Coulomb finite-size effects in quasi-2D systems

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Outline

- Background - Coulomb interactions and the simulation of extended systems

- Motivation for implementing an alternative quasi-2D interaction

- Results

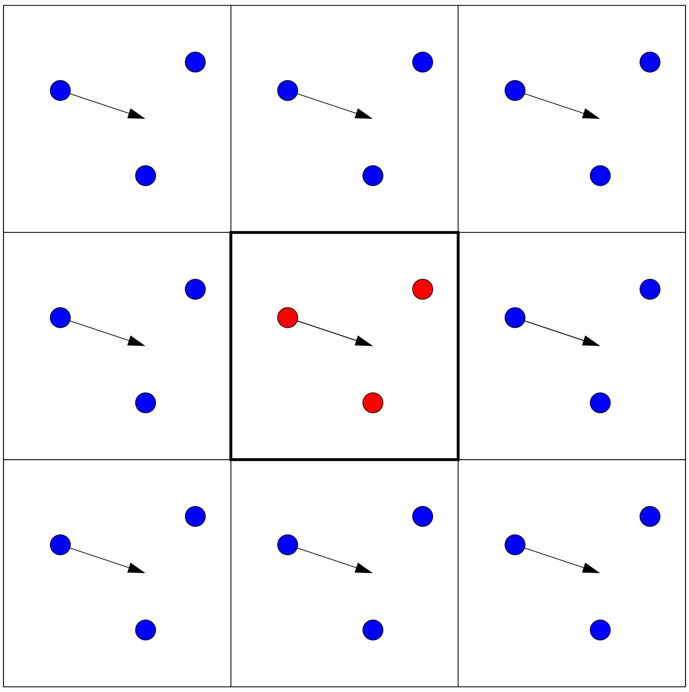
- More theory and conclusions

Background: simulation of extended systems

- Quantum Monte Carlo simulations are limited to thousands of electrons - not enough to simulate a bulk system

- The use of a supercell with periodic boundary conditions is required

- This leads to finite-size errors



Coulomb energy in supercell simulations

- Two categories of finite-size error have been identified in earlier work:
  - Independent-particle
  - Coulomb

- Independent-particle finite-size errors exist because the smooth density of states of a bulk material is replaced with a set of discrete points

- They may also be thought of as $\mathbf{k}$-point sampling errors

Coulomb finite-size errors

- To evaluate the energy during a simulation, it is necessary to know the potential due to an infinite lattice of charges

- Direct summation of potentials does not work - the sum is only conditionally convergent

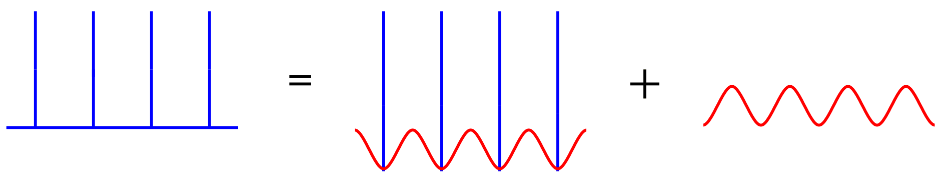
- This problem was traditionally solved by using the Ewald sum, which gives the periodic solution to Poisson's equation

The quasi-2D Ewald sum

- The aim is to evaluate the potential due to the charge distribution
$$\rho(\mathbf{r}) = \sum_{\mathbf{R}} \delta(\mathbf{r} - \mathbf{R})$$
where $\mathbf{R}$ is a 2D lattice vector

- The 3D Ewald method is to rewrite the charge distribution so that it consists of a smooth part (which will be evaluated in reciprocal space) and a strongly-localized part (which will be evaluated in real space)

- This becomes slightly more complicated for quasi-2D systems



- The density is split up into three parts:

$$\rho_1 = \sum_{\mathbf{R}} \left(\delta(\mathbf{r} - \mathbf{R}) - \frac{1}{\pi\sqrt{\pi}\sigma^3} e^{-(\mathbf{r}-\mathbf{R})^2/\sigma^2} \right)$$

$$\rho_2 = \sum_{\mathbf{R}} \frac{1}{\pi\sqrt{\pi}\sigma^3} e^{-(\mathbf{r}-\mathbf{R})^2/\sigma^2} - \frac{1}{\sqrt{\pi}\sigma A} e^{-z^2/\sigma^2}$$

$$\rho_3 = \frac{1}{\sqrt{\pi}\sigma A} e^{-z^2/\sigma^2}$$

- The resultant potential has the form

$$v_{\mathrm{E}}(\mathbf{r}) = \sum_{\mathbf{R}} f_1(\mathbf{r}, \mathbf{R}, \sigma) + \sum_{\mathbf{k}} f_2(\mathbf{r}, \mathbf{k}, \sigma) + f_3(z)$$

- The parameter σ determines the rate of convergence of the two sums

Motivation for an alternative quasi-2D interaction

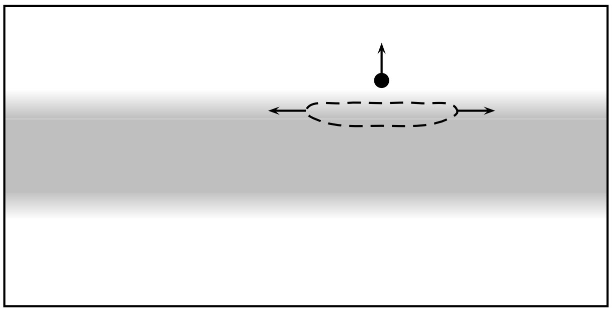
- In 3D, the Model Periodic Coulomb interaction was very successful - finite-size errors and calculation time were reduced significantly

- Recent studies (using non-QMC methods) of the quasi-2D electron gas gave results for the surface energy in disagreement with those obtained using QMC

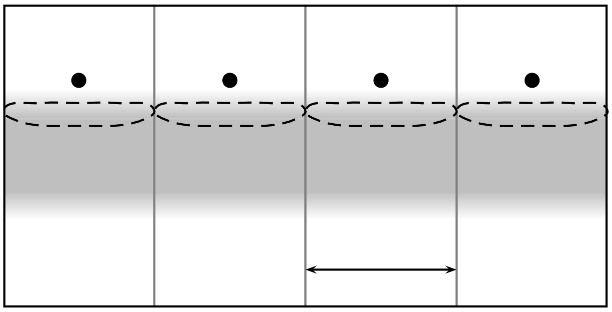
- Possible sources of error in these QMC calculations should be investigated to establish the validity of QMC as a tool for studying extended quasi-2D systems

Where does the Ewald interaction go wrong?

- Consider what happens when an electron wanders far from the surface:



- Result of using the Ewald interaction:



- The electron interacts with an unphysical capacitor-like array of charge

The Coulomb energy

- Definitions:
  - The Ewald interaction is v_{E}
  - The self-interaction energy is
$$\xi = \lim_{\mathbf{r}\to\mathbf{0}} \left(v_{\mathsf{E}}(\mathbf{r}) - \frac{1}{r} \right)$$
  - There are N electrons (charge 1) positioned at r_i
  - The background charges q_α (nuclei?) are positioned at d_α

- The Coulomb energy operator is then

$$\begin{aligned} U_{\mathsf{C}} &= \sum_{i>j} v_{\mathsf{E}}(\mathbf{r}_{ij}) + \frac{1}{2} N\xi + \sum_{i,\alpha} q_\alpha v_{\mathsf{E}}(\mathbf{r}_i - \mathbf{d}_\alpha) \\ &\quad + \sum_{\alpha>\beta} q_\alpha q_\beta v_{\mathsf{E}}(\mathbf{d}_{\alpha\beta}) + \frac{1}{2} \left(\sum_\alpha q_\alpha^2 \right) \xi \end{aligned}$$

- The electron-electron part of the Coulomb energy is

$$U^{\mathsf{EW}}_{\mathsf{e-e}} = \langle \sum_{i>j} v_{\mathsf{E}}(\mathbf{r}_{ij}) \rangle + \frac{1}{2} N \xi$$

- In terms of the one-electron density matrix $n(\mathbf{r})$ and the exchange-correlation functional $n_{\mathsf{XC}}(\mathbf{r}, \mathbf{r}')$, this becomes

$$U^{\mathsf{EW}}_{\mathsf{e-e}} = U_{\mathsf{Ha}} + U^{\mathsf{EW}}_{\mathsf{XC}}$$

with

$$U_{\mathsf{Ha}} = \frac{1}{2} \int \mathrm{d}\mathbf{r}\, \mathrm{d}\mathbf{r}'\, n(\mathbf{r}) n(\mathbf{r}') v_{\mathsf{E}}(\mathbf{r} - \mathbf{r}')$$

$$U^{\mathsf{EW}}_{\mathsf{XC}} = \frac{1}{2} \int \mathrm{d}\mathbf{r}\, \mathrm{d}\mathbf{r}'\, n(\mathbf{r}) n_{\mathsf{XC}}(\mathbf{r}, \mathbf{r}') [v_{\mathsf{E}}(\mathbf{r} - \mathbf{r}') - \xi]$$

The problem with the Ewald sum

- v_{E} is the right interaction in U_{Ha} but the interaction between electron and XC hole should be *exactly* $1/r$

- This is because the XC hole is always contained entirely within the simulation cell and should not be duplicated outside

- The solution is to replace the original electron-electron interaction energy with

$$
\begin{aligned}
U_{\mathsf{e-e}}^{\mathsf{MPC}} &= \langle \sum_{i>j} f(\mathbf{r}_{ij}) \rangle \\
&+ \langle \sum_{i} \frac{1}{2} \int d\mathbf{r}\, n(\mathbf{r}) \left[v_{\mathsf{E}}(\mathbf{r}-\mathbf{r}_i) - f(\mathbf{r}-\mathbf{r}_i) \right] \rangle
\end{aligned}
$$

$f(\mathbf{r})$ is the minimum-image $1/r$ interaction

The MPC interaction

- Some algebra shows that the new interaction has
  - v_{E} in the Hartree energy ✓
  - $1/r$ in the XC energy ✓
- In addition, it should be considerably faster: the old interaction required $\mathcal{O}[N^2]$ calculations of the costly function v_{E}
- In contrast, the only $\mathcal{O}[N^2]$ term in the MPC is the simple $1/r$
- The rest of the interaction is effectively a one-body potential

Evaluating the one-body part

- The one-body term

$$\sum_i \frac{1}{2} \int \mathrm{d}\mathbf{r}\, n(\mathbf{r}) \left[v_{\mathsf{E}}(\mathbf{r} - \mathbf{r}_i) - f(\mathbf{r} - \mathbf{r}_i) \right]$$

  is evaluated as

$$\Omega \sum_i \sum_{\mathbf{k}} n_{\mathbf{k}}^* g_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}_i}$$

- $n_{\mathbf{k}}$ and $g_{\mathbf{k}}$ are the 3D Fourier transforms of $n(\mathbf{r})$ and $[v_{\mathsf{E}}(\mathbf{r}) - f(\mathbf{r})]$

- This brings a big speed advantage - most of the work is now in the pre-calculation

- There is a small subtlety - overlapping must be avoided

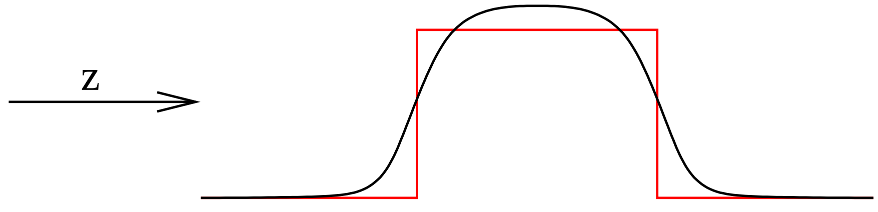
The test system

- An electron gas moves in the potential of a positive background

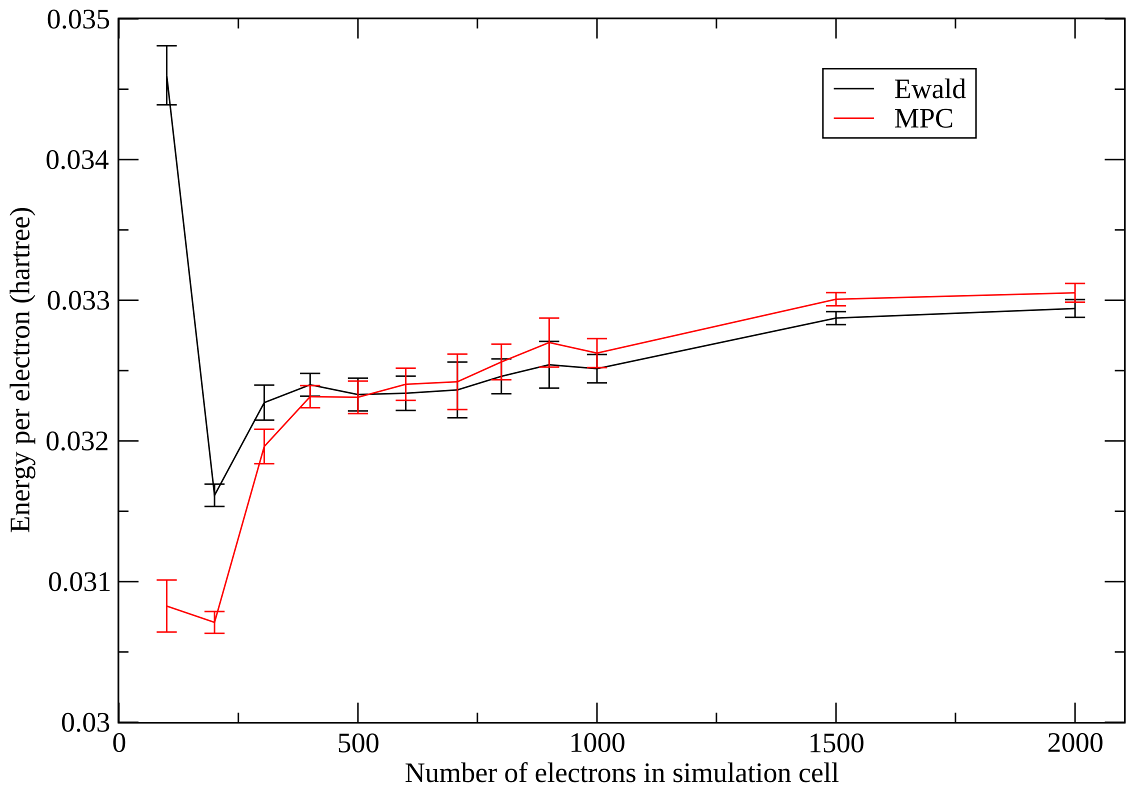
- The background charge has uniform density over a finite range in the z-direction

- The number of electrons in the simulation determines the (2D) size of the simulation cell, which is charge neutral

- Density is given by $r_s = 2.07$, slab width 18.63 a.u.



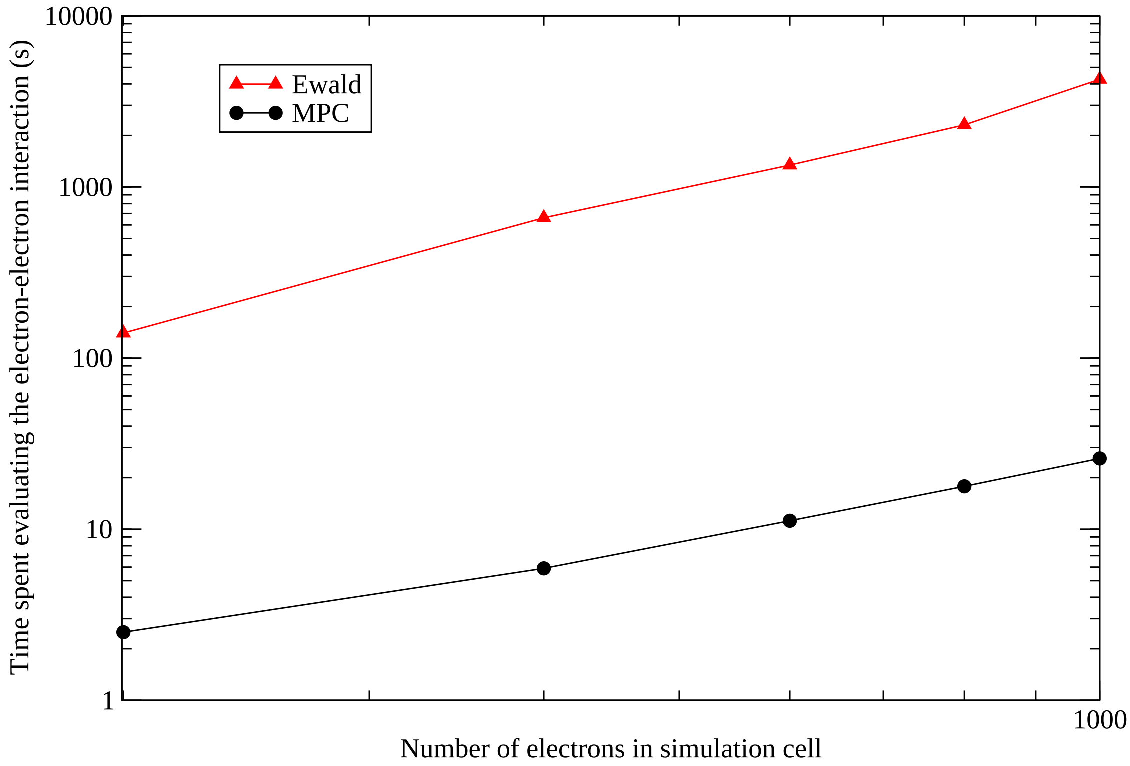
Results from VMC



- The VMC calculations were carried out using CASINO with wave functions generated by density-functional methods in the LDA

- Independent-particle finite-size error corrections have been applied

Timing results



- The timings were based on an 8000-move VMC simulation

- The time for the MPC pre-calculation is not included - for any serious simulation this is negligible

Why does the MPC appear not to reduce finite-size errors?

- The error expected to be incurred by the use of the Ewald sum is
$$\frac{1}{2}\int d\mathbf{r}\, d\mathbf{r}'\, n(\mathbf{r}) n_{\mathsf{XC}}(\mathbf{r},\mathbf{r}')[v_{\mathsf{E}}(\mathbf{r}-\mathbf{r}') - \xi - f(\mathbf{r}-\mathbf{r}')]$$

- An estimate of this error may be obtained by expanding $(v_{\mathsf{E}}(\mathbf{r}) - \xi)$ for small r, since $n_{\mathsf{XC}}(\mathbf{r},\mathbf{r}')$ is expected to be short-ranged

- The expansion gives
$$v_{\mathsf{E}}(\mathbf{r}) - \xi \;=\; \frac{1}{r} - \frac{C}{L^3}\left(z^2 - \frac{r_{\parallel}^2}{2}\right)$$
to order r^4, where $C = 4\beta(3/2)\zeta(3/2)$ and L is the lattice parameter; terms involving e^{-L^2/σ^2} have also been neglected

- It is interesting to compare this with the situation in 3D, where the expansion is

$$[v_{\mathsf{E}}(\mathbf{r}) - \xi]_{3\mathsf{D}} = \frac{1}{r} - \frac{2\pi r^2}{3L^3}$$

- In 3D the correction to $1/r$ is spherically-symmetric

- The resulting error estimate for the 3D interaction is

$$-\frac{\pi}{3L^3}\int d\mathbf{r}\, d\mathbf{r}'\, n(\mathbf{r}) n_{\mathsf{XC}}(\mathbf{r},\mathbf{r}')[(\mathbf{r}-\mathbf{r}')^2]$$

- For the quasi-2D interaction, this becomes

$$-\frac{C}{2L^3}\int d\mathbf{r}\, d\mathbf{r}'\, n(\mathbf{r}) n_{\mathsf{XC}}(\mathbf{r},\mathbf{r}') \left[(z-z')^2 - \frac{(\mathbf{r}_{\parallel}-\mathbf{r}'_{\parallel})^2}{2}\right]$$

- In the quasi-2D version, the expansion indicates that a large cancellation of errors is expected, as long as $n_{\mathsf{XC}}(\mathbf{r}, \mathbf{r}')$ does not depend on the direction of $(\mathbf{r} - \mathbf{r}')$

- For the test system studied here, this is true in the bulk, but not near the surfaces

- However, near the surfaces the XC hole expands and the simple $\mathcal{O}[r^2]$ expansion may no longer be appropriate - further cancellation of errors is possible

Conclusions

- The quasi-2D MPC does not significantly reduce Coulomb finite-size errors
- However, it offers a very large speed improvement over the Ewald sum, which makes it worthwhile to implement
- Do DMC results show the same pattern as VMC? In other words, does the quality of the trial wave function matter here?