Quantum Monte Carlo modelling of the spherically averaged structure factor of a many-electron system

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The interaction and exchange-correlation contributions to the ground-state energy of an arbitrary many-electron system can be obtained from a spherical average of the wavevector-dependent diagonal structure factor (SF). We model the continuous-k spherically averaged SF using quantum Monte Carlo calculations in finite simulation cells. We thus derive a method that allows to substantially reduce the troublesome Coulomb finite-size errors that are usually present in ground-state energy calculations. To demonstrate this, we perform variational Monte Carlo calculations of the interaction energy of the homogeneous electron gas. The method is, however, equally applicable to arbitrary inhomogeneous systems.

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Together with density-functional theory (DFT) [1, 2], Quantum Monte Carlo (QMC) calculations belong to the bedrock of computational solid state physics [3]. One major problem, the focus of this paper, encountered in QMC solid-state applications are the Coulomb finite-size effects. These originate in the periodic Ewald interaction that is typically used to model the electron-electron (e-e) Coulomb interaction in a periodic geometry [4]. When using the Ewald interaction, the long-range nature of the Coulomb interaction yields spurious contributions to the interaction energy caused by the interaction of an electron with the periodically repeated copies of its exchange-correlation (xc) hole. Such finite-size effects are usually dealt with by increasing the system size and monitoring the convergence of the relevant data. However, the Coulomb finite-size errors of the interaction energy are known to scale as 1/N, N being the number of electrons in the supercell, and convergence is therefore slow [5, 6]. An alternative involves replacing the periodic Ewald interaction by a "model periodic Coulomb" (MPC) interaction that converges faster [7, 8].

In this Letter, we present an approach that reduces finite-size errors by keeping the true Coulomb interaction and going to the core of the issue by using QMC to model the spherical average of the diagonal structure factor (SF) of extended systems. This is in contrast to a paper [9] we recently learnt of that uses the (non-spherically averaged) SF to correct QMC data at long wavelengths. Our model (see Fig. 1) assumes

$$U_{xc} = \frac{N}{\pi} \int dk \left( S_k - 1 \right),$$

where $S_k$ is the spherical average of the diagonal structure factor $S_k(k)$:

$$S_k = 1 + \frac{4\pi}{N} \int dr \, n(r) \, \int du \, u^2 \frac{\sin(ku)}{ku} n_{xc}(r, u),$$

$n(r)$ being the electron density at $r$.

Implicitly we are considering an infinite system: $k$ is a continuous variable. However, $S_k$ for a QMC system contains irregularly spaced delta peaks that on integration give the QMC $U_{xc}$. Our model (see Fig. 1) assumes from alternative calculations based on, e.g. the random-phase approximation (RPA) which is known to describe collective excitations correctly and becomes exact at long wavelengths [11]. We aim to have the best of both worlds!

The method we propose bears some resemblance to the MPC interaction. However, while the MPC modifies the interaction, here we keep the standard Coulomb interaction and model the QMC correlations in a $k$ dependent way. The advantage is that our method ought to yield improvements where others fail [12], e.g. the exchange hole is known to be long-ranged, decaying as $1/r^4$. In a finite simulation cell this results in a finite size error of the exchange energy $\propto N^{-2/3}$. The error at large $r$, however, corresponds to $S_k$ at small $k$ where it can be replaced easily by the correct asymptotic value.

The interaction energy of an arbitrary many-electron system is usually expressed as the sum of the Hartree energy (which in the case of an infinite Jellium model is exactly cancelled by the Coulomb energy due to the presence of the positive background) and the so-called xc interaction energy $U_{xc}$. $U_{xc}$ corresponds to the attractive interaction between each electron and its own xc hole. Starting from the spherical average $n_{xc}(r, u)$ of the xc hole density $n_{xc}(r, r')$ at $r'$ around an electron at $r$, one finds

$$U_{xc} = \frac{N}{\pi} \int dk \left( S_k - 1 \right),$$

where $S_k$ is the spherical average of the diagonal structure factor $S_k(k)$:

$$S_k = 1 + \frac{4\pi}{N} \int dr \, n(r) \, \int du \, u^2 \frac{\sin(ku)}{ku} n_{xc}(r, u),$$

$n(r)$ being the electron density at $r$.

Implicitly we are considering an infinite system: $k$ is a continuous variable. However, $S_k$ for a QMC system contains irregularly spaced delta peaks that on integration give the QMC $U_{xc}$. Our model (see Fig. 1) assumes
that correlations are non-periodic and beyond a cutoff radius \(u_0\) are due only to variations in the density, so that beyond \(u_0\) there is no contribution to \(U_{xc}\). For \(u_0\), we choose the Wigner-Seitz radius \(u_{WS}\) of the simulation cell, and the structure factor \(S_k\) can then be sampled directly during the QMC run. We find:

\[
S_k = S_k^I + S_k^{II},
\]

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

\[
S_k^{II} = -\frac{3}{2N} \sum_q \tilde{g}(\tilde{k}, \tilde{q}) \tilde{n}_q \tilde{n}_{-q},
\]

\[
\tilde{g}(\tilde{k}, \tilde{q}) = \frac{1}{k \tilde{q}} \left( \frac{\sin (\tilde{k} - \tilde{q}) \tilde{k} - \tilde{q}}{\tilde{k} - \tilde{q}} - \frac{\sin (\tilde{k} + \tilde{q}) \tilde{k} + \tilde{q}}{\tilde{k} + \tilde{q}} \right),
\]

using the dimensionless quantities \(\tilde{n}_q = V n_q\), \(\tilde{k} = ku_0\), and \(\tilde{q} = |q|u_0\). \(f = 4\pi u_0^3/(3V)\) is the volume fraction of the super cell that contributes to \(S_k^I\); \(V\) is its total volume, and \(n_q\) denotes the Fourier transform of the electron density \(n(\mathbf{r})\). Apart from \(n(\mathbf{r})\) the sampling of \(S_k\) only needs \(|\mathbf{r}_j - \mathbf{r}_i|\) which is readily available in most QMC codes making the SF easy to implement. \(S_k^{II}\), which is due solely to variations in the density, cancels the Hartree contribution \(14\) to Eq. \(4\). Note that the \(k\) is continuous even in the case of a periodic system for which the \(q\) vectors are discrete. This is deliberate, as the sampling of a periodic QMC system models an extended (non-periodic, continuous \(k\)) system.

Equations \(4\) and \(5\) do not include the entire xc hole in the QMC sampling, as \(f < 1\). As a result, our raw SF differs from zero at \(k = 0\). This corresponds to the amount of the xc hole that is missed and which is located in the corners of the simulation cell beyond the cutoff radius \(15\). However, due to the periodic boundary conditions the QMC description in these corners is unlikely to be accurate, so not much information is lost. Below we show that some of the residual error can be corrected for easily and efficiently.

We performed Hartree-Fock (HF) and Variational Monte Carlo (VMC) calculations for the homogeneous electron gas, using the CASINO package \(16\). The calculations employ plane-wave Slater determinants with and without a Jastrow factor. The latter corresponds to HF calculations where the exact result is known \(11\). The systems we studied are non-polarised in a face-centered cubic simulation cell with the number of electrons ranging from \(2 \times 27\) to \(2 \times 307\) at \(r_s = 1\). This corresponds to a Wigner-Seitz radius \(u_{WS}\) ranging from \(3.420\) to \(7.689\) in atomic units, which we use throughout. The interaction energy is evaluated using either our SF-based approach or the standard Ewald interaction. The SF is sampled at 1000 equally spaced points ranging from 0 to 10. In the case of VMC calculations, the Jastrow factor was converged using several iterations of variance minimisation.

Let us first look at a pure Slater determinant of plane waves. Fig. \(2\) plots our HF calculation of the SF next to the exact Hartree-Fock SF. Fig. \(3\) shows the convergence of \(U_{xc}\) to the known HF (exchange) energy. The Ewald data shows the familiar finite-size errors, while the
SF yields an interaction (exchange) energy that is essentially flat, consistent with the elimination of the Coulomb finite-size error.

A similar analysis can be performed with the correlated Slater-Jastrow many-electron wavefunction (Figs. 4 and 5). As in the case of the HF calculation, the Ewald data exhibits finite-size errors, which should scale as $1/N$. In contrast, our SF-based calculations exhibit a systematic error with the opposite sign. The Coulomb finite-size error has been eliminated, but we are missing a bit of the xc hole (located at the corners of the simulation cell), which yields a structure factor $S_k$ that differs from zero at $k = 0$ resulting in an erroneous xc interaction energy.

We now analyse the behavior of the structure factor $S_k$ at small $k$. As the system size increases, one would expect the SF to improve at small $k$. Fig. 2 shows our variational HF calculation of the SF, for two systems. The SF is essentially correct beyond a system-size dependent minimum $k_0$. At $k < k_0$, the SF levels off and at $k = 0$ approaches a value that equals the error in the xc hole. The crossover $k_0$ obviously goes to zero as the system size increases. Since our xc-hole is expected to be accurate inside a sphere of radius $u_0$, one expects the SF to be accurate beyond $2\pi/(2u_0)$, $2u_0$ being the characteristic length scale of the simulation cell. Indeed, a cutoff $k_0 = \pi/u_0$ seems plausible. We have looked at the $k_0$ values at which our HF structure factor and the exact one start to diverge markedly, and we have found $k_0 \sim 4.2/u_0$. This rough estimate implies an accurate HF xc hole within a radius ~$3u_0/4$ from a given electron. Using $k_0 = 4.2/u_0$ and letting our calculated HF structure factor go to 0 linearly at smaller $k$ produces a new corrected estimate of $U_{xc}$ shown in Fig. 3. There is no longer a systematic error due to the system size and the corrected SF exhibits fluctuations that are considerably smaller than those of the uncorrected SF. Statistical noise and a shell structure remain, of course.

Figs. 4-5 repeat the analysis for the correlated Slater-Jastrow wavefunction. Here we use the VMC SF of the largest system as the reference. Interestingly, the VMC structure factor seems to remain correct at unexpectedly small values of $k$. We have found $k_0 \sim 2.1/u_0$, corresponding to a correct xc hole up to a surprisingly large $u = 1.5u_0$! Possibly, $S_0 = 0$ poses such a strong constraint on the relatively shapeless SF that the SF has little choice but to be accurate at “too small” $k$ especially as in contrast to the HF case, the true interacting
SF is also quadratic for $k \to 0$ [18]. The behavior of the SF around $k = 0$ is therefore qualitatively correct. Nevertheless, a correction is needed. We chose a simple scheme, multiplying $S(k)$ by $k/k_0$ when $k < k_0$. We did not use the RPA for interpolation as its region of validity seems to begin at values of $k$ smaller than our smallest $k_0$ (see also Fig. [1]). By looking at the final convergence of the xc interaction energy $U_{xc}$ with system size, we see again that the estimates for $U_{xc}$ are noisy but essentially flat, which is a signature of Coulomb finite-size errors having been eliminated.

QMC being inherently statistical in nature, we close with a discussion of error bars. Errors of the SF at different $k$ are correlated and so the direct evaluation of an error for an xc interaction energy $U_{xc}$ derived in the way described here is non-trivial. However, observe that in a finite system the SF-based $U_{xc}$ and the usual $U_{xc}$ coincide. Even for an infinite system, as the simulation cell increases their values become more and more similar as they contain similar if not identical information. Hence, it seems reasonable to assume that the error bars of the standard $U_{xc}$ can be used for the SF data. We have evaluated both the SF-based and the standard $U_{xc}$ for a homogeneous electron gas with $2 \times 51$ electrons, for 10 statistically independent yet identical runs averaging over 1000 QMC steps. The estimates for $U_{xc}$ differ by an offset, due to the different finite-size errors, nevertheless, the estimated standard deviations are similar: 0.00182 using the Ewald interaction, 0.00216 using the uncorrected SF, and 0.00173 using the corrected SF. These results are consistent with an error bar of 0.0015 derived by blocking. The estimates for $U_{xc}$ were correlated, with the correlation between the Ewald calculation and the uncorrected and corrected SF-based calculations being 0.64 and 0.74 respectively. The two SF-based calculations had a correlation coefficient of 0.88. Thus the error-bars for the standard Ewald data can be used also for the SF based data.

In conclusion, we have devised a new method to evaluate QMC xc interaction energies $U_{xc}$ that do not suffer from spurious interactions of electrons with periodic copies of their xc hole. The method is robust and easy to implement. Applying our method to Slater and Slater-Jastrow type many-body wavefunctions of a homogeneous electron gas, we have shown how to efficiently handle and eliminate residual Coulomb finite-size errors. Our approach is equally applicable to arbitrary inhomogeneous many-electron systems. Spherical averaging reduces the information contained in any QMC system to a smooth one-dimensional curve. Each value of $S(k)$ therefore contains more information (hence less statistical noise) than $S(k, -k)$ and no spherical self-averaging need be assumed. In future, we aim to apply our method to the case of Jellium surfaces and real solids. In the case of the homogeneous electron gas that we have considered here, we have shown that SF-based calculations of the xc interaction energy can be improved considerably by simply letting the SF go to the correct long-wavelength limit at $k = 0$. For more complex inhomogeneous many-electron systems it might be advantageous, however, to splice together structure factors obtained from RPA at small $k$ and QMC at larger $k$.

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