Quantum Monte Carlo modeling 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 wave-vector-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 us 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,[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 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 paper, 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 by Chiesa *et al.*[9] We recently learn of that using the random-phase approximation (RPA) in conjunction with the (nonspherically averaged) SF to correct QMC data at long wavelengths for the homogeneous electron gas and silicon (diamond structure) at ambient pressure. While their method also allows for the correcting of some finite-size errors appearing in the kinetic energy, our method has several advantages. Apart from the density, the sampling of the spherically averaged SF only needs the electron separation $|\mathbf{r}_j-\mathbf{r}_i|$, which is readily available in QMC codes, making our method easy to implement. In addition, no spherical self-averaging need be assumed. It is not obvious why this should happen in strongly inhomogeneous systems where our method still yields a smooth and continuous curve. The last property—continuity—implies that we are describing an infinite system right from the outset.

Our starting point is the link between the interaction energy and the spherically averaged wave-vector-dependent diagonal SF S_k of an arbitrary many-electron system. Since large $\mathbf{k}$ wave vectors are related to small electron separations, the large-k behavior of QMC simulations ought to be correct. This is not the case for the small-k behavior (long wavelengths), which, in the case of a finite simulation cell, yields spurious Ewald interactions. However, the long-range (small-k) behavior can be obtained differently, either from the known constraint $S_{k\to 0}=0$ (Ref. 10) or from alternative calculations based on, e.g., the 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 canceled 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 $n_{xc}(\mathbf{r},u)$ of the xc hole density $n_{xc}(\mathbf{r},\mathbf{r}')$ at $\mathbf{r}'$ around an electron at $\mathbf{r}$, one finds,[13] in atomic units which we use throughout the paper,

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

where S_k is the spherical average of the diagonal structure factor $S_{\mathbf{k},\mathbf{k}}$:

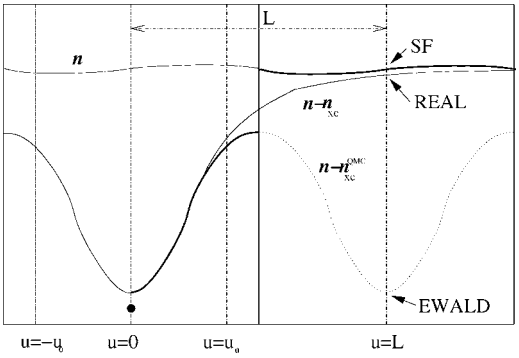

FIG. 1. An electron at $u=0$ inside a box of size L is surrounded by a periodic xc hole n_{xc}^{QMC}. U_{xc} is the Coulomb energy between the electron and its xc hole n_{xc}. Our method (the bold line in the figure) effectively replaces $n-n_{xc}^{QMC}$ (EWALD in the figure) by the density n (SF in the figure) beyond a given cutoff u_0. Clearly, the interaction between an electron and its xc hole at $u=L,2L,\ldots$, is more accurate (i.e., closer to REAL) and converges much faster than in the standard QMC case (EWALD). Close to the boundary of the box, n_{xc} and n_{xc}^{QMC} diverge as both have to integrate to -1. Since n_{xc} in the SF case jumps to 0 at u_0, this sum rule is violated, but the resulting error can be corrected easily (see text). Due to the effective nonperiodicity of the xc hole marked SF, the resulting structure factor is continuous from the outset.

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

with $n(\mathbf{r})$ being the electron density at $\mathbf{r}$.

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 nonperiodic 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

$$S_k = 1 + S_k^I + S_k^{II}, \qquad (3)$$

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

$$S_k^{II} = -\frac{3}{2}\frac{f}{N}\sum_{\boldsymbol{q}} \tilde{g}(\tilde{k},\tilde{q})\tilde{n}_{\boldsymbol{q}}\tilde{n}_{-\boldsymbol{q}}, \qquad (5)$$

$$\tilde{g}(\tilde{q},\tilde{k}) = \frac{1}{\tilde{k}\tilde{q}}\left[\frac{\sin(\tilde{k}-\tilde{q})}{\tilde{k}-\tilde{q}} - \frac{\sin(\tilde{k}+\tilde{q})}{\tilde{k}+\tilde{q}}\right], \qquad (6)$$

using the dimensionless quantities $\tilde{n}_{\boldsymbol{q}} = V n_{\boldsymbol{q}}$, $\tilde{k} = k u_0$, and $\tilde{q} = |\mathbf{q}| u_0$. $f = 4\pi u_0^3/(3V)$ is the volume fraction of the supercell that contributes to S_k^I, V is its total volume, and $n_{\boldsymbol{q}}$ denotes the Fourier transform of the electron density $n(\mathbf{r})$. 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 $\boldsymbol{q}$ vectors are discrete. This is deliberate, as the sampling of a periodic QMC system models an extended (nonperiodic, continuous k) system.

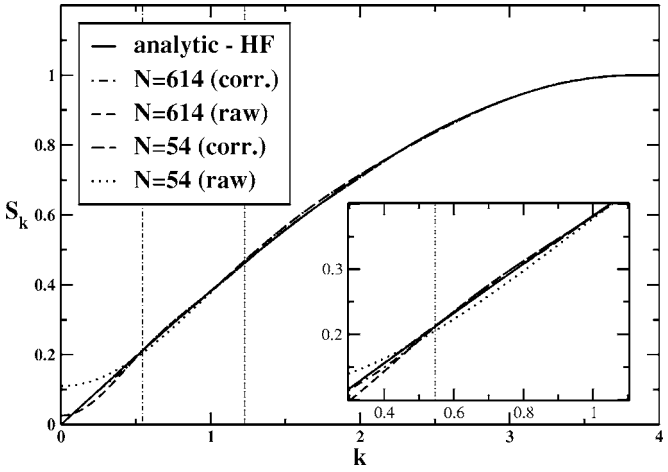

FIG. 2. This figure shows the raw and corrected Hartree-Fock SFs for the smallest and the largest system (2×27 and 2×307 electrons, respectively) as well as the exact result. For details of the correction, see main text. The vertical lines indicate the cutoffs used.

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 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 nonpolarized in a face-centered-cubic simulation cell with the number of electrons ranging from 2×27 to 2×307 at $r_s=1$. This corresponds to a Wigner-Seitz radius u_{WS} ranging from 3.420 to 7.689. 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 minimization.

Let us first look at a pure Slater determinant of plane waves. Figure 2 plots our HF calculation of the SF next to the *exact* Hartree-Fock SF. Figure 3 shows the convergence of U_{xc} to the known HF (exchange) energy. The Ewald data show 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 wave function (Figs. 4 and 5). For this system, we also plot the total energy in Fig. 6, where the kinetic term has been corrected by subtracting ΔT

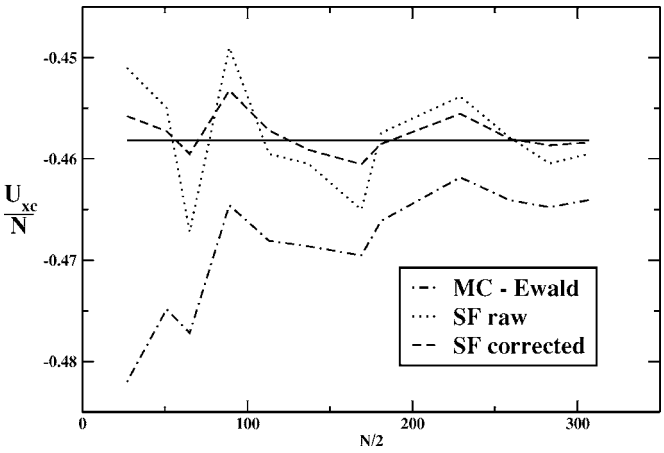

FIG. 3. Convergence of the potential energy with system size (2×27 to 2×307 electrons) using a Slater determinant only. The solid line is the HF result for an infinite system.

$=T_{HF}(N)-T_{HF}(N=\infty)$, which reduces the finite-size errors of the kinetic energy. The corresponding total energy for HF is not shown; once it has been corrected using ΔT, it is just the same as the HF U_{xc} shifted by a constant $T_{HF}(N=\infty)=1.1050$. In contrast, the corrected T_{QMC} still contains finite-size errors of a similar order as the finite-size errors in SF U_{xc}.

As in the case of the HF calculation, the Ewald data exhibit 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 analyze 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. Figure 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

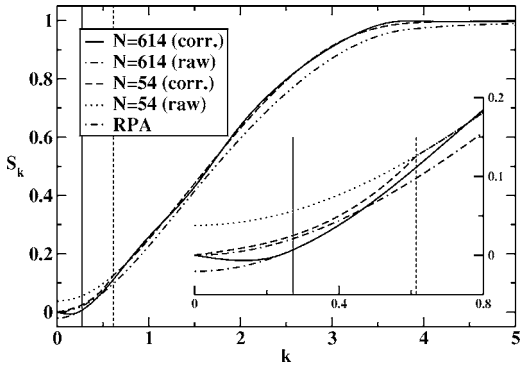

FIG. 4. This figure shows the raw and corrected Slater-Jastrow SFs for the smallest and the largest system (2×27 and 2×307 electrons, respectively). For details of the correction, see main text. The vertical lines indicate the cutoffs used. The RPA SF is also shown. It seems incorrect for $k>0.5$. Hence, only for systems large enough such that $0.5\gtrsim k_c$ would the interpolation with the RPA SF improve U_{xc}.

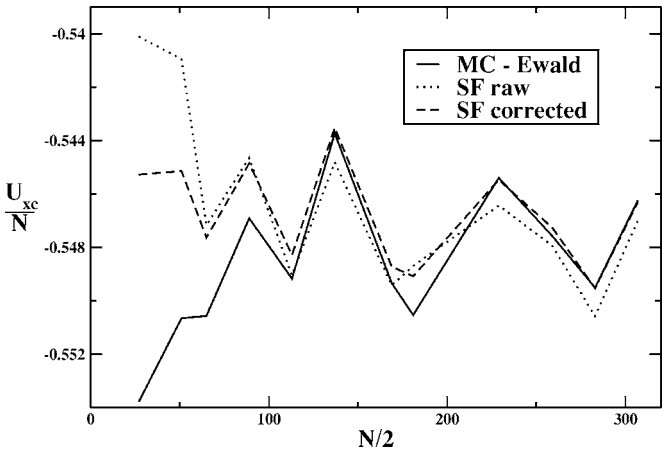

FIG. 5. Convergence of the potential energy with system size (2×27 to 2×307 electrons) using a Slater-Jastrow wave function. The standard Ewald result is shown next to the raw and corrected SF results.

$k<k_0$, the SF levels off, and at $k=0$, approaches a value that equals the error in the magnitude of 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 $2\pi/(2u_0)$, with $2u_0$ 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 $k_0\sim4.2/u_0$. This rough estimate implies an accurate HF xc hole within a radius of $\sim3u_0/4$ from a given electron. Using $k_0=4.2/u_0$ and letting our calculated

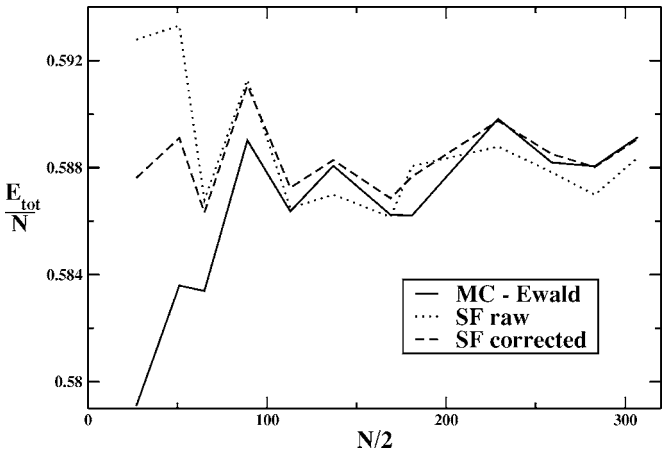

FIG. 6. Convergence of the total energy with system size (2×27 to 2×307 electrons) using a Slater-Jastrow wave function. This figure shows the sum of U_{xc}, as in Fig. 5 and $T_{QMC}-\Delta T$ (see main text for details). The standard Ewald result is shown next to the raw and corrected SF results. The scale is the same as for U_{xc} in Fig. 5. The improvement for the total energy using the SF seems better than that for U_{xc} alone. This is due to the residual systematic $1/N$ error in ΔT being additive in the case of the Ewald data but canceling a residual $1/N$ error in the SF U_{xc} with opposite sign (not shown, probably an artifact). Also the fluctuations at large N appear smaller.

HF structure factor go to 0 linearly at smaller k produce 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.

Figures 4 and 5 repeat the analysis for the correlated Slater-Jastrow wave function. Additionally, Fig. 6 plots the total energy. Here, we use the VMC SF of the largest system as the reference.[18] 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 $u=1.5u_0$. For $k>k_0$, the SFs were essentially identical to our best SF coming from the largest system with 2×307 electrons. Possibly, $S_0=0$ poses such a strong constraint on the relatively shapeless[17] SF that the SF has little choice but to be accurate at "too small" k; especially, in contrast to the HF case, the true interacting SF is also quadratic for $k\rightarrow 0$.[18] The behavior of the SF around $k=0$ is therefore qualitatively correct. Nevertheless, a correction is needed. It is easy to think of and implement interpolation schemes. We looked at many different ones, but in the end, we chose to present results using the simplest one, multiplying S_k by k/k_0 when $k<k_0$. This turned out to be sufficient as the details of the interpolation (e.g., a small incorrect linear term at $k=0$ when using the simple scheme, see Fig. 4) do not matter, as they only have a small effect on the total k integral that yields U_{xc}. 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 (i.e., for very large system, see also Fig. 4). 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.

With 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 nontrivial. However, observe that in a finite system, the SF-based U_{xc} and the usual U_{xc} coincide. Even for a 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 2×51 electrons for ten 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 for a single run are similar: 0.001 82 using the Ewald interaction, 0.002 16 using the uncorrected SF, and 0.001 73 using the corrected SF. These results are consistent with an error bar of the Ewald energy of 0.0015 derived for in single run 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 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[17] and easy to implement. Applying our method to Slater and Slater-Jastrow-type many-body wave functions 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 $S_{\mathbf{k},-\mathbf{k}}$, and no spherical self-averaging need be assumed. In the 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 such as surfaces, it might be advantageous, however, to splice together structure factors obtained, e.g., from RPA at small k and QMC at larger k.

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[14] For a homogeneous infinite many-electron system, this term becomes the more familiar $S_k = N\delta_{k,0}$.
[15] Interestingly, for some Slater-Jastrow wave functions, $S_{k=0} < 0$, suggesting that too much electron density was expelled from the vicinity of an electron. This might be an artifact of the specific Jastrow function we used.
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[17] Incidentally, due to the SF's shapelessness, accurate integrals can be obtained efficiently using relatively coarse grids.
[18] The correct structure factor of a homogeneous electron gas goes as $S_k = k^2/2\omega_p$ for $k \to 0$. $\omega_p = (4\pi n)^{1/2}$ is the bulk-plasmon energy, where n is the electron density.