Finite-Size Error in Many-Body Simulations with Long-Range Interactions

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We discuss the origin of the finite-size error of the energy in many-body simulation of systems of charged particles and we propose a correction based on the random-phase approximation at long wavelengths. The correction is determined mainly by the collective charge oscillations of the interacting system. Finite-size corrections, both on kinetic and potential energy, can be calculated within a single simulation. Results are presented for the electron gas and silicon.

The accurate calculation of properties of systems containing electrons is a very active field of research. Among the possible numerical approaches, quantum Monte Carlo methods are unique in their ability to produce reliable ground state properties at a reasonable computational cost [1]. However, in the simulation of bulk systems, calculations are necessarily performed using a finite number of electrons. In order to reduce the ensuing finite size errors, the system and, hence, the pair interaction are made periodic in a supercell with basis vectors \( \{ \mathbf{L}_a \}_{a=1,2,3} \). (In the case of a crystal these vectors define a supercell of the unit cell.) This is achieved by using the Fourier components of the interaction at the reciprocal wave vectors of the supercell, i.e., \( \mathbf{k} \) such that \( \exp(i \mathbf{k} \cdot \mathbf{L}_a) = 1 \). Singular long-ranged potentials, such as the Coulomb interaction, are computed by splitting the sum into a portion in real and reciprocal space [2]. Although using the periodized potential reduces the finite-size effects, some error still remains; the one on the energy, for example, often exceeds the statistical noise and other errors characteristic of quantum simulations [3]. Finite-size scaling is possible, but difficult, because the cost of a simulation increases rapidly with the number of particles in the supercell. Here we present an approach that reduces the finite-size errors.

For a supercell of volume \( \Omega \) containing \( N \) electrons, the electron-electron potential energy is conveniently written in Fourier space as

\[
V_N = \frac{2\pi e^2}{\Omega} \sum_{k \neq 0} \frac{1}{k^2} (\rho_k \rho_{-k} - N),
\]

where \( \rho_k = \sum_j \exp(i \mathbf{k} \cdot \mathbf{r}_j) \) and \( e \) is the electron charge. The boundary conditions on the wave function can be chosen as \( \Psi(\mathbf{r}_j + \mathbf{L}_a) = \exp(i \theta_a) \Psi(\mathbf{r}_j) \), where \( \theta_a \) is the “twist” of the phase in the \( a \)th direction. Periodic boundary conditions have \( \theta_a = 0 \). When there is no long-range order, finite-size errors are reduced by averaging over twists (i.e., \( k \)-point sampling or Brillouin zone integration) [4]. This comes at little cost in simulations since the average is also effective in reducing the statistical noise. Even when this is done, the expectation value of the potential energy remains expressed as a series over \( \mathbf{k} \) vectors and is determined by the static structure factor \( S_N(\mathbf{k}) = \langle \rho_k \rho_{-k} \rangle / N \). 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.

The error on the potential energy per particle, using a simulation box with \( N \) particles, is therefore given by

\[
\Delta V_N = e^2 \frac{2}{4\pi^2} \int \frac{S(\mathbf{k}) - 1}{k^2} d\mathbf{k} - \frac{2\pi e^2}{\Omega} \sum_{k \neq 0} \frac{S_N(\mathbf{k}) - 1}{k^2},
\]

where \( S(\mathbf{k}) \) is the structure factor in the thermodynamic limit. The leading order contribution to the error is given by the Madelung constant, \( \nu_M \), and corresponds to the difference \(-e^2 \int (2\pi k)^{-2} d\mathbf{k} + 2\pi e^2 \Omega^{-1} \sum_{k \neq 0} k^{-2}\). It scales as \( N^{-1/3} \) because of the omission of the \( k = 0 \) contribution from the sum and its value is proportional to \( e^2 \int (2\pi k)^{-2} d\mathbf{k} \), where \( D \) is a domain of volume \((2\pi)^3/\Omega\).

Although \( \nu_M \) is usually introduced using a real space picture, as the interaction between images, the above perspective can be easily generalized to the next order correction. The remaining part of the error is determined by (i) the substitution of \( S(\mathbf{k}) \) by the computed \( S_N(\mathbf{k}) \) and (ii) the discretization of \( e^2 \int d\mathbf{k} S(\mathbf{k})(2\pi k)^{-2} \). The behavior of \( S(\mathbf{k}) \) at large \( k \) is determined by the short range correlation and can be neglected. This is apparent if the potential is decomposed in a short- and long-range part. The long-range part, whose expectation value is affected by the finite size, decays quickly to 0 in reciprocal space so that the behavior of \( S(\mathbf{k}) \) at large \( k \) is irrelevant. Moreover, in the limit \( k \to 0 \), one knows that the random-phase approximation becomes exact and describes independent density-fluctuation modes [5]. In the small \( k \) region the random-phase approximation suggests

\[
S(\mathbf{k}) \approx S_N(\mathbf{k})
\]

and implies that the leading order contribution to the error comes from point (ii) above. It is an integration error that, analogously to the Madelung constant, comes from the
omission of the \( k = 0 \) volume element from the energy sum. Scaling of the finite-size errors is then determined to leading order by this missing contribution, i.e., \( \epsilon^2 \int_D S(k)(2\pi)^{-2}dk \), where \( D \) is a domain centered on \( k = 0 \) whose volume equals \((2\pi)^3/\Omega\). This, together with the characteristic quadratic behavior of \( S(k) \) for correlated charged systems, leads straightforwardly to the well-known \( 1/\Omega \) scaling of the error [6]. Thanks to the validity of the random-phase approximation, \( S(k) \) can be determined in the small-\( k \) region either analytically or from a knowledge of the \( S_N(k) \) computed in the simulation. Once \( S(k) \) is known, one can accurately compute the correction.

We looked at jellium as a test case to judge to what extent Eq. (3) is verified. Results for \( S_N(k) \) computed in variational Monte Carlo simulations at \( \epsilon = 10 \) 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. It is important to distinguish between the effects due to momentum quantization and long-range correlation. When using a twisted boundary condition \( \theta \) in a cubic cell, the kinetic energy is given in terms of the momentum distribution by

\[
T_N = \frac{\hbar^2}{2m} \sum_k n_N(k + \theta/L)(k + \theta/L)^2, \tag{4}
\]

where \( m \) is the electron mass. When using a single twist, for example, periodic boundary conditions, the finite-size error is, once again, composed of two contributions: the integration error and the error in approximating the exact momentum distribution, \( n \), with \( n_N \). To better understand the latter point, consider the Fourier transform of the momentum distribution and long-range correlation. When using a twisted boundary condition \( \theta \) in a cubic cell, the kinetic energy is

\[
\Psi = \Psi_{sl} \exp \left[ -\frac{1}{2\Omega} \sum_{k=\pm} u_N(k) \rho_k \rho_{-k} \right]. \tag{5}
\]

where \( \Psi_{sl} \) only contains short range correlations and \( u_N(k) \) decays quickly to 0 as \( k \) increases and diverges as \( k^{-2} \) at small \( k \). Because of this divergence, \( u_N \) converges very slowly to its thermodynamic value and the average over twists provides only a partial correction. Although one can address the bias on the momentum distribution directly [9], we here employ a different route. Thanks to Green’s identity the kinetic energy per particle is written as \( T_N = -\hbar^2 \sum k^2 \ln|\Psi|^2/4mN \) [10] with a contribution coming from the Jastrow potential, \( T_{N,j}^j \), given by

\[
T_{N,j} = -\frac{\hbar^2}{4m\Omega} \sum_{k \neq 0} k^2 u_N(k)[S_N(k) - 1]. \tag{6}
\]

If \( u(k) \) is the optimal Jastrow potential in the thermodynamic limit, the leading order error of \( T_N \) has a similar mathematical structure to that of Eq. (2):

\[
\Delta T_N = -\frac{\hbar^2}{4m(2\pi)^3} \int dk k^2 u(k) - \frac{\hbar^2}{4m\Omega} \sum k^2 u_N(k). \tag{7}
\]

It is an integration error provided \( u_N(k) \) does not depend on the system size. This must be the case whenever Eq. (3) is satisfied since a difference in \( u_N(k) \) would necessarily imply a difference in \( S_N(k) \). Under this assumption \( \Delta T_N \) scales as \( 1/N \), as a result of the omission of the \( k = 0 \) term in Eq. (6).

To compute \( \Delta V_N \) and \( \Delta T_N \) we use the Poisson sum formula \( \sum_L \xi(L) = \Omega^{-1} \sum k \xi(k) \), where \( \xi \) and \( \zeta \) are a

FIG. 1 (color online). Lower panel: static structure factor for the electron gas at \( \epsilon = 10 \). Upper panel: \( \Delta S = S_N(k) - S_{66}(k) \). The difference is computed using a spline function interpolation of \( S_{66} \).
given by long-range correlations to kinetic and potential energy is with cubic symmetry, drastically reduces the number of needed to be the number of inequivalent pockets. This, together with can exploit this fact to reduce the number of twist angles to each pocket the energy dependence on \( \theta \).

One sets \( \xi(0) \) equal to the \( k = 0 \) limit of \( 2\pi^2 S(k)k^2 \) or \( h^2 k^2 u(k)/4m \) for the leading order correction to the potential and kinetic energy, respectively.

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 \( \omega_p \) is the plasma frequency. In our tests, the wave function had a backflow-Jastrow form \([11]\) and simulations were performed in the grand-canonical ensemble with final energies averaged over twist angles. Thanks to the translational invariance of the Hamiltonian, the wave function factorizes as \( \exp(i\theta\sum r_j/L)\Phi \), where \( \Phi \), the periodic part, is invariant in a finite pocket of \( k \) space around each twist angle. In each pocket the energy dependence on \( \theta \) is trivial and one can exploit this fact to reduce the number of twist angles to be the number of inequivalent pockets. This, together with cubic symmetry, drastically reduces 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 is given by \( \Delta V_N = \Delta T_N = \hbar\omega_p/4N \). Corrected and uncorrected variational energies are shown in Fig. 2 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 ({\( r_s = 2.0 \)). Calculations were performed using the CASINO \([12]\) code, a Slater-Jastrow wave function, a Hartree-Fock pseudopotential \([13,14]\), and periodic boundary conditions. The orbitals used for the trial function (Hartree-Fock) were from the CRYSTAL98 code \([15]\). To eliminate the effects of momentum quantization we used a correction based on the density functional eigenvalues of those single-particle states periodic in the simulation cell. Although this is quite common practice, it represents an uncontrolled approximation and results depend weakly on the functional employed (we used the local density approximation). The parameters in the Jastrow potential and a one-body term were optimized. The two-particle Jastrow factor was made up by a spherical short range part and a plane wave expansion including 3 shells of \( k \) points for a total of 11 parameters \([16]\). One needs the plane wave expansion to accurately reproduce the behavior of the optimal Jastrow factor at small \( k \), especially in the case of small simulation cells. To further eliminate errors in the wave function we correct the diffusion Monte Carlo value of \( S_N(k) \) by \( S_N(k) = S_N(k)_{\text{VMC}} - S_N(k)_{\text{DMC}} \) which leads to an estimate correct to second-order in the wave function. The behavior of \( S_N(k) \) and \( u_N(k) \) for different \( N \) is reported in Fig. 3.

For Eq. (8) we assumed \( S(k) = 1 - \exp(-\alpha k^2) \) and \( u(k) = 4\pi a[k^2 - (k^2 + a^{-1})]^{-1} \) \([17]\). When \( k \) is expressed in atomic units, the optimal value of \( \alpha \) 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. 4. Even for the smallest cell (cubic, with 8 Si atoms), the residual finite-size 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. Two of the calculations were repeated using the model periodic Coulomb (MPC) interaction [18] and results, after momentum quantization effects were removed, are reported in Fig. 4. The MPC interaction removes the bias in $\langle V_N \rangle$ and leads to potential energies in close agreement (within 0.5 mHartree/electron) with those of this Letter. A more subtle point, that lies outside the scope of this work, is to what extent the MPC interaction affects the behavior of $u_N(k)$ and, consequently, the value of $\Delta T_N$.

To conclude, we propose a way to estimate the errors in the potential and kinetic energy under the assumption that the low $k$ behavior of the correlation factor is unchanged upon variation of the simulation cell size. This scheme is suggested by the random-phase approximation that describes independent collective mode in the limit $k \rightarrow 0$. The dominant finite-size errors on potential and kinetic energy are integration errors that can be estimated by using the properties of the charge structure factor and the Jastrow potential at long wavelength. The behavior of these quantities in the small $k$ limit can either be obtained analytically (e.g., for the electron gas) or from results with accurate optimized trial wave functions. This approach can be used to obtain energies close to the thermodynamic limit without performing a scaling analysis using different sized systems or assuming the finite-size behavior is given by Fermi liquid theory or approximated by density functional theory.

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[3] For example, the time-step bias and the fixed node error.
[6] This is only true for those wave functions that properly describe charge fluctuations in Coulomb systems (as is the case in this Letter, thanks to the Jastrow potential). In independent-particle approaches, gapless systems are characterized by $S(k) \approx k$ at small $k$ and the error is expected to scale as $\Omega^{-2/3}$.