

Ewald Interactions and Finite-Size Errors

Neil Drummond

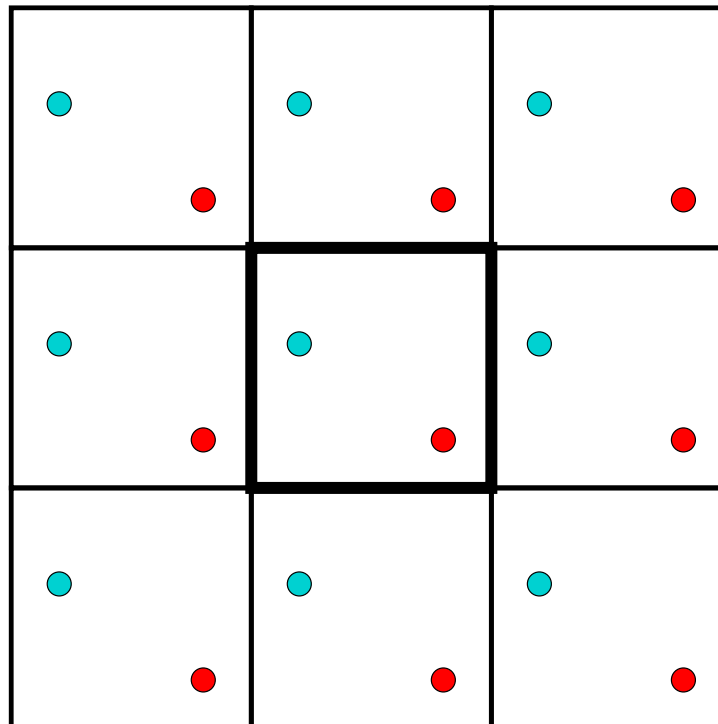
TCM Group, Cavendish Laboratory, University of Cambridge

2007 Summer School on Computational Materials Science
University of Illinois at Urbana-Champaign, USA

Friday 13th July, 2007

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 numbers 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:

$$V(\mathbf{r}_1, \dots, \mathbf{r}_N) = \sum_{\mathbf{R}} \sum_{i>j} \frac{q_i q_j}{|\mathbf{r}_i - \mathbf{r}_j - \mathbf{R}|},$$

where q_i is the charge of particle i 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

¹P. 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

- Poisson's equation for the electrostatic potential:

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

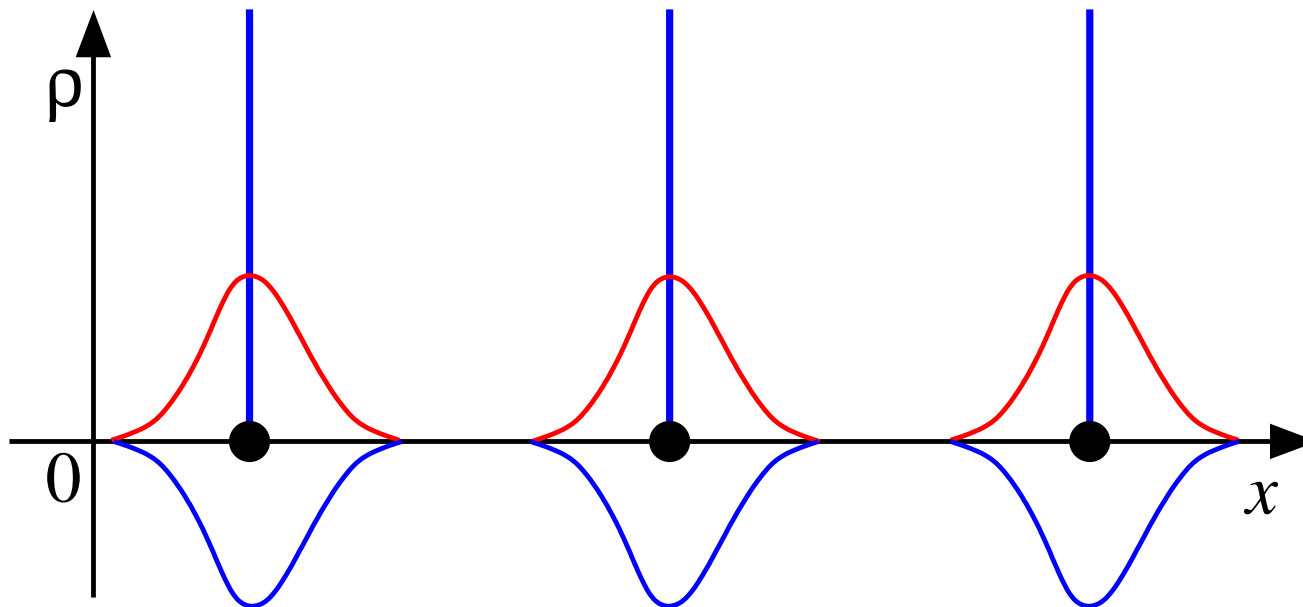
- Hence the Fourier components are related by

$$\Phi_{\mathbf{G}} = \frac{4\pi\rho_{\mathbf{G}}}{|\mathbf{G}|^2}.$$

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 Ewald Interaction (V): the Reciprocal-Space Sum

- The Fourier components of ρ_a are

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

- Hence the electrostatic potential due to ρ_a is

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

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

- Consider a Gaussian charge distribution centred on the origin:

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

The electrostatic potential is

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

- 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

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

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

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

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

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

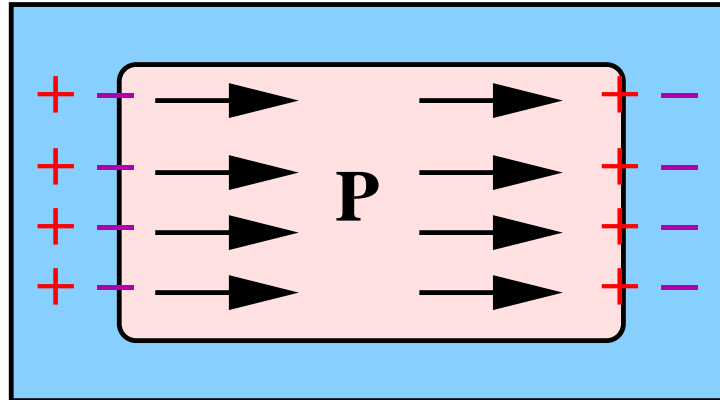
where

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

- Fourier transform of $v_E(\mathbf{r})$ is $v_E(\mathbf{G}) = 4\pi/|\mathbf{G}|^2$. Fourier series for v_E is not convergent; interpret $v_E(\mathbf{G})$ as a distribution.

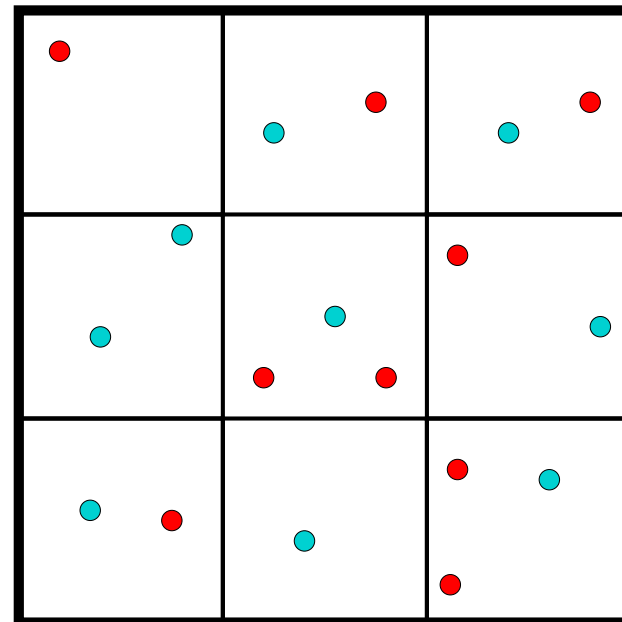
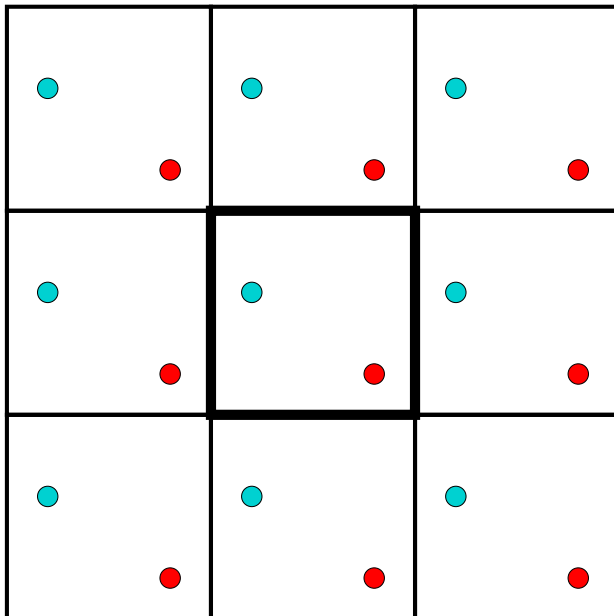
The Ewald Interaction (IX): Comments

- Ewald energy V is independent of γ . Larger values of γ make real-space sum more rapidly convergent; smaller values make reciprocal-space sum more rapidly convergent.
- 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*.



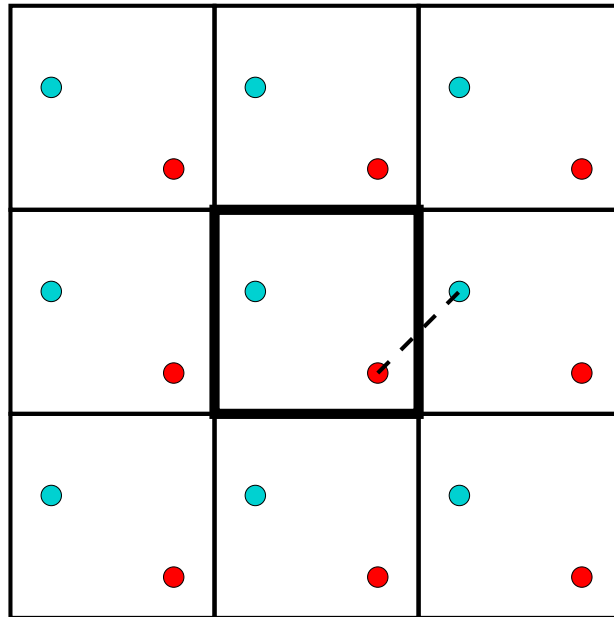
Simulation and Primitive Unit Cells

- 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-ranged.
- Must build simulation cell from several primitive cells.



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} .

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

- Nonzero \mathbf{k}_s : **twisted boundary conditions** (see later).
- Use ideas from band structure; e.g., for insulators choose \mathbf{k}_s to be Baldereschi point.

²G. 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 \mathbf{k} 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 $E_{\text{QMC}}(n) - E_{\text{QMC}}(\infty) \propto [E_{\text{DFT}}(n) - E_{\text{DFT}}(\infty)]$ where $E(n)$ is the energy obtained using an $n \times n \times n$ \mathbf{k} -point mesh.
- Hence can use DFT (or HF) 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.

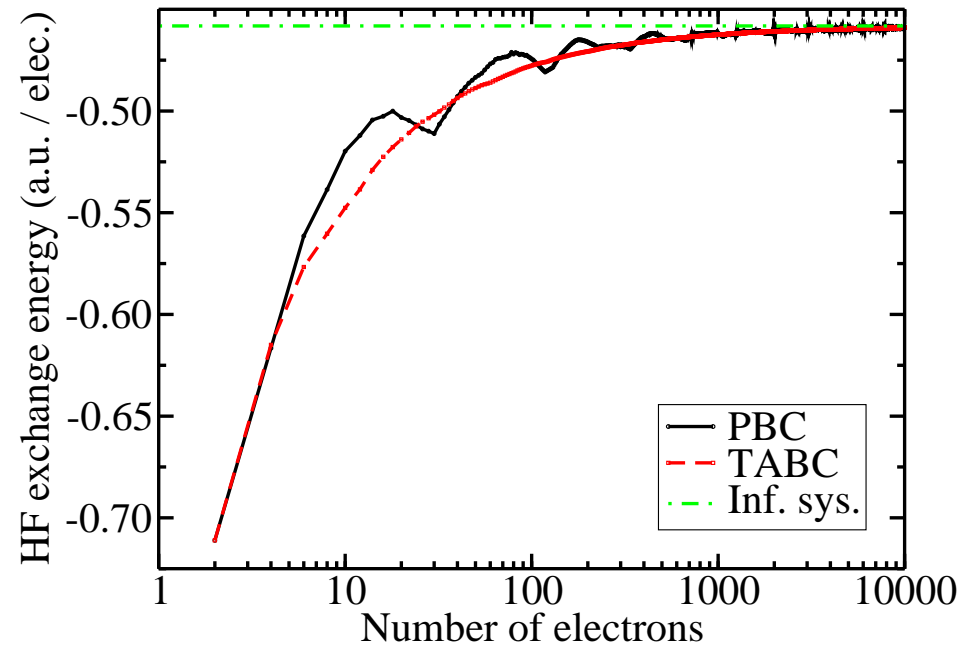
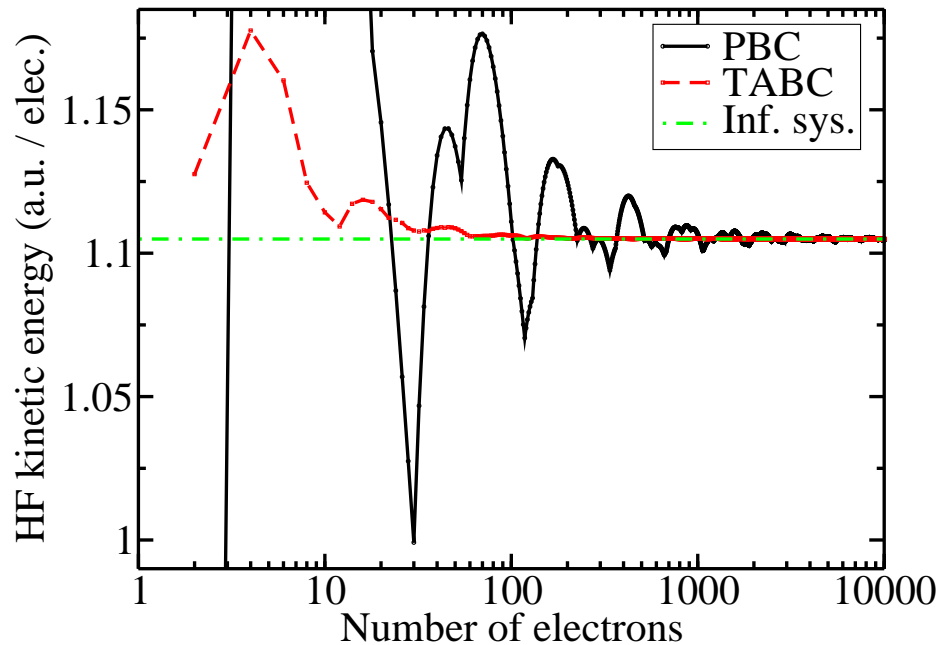
Twist Averaging (I)

- **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} is an integer multiple of the simulation-cell reciprocal lattice vectors in the first Brillouin zone of the primitive 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 $\psi_{\mathbf{k}}(\mathbf{r}) = \exp[i(\mathbf{k} + \mathbf{k}_s) \cdot \mathbf{r}]u_{\mathbf{k}}(\mathbf{r})$.
- **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.

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

Twist Averaging (II)

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.:



Twist averaging greatly dampens the energy fluctuations caused by shell filling.

Making Real Orbitals (I)

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

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

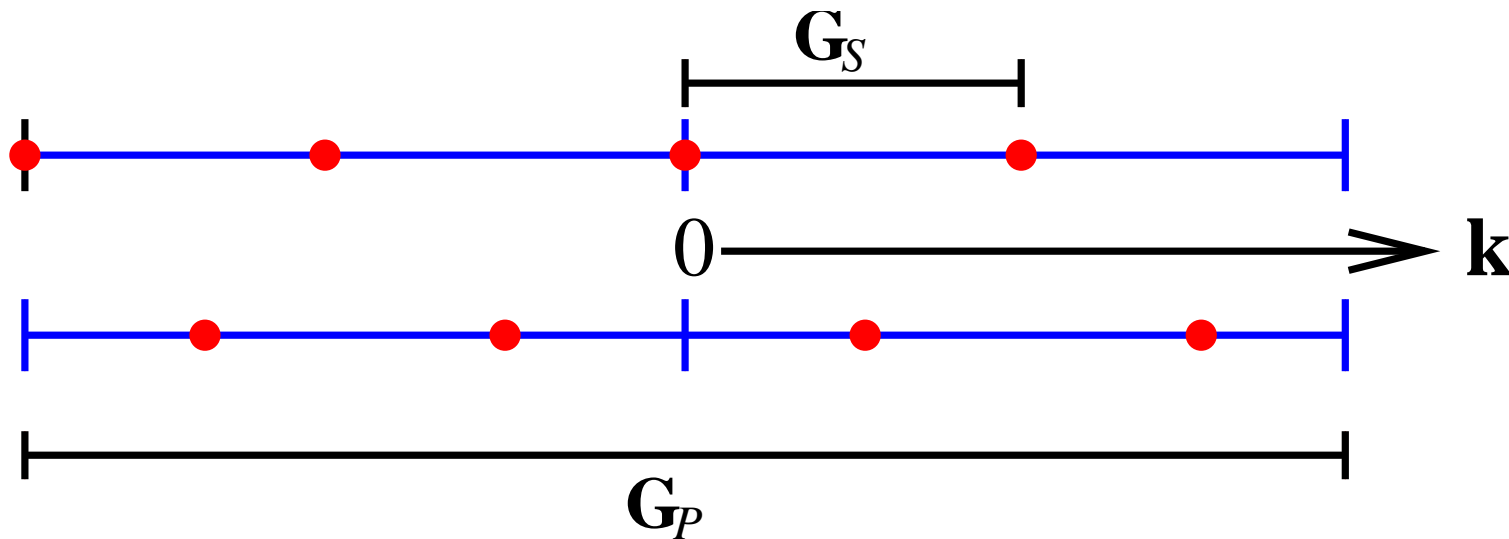
- Nonsingular linear transformations of the columns of the Slater determinant leave the wave function unchanged (up to normalisation).
- So can replace occupied orbitals $\psi_{\mathbf{k}}$ and $\psi_{-\mathbf{k}}$ by

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

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

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

$$E_N = E_\infty + a (T_N^{\text{HF}} - T_\infty^{\text{HF}}) - \frac{b}{N},$$

where a , b and E_∞ are fitting parameters and T_N^{HF} is the Hartree–Fock (or DFT) kinetic energy of an N -particle system.

- For electron gases etc. T_∞^{HF} can be calculated exactly; otherwise it must be taken from a HF/DFT calculation with a fine \mathbf{k} -point mesh.
- 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.
- Better to correct finite-size errors than to rely on fitting.

Static Structure Factors

Spin-resolved static structure factor:

$$S_{\alpha\beta}(\mathbf{r}, \mathbf{r}') = \frac{1}{N} \langle [\hat{\rho}_\alpha(\mathbf{r}) - \rho_\alpha(\mathbf{r})][\hat{\rho}_\beta(\mathbf{r}') - \rho_\beta(\mathbf{r}')] \rangle$$

where $\hat{\rho}_\alpha(\mathbf{r}) = \sum_i \delta(\mathbf{r} - \mathbf{r}_{i\alpha})$ is the density operator and $\rho_\alpha(\mathbf{r}) = \langle \hat{\rho}_\alpha(\mathbf{r}) \rangle$ is the density for electrons of spin α . N.B. $\hat{\rho} = \sum_\alpha \hat{\rho}_\alpha$ and $S = \sum_{\alpha,\beta} S_{\alpha\beta}$.

Translationally averaged structure factor:

$$S_{\alpha\beta}(\mathbf{r}) = \frac{1}{\Omega} \int_{\Omega} S_{\alpha\beta}(\mathbf{r}' + \mathbf{r}, \mathbf{r}') d\mathbf{r}'.$$

Fourier transform of the translationally averaged structure factor:

$$S_{\alpha\beta}(\mathbf{G}) = \frac{1}{N} \left(\langle \hat{\rho}_\alpha(\mathbf{G}) \hat{\rho}_\beta^*(\mathbf{G}) \rangle - \rho_\alpha(\mathbf{G}) \rho_\beta^*(\mathbf{G}) \right),$$

where $\hat{\rho}_\alpha(\mathbf{G}) = \sum_i \exp(-i\mathbf{G} \cdot \mathbf{r}_{i\alpha})$ is the Fourier transform of the density operator.

Interaction Energy in Terms of the Structure Factor

$$\begin{aligned} V_{ee} &= \frac{Nv_M}{2} + \frac{\int |\Psi(\mathbf{R})|^2 \frac{1}{2} \sum_{i \neq j} v_E(\mathbf{r}_i - \mathbf{r}_j) d\mathbf{R}}{\int |\Psi(\mathbf{R})|^2 d\mathbf{R}} \\ &= \frac{1}{2} \int \int [\rho(\mathbf{r}, \mathbf{r}') - \rho(\mathbf{r})\rho(\mathbf{r}')] [v_E(\mathbf{r} - \mathbf{r}') - v_M] d\mathbf{r} d\mathbf{r}' \\ &\quad + \frac{1}{2} \int \int v_E(\mathbf{r} - \mathbf{r}') \rho(\mathbf{r})\rho(\mathbf{r}') d\mathbf{r} d\mathbf{r}' \\ &= \frac{N}{2} \left(\sum_{\mathbf{G} \neq 0} \frac{4\pi}{\Omega |\mathbf{G}|^2} [S(\mathbf{G}) - 1] + v_M \right) + \sum_{\mathbf{G} \neq 0} \frac{2\pi\Omega}{|\mathbf{G}|^2} \rho(\mathbf{G})\rho^*(\mathbf{G}), \end{aligned}$$

where $\rho(\mathbf{r}, \mathbf{r}') = \left\langle \sum_{i \neq j} \delta(\mathbf{r} - \mathbf{r}_i) \delta(\mathbf{r}' - \mathbf{r}_j) \right\rangle$ is the pair density.

First term: **exchange-correlation energy** (interaction of electrons with their XC 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 XC hole should be $1/r$.
- This is enforced in the **model periodic Coulomb** interaction.⁴

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

Model Periodic Coulomb Interaction (I)

- MPC interaction operator:

$$\begin{aligned}\hat{H}_{ee} &= \frac{1}{2} \sum_{i \neq j} f(\mathbf{r}_i - \mathbf{r}_j) + \sum_i \int \rho(\mathbf{r}) [v_E(\mathbf{r}_i - \mathbf{r}) - f(\mathbf{r}_i - \mathbf{r})] d\mathbf{r} \\ &\quad - \frac{1}{2} \int \rho(\mathbf{r}) \rho(\mathbf{r}') [v_E(\mathbf{r} - \mathbf{r}') - f(\mathbf{r} - \mathbf{r}')] d\mathbf{r} d\mathbf{r}',\end{aligned}$$

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

- Electron-electron interaction energy:

$$\begin{aligned}\langle \hat{H}_{ee} \rangle &= \frac{1}{2} \int \rho(\mathbf{r}) \rho(\mathbf{r}') v_E(\mathbf{r} - \mathbf{r}') d\mathbf{r} d\mathbf{r}' \\ &\quad + \int \int [\rho(\mathbf{r}, \mathbf{r}') - \rho(\mathbf{r}) \rho(\mathbf{r}')] f(\mathbf{r} - \mathbf{r}') d\mathbf{r} d\mathbf{r}',\end{aligned}$$

i.e. Hartree energy + XC 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 HF calculation.
- The error due to this approximation is $\mathcal{O}(\rho - \rho_A)^2$. Furthermore the operator $(v_E - f)$ 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.

Model Periodic Coulomb Interaction (III)

- First term of MPC interaction is evaluated in real space, second term is evaluated in reciprocal space and third term is a constant:

$$\hat{H}_{ee} = \frac{1}{2} \sum_{i \neq j} f(\mathbf{r}_i - \mathbf{r}_j) + \frac{1}{\Omega} \sum_i \sum_{\mathbf{G} \neq 0} \left[\frac{4\pi}{|\mathbf{G}|^2} - f_{\mathbf{G}} \right] \rho_{A,\mathbf{G}} e^{i\mathbf{G} \cdot \mathbf{r}_i} + \left(-\frac{1}{\Omega} \sum_i f_0 \rho_{A,0} - \frac{1}{2\Omega} \sum_{\mathbf{G} \neq 0} \left[\frac{4\pi}{|\mathbf{G}|^2} - f_{\mathbf{G}} \right] \rho_{A,\mathbf{G}}^* \rho_{A,\mathbf{G}} + \frac{1}{2\Omega} f_0 \rho_{A,0}^* \rho_{A,0} \right).$$

- Fourier coefficients $f_{\mathbf{G}}$ are evaluated numerically. Requires care because $f(\mathbf{r})$ diverges at $\mathbf{r} = \mathbf{0}$ and is non-differentiable at the boundary of the Wigner-Seitz cell.

Finite-Size Correction to the XC Energy (I)

- Charge density and hence Hartree energy converge rapidly with system size.
- Form of structure factor converges rapidly with system size.
- So the finite-size error in the Ewald interaction energy is⁵:

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

where D is a sphere of volume $(2\pi)^3/\Omega$ centred on the origin.⁶

⁵S. Chiesa *et al.*, Phys. Rev. Lett. **97**, 076404 (2006).

⁶To see this, insert factors of $\exp(-\epsilon|\mathbf{k}|^2)$ and $\exp(-\epsilon|\mathbf{G}|^2)$ in the integrand and summand and choose $\kappa = 1/(2\sqrt{\epsilon})$ in the Ewald expression for v_M ; finally take the limit $\epsilon \rightarrow 0$.

Finite-Size Correction to the XC Energy (II)

- $S(\mathbf{k}) \propto |\mathbf{k}|^2$ at small \mathbf{k} , so ΔV is $\mathcal{O}(N^0)$, i.e. error in interaction energy per particle is $\mathcal{O}(N^{-1})$.
- Finite-size correction is an alternative to using MPC. (Don't use both!)
- Insert $f(r) = v_E(r) - v_M - 2\pi\mathbf{r}^T W \mathbf{r} / (3\Omega) + \dots$ into MPC XC energy; find that XC correction ΔV arises from quadratic term.⁷
- MPC is “perfect” if XC hole fits into sim. cell; adding ΔV to the Ewald energy is then merely an approximation to the MPC; however, if XC hole does not fit into sim. cell then MPC is not perfect and the finite-size correction can make use of known form of $S(\mathbf{k})$ at small k . Not yet clear which is best.
- For a homogeneous electron gas, *random phase approximation* implies that $S(\mathbf{k}) = |\mathbf{k}|^2 / (2\omega_p)$ for small \mathbf{k} , where $\omega_p = \sqrt{4\pi N / \Omega}$ is the plasma frequency.
- Hence $\Delta V = \omega_p / 4$ for a HEG.

⁷W. M. C. Foulkes, unpublished.

Finite-Size Correction to the XC Energy (III)

Results for a 3D electron gas, $r_s = 3$ a.u.:

N	$E_{\text{MPC}} - E_{\text{Ewald}}$ (a.u.)	$\omega_p/(4N)$ (a.u.)
54	0.0015(1)	0.00154
102	0.0008(1)	0.000817
226	0.00037(6)	0.000369

E_{Ewald} is total SJ-DMC energy per particle obtained using Ewald interaction.

E_{MPC} is total SJ-DMC energy per particle obtained using MPC interaction.⁸

⁸ E_{Ewald} was used in the branching factor in DMC, so the kinetic energy is the same in the two cases.

Finite-Size Correction to the Kinetic Energy (I)

- The two-body correlations described by the Jastrow factor are long ranged.
- 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.⁹
- Write Ψ as the product of a long-ranged two-body Jastrow factor $\exp(u_{\alpha\beta})$, which has the periodicity of the simulation cell and inversion symmetry, and a part consisting of everything else, Ψ_s :

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

⁹S. Chiesa *et al.*, Phys. Rev. Lett. **97**, 076404 (2006).

Finite-Size Correction to the Kinetic Energy (II)

- “TI” kinetic-energy estimator:

$$T(\mathbf{R}) = \frac{-1}{4} \nabla^2 \log(\Psi) = T_s(\mathbf{R}) - \frac{1}{8\Omega} \sum_{\alpha, \beta} \sum_{\mathbf{G} \neq \mathbf{0}} u_{\alpha\beta}(\mathbf{G}) \nabla^2 [\hat{\rho}_\alpha^*(\mathbf{G}) \hat{\rho}_\beta(\mathbf{G})],$$

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

- Use $\nabla^2 [\hat{\rho}_\alpha^*(\mathbf{G}) \hat{\rho}_\beta(\mathbf{G})] = -2|\mathbf{G}|^2 [\hat{\rho}_\alpha^*(\mathbf{G}) \hat{\rho}_\beta(\mathbf{G}) - N_\alpha \delta_{\alpha\beta}]$ to show that

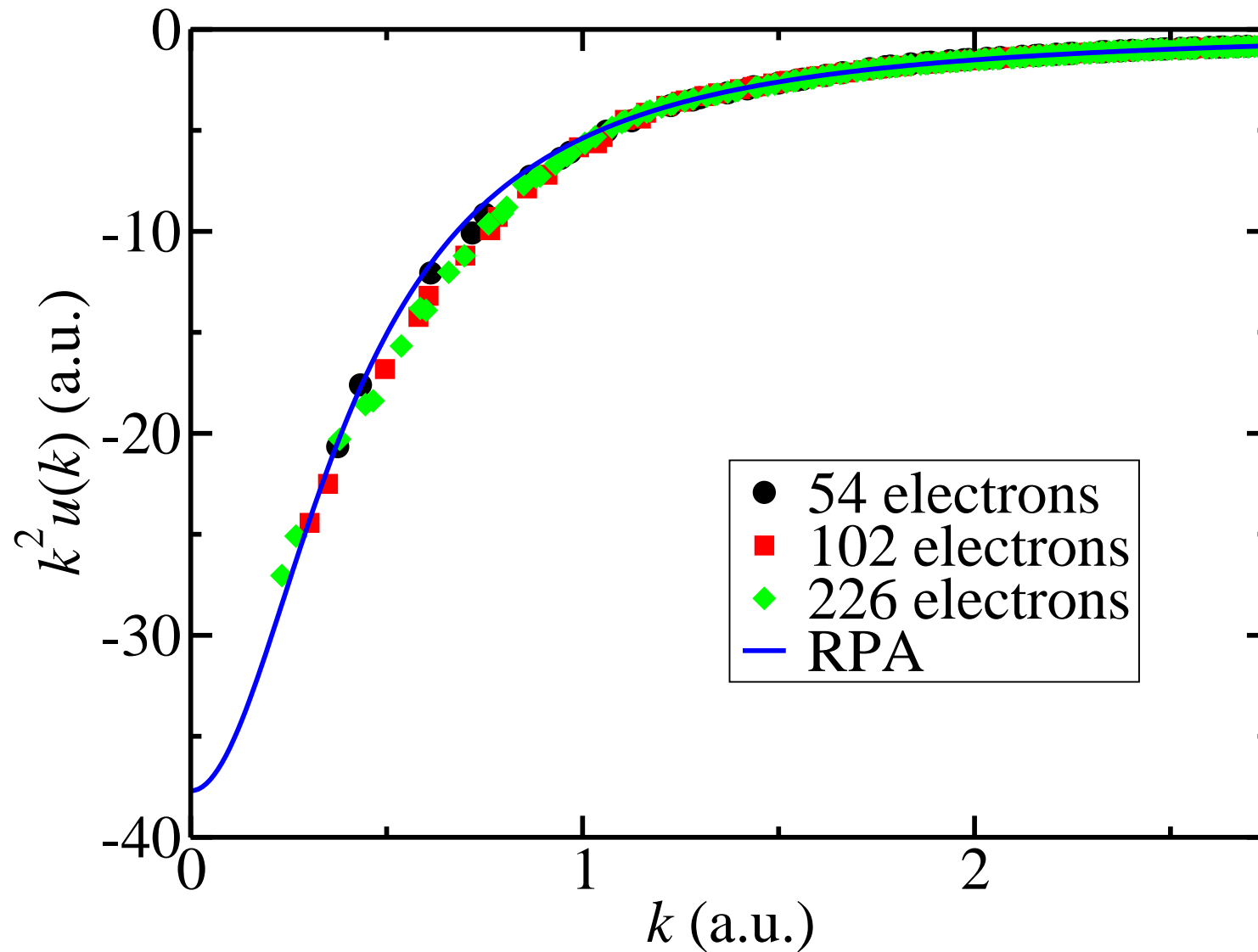
$$\langle T \rangle = \langle T_s \rangle + \frac{1}{4\Omega} \sum_{\mathbf{G} \neq \mathbf{0}} |\mathbf{G}|^2 \left(\sum_{\alpha, \beta} u_{\alpha\beta}(\mathbf{G}) \langle \hat{\rho}_\alpha^*(\mathbf{G}) \hat{\rho}_\beta(\mathbf{G}) \rangle - \sum_{\alpha} N_\alpha u_{\alpha\alpha}(\mathbf{G}) \right).$$

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

$$\langle T \rangle = \langle T_s \rangle + \frac{N}{4\Omega} \sum_{\mathbf{G} \neq \mathbf{0}} |\mathbf{G}|^2 \sum_{\alpha, \beta} u_{\alpha\beta}(\mathbf{G}) S_{\alpha\beta}^*(\mathbf{G}) - \frac{1}{4\Omega} \sum_{\mathbf{G} \neq \mathbf{0}} |\mathbf{G}|^2 \sum_{\alpha} N_\alpha u_{\alpha\alpha}(\mathbf{G}).$$

Finite-Size Correction to the Kinetic Energy (III)

$u_{\alpha\alpha}(\mathbf{k})$ has roughly the same form at different system sizes:



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 $\langle T \rangle$.
- The finite-size correction is therefore

$$\Delta T = - \sum_{\alpha} \frac{N_{\alpha}}{4(2\pi)^3} \int_0^D 4\pi k^2 \times k^2 \bar{u}_{\alpha\alpha}(k) dk$$

in 3D, where $\bar{u}(k)$ is the spherical average of $u(\mathbf{k})$ and D is the radius of a sphere of volume $(2\pi)^3/\Omega$.

Finite-Size Correction to the Kinetic Energy (V)

Infinite-system “random phase approximation” Jastrow factor for same-spin electrons:

$$u_{\alpha\alpha}(\mathbf{k}) = -4\pi A \left(\frac{1}{k^2} - \frac{1}{k^2 + 1/(2A)} \right).$$

where A is a parameter to be determined by fitting. Hence

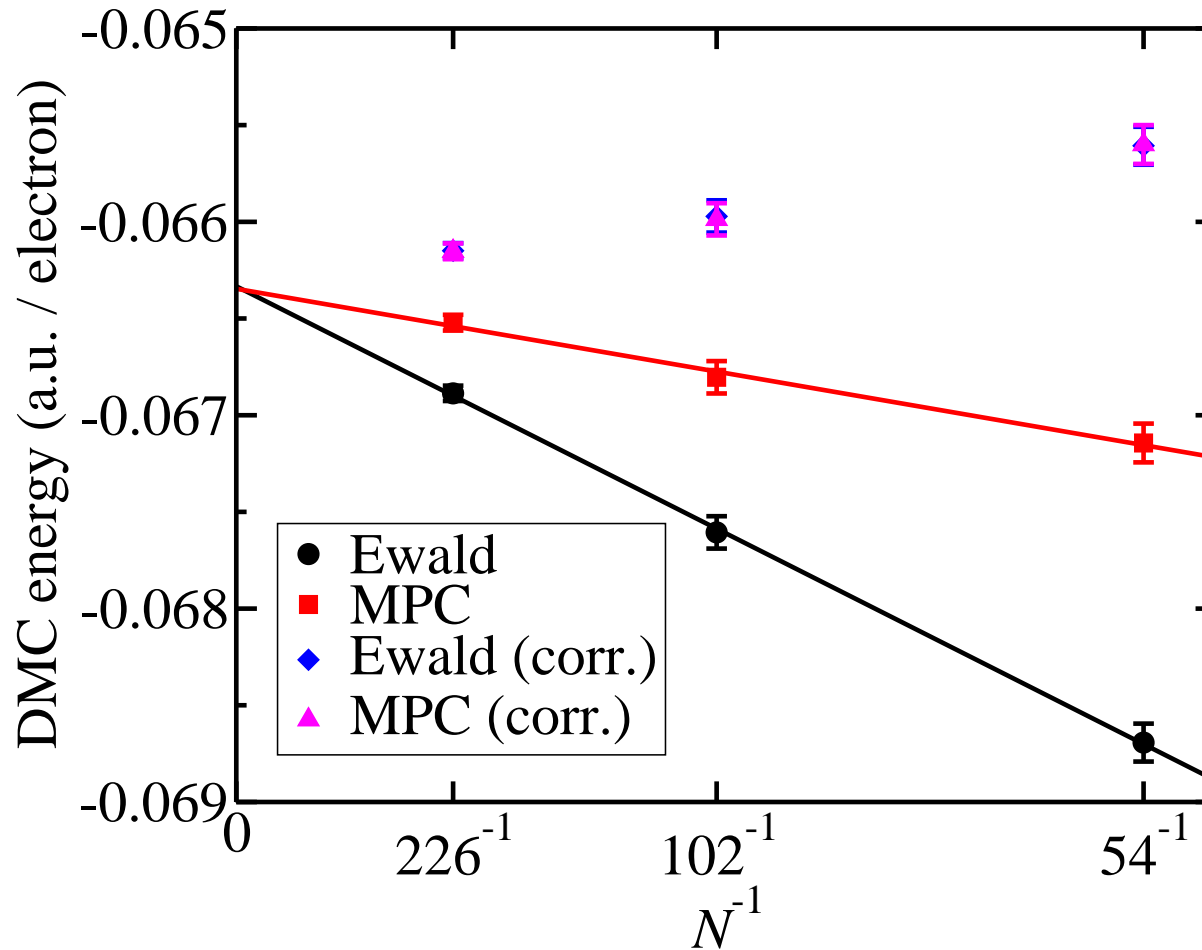
$$\begin{aligned} \Delta T &= \frac{N}{4\pi} \left(D - \frac{\tan^{-1}(\sqrt{2AD})}{\sqrt{2A}} \right) \\ &= \frac{\pi N A}{\Omega} + \mathcal{O}(N^{-2/3}), \end{aligned}$$

so the error in the KE per particle falls off as $\mathcal{O}(N^{-1})$.

- Homogeneous electron gas has $A = 1/\omega_p$, where ω_p is the plasma frequency.
- Hence leading-order correction to the KE is $\Delta T = \omega_p/4$ for a HEG.

Example: Finite-Size Errors in a 3D HEG

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



Correction: $\omega_p/(2N)$ for Ewald data and $\omega_p/(4N)$ for MPC data.

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):
 1. *Use a large finite simulation cell!*
 2. *Twist average to reduce single-particle finite-size errors.*
 3. *Extrapolate to infinite system size using fitting formulae.*
 4. *Use MPC interaction to reduce Coulomb finite-size biases.*
 5. *Add corrections to the kinetic and potential energy to account for differences between finite- and infinite-system two-body Jastrow factor and structure factor.*
- Can usually expect reasonable cancellation of finite-size biases when energy differences are taken.