Modelling the spherically averaged structure factor in Quantum Monte Carlo Calculations

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Introduction

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- Monte Carlo calculations deal with finite systems.
- Infinite solids are implemented using periodically repeated simmulation cells of volume V.
- Correlation within the cell usually converges well.
- The xc hole is also repeated periodically which leads to spourious errors in the interaction energy. This is due to the long range nature of teh Coulomb interaction.
- Ewald energies converge slowly with system size.

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We need to separate the Monte Carlo data at large electron-electron distances from data at short distances. An object that seperates the correlations according to the length scale yet is simple, is the one dimensional spherically averaged structure factor $S(k)$

Correlations I

In terms of

$$\tilde{S}(\boldsymbol{u}) = \left(\left\langle \sum_{i \neq j} \delta(\boldsymbol{r}_j - \boldsymbol{r}_i - \boldsymbol{u}) \right\rangle - \int n(\boldsymbol{r}) n(\boldsymbol{r} + \boldsymbol{u}) d^3 r \right) \quad (1)$$

the xc energy can be written as

$$U_{xc} = \frac{1}{2} \int \frac{\tilde{S}(\boldsymbol{u})}{u} d^3 u = \frac{N}{\pi} \int dk \, (S_k - 1) \quad (2)$$

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Problem: The structure factor (SF) is essentially the Fourier transform of $\tilde{S}$. Since we have a periodic system $S(k)$ will consist of irregularly spaced delta peaks.

Correlation II

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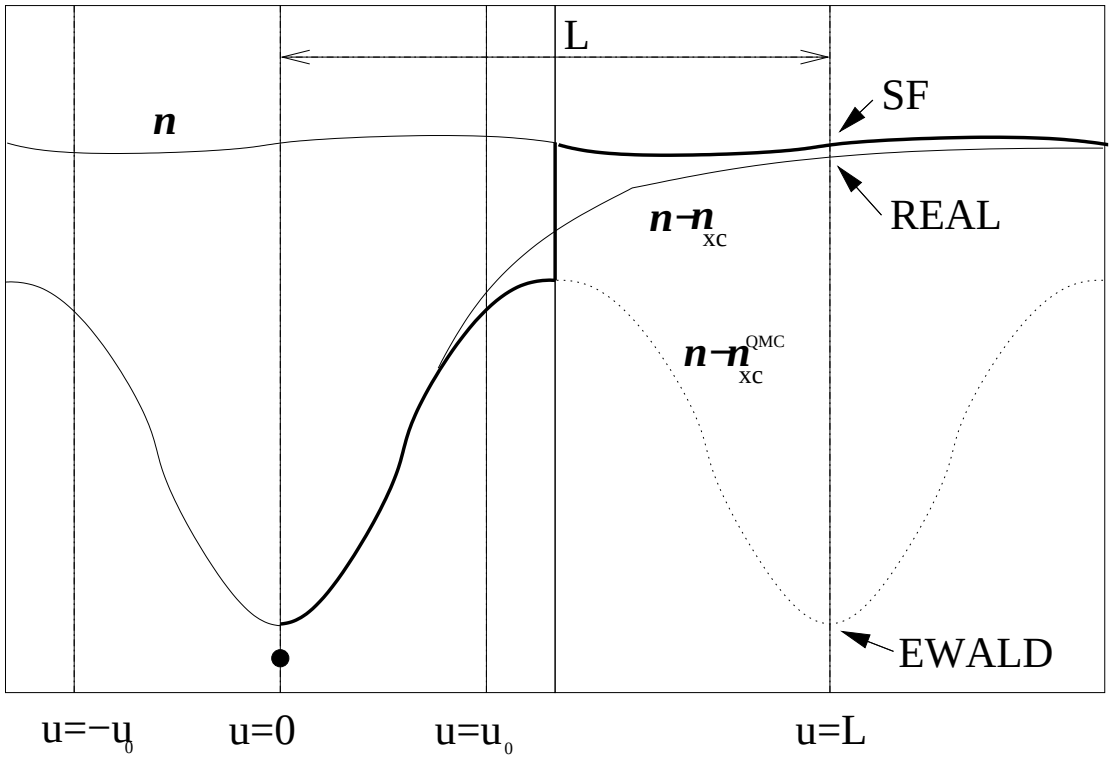

Correlation III

$$S_k = 1 + S_k^I + S_k^{II}, \tag{3}$$

The spherically averaged Fourier transform of the interaction term yields:

$$S_k^I = \frac{1}{N} \left\langle \sum_{i \neq j} \frac{\sin k|\boldsymbol{r}_j - \boldsymbol{r}_i|}{k|\boldsymbol{r}_j - \boldsymbol{r}_i|} \Theta\left(u_0 - |\boldsymbol{r}_j - \boldsymbol{r}_i|\right) \right\rangle_{QMC}, \tag{4}$$

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The Hartree term S_k^{II} is more complicated:

Correlation IV

Using $n(\boldsymbol{r}) = \sum_{\boldsymbol{q}} e^{i\boldsymbol{q}\boldsymbol{r}} n(\boldsymbol{q})$ it follows that

$$\int n(\boldsymbol{r}) n(\boldsymbol{r}+\boldsymbol{u}) d^3r = \sum_{\boldsymbol{q},q'} n(\boldsymbol{q}) n(\boldsymbol{q}') e^{i\boldsymbol{q}\boldsymbol{r}} e^{i\boldsymbol{q}'\boldsymbol{r}+\boldsymbol{u}} d^3r \quad (5)$$

and we get $S^{II}(\boldsymbol{u}) = V \sum_{\boldsymbol{q}} n(\boldsymbol{q}) n(-\boldsymbol{q}) e^{-i\boldsymbol{q}\boldsymbol{u}}$. Using

$$S^{II}(k) = \int_{|\boldsymbol{u}| \le u_0} \frac{\sin k|\boldsymbol{u}|}{k|\boldsymbol{u}|} S_{II}(\boldsymbol{u}) d^3u \quad (6)$$

gives

$$\begin{aligned} S_{II}(k) &= \frac{V}{k} \cdot \sum_{\boldsymbol{q}} n(\boldsymbol{q}) n(-\boldsymbol{q}) \quad (7) \\ &\left\{ \int_{|\boldsymbol{u}| \le u_0} \frac{\sin k|\boldsymbol{u}|}{|\boldsymbol{u}|} e^{-i\boldsymbol{q}\boldsymbol{u}} d^3u \right\} \end{aligned}$$

Correlation V

Interestingly this can be evaluated and yields

$$S_k^{II} = -\frac{3}{2}\frac{f}{N}\sum_{\boldsymbol{q}} \tilde{g}(\tilde{k},\tilde{q})\tilde{n}_{\boldsymbol{q}}\tilde{n}_{-\boldsymbol{q}}, \tag{8}$$

$$\tilde{g}(\tilde{q},\tilde{k}) = \frac{1}{\tilde{k}\tilde{q}}\left(\frac{\sin(\tilde{k}-\tilde{q})}{\tilde{k}-\tilde{q}} - \frac{\sin(\tilde{k}+\tilde{q})}{\tilde{k}+\tilde{q}}\right), \tag{9}$$

using the dimensionless quantities $\tilde{n}_{\boldsymbol{q}} = Vn_{\boldsymbol{q}}$, $\tilde{k} = ku_0$, and $\tilde{q} = |\boldsymbol{q}|u_0$. $f = 4\pi u_0^3/(3V)$ is the volume fraction of the super cell that contributes to S_k^I.
Note that k is continous even if the $\boldsymbol{q}$'s are discreete.

Correlation VI

The following expansions may be used:
For $k, q \ll 1$ one gets:

$$\tilde{g} = 1 - \frac{1}{10}\left(\tilde{k}^2 + \tilde{q}^2\right) + \frac{1}{840}\left(3\tilde{k}^2 + \tilde{q}^2\right)\left(\tilde{k}^2 + 3\tilde{q}^2\right) + \ldots \quad (10)$$

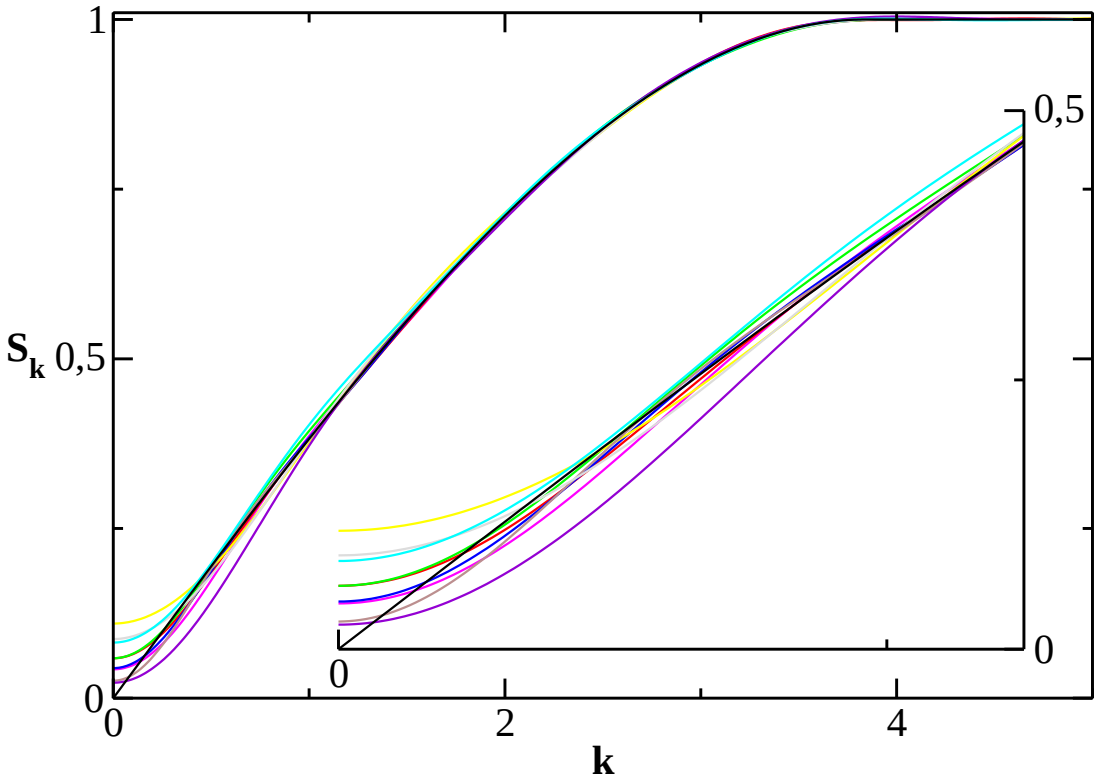
If only one of the two arguments is small - note $\tilde{g}$ is symmetric - the following holds, e.g. for $q \ll 1$:

$$\begin{aligned} \frac{\tilde{g}}{3} = & \frac{\sin\tilde{k}}{\tilde{k}^3} - \frac{\cos\tilde{k}}{\tilde{k}^2} + \tilde{q}^2\left[\frac{\sin\tilde{k}}{\tilde{k}^3}\left(\frac{1}{\tilde{k}^2} - \frac{1}{2}\right)\right. \\ & \left. - \frac{\cos\tilde{k}}{\tilde{k}^2}\left(\frac{1}{\tilde{k}^2} - \frac{1}{6}\right)\right] + \tilde{q}^4\left[\frac{\sin\tilde{k}}{\tilde{k}^3}\left(\frac{1}{\tilde{k}^4} - \frac{1}{2\tilde{k}^2} + \frac{1}{24}\right)\right. \\ & \left. - \frac{\cos\tilde{k}}{\tilde{k}^2}\left(\frac{1}{\tilde{k}^4} - \frac{1}{6\tilde{k}^2} + \frac{1}{120}\right)\right] \ldots \end{aligned} \quad (11)$$

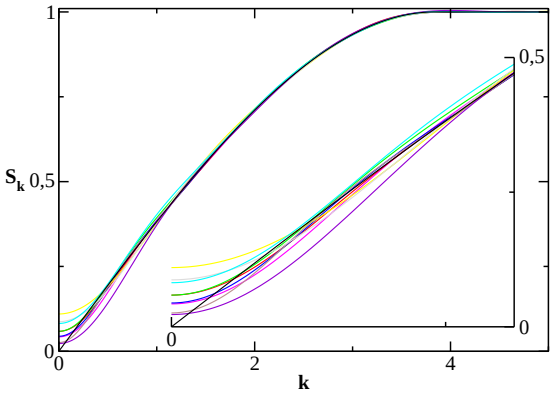
Results

An example

The spherically averaged structure factor at $r_s = 1$ for a slater determinant (HF system) ($N = 54$ upto $N = 614$):



A structure factor



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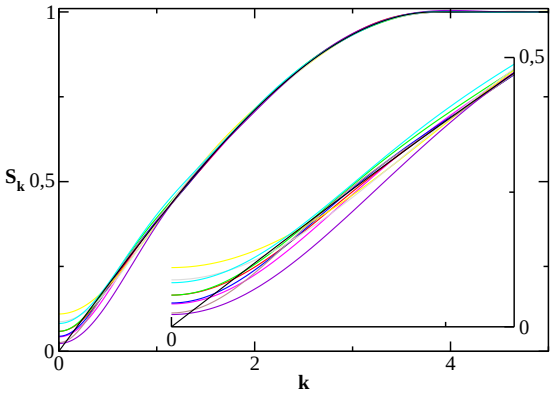

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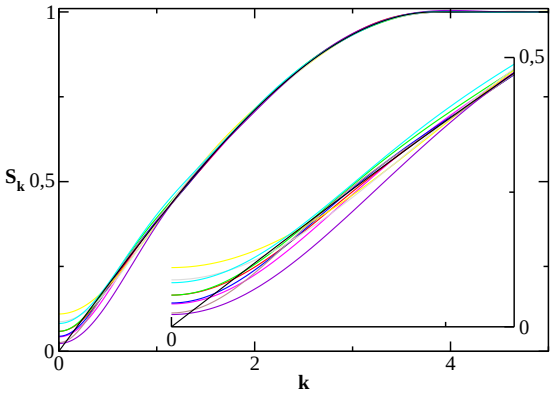

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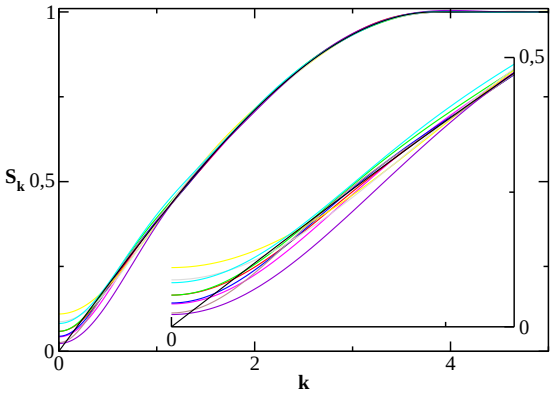

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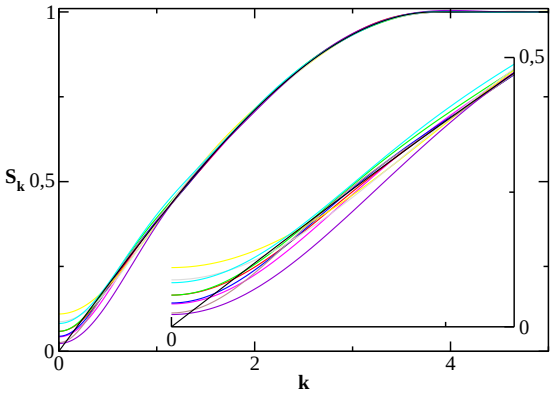

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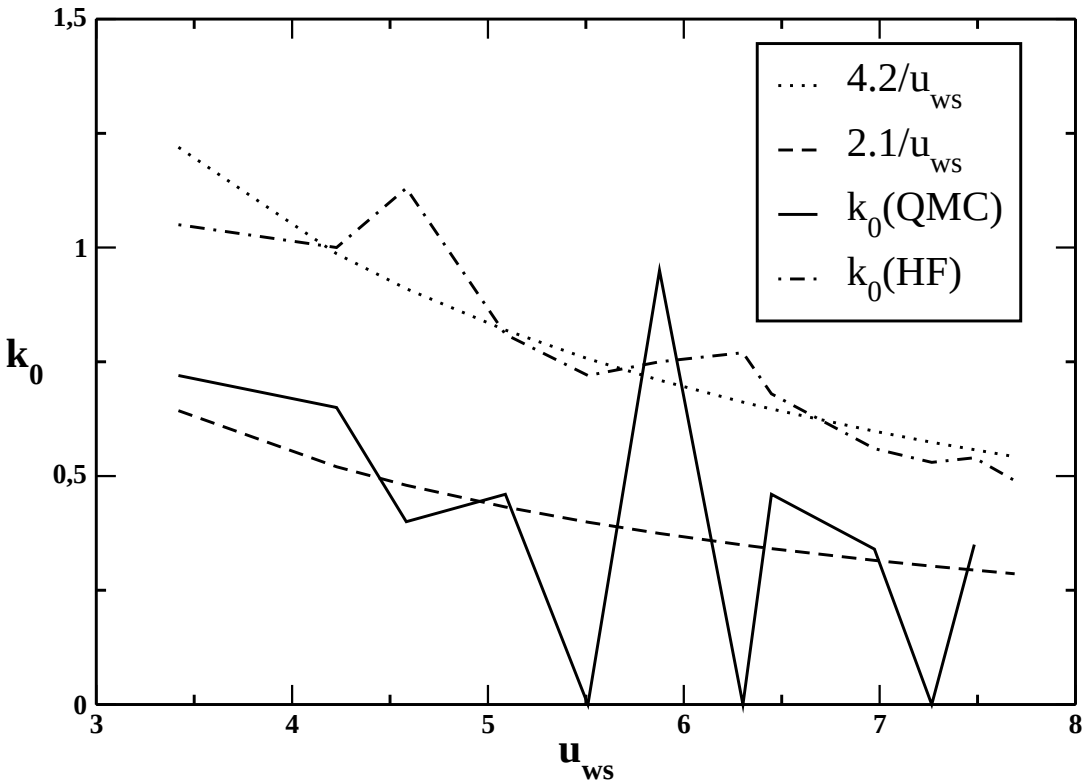
Solution: Below a simmulation cell dependent cutoff we replace the raw MC structure factor with something else.

Slide 1

By "inspection" we get for k_0:



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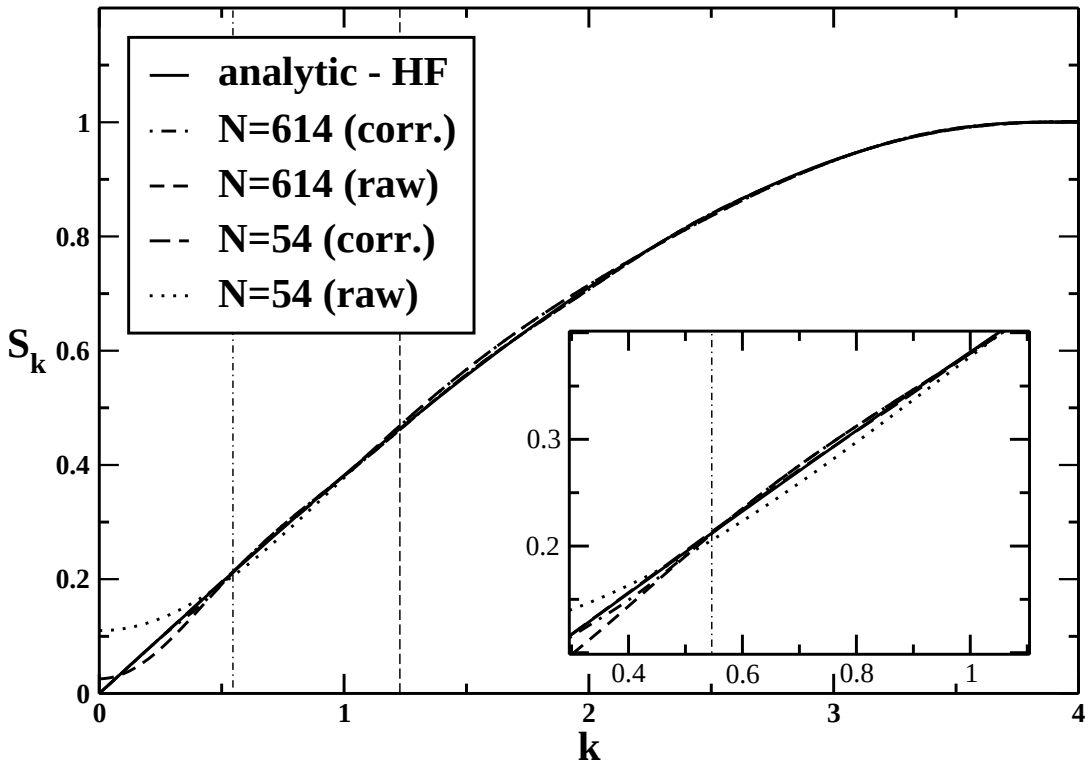
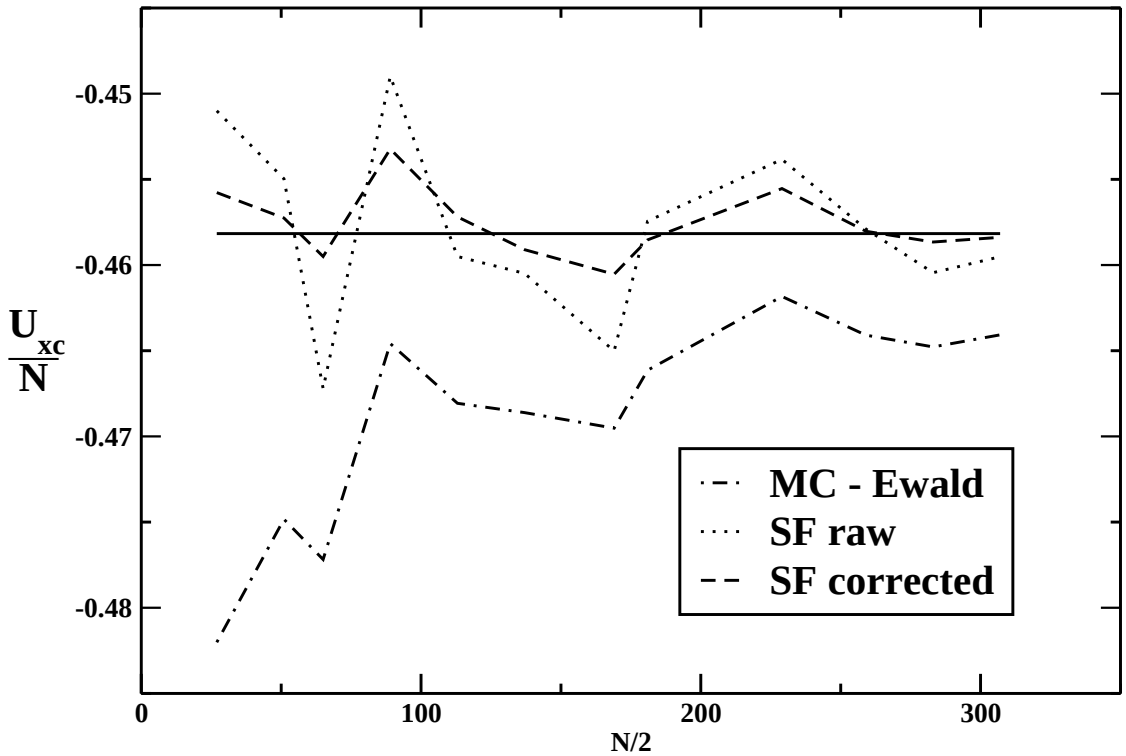
- As the system size increases $k_0 \longrightarrow 0$ and hence the correction term goes to zero.
- Convergence is guaranteed, improvment depends on a good choice of the correction and the cutoff.

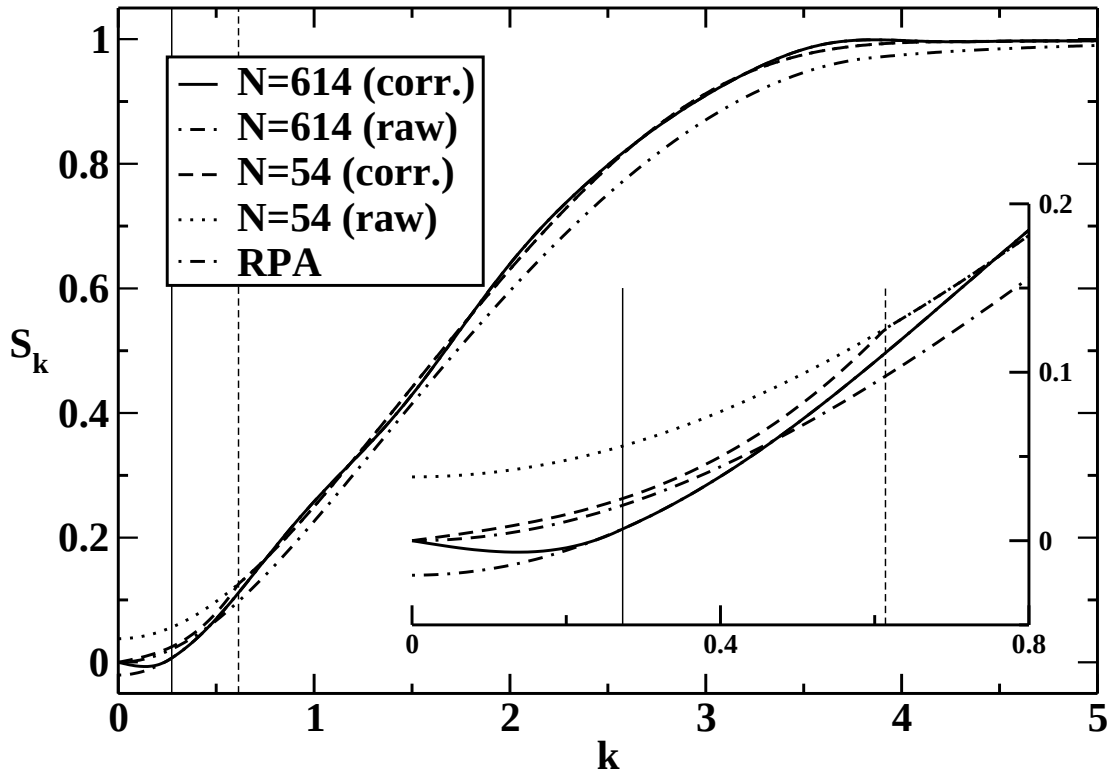
An improved HF structure factor



HF SF potential energy

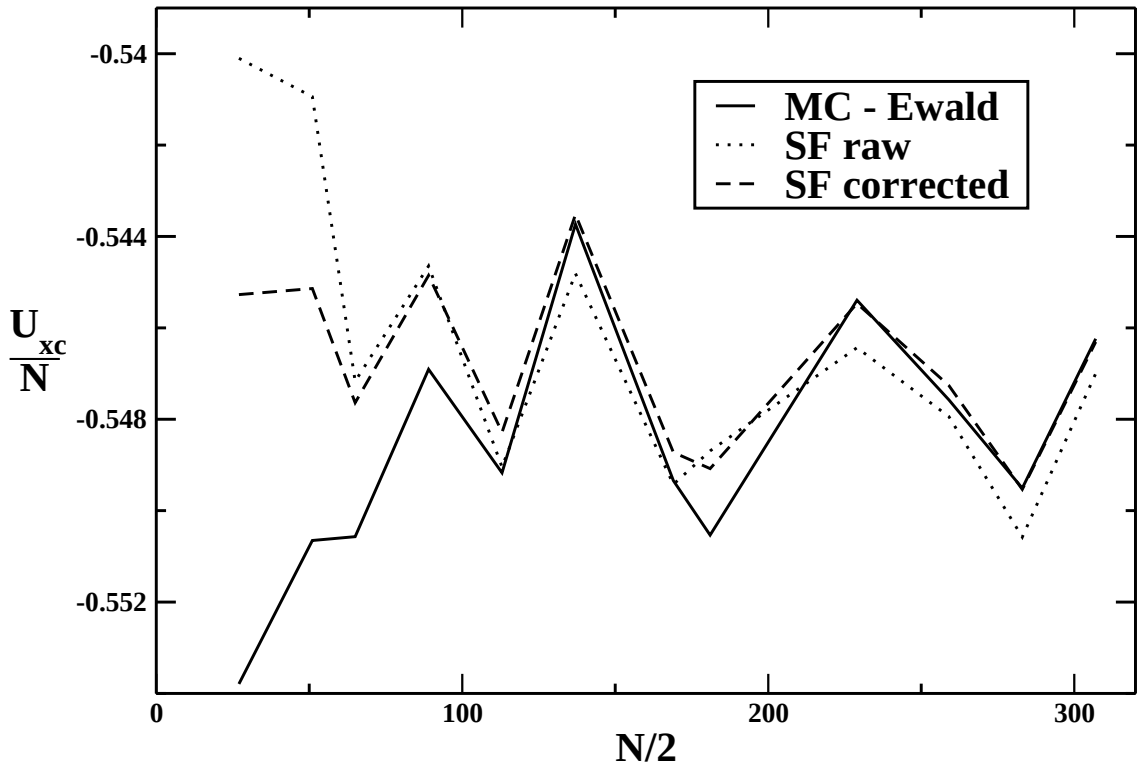


Fully interacting (QMC) structure factor

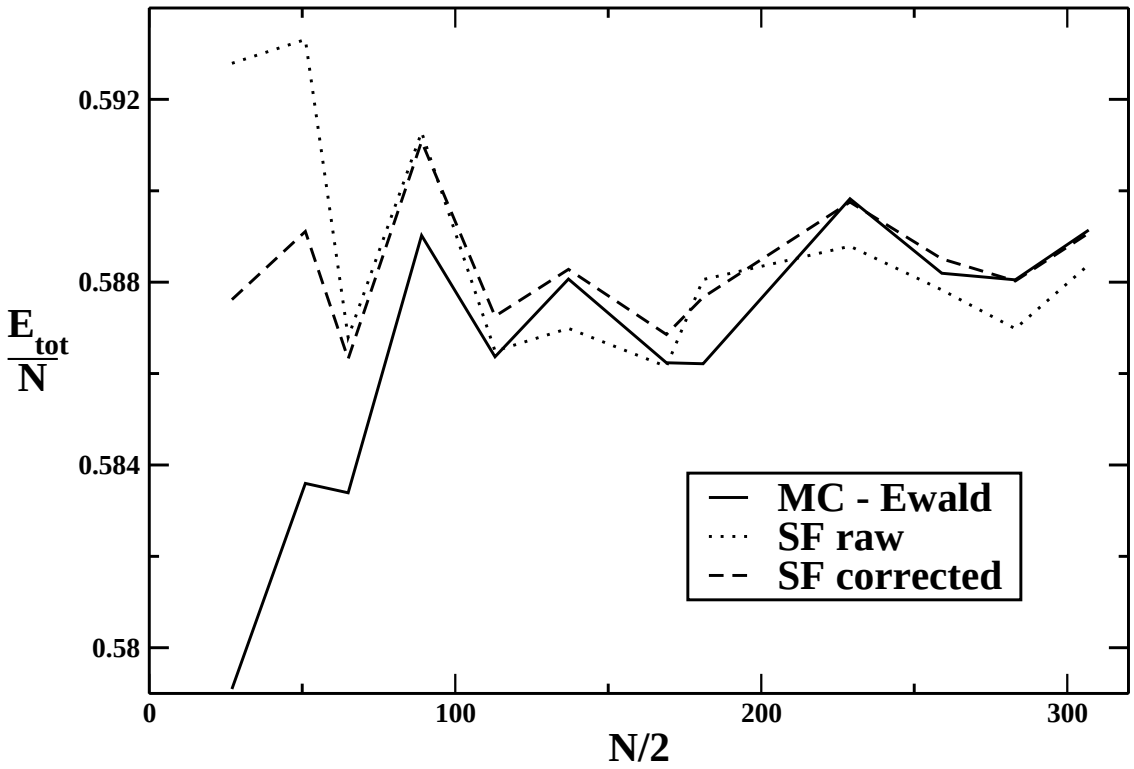


RPA SF $\neq$ QMC SF for $k > 0.5$. Hence, an RPA based correction term is only usfull for the largest systems.

... the corresponding potential energy



... and total energy



Under construction ...

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$$\left. - \int \rho(\boldsymbol{r})\rho(\boldsymbol{r}')f(|\boldsymbol{r} - \boldsymbol{r}'|)\Theta(u_0 - |\boldsymbol{r} - \boldsymbol{r}'|)d\boldsymbol{r}d\boldsymbol{r}'\right)$$

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where f(r)=1/r. In comparison MPC gives $U_{xc} =$

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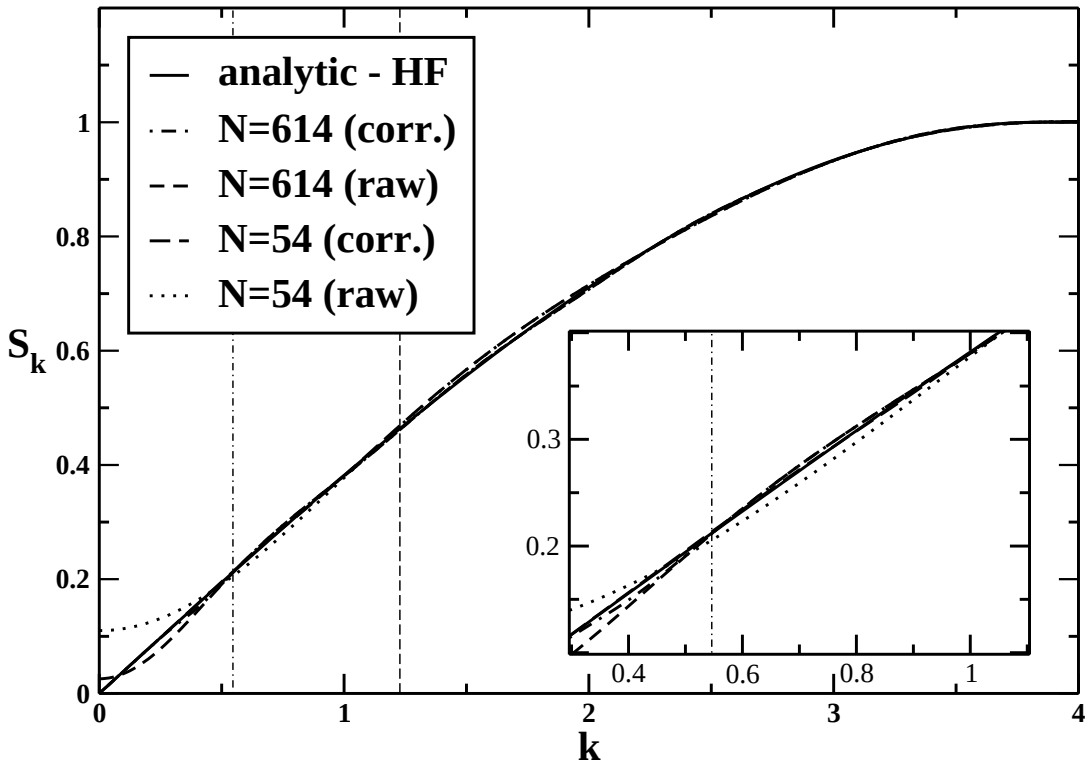
So what is the point....
Lets us look at the HF structure factor again:

SF and MPC III



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- The cause: implicitly we are always dealing with a finite system.
- Only ensuring $S(k) = 0$ is not sufficient in the case of HF.
- The correction term can in principle deal with the wrong assymptotic behaviour too.

Outlook

- Surfaces: Using a structure factor based correction term might improve the convergence in slab or surface calculations.

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- Linking the potential and kinetic energy via coordinate scaling or the Virial theorem might yield a finite size corection term for the kinetic energy.

Conclusions

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- $S(k)$ offers an obvious way to splice together long and short range correlations from different sources.
- Not only the value $S(k = 0)$ must be correct, but also its shape at $k \approx 0$, in order to ensure good convergence. Not all systems behave quadratically around $k = 0$ and a flexible SF based correction term might be of help.