Random phase approximation and the finite size errors in many body simulations

Simone Chiesa*, D. M. Ceperley[†], R. M. Martin[†] and Markus Holzmann**

*Dept. of Physics, University of California Davis, CA 95616 *Dept. of Physics, University of Illinois Urbana-Champaign, Urbana, IL 61801 **LPTMC, UMR 7600 of CNRS, Université P. et M. Curie, Paris, France

Abstract. We address the problem of finite size errors on the energy computed in quantum Monte Carlo simulations. We introduce a scheme based on the random phase approximation that, within a single calculation, allows to retrieve the leading order correction and produces practically converged results for modest numbers of particles. Applications to the electron gas and silicon are presented.

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In the simulation of bulk systems via quantum Monte Carlo methods[1] the main source of systematic error is related to the relatively small number of particles that can be practically handled. The aim of this paper is to show that such a finite size error on the energy can be corrected using the information collected in a single simulation performed using a small number of particles.

In order to simulate an infinitely extended system, one defines a superlattice with basis vectors $\{\mathbf{L}_{\alpha}\}_{\alpha=1,2,3}$ and explicitly considers only a finite number of particles $N = \Omega/n$ where $\Omega = |\mathbf{L}_1 \cdot (\mathbf{L}_2 \times \mathbf{L}_3)|$ and *n* is the desired average density. The (infinitely many) remaining particles are periodic images of these *N* so that the potential energy is periodic and given by

$$V_{e-e} = \sum_{i < j} \sum_{\mathbf{L}} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j + \mathbf{L}|} + V_{\text{background}} = \frac{2\pi e^2}{\Omega} \sum_{\mathbf{k} \neq 0} \frac{1}{k^2} (\rho_{\mathbf{k}} \rho_{-\mathbf{k}} - N)$$
(1)

where $\rho_{\mathbf{k}} \equiv \sum_{i} \exp(i\mathbf{k}\mathbf{r}_{i})$ and \mathbf{k} , the reciprocal lattice vectors, satisfy $\exp(i\mathbf{k}\mathbf{L}_{\alpha}) = 1$. In practice, none of the forms in Eq.1 is used in simulations: the Coulomb interaction is split in a divergent short range part treated in real space and a smooth long range part handled in reciprocal space[2]. For the purpose of this paper however, it is most convenient to focus on the reciprocal space form. Because of the periodicity of the Hamiltonian, the boundary conditions on the wave function can be chosen as $\Psi(..\mathbf{r}_i + \mathbf{L}_{\alpha}..) = \exp(i\theta_{\alpha})\Psi(..\mathbf{r}_{i}..)$ where θ_{α} is the "twist" of the phase in the α th direction and lies in the interval $[-\pi, \pi)[3, 4]$. When using a single twist the expectation value of the potential energy is determined by the static structure factor $S_{\theta,N}(\mathbf{k}) = \langle \rho_{\mathbf{k}}\rho_{-\mathbf{k}}\rangle_{\theta,N}/N$. As the system size increases, the mesh of \mathbf{k} vectors gets finer and the series eventually converges to an integral corresponding to the exact thermodynamic limit. At finite N, the only effect of averaging over $\boldsymbol{\theta}$ is to replace $S_{\theta,N}$ with $S_N(\mathbf{k}) = (2\pi)^{-3} \int d\boldsymbol{\theta} S_{\theta,N}(\mathbf{k})$. This does not change the reciprocal lattice mesh and twist-averaging is therefore expected to have a

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FIGURE 1. Left: Static structure factor for the electron gas at $r_s = 10$ (lower panel) and $\Delta S = S_N(k) - S_{66}(k)$. The difference is computed using a spline function interpolation of S_{66} . Right: Energies per particle of the electron gas at $r_s = 10$ in Rydberg as a function of the inverse particle number. Circles are the Monte Carlo energies averaged over twist angles. Squares are the energies after the additional $\hbar \omega_p/2N$ correction (see text).

minor effect on the error in the potential energy.

The error using a simulation box with N particles is therefore given by

$$\Delta V \equiv \frac{e^2}{4\pi^2} \int \frac{S_{\infty}(\mathbf{k}) - 1}{k^2} d\mathbf{k} - \frac{2\pi e^2}{\Omega} \sum_{\mathbf{k} \neq 0} \frac{S_N(\mathbf{k}) - 1}{k^2}.$$
 (2)

After the Madelung constant has been taken into account[5] the remaining part of the error is determined by i) the substitution of $S_{\infty}(\mathbf{k})$ by the computed $S_N(\mathbf{k})$ and ii) the discretization of the integral of $e^2 S(\mathbf{k})(4\pi^2k^2)^{-1}$. In the small *k* region the random-phase approximation suggests $S_{\infty}(\mathbf{k}) \simeq S_N(\mathbf{k})$ and implies that the leading order contribution to the error comes from point ii) above: it is an integration error that originates from the omission of the $\mathbf{k} = 0$ volume element from the energy sum. Thanks to the validity of the random-phase approximation one also knows $S(\mathbf{k}) \sim k^2$ with a prefactor that can be determined either analytically or from a knowledge of the $S_N(\mathbf{k})$ computed in the simulation. Once the prefactor is known, one can accurately compute the correction.

We looked at jellium as a test case to judge to what extent the *ansatz* $S_{\infty}(\mathbf{k}) = S_N(\mathbf{k})$ is verified. Results for $S_N(k)$ computed in variational Monte Carlo simulations at $r_s = 10$ for 12, 24 and 54 particles are shown in Fig.1. As we increase the number of particles, the grid of k points for which S_N is defined shifts, but the values of S_N fall on a smooth curve, independent of N.

Let us now consider the kinetic energy. When using a twisted boundary condition $\boldsymbol{\theta}$ in a cubic supercell, the kinetic energy is given in terms of the momentum distribution $n_{\boldsymbol{\theta},N}(\mathbf{k}) = \langle c_{\mathbf{k}}^{\dagger} c_{\mathbf{k}} \rangle_{\boldsymbol{\theta},N}$ by

$$T = \frac{\hbar^2}{2m} \sum_{\mathbf{k}} n_{\boldsymbol{\theta},N}(\mathbf{k} + \boldsymbol{\theta}/L) |\mathbf{k} + \boldsymbol{\theta}/L|^2$$
(3)

At variance with the potential energy case, the reciprocal lattice over which the summation is performed is shifted by θ/L so that when the average over twist is performed one gets

$$T = \frac{\hbar^2}{2m(2\pi)^3} \int d\boldsymbol{\theta} \sum_{\mathbf{k}} n_{\boldsymbol{\theta},N}(\mathbf{k} + \boldsymbol{\theta}/L)(\mathbf{k} + \boldsymbol{\theta}/L)^2.$$
(4)

This is the exact thermodynamic limit if the condition $n_{\theta,N} = n_{\infty}$ is satisfied at those reciprocal vectors where $n_{\theta,N}$ is defined. In practice, the error in the twist angle integration can be made arbitrarily small by increasing the density of twist angles.

The assumption $n_{\theta,N} = n_{\infty}$ is however not satisfied in a many body system. The average over twist is important and must be performed. However, as we shall show, it does not go all the way to eliminate the finite size error on *T*. To understand why, we first need to remember some known features of the exact ground state wave function. In charged systems the interaction causes the wave function to have a long range charge-charge correlation factor: the Jastrow potential. Within the random phase approximation the ground state of the system is described by a collection of dressed particles interacting via short range forces and quantized coherent modes, the plasmons. Accordingly, the many-body wave function factorizes as[6]

$$\Psi = \Psi_{\mathbf{s.r.}} \exp(J) = \Psi_{\mathbf{s.r.}} \exp\left[-\frac{1}{2\Omega} \sum_{\mathbf{k} \neq 0} u_{\mathbf{k}} \rho_{\mathbf{k}} \rho_{\mathbf{k}}^{\dagger}\right]$$
(5)

where $\Psi_{s.r.}$ only contains short range correlations and u_k decays quickly to 0 as k increases and diverges as k^{-2} at small k.

We now focus on one twist and consider the Fourier transform of $n_{\theta,N}(\mathbf{k})$: the one body density matrix $\gamma(\mathbf{r}) = \frac{1}{\Omega} \sum_{\mathbf{k}} n_{\theta,N}(\mathbf{k}) \exp(i\mathbf{k}\mathbf{r})$. This quantity can be directly expressed in terms of the wave function as

$$\gamma(\mathbf{r}) = \frac{1}{N} \sum_{\alpha=1}^{N} \left\langle \frac{\Psi(\mathbf{r}_1, \mathbf{r}_2 \dots \mathbf{r}_\alpha + \mathbf{r}, \dots)}{\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots)} \right\rangle$$
(6)

and determines the kinetic energy per particle as $T = -\frac{\hbar}{2mn} \nabla^2 \gamma(\mathbf{r})|_{\mathbf{r}=0}$. The correct prescription to compute $\gamma(\mathbf{r})$ consists in displacing particle α by \mathbf{r} keeping all the remaining ones fixed. However, due to the periodic setup of the system, Eq.6 describes a global shift of α and all its images. Such an error cannot be addressed by averaging over boundary conditions since the violation of the "correct prescription" happens regardless of the value of the twist. All of this is fairly irrelevant for the short range part of the wave function since the ratio $\Psi_{s.r.}(\mathbf{r}_1, \mathbf{r}_2...\mathbf{r}_{\alpha} + \mathbf{r}, ...)/\Psi_{s.r.}(\mathbf{r}_1, \mathbf{r}_2...)$ is sensitive only to particles lying close to α (within some characteristic short range correlation length) and the images fall quickly out of this region upon increasing the supercell size. Matters are different for the long range Jastrow potential so that, as pointed out by Magro and Ceperley[7], it is necessary to retain the leading order contribution to the difference between the periodic Jastrow potential and the fixed-image one. This is given by

$$\Delta J(\mathbf{r}) \equiv \frac{1}{2\Omega} \sum_{\mathbf{k} \neq 0} u_{\mathbf{k}} (1 - \exp(i\mathbf{k} \cdot \mathbf{r})) - \frac{1}{2(2\pi)^3} \int d\mathbf{k} u_{\mathbf{k}} (1 - \exp(i\mathbf{k} \cdot \mathbf{r}))$$
(7)



FIGURE 2. Left: Structure factor (left panel) and Jastrow potential (right panel) for diamond silicon at ambient pressure. The continuous lines are fit to the data (see text). The Jastrow potential shows a k^{-2} divergence at small k that was not explicitly imposed but obtained through energy variance minimization. Right: Diffusion Monte Carlo energies per electron in diamond Silicon at $r_s = 2.0$. Energies and the S(k) and u(k) used to compute the correction are all obtained in simulations with the same number of particles. The smallest cell is the conventional FCC cubic cell of diamond. The two intermediate ones are, respectively, $2 \times 2 \times 2$ and $3 \times 3 \times 3$ supercells of the primitive cell. The largest one is a $2 \times 2 \times 2$ supercell of the conventional cubic cell.

so that the corrected density matrix becomes $\gamma_{\text{corr}} = \gamma \exp(\Delta J)$. Since $\Delta J(0) = 0$, $\nabla \gamma|_{\mathbf{r}=0} = 0$ and $\gamma(0) = n$ the kinetic error is given by $\Delta T = -\frac{\hat{n}}{2m} \nabla^2 \Delta J(\mathbf{r})|_{\mathbf{r}=0}$ and, by using Eq.7, can be explicitly written as

$$\Delta T = \frac{\hbar^2}{4m(2\pi)^3} \int d\mathbf{k} k^2 u_k - \frac{\hbar^2}{4m\Omega} \sum_{\mathbf{k} \neq 0} k^2 u_k.$$
(8)

This is again an integration error provided u_k does not depend on the system size. As before such an error originates primarily from the omission of the k = 0 contribution. That u_k is independent of N is strongly suggested by the fact that a difference in u_k would necessarily imply a difference in $S(\mathbf{k})$ contrary to the random phase approximation. Within this approxiation $u_k \sim 1/k^2$ so that, once again, we need to determine a prefactor to estimate the error.

We first apply these corrections to the electron gas for which the small k limits of S(k)and u(k) are known from the random phase approximation as, respectively, $\hbar k^2/2m\omega_p$ and $4\pi e^2/\hbar\omega_p k^2$ where ω_p is the plasma frequency. In our tests, the wave function had a backflow-Jastrow form[8] and simulations were performed in the grand-canonical ensemble. Symmetries can be used to drastically reduce the number of needed twist angles to between 20 - 200 for an unpolarized system with $N \sim 10 - 100$. The leading order correction due to long range correlations to kinetic and potential energy are equal and sum up to a total error $\Delta_N = \hbar\omega_p (2N)^{-1}$. Corrected and uncorrected variational energies are shown in Fig.1 for $r_s = 10$. Diffusion Monte Carlo values are uniformly shifted to lower energy by 0.6 mRyd/electron and show similar behavior. One can see that the bias due to the small size of the simulation cell is tremendously reduced, so that the N = 12 case is already satisfactory.

As a second example we considered the diamond structure of silicon at ambient pressure ($r_s = 2.0$). Most of the computational details can be found elsewhere[5]. Here, it is only worth stressing that the correct analytical behavior of the Jastrow potential at low *k* is automatically retrieved by variance minimization[9]. This is crucial for more complicated systems where there is no explicit form for the prefactors. Structure factor and Jastrow potential for different system size are presented in Fig.2.

We fit the parametric form $S(k) = 1 - \exp(-\alpha k^2)$ and $u(k) = 4\pi a[k^{-2} - (k^2 + a^{-1})^{-1}][10]$ to extract the sought prefactors. It is particularly remarkable that a 1-parameter form is capturing so well the behavior of a Jastrow potential which was optimized using more than 10 parameters. When k is expressed in atomic units, the optimal value of α and a were found to be 0.72 and 1.0 respectively, leading to corrections of 0.13/N and 0.092/N Hartree per electron for potential and kinetic energy. Results after the two corrections were applied are shown in Fig.2. Even for the smallest cell (cubic, with 8 Si atoms), the error in the energy is of the order of 1 mHartree/electron (0.1 eV/atom) when compared to the value extrapolated for the infinite size.

To summarize, we introduced a scheme to compute the correction to finite size error in the kinetic and potential energy in quantum Monte Carlo simulations. Madelung constant, Brillouin zone integration and the two 1/L contributions to the error addressed in this paper fall all out naturally from a reciprocal space approach as integration errors. The scheme is based on the determination of the low-k behavior of the structure factor and the Jastrow potential and greatly benefits of the random phase approximation that prescribes the power law behavior of such quantities.

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