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Elimination of Coulomb finite-size effects in quantum many-body simulations

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(Received 17 December 1996)

A model interaction is introduced for quantum many-body simulations of Coulomb systems using periodic boundary conditions. The interaction gives much smaller finite size effects than the standard Ewald interaction and is also much faster to compute. Variational quantum Monte Carlo simulations of diamond-structure silicon with up to 1000 electrons demonstrate the effectiveness of our method. [S0163-1829(97)51408-1]

Many-body simulation techniques such as the variational[1] and diffusion[2] quantum Monte Carlo (QMC) methods are capable of yielding highly accurate results for correlated systems. Large systems are normally modeled using a finite simulation cell subject to periodic boundary conditions. This, however, introduces "finite size effects" which are often very important, particularly for systems with long ranged interactions such as the Coulomb interaction. In this paper we introduce a method for dealing with long ranged interactions in quantum many-body simulations which greatly reduces these finite size effects. This method is a generalization of one we developed earlier for homogeneous systems such as jellium.[3] We illustrate our method with variational QMC calculations on diamond-structure silicon. The ideas described in this paper are of wide generality and can be applied to other quantum many-body schemes, such as the HF and "*GW*" (Ref. 4) methods, and to long ranged interactions other than the Coulomb interaction.

The finite size effects encountered in QMC calculations for electronic systems can be divided into two terms: (i) the independent particle finite size effect (IPFSE) and (ii) the Coulomb finite size effect (CFSE).[3,5] The IPFSE and CFSE are most easily defined with reference to results of local density approximation (LDA) calculations. The IPFSE is the difference between the LDA energies per atom in the finite and infinite systems and the CFSE is the remainder of the finite size error. Recently we presented a method[6] for reducing the IPFSE in insulating systems by using the "special *k*-points" method borrowed from band-structure theory.[7] This method reduces the IPFSE by an order of magnitude and leaves the CFSE as the dominant finite size effect. The CFSE, which is the subject of this work, arises from the long range of the Coulomb interaction and is therefore of wide significance in many-body simulations.

We illustrate the CFSE by comparing the results of LDA and Hartree-Fock calculations. To define the LDA and HF energies for simulation cells with periodic boundary conditions we must specify the form of the model electron-electron interaction used. This interaction acts only between the charges within the simulation cell, but is intended to model the forces that would act in the center of an infinite array of identical copies of that cell. Unfortunately, sums of Coulomb $1/r$ potentials in extended systems are only conditionally convergent, and hence these forces are not uniquely defined until the boundary conditions at infinity have been specified. It is standard to calculate the potential (and hence the forces) by solving Poisson's equation subject to periodic boundary conditions, in which case the model interaction
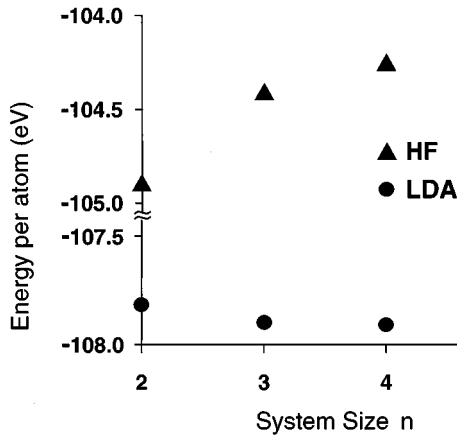
FIG. 1. LDA and HF energies per atom of diamond-structure silicon as a function of the size of the simulation cell, which consists of $n \times n \times n$ primitive unit cells.

between electrons in the cell becomes the well-known Ewald interaction.[8]

In Fig. 1 we show the LDA and HF energies per atom of diamond-structure silicon as a function of simulation cell size, calculated using norm-conserving pseudopotentials and a plane wave basis set. We sample a single k point in the Brillouin zone (BZ) of the simulation cell, whose translation vectors are n times those of the primitive unit cell.[6] The k point unfolds into an $n \times n \times n$ mesh in the BZ of the primitive unit cell. The k point we have chosen is an L point of the supercell BZ, which is equivalent to using a ''special k-points'' method giving very good results.[6,7] We have studied simulation cells with $n = 2,3,4,5$, which, for the diamond structure, corresponds to 16,54,128,250 atoms, respectively. To facilitate comparison between the LDA and HF results we have used the LDA orbitals to calculate the HF energies, so that the energy differences arise solely from the difference between the LDA exchange-correlation (XC) energy and the HF exchange energy. Figure 1 shows that the LDA energy converges very rapidly with simulation cell size, whereas the HF exchange energy converges very slowly. For $n = 3$ the finite size error in the LDA energy (IPFSE) is 0.012 eV per atom, which is much smaller than the HF finite size error of -0.211 eV per atom. The slow convergence of the HF exchange energy with the density of BZ sampling (which is equivalent to the size of the simulation cell) is well known and is usually solved by increasing the quality of the BZ integration. This solution is costly even in HF, and would be prohibitive in QMC calculations; the required computer time is roughly proportional to the cube of the number of electrons in the simulation cell and hence to the ninth power of n.

In the past, corrections for the CFSE in QMC simulations have been applied using results for different simulation cell sizes and extrapolating to the infinite cell size limit.[5,6] This empirical procedure is very costly and not particularly accurate. Such calculations have established that the CFSE is approximately inversely proportional to the number of electrons in the simulation cell, a result which is borne out by the HF data of Fig. 1. We now illustrate the fact that the CFSE is a crucial issue affecting the accuracy of many-body calculations for Coulomb systems. A standard problem in electronic

structure theory is to calculate the energy required to create a point defect. This is done by subtracting the energy of the perfect crystal from that of a large simulation cell containing a single defect. Taking the example of the $n = 3$ (54 atom) simulation cell of silicon, we find (see Fig. 1) that the CFSE error in the HF energy of the whole simulation cell is -11 eV, while in the fully correlated QMC calculation (see below) it is about -5 eV. In either case it is much larger than the energies of interest, which are often tenths of an eV per simulation cell. Moreover, since the CFSE per atom is approximately inversely proportional to the number of atoms in the simulation cell, the CFSE for the whole cell is almost independent of n.[9] Of course there will be a cancellation between the CFSEs in the perfect and defective solids, which will become more complete as the size of the simulation cell increases, so that eventually the energy difference will converge. However, we must expect that the incomplete cancellation of errors for finite simulation cells will lead to a significant uncertainty in the defect energy.

We now describe the origin of the CFSE in more detail. We write the total energy of the finite simulation cell as the sum of kinetic, electron-ion, and electron-electron interaction energies. We further split the electron-electron interaction energy into Hartree and XC contributions:

$$E_{e\text{-}e} = \frac{1}{2} \int_{\text{cell}} \rho(\mathbf{r}) \rho(\mathbf{r}') v(\mathbf{r} - \mathbf{r}') d\mathbf{r} d\mathbf{r}'$$

$$+ \frac{1}{2} \int_{\text{cell}} \rho_{\text{XC}}(\mathbf{r}', \mathbf{r}) \rho(\mathbf{r}) v(\mathbf{r} - \mathbf{r}') d\mathbf{r} d\mathbf{r}', \qquad (1)$$

where v is the model interaction, ρ is the electron density, and ρ_{XC} is the XC hole. In HF theory the XC hole is replaced by the exchange hole, but the expression for $E_{e\text{-}e}$ is otherwise the same. Note that the entire XC hole, with an integrated charge equal to a deficit of one electron, is always contained within the simulation cell (which is the entire physical system). Normally the charge density converges quite rapidly with simulation cell size. An extreme example is jellium, where the charge density is exact for all simulation cell sizes but the CFSE is still present. Therefore the convergence of the charge density with simulation cell size is not the cause of the CFSE. Calculations of pair correlation functions (e.g., Ref. 3) show that they also converge rapidly with simulation cell size, and therefore the convergence of ρ_{XC} is not the cause of the CFSE either.

We have found that the CFSE is due to the use of the Ewald interaction. Expanding the Ewald interaction[10] yields

$$v_{\text{Ewald}}(\mathbf{r}) = \frac{1}{r} + \frac{2\pi}{3\Omega} \mathbf{r}^T \cdot \mathbf{D} \cdot \mathbf{r} + \mathcal{O}\left(\frac{r^4}{\Omega^{5/3}}\right), \qquad (2)$$

where Ω is the volume of the simulation cell, and the tensor $\mathbf{D}$ depends on the geometry of the simulation cell. (For a cubic cell $\mathbf{D}$ is the identity matrix.) The deviations from $1/r$ model the effects of charges ''outside'' the simulation cell. In the XC integral, however, the interaction between each electron and its XC hole should be exactly $1/r$, independent of the size of the simulation cell. For very large simulation cells the $1/r$ term in the expansion of the Ewald interaction dominates, but for typical cell sizes the second term is significant and produces a finite size error propor-
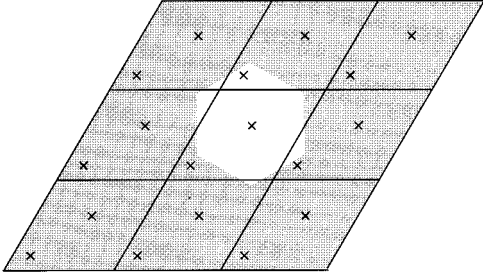
FIG. 2. An illustration of our interaction for a rhombohedral simulation cell containing two electrons (crosses). The hexagonal clear window centered on one of the electrons has the shape of the Wigner-Seitz cell of the simulation cell.
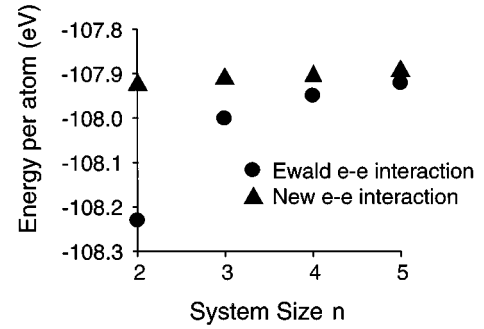

FIG. 3. The energy per atom of diamond-structure silicon as a function of simulation cell size, from variational QMC calculations using the Ewald electron-electron interaction and our interaction. The statistical error bars are smaller than the size of the symbols.

tional to $1/\Omega$ in the XC energy per electron. The XC energy is negative and the extra unphysical interaction makes the XC energy more negative. These observations explain why the HF energies in Fig. 1 converge with increasing simulation cell size (i) from below and (ii) with an error which is roughly inversely proportional to the number of electrons in the simulation cell.

The success of the LDA is often ascribed to the fact that it preserves the sum rule that the XC hole contains unit charge. When using many-body wave functions, as in QMC techniques, this sum rule is automatically satisfied and the important point is simply to make sure that the interaction with the XC hole has the proper $1/r$ form. In many cases the XC hole is well localized around each electron, so we should be able to simulate the XC interaction using relatively small simulation cells.

The two requirements for a model Coulomb interaction, which gives small CFSEs in simulations employing periodic boundary condition, are now clear. The model Coulomb interaction should (i) reproduce the proper Hartree interaction [first term in Eq. (1)] and (ii) be exactly $1/r$ for the interaction with the XC hole. The Ewald interaction satisfies (i), but violates (ii). An interaction energy satisfying both requirements is

$$E_{e\text{-}e} = \frac{1}{2} \int_{\text{cell}} \rho(\mathbf{r})\rho(\mathbf{r}')[v_{\text{Ewald}}(\mathbf{r}-\mathbf{r}') - f(\mathbf{r}-\mathbf{r}')]d\mathbf{r}d\mathbf{r}'$$

$$+ \int_{\text{cell}} |\Psi|^2 \sum_{i>j} f(\mathbf{r}_i-\mathbf{r}_j)\Pi_k d\mathbf{r}_k, \qquad (3)$$

where $f(\mathbf{r})$ is the $1/r$ Coulomb interaction treated within the ''nearest image'' convention, which corresponds to reducing the vector $\mathbf{r}$ into the Wigner-Seitz cell of the simulation cell.[11] The second term in Eq. (3) contributes both Hartree and XC terms. The Hartree contribution cancels the unwanted $f(\mathbf{r}-\mathbf{r}')$ term in the first integral, and the XC contribution involves the $f(\mathbf{r}-\mathbf{r}')$ interaction, which has the required $1/|\mathbf{r}-\mathbf{r}'|$ form at small separations. Of course, for consistency, we should apply the same prescription to all the interactions in the system, i.e., electron-electron, electron-ion, and ion-ion terms. However, if we model the ions as classical particles with well defined positions, then the XC terms from the electron-ion and ion-ion terms vanish and only Hartree-like terms involving the Ewald interaction re-

main. This analysis justifies our procedure of retaining the Ewald interaction for the electron-ion and ion-ion interactions. One consequence of this is that the forces on the ions are continuous functions of the ionic positions, which means that our scheme is suitable for use in quantum molecular dynamics calculations.

The Schrödinger equation may be ''derived'' by minimizing an energy functional, $E[\Psi] = \langle\Psi|\hat{H}|\Psi\rangle$, where Ψ is a normalized wave function. If a similar procedure is carried out for a functional including the electron-electron interaction of Eq. (3), the electron-electron interaction operator in the resulting Schrödinger-like equation is

$$\hat{H}_{e\text{-}e} = \sum_{i>j} f(\mathbf{r}_i-\mathbf{r}_j) + \sum_i \int_{\text{cell}} [v_{\text{Ewald}}(\mathbf{r}_i-\mathbf{r})$$

$$- f(\mathbf{r}_i-\mathbf{r})]\rho(\mathbf{r})d\mathbf{r}. \qquad (4)$$

The total electron-electron energy, $E_{e\text{-}e}$, is then the expectation value of $\hat{H}_{e\text{-}e}$ minus a double counting term for the electrostatic interactions. For systems where the charge density is uniform, the interaction reduces to a truncated Coulomb interaction (plus a constant), which is precisely the form we proposed for homogeneous systems.[3] Since the Ewald potential may be interpreted as the potential in an infinite periodic lattice with a particular choice of boundary conditions at infinity,[12,3] the interaction of Eq. (4) may be illustrated as in Fig. 2. This depicts a rhombohedral simulation cell containing two electrons, on one of which is centered a hexagonal window corresponding to the Wigner-Seitz cell of the simulation cell. The electron at the center of the window experiences a $1/r$ interaction with all the other electrons within the window (one in this case) and an electrostatic interaction with the electronic charge density of the shaded region outside of the window.

In a variational QMC calculation the electronic charge density appearing in Eq. (4) may be accumulated during the simulation and the interaction energy evaluated afterwards. In a diffusion QMC calculation this is not possible and one must know the charge density before starting the calculation. To overcome this problem we use the LDA charge density in Eq. (4). It would be possible to update this charge density afterwards and perform a self-consistent calculation. However, LDA charge densities are normally remarkably good and, moreover, the interaction energy is insensitive to the

quality of the charge density used because $v_{\text{Ewald}}(\mathbf{r}) - f(\mathbf{r})$ differs significantly from zero only when $|\mathbf{r}|$ is large. We have found this approximation to be so successful that for convenience we also use it for variational QMC calculations and in the procedures for optimizing wave functions. We note that a successful QMC calculation requires a reasonable approximation to the wave function itself, so that the requirement of a reasonable approximation to the charge density is not a serious limitation.

We now illustrate the effectiveness of our procedure with a set of variational QMC calculations for the silicon simulation cells listed earlier. The techniques employed are similar to those described elsewhere.[6,13] We use variational Slater-Jastrow wave functions containing 24 parameters,[13] which are optimized by minimizing the variance of the energy.[14] The single particle functions were obtained from LDA calculations and were the same as those used in Fig. 1. We have optimized the wave functions using Hamiltonians with the Ewald interaction and with our interaction, but even for the smallest simulation cells the wave functions obtained were virtually identical. This shows that properties other than the energy are not significantly affected by the change in the interaction term. We have also tested the sensitivity to the charge density used in the Hamiltonian of Eq. (4). Using the charge densities obtained from an $n=2$ LDA calculation and from a fully converged LDA calculation makes no detectable difference to the calculated energies. Figure 3 shows the energy per atom obtained from variational QMC calculations using our interaction and the Ewald interaction. It is clear that the use of our interaction greatly reduces the CFSE. This interaction is also successful in HF calculations, reducing the CFSE shown in Fig. 1 by a factor of about 3. Finally, we note that our interaction is much faster to compute than the Ewald interaction.

In summary, we have traced the source of the troublesome Coulomb finite size errors in quantum many-body calculations for periodic simulation cells to the use of the Ewald interaction, which gives a spurious cell-size-dependent contribution to the electron-electron interaction energy. We have devised a model electron-electron interaction which eliminates this problem, based on the idea that the exchange-correlation hole is short ranged. Variational QMC calculations with up to 1000 electrons show that the interaction gives much smaller finite size effects than the Ewald interaction. This development will allow for significantly more accurate simulations of correlated electron systems.

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[10] Note that our definition of the Ewald interaction differs by a constant from that used by many other authors. Our Ewald interaction satisfies Eq. (2) but does not average to zero over the simulation cell.

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