Green's Function Monte Carlo Method for Liquid ^{3}He

Michael A. Lee, K. E. Schmidt, and M. H. Kalos

Courant Institute of Mathematical Sciences, New York, New York 10012

and

G. V. Chester

Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York 14853

The Green's-function Monte Carlo method, which yields an exact ground-state solution to the Schrödinger equation for Bose systems, is applied to liquid ^{3}He, a fermion system. With the use of a technique that projects out states of selected symmetry, strict upper bounds to the ground-state energy of many-fermion systems have been constructed. An upper bound has been found for liquid ^{3}He of $-2.20 \pm 0.05\,°K$ at the experimental equilibrium density. This energy is more than $1\,°K$ below Jastrow variational results and much nearer the experimental value of $-2.47 \pm 0.01\,°K$.

PACS numbers: 67.50.Dg

The Green's-function Monte Carlo (GFMC) method has been shown to be an exact and flexible method of obtaining the ground-state energy and structure of Bose systems. The method is described in detail in several references.[1,2] Since the initial presentation of practical GFMC calculations for Bose systems a decade ago, an outstanding problem has been to devise similar methods for fermion systems.[3] In this paper we show how the GFMC method can be applied to obtain upper bounds to the ground-state energy of many-fermion systems.

Although the technique presented here formally converges to the exact fermion wave function and energy, the computer time required for iterating the equations n times, so as to obtain a fixed statistical error in each iterate, increases exponentially with n; thus, continued iteration to demonstrate convergence will become prohibitive at some point. However, at each iteration our method yields an energy which is an upper bound to the true ground-state energy, and which converges monotonically. Therefore, useful results can be extracted before available computational resources are exceeded.

The GFMC method employs the Monte Carlo technique to iterate the integral equation

$$\psi^{n+1}(R) = E_0 \int G(R,R')\psi^n(R')dR' \tag{1}$$

with $G(R,R')$ defined by

$$HG(R,R') = \delta(R-R'). \tag{2}$$

Here R stands for the coordinates of the N particles in the system; ψ^n is the wave function obtained after n iterations of the equation; and E_0, H, and $G(R,R')$ are the ground-state energy, the

Hamiltonian, and the Green's function, respectively. The salient feature of the method is that when the iteration of Eq. (1) has converged, the ground-state wave function obtained is not analytic, but rather a set of configurations of the particles drawn from the exact ground-state wave function $\psi_0(R)$. The calculation of the desired expectation values is accomplished by evaluating appropriate many-body integrals at this set of configurations. These techniques are described adequately elsewhere.[1,2] We will confine our attention to the evaluation of the energy.

The calculation begins by choosing a trial fermion wave function, ψ_T, that is totally antisymmetric under interchange of particles of like spin. This wave function serves the purpose of being $\psi_F^0(R)$, the starting solution to be iterated. It also provides our energy weighting function.

Let $\{\psi_i\}$ denote the eigenfunctions of the Hamiltonian H. Some of these functions will be symmetric, others antisymmetric, and many will have mixed symmetries. Also let ψ_F^n be the wave function obtained from the nth iteration of Eq. (1) with $\psi_F^0 = \psi_T$. We define the "mixed energy" at the nth iteration to be

$$E_F^n = \langle\psi_T|H|\psi_F^n\rangle/\langle\psi_T|\psi_F^n\rangle. \tag{3}$$

We will show that for all n, $E_F^n \geq E_F$ the true Fermi ground-state energy.

The Green's function $G(R,R')$ and ψ_F^n can be expanded in the complete set of states $\{\psi_i\}$ as

$$\psi_F^n = \sum_i a_i^n \psi_i(R), \tag{4}$$

and

$$G(R,R') = \sum_i \psi_i^*(R)\psi_i(R')/E_i. \tag{5}$$

The zero point of the energy has been chosen so that all $E_l > 0$. From Eqs. (1), (4), and (5) we can write a recursion relation for the $a_l{}^n$:

$$a_l{}^{n+1} = (E_0/E_l) a_l{}^n. \tag{6}$$

This relation and the orthogonality of the ψ_l's can be combined to give

$$E_F{}^n = \frac{\langle \psi_T | H | \psi_F{}^n \rangle}{\langle \psi_T | \psi_F{}^n \rangle} = \frac{\langle \psi_M{}^n | H | \psi_M{}^n \rangle}{\langle \psi_M{}^n | \psi_M{}^n \rangle} \geq E_F, \tag{7}$$

where

$$\psi_M{}^n = \sum_l (E_0/E_l)^{n/2} a_l{}^0 \psi_l. \tag{8}$$

The mixed energy is exactly equivalent to the expectation value of the Hamiltonian with $\psi_M{}^n$, and is therefore greater than or equal to the exact ground-state energy. As $n \to \infty$, only the lowest-energy state with nonzero $a_l{}^0$ will contribute. Since ψ_T is chosen to be antisymmetric, this will be a Fermi state. This proof is valuable because ψ_T, not $\psi_F{}^n$, is known analytically and only the mixed energy can be evaluated in our Monte Carlo procedure. We note that this proof makes no assumptions about the fermion nature of the problem. It is equally true for bosons if ψ_T is not orthogonal to the Bose ground state.

In the actual calculation, configurations are sampled with the appropriate probabilities from the Green's functions and wave functions. Hence, all quantities have some statistical uncertainty.

Since probability densities must be positive definite, it is necessary to separate the fermion wave function into two positive parts, i.e.,

$$\psi_F{}^n = \psi_F{}^{n(+)} - \psi_F{}^{n(-)}. \tag{9}$$

The $\psi_F{}^{0(+)}$ ($\psi_F{}^{0(-)}$) is chosen to be zero where ψ_T is negative (positive). All the required integrals, e.g., Eq. (1), are linear in $\psi_F{}^n$ and can be evaluated for $\psi_F{}^{n(+)}$ and $\psi_F{}^{n(-)}$ separately. Since $\psi_F{}^{n(+)}$ and $\psi_F{}^{n(-)}$ are not individually orthogonal to lower-energy nonfermion states, each iteration of Eq. (1) introduces into $\psi_F{}^{n+1(\pm)}$ increasingly larger nonfermion components. Though these components in the full $\psi_F{}^n$ cancel on the average, their contribution to the statistical uncertainty of the expectation value does not. Eventually the Bose ground state dominates $\psi_F{}^{n(\pm)}$ and the computational time for fixed uncertainty increases exponentially with n.

We have completed calculations using two different initial trial wave functions. The first trial function which we used was a simple Slater-Jastrow wave function:

$$\psi_{T1} = \psi_J \det[\exp(i\vec{k}_i \cdot \vec{r}_j)],$$
$$\psi_J = \exp[-\tfrac{1}{2} \sum_{i<j} u(r_{ij})], \tag{10}$$

where the det stands for a determinant for each spin state. The second trial function included both symmetric three-body correlations and backflow correlations in the determinants:

$$\psi_{T2} = \psi_3 \det(\exp\{i\vec{k}_i \cdot [\vec{r}_j + \sum_{l \neq j} \eta(r_{lj})\vec{r}_{lj}]\}), \quad \psi_3 = \exp[-\tfrac{1}{2}\sum_{i<j} u(r_{ij}) - \tfrac{1}{2}\sum_l \sum_{i<j \neq l} \xi(r_{li})\xi(r_{lj})\vec{r}_{li} \cdot \vec{r}_{lj}]. \tag{11}$$

The wave function ψ_{T2} gives a substantially improved energy over that of ψ_{T1} in standard variational calculations. The variational calculations with these two forms for a trial wave function are described in detail elsewhere.[4] Our results are summarized in Figs. 1–3. All calculations were done at the experimental equilibrium denstiy of liquid ^{3}He.

Figure 1 shows the energy as a function of iteration for both trial wave functions. The energies at $n = 0$ are quite different; however they come close together at large n.

Figures 2 and 3 show the overlap integrals $\langle \psi_T | \psi_F{}^n \rangle$, and the boson component energies of each wave function as a function of iteration n. The boson component of $\psi_F{}^n$ clearly dominates the calculation asymptotically.

These calculations give a significantly better upper bound for liquid ^{3}He (-2.20 ± 0.05 °K) than ever obtained before. A discrepancy remains be-

tween our results and the experimental value of the energy -2.47 ± 0.01 °K.[5] In Fig. 1, it appears that both wave functions approach an energy of -2.2 °K, about 0.3 °K above the experimental value. There are several possible explanations for the difference between theory and experiment: (1) The procedure has not converged; (2) the ^{3}He potential is incorrect; (3) the finite number of particles simulated could affect the energy; (4) the trial wave function could be nearly orthogonal to the Fermi ground state.

The question of convergence is difficult to answer. Figure 1 itself is ambiguous. To check the convergence adequately, it may be necessary to iterate to an n of the order of 70–100. To get an accuracy of 0.05 °K then would require more than an order of magnitude more computation time. Such a calculation is feasible.

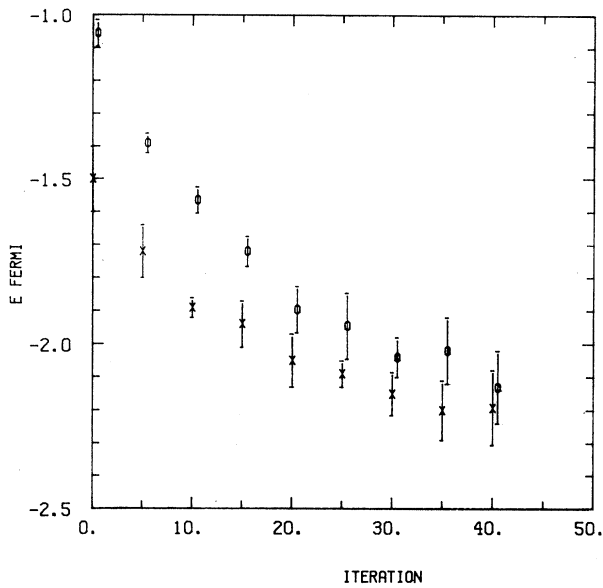The two-body potential we have used is the

729

FIG. 1. Energy of the ^{3}He wave function calculated every five iterations of Eq. (1). The circles are results for the initial choice of a plain Slater-Jastrow wave function lEq. (10)l. The crosses are obtained by using the full wave function including backflow and triplet correlations lEq. (11)l. A slight lateral displacement of one set of results has been made for additional clarity.
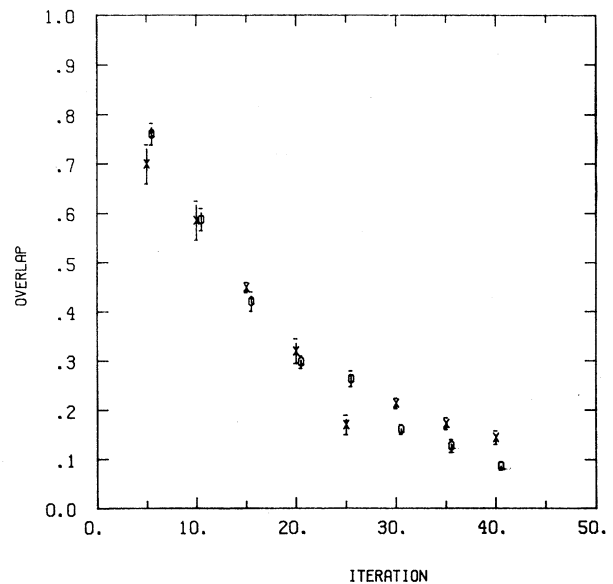

FIG. 2. The overlap of the fermion wave functions with the initial trial fermion wave functions. Symbol identification is the same as in Fig. 1.

HFDHE2 potential of Aziz et al.[6] and is known to yield excellent results for liquid ^{4}He,[7] but has not been tested near the ^{3}He equilibrium density. We estimate that this might give an error of about ± 0.1 °K. Variational calculations[8] suggest that the difference in the energy between a system of the 38 particles that we used and an infinite system is about 0.15–0.2 °K and will raise the energy. Thus the discrepancy with experiment may be as large as 0.5 °K.

In conclusion, we have shown that GFMC methods may be employed to greatly improve upon standard variational wave functions. It will be important to determine the source of our discrepancy with experiment. If this difference is not due to slow convergence, then this method is feasible for investigating the exact properties of many-fermion systems.

In the near future we plan to publish a more complete discussion of the question of exact and asymptotically stable fermion algorithms in which the computational time goes linearly with the number of iterations, including one which we find functional in small systems. Also we plan to test the helium potential by solving the ^{3}He-in-

^{4}He mixture problem in the low-concentration limit, since experimental data are available in this system.
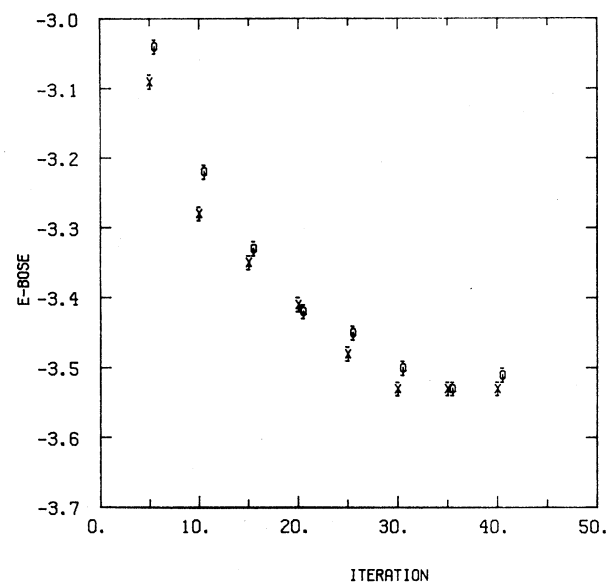
FIG. 3. Energy of the mass-3 boson component of $\psi_F^{\pm}$ for the two choices of initial wave function. The correct mass-3 boson energy is − 3.54 ± 0.01 °K. Symbol identification is the same as in Fig. 1.

[1]M. H. Kalos, D. Levesque, and L. Verlet, Phys. Rev. A **9**, 2178 (1974); D. Ceperley and M. H. Kalos, in *Monte Carlo Methods in Statistical Physics*, edited by K. Binder (Springer-Verlag, Berlin, 1979).

[2]P. A. Whitlock, D. M. Ceperley, G. V. Chester, and M. H. Kalos, Phys. Rev. B **19**, 5598 (1979).

[3]D. M. Arnow, M. H. Kalos, K. E. Schmidt, M. A. Lee, Bull. Am. Phys. Soc. **25**, 429 (1980); D. Ceperley and B. Alder, Phys. Rev. Lett. **45**, 566 (1980); J. B. Anderson, J. Chem. Phys. **73**, 3897 (1980).

[4]M. H. Kalos, K. E. Schmidt, Michael A. Lee, and G. V. Chester, to be published.

[5]T. R. Roberts, R. H. Sherman, and S. G. Sydoriak, J. Res. Nat. Bur. Stand. Sect. A **68**, 567 (1964).

[6]R. A. Aziz, V. P. S. Nain, J. S. Carley, W. J. Taylor, and G. T. McConville, J. Chem. Phys. **70**, 4330 (1979).

[7]M. H. Kalos, Michael A. Lee, P. A. Whitlock, and G. V. Chester, to be published.

[8]D. Ceperley, G. V. Chester, and M. H. Kalos, Phys. Rev. B **16**, 3081 (1977).

Metal-Surface Reconstruction Induced by Adsorbate: Fe(110)$p(2\times2)$-S

H. D. Shih[a] and F. Jona

Department of Materials Science and Engineering, State University of New York, Stony Brook, New York 11794

and

D. W. Jepsen and P. M. Marcus

IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598

(Received 19 December 1980)

Reconstruction of the Fe(110) surface by a quarter monolayer of S is shown by low-energy electron-diffraction intensity analysis to correspond to a model in which hard-sphere atoms displace to a unique jamming point. After reconstruction the S atoms sit in fourfold hollows of touching Fe atoms with S-Fe bond lengths of 2.17 and 2.36 Å. A general construction for 2×2 reconstructions with rectangular symmetry is given and applied to this case and to Ni(001)(2×2)-C.

Clean metal surfaces generally do not reconstruct, i.e., rearrange the atoms of the surface layers to give a different unit cell than the bulk.[1] However, when the surface has an ordered adsorbate with a different unit cell than the substrate bulk, reconstruction of the top substrate layers to the adsorbate unit cell and symmetry[2] should be universal. The atom displacements from bulk positions are small for the low-index (high–packing-density) surfaces commonly studied, since the range of movement is limited by the jamming of atoms against each other. A successful quantitative study has previously been carried out for only one case, Ni(001)(2×2)-C by low-energy electron-diffraction (LEED) intensity analysis.[3] We report here the case of Fe(110)$p(2\times2)$-S also studied by LEED intensity analysis, which resembles the Ni case, but shows interesting differences. In both cases an adsorbate atom is situated in a fourfold hollow site of the metal

surface, i.e., a hollow surrounded by four atoms, not necessarily at the same distance, and the presence of the adsorbate induces a 2×2 reconstruction which enlarges that hollow by contracting other hollows. However, in the Fe case there is rectangular symmetry and the reconstruction is induced by a quarter monolayer of S atoms, whereas in the Ni case the structure retains fourfold rotational (but not square) symmetry and is induced by a half monolayer of C atoms. In the Fe case, the analysis shows that both adsorbate and reconstructed substrate have 2×2 symmetry, hence an intensity analysis is required to determine that the Fe atoms have moved from their bulk positions; in the Ni case, the adsorbate has $c(2\times2)$ symmetry and the presence of additional diffracted beams indicates directly that the substrate has a $p(2\times2)$ reconstruction. The anisotropy of the Fe case suggests a simple mechanism in which the S atom increases the two shorter