \frac{N}{4\pi^2} \int \frac{S(\mathbf{k})}{k^2} d\mathbf{k} - \frac{2\pi N}{\Omega} \sum_{\mathbf{G} \neq 0} \frac{S(\mathbf{G})}{G^2} \approx \frac{2\pi N}{\Omega} \lim_{k \rightarrow 0} \frac{\bar{S}(k)}{k^2},\end{aligned}$$

i.e., the leading-order correction is the missing $\mathbf{G} = \mathbf{0}$ term in the sum.⁷

- ΔV is $\mathcal{O}(N^0)$, i.e. correction to interaction energy per particle is $\mathcal{O}(N^{-1})$.

⁶ S. Chiesa *et al.*, Phys. Rev. Lett. **97**, 076404 (2006).

⁷ To get from the first line to the second, insert factors of $\exp(-\epsilon k^2)$ and $\exp(-\epsilon G^2)$ in the integrand and summand and choose $\gamma = 1/(2\sqrt{\epsilon})$ in the Ewald expression for v_M ; finally take the limit $\epsilon \rightarrow 0$. Note that $\bar{S}(k) = \kappa k^2 + \mathcal{O}(k^4)$.

Finite-Size Correction to the Exchange–Correlation Energy (II)

- Summary: add $(2\pi N/\Omega) \lim_{\mathbf{k} \rightarrow 0} \bar{S}(k)/k^2$ to correct exchange–correlation energy.
 - Can show that the residual error is $\mathcal{O}(N^{-1})$ in cubic systems and $\mathcal{O}(N^0)$ in noncubic systems with noncubic sim. cells.⁸
 - *In noncubic systems, try to use a (nearly) cubic simulation cell.*
- Finite-size correction and MPC are both essentially exact for cubic systems; results ought to agree.
 - Can prove equivalence directly.
- For an electron gas, *random phase approximation* implies that $S(\mathbf{k}) = k^2/(2\omega_p)$ for small \mathbf{k} , where $\omega_p = \sqrt{4\pi N/\Omega}$ is the plasma frequency.
 - Hence $\Delta V = \omega_p/4$ for an electron gas.

⁸ N. D. Drummond *et al.*, Phys. Rev. B **78**, 125106 (2008).

Finite-Size Correction to the Exchange–Correlation Energy (III)

r_s	N	$(E_{\text{MPC}} - E_{\text{Ew}})/N$ (a.u. / elec.)	$\Delta V_{\text{Ew}}/N$ (a.u. / elec.)
1	54	0.007 81(1)	0.008 02
1	102	0.004 137(9)	0.004 245
1	226	0.001 89(1)	0.001 92
3	54	0.001 551(4)	0.001 543
3	102	0.000 802(2)	0.000 817
3	226	0.000 365(1)	0.000 369
10	54	0.000 242(1)	0.000 254
10	102	0.000 131 9(4)	0.000 134 2
10	226	0.000 060 5(7)	0.000 060 6

- E_{Ew} is total SJ-DMC energy per particle obtained using Ewald interaction.
- E_{MPC} is total SJ-DMC energy per particle obtained using MPC interaction.⁹
- MPC and finite-size-corrected Ewald results are very similar.

⁹ E_{Ew} was used in the branching factor in DMC, so the kinetic energy is the same in the two cases.

MPC v. Exchange–Correlation Correction

- MPC is accurate in both noncubic and cubic systems. Exchange–correlation correction may not work so well in noncubic systems.
- Exchange–correlation correction can make use of analytic results for long-range behaviour.
- MPC doesn't require structure factor (or expansion of structure factor in spherical harmonics at $\mathbf{k} = \mathbf{0}$).
- Exchange–correlation correction is a more general method. MPC is only applicable when the leading-order errors are due to slow convergence of v_E ; doesn't help when errors are due to slow convergence of exchange–correlation hole, e.g. in Hartree–Fock theory.

Finite-Size Correction to the Kinetic Energy (I)

- The two-body correlations described by the Jastrow factor are long-range.
- They are restricted in a finite simulation cell: leads to bias in kinetic energy.
- Correct for this by interpolating Fourier transformation of two-body Jastrow factor.¹⁰
- Write Ψ as the product of a long-range two-body Jastrow factor $\exp(u)$, which has the periodicity of the simulation cell and inversion symmetry, and a part consisting of everything else, Ψ_s :

$$\begin{aligned}\Psi &= \Psi_s \exp \left(\sum_{i>j} u(\mathbf{r}_i - \mathbf{r}_j) \right), \\ &= \Psi_s \exp \left(\frac{1}{2\Omega} \sum_{\mathbf{G} \neq 0} u(\mathbf{G}) \hat{\rho}^*(\mathbf{G}) \hat{\rho}(\mathbf{G}) + K \right).\end{aligned}$$

¹⁰ S. Chiesa *et al.*, Phys. Rev. Lett. **97**, 076404 (2006).

Finite-Size Correction to the Kinetic Energy (II)

- “TI” kinetic-energy estimator:

$$\hat{T} = \frac{-1}{4} \nabla^2 \log(\Psi) = \hat{T}_s - \frac{1}{8\Omega} \sum_{\mathbf{G} \neq 0} u(\mathbf{G}) \nabla^2 [\hat{\rho}^*(\mathbf{G}) \hat{\rho}(\mathbf{G})],$$

where $T_s = -\nabla^2 \log(\Psi_s)/4$.

- Use $\nabla^2 [\hat{\rho}^*(\mathbf{G}) \hat{\rho}(\mathbf{G})] = -2G^2 [\hat{\rho}^*(\mathbf{G}) \hat{\rho}(\mathbf{G}) - N]$ to show that

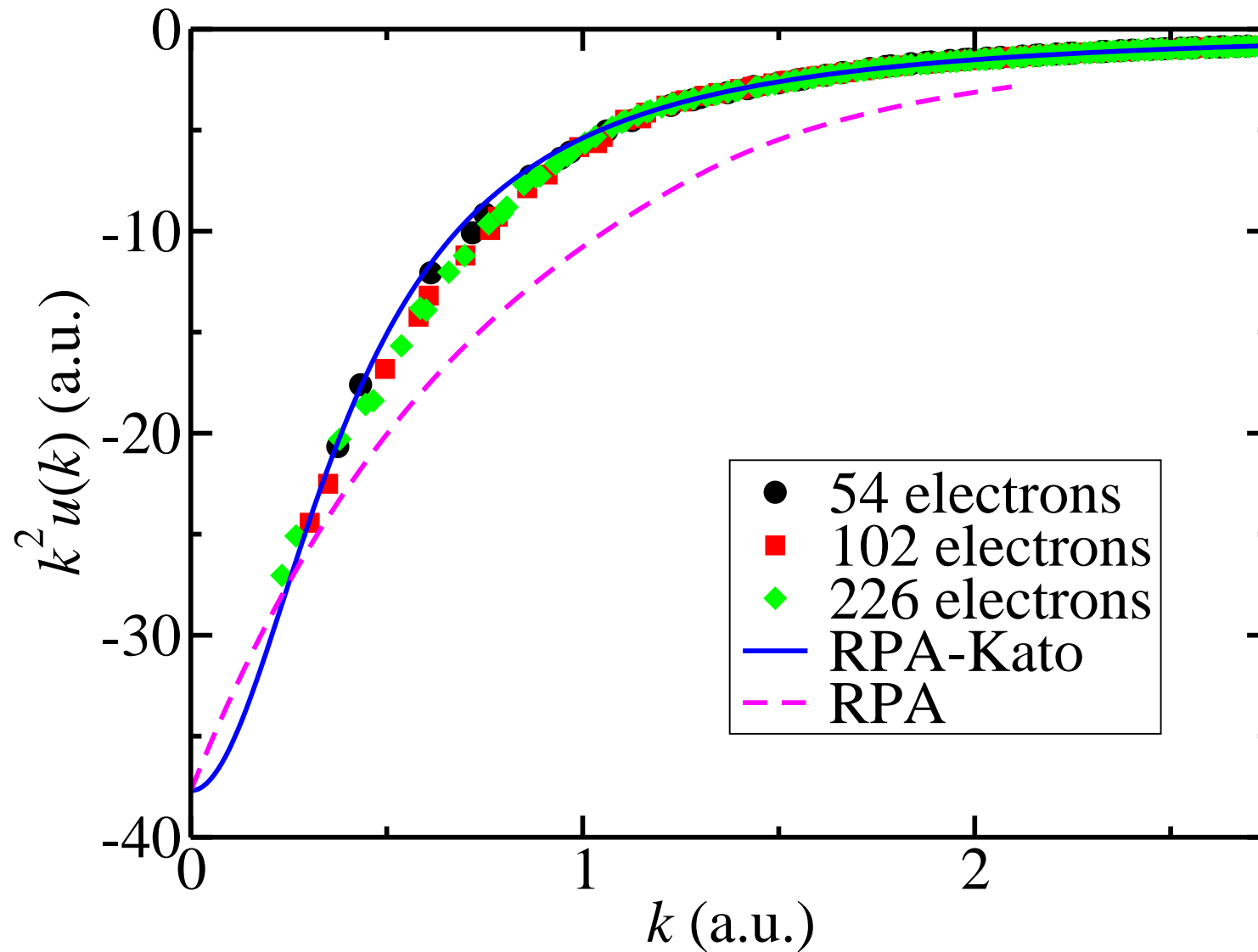
$$\langle T \rangle = \langle T_s \rangle + \frac{1}{4\Omega} \sum_{\mathbf{G} \neq 0} G^2 [u(\mathbf{G}) \langle \hat{\rho}^*(\mathbf{G}) \hat{\rho}(\mathbf{G}) \rangle - Nu(\mathbf{G})].$$

- $\rho(\mathbf{k})$ is only nonzero for \mathbf{G} vectors of the primitive lattice. Assuming the sum runs only over small \mathbf{G} ,

$$\langle T \rangle = \langle T_s \rangle + \frac{N}{4\Omega} \sum_{\mathbf{G} \neq 0} G^2 u(\mathbf{G}) S^*(\mathbf{G}) - \frac{N}{4\Omega} \sum_{\mathbf{G} \neq 0} G^2 u(\mathbf{G}).$$

Finite-Size Correction to the Kinetic Energy (III)

$u(\mathbf{k})$ has same form at different N . It diverges as k^{-2} , so $\lim_{k \rightarrow 0} k^2 \bar{u}(k)$ exists.



Finite-Size Correction to the Kinetic Energy (IV)

- In the infinite system limit, the sum over \mathbf{G} should be replaced by an integral.
- Leading-order finite-size error is the omission of the $\mathbf{G} = \mathbf{0}$ contribution in the third term in the expression for $\langle T \rangle$. Gives a correction¹¹

$$\Delta T_A \approx -\frac{N}{4\Omega} \lim_{k \rightarrow 0} k^2 \bar{u}(k).$$

- For an electron gas, random phase approximation (RPA) implies that $\lim_{k \rightarrow 0} k^2 \bar{u}(k) = -4\pi/\omega_p$.
 - Hence $\Delta T_A = \omega_p/4$.
- Unfortunately, the next-to-leading-order correction ΔT_B is also important.¹²
- Residual single-particle finite-size errors in the canonical-ensemble twist-averaged data are also significant. These errors can be estimated within Hartree–Fock theory.

¹¹ S. Chiesa *et al.*, Phys. Rev. Lett. **97**, 076404 (2006).

¹² N. D. Drummond *et al.*, Phys. Rev. B **78**, 125106 (2008).

Higher-Order Corrections to the Kinetic Energy

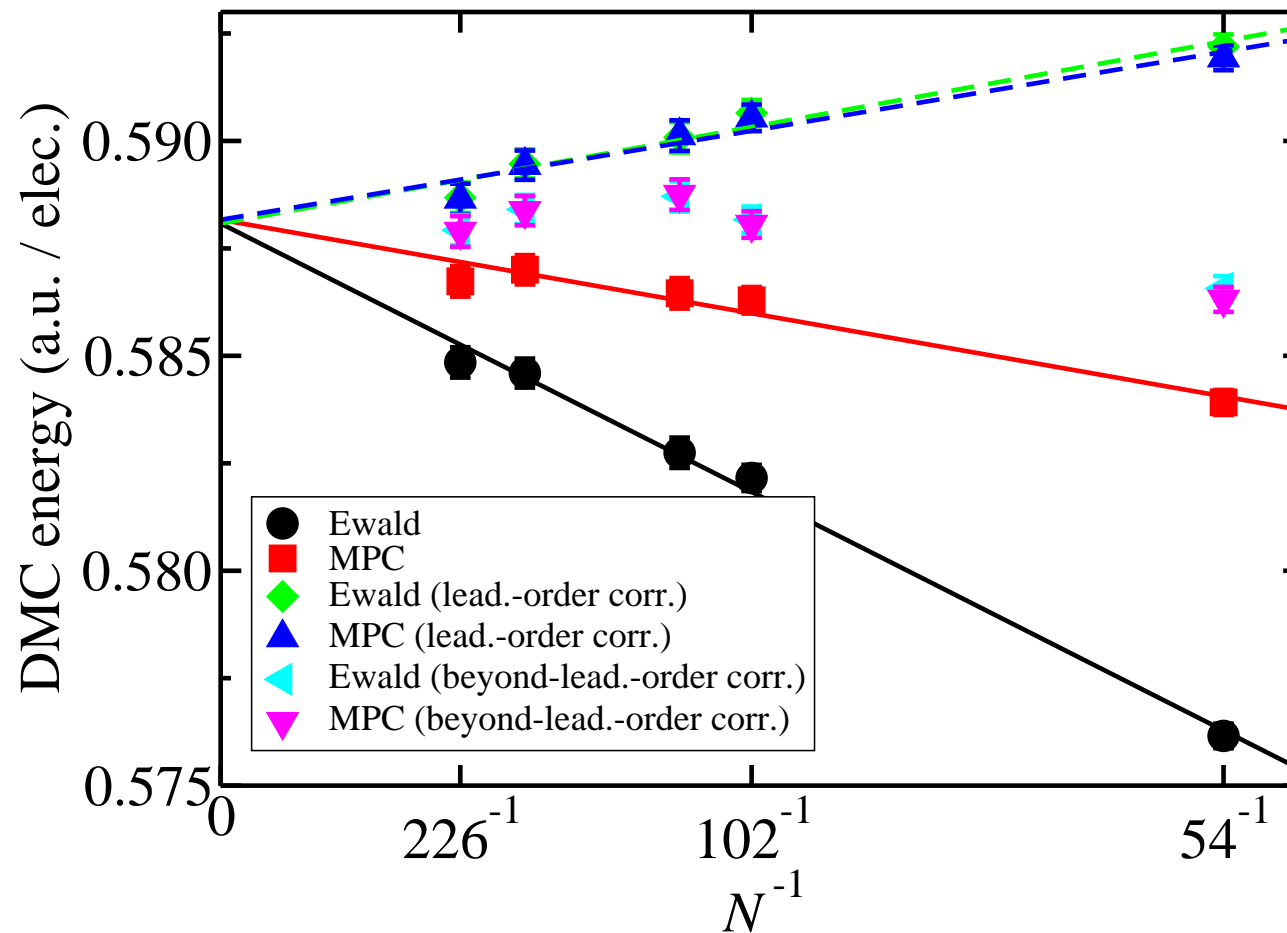
- Magnitude of finite-size corrections to the kinetic energy of 3D electron gases:

r_s (a.u.)	N	KE error (a.u. per elec.)		
		Single-particle corr.	ΔT_A	ΔT_B
1	54	-0.002 8	0.008 0	-0.001 6
1	130	-0.000 65	0.003 33	-0.000 48
3	54	-0.000 31	0.001 54	-0.000 17
3	130	-0.000 072	0.000 641	-0.000 054
10	54	-0.000 027	0.000 254	-0.000 015
10	130	-0.000 006	0.000 105	-0.000 005

- Residual single-particle error is comparable with next-to-leading order correction (ΔT_B).

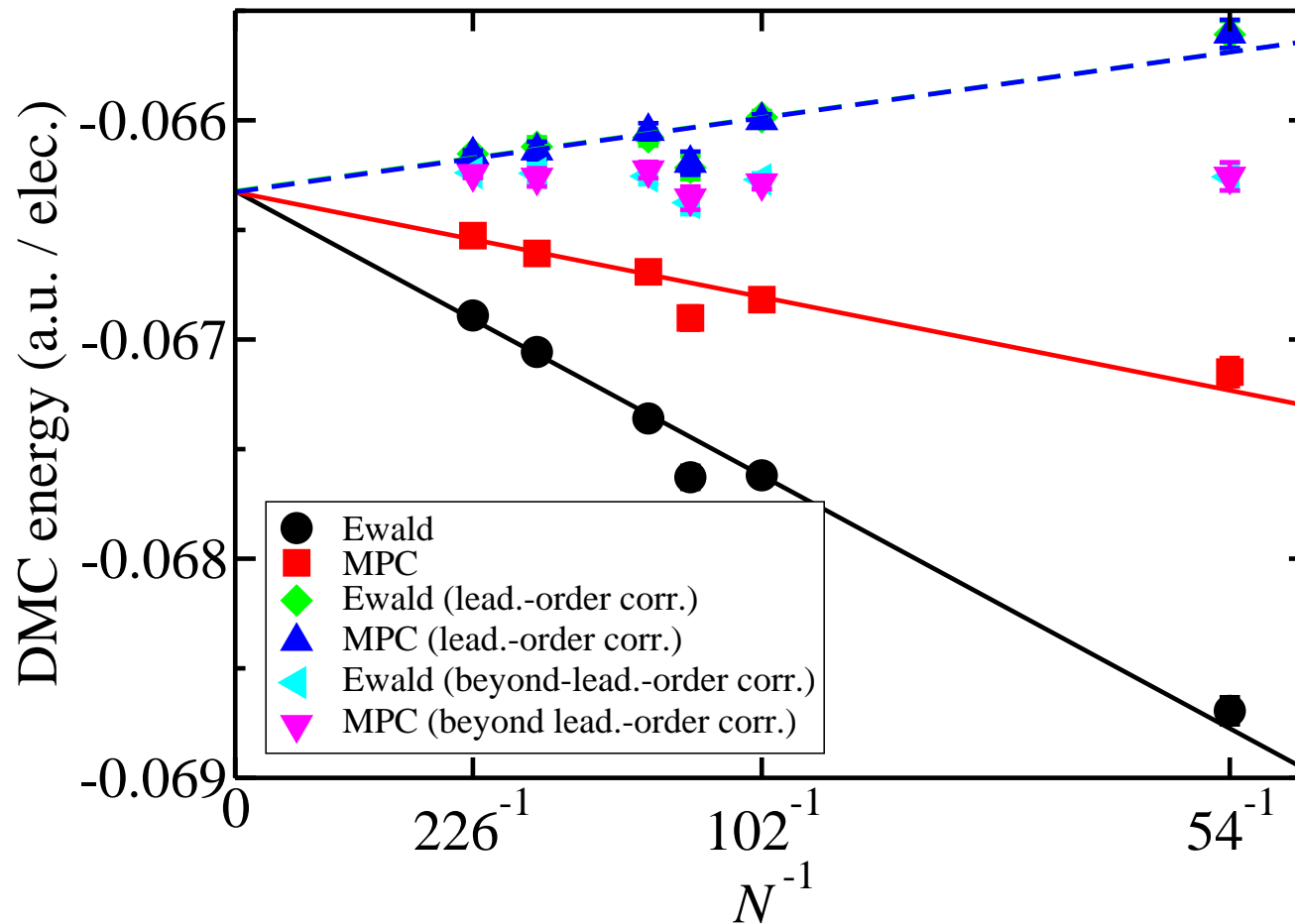
Finite-Size Errors in a 3D Electron Gas (I): High Density

- DMC results for a 3D electron gas, $r_s = 1$ a.u. (using twist averaging and a Slater–Jastrow wave function):



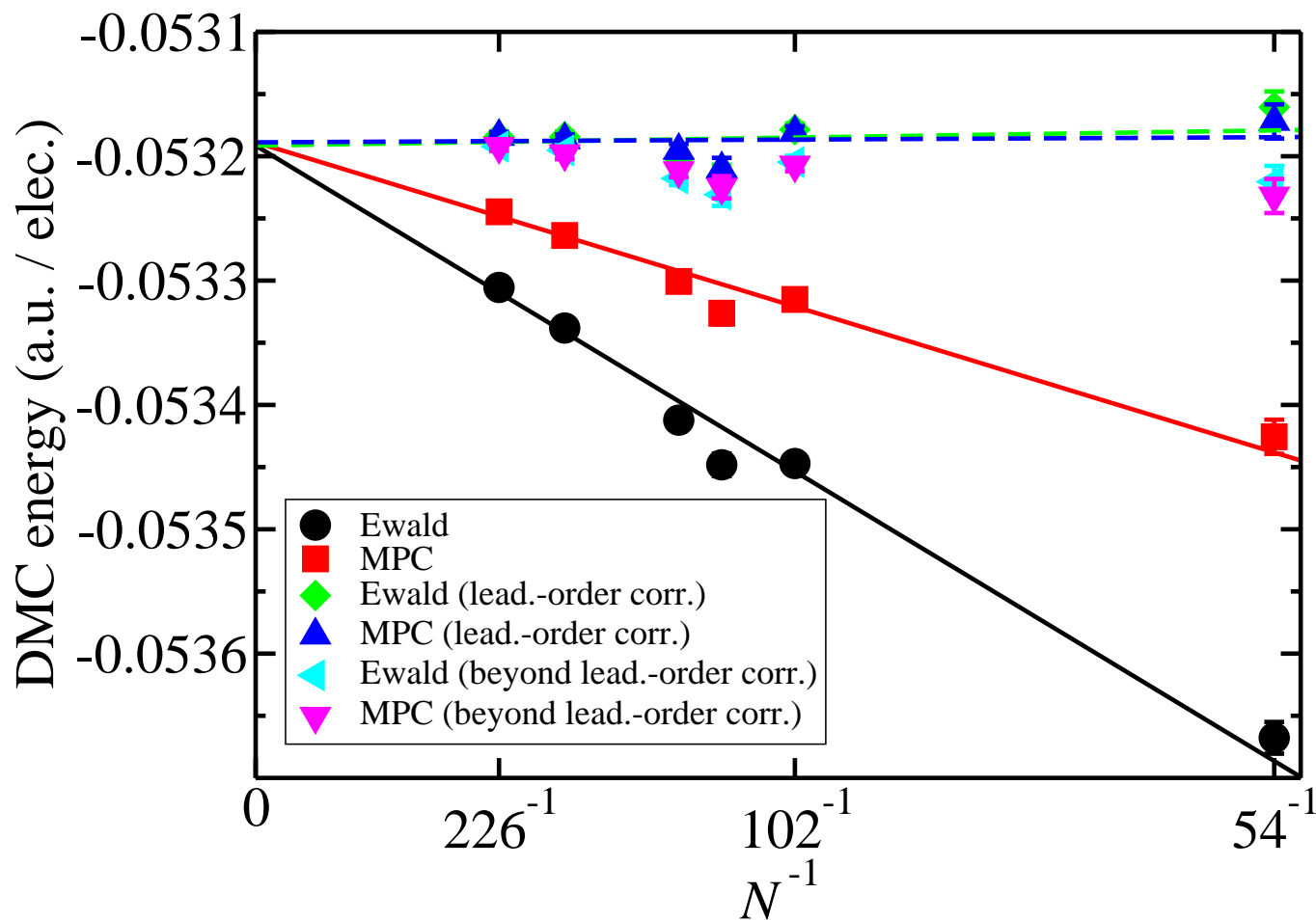
Finite-Size Errors in a 3D Electron Gas (II): Intermediate Density

- DMC results for a 3D electron gas, $r_s = 3$ a.u. (using twist averaging and a Slater–Jastrow wave function):



Finite-Size Errors in a 3D Electron Gas (III): Low Density

- DMC results for a 3D electron gas, $r_s = 10$ a.u. (using twist averaging and a Slater–Jastrow wave function):

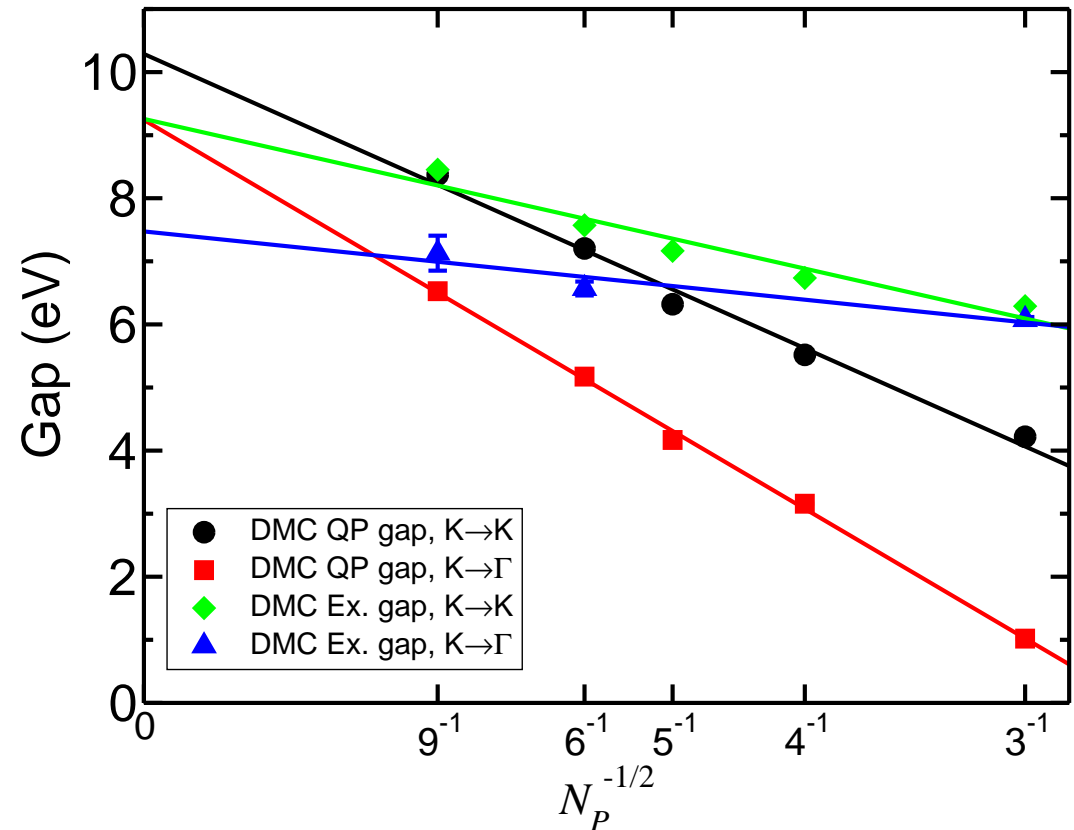


2D-Periodic Systems

- Can carry out similar analysis for 2D-periodic systems.
- Leading order error in total energy per particle goes as $N^{-1/4}$.
- Theory of corrections doesn't work so well because exchange–correlation hole is relatively long-range and therefore slowly convergent with system size.

Finite-Size Errors in Other Quantities

- We have discussed finite-size errors in the total energy.
- The density converges very rapidly with system size.
- The convergence of the pair density is limited by the fact that its r^{-8} tail is truncated.
- Open research questions: what can we say about finite-size errors in excitation energies? In 2D they are extremely significant.



DMC quasiparticle and excitonic bandgaps in a boron nitride monolayer appear to fall off as the reciprocal of the linear size of the cell.

Finite-Size Exchange–Correlation Functional

- **DFT correction to finite-size error in QMC¹³**: use DMC energies for electron gases to construct finite-size LDA exchange–correlation functionals, then use these functionals to evaluate finite-size corrections for real systems within DFT.
- **Finite-size LDA**: exchange–correlation energy at a point in space with density ρ is equal to the exchange–correlation energy of a finite electron gas of density ρ in a periodic cell whose volume is equal to the unfolded supercell volume of the real system.
- Evaluate finite-size correction as difference between a highly converged DFT energy with the usual (infinite-system) LDA and the finite-size LDA energy for a \mathbf{k} -point sampling corresponding to the QMC calculation to be corrected.
- *Single-particle and long-range finite-size errors are corrected simultaneously in this approach.*
- Effects due to shape of simulation cell, etc., are neglected.

¹³ H. Kwee *et al.*, Phys. Rev. Lett. **100**, 126404 (2008).

Conclusions

- QMC simulations of periodic systems suffer from finite-size errors.
- Finite-size errors **must** be accounted for in any QMC study of condensed matter.
- Methods for dealing with finite-size errors (use appropriate combinations of these; don't add the exchange–correlation correction to the MPC energy, for example!):
 1. *Use a large finite simulation cell!*
 2. *In noncubic systems choose the simulation cell to be as nearly cubic as possible.*
 3. *Make a sensible choice of \mathbf{k}_s (offset to the grid of \mathbf{k} vectors).*
 4. *Twist average to reduce single-particle finite-size errors.*
 5. *Extrapolate to infinite system size using fitting formulae.*
 6. *Use MPC interaction to reduce Coulomb finite-size biases.*
 7. *Add corrections to the kinetic and exchange–correlation energies to account for the difference between a sum with a missing term and an integral.*
 8. *Add correction evaluated within DFT using infinite- and finite-cell LDA functionals.*
- Sometimes have cancellation of finite-size biases when energy differences are taken.