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Structure of the ground-state wave function of quantum fluids and "exact" numerical methods

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The problem of how to extract information on the structure of the exact ground-state wave function of a Bose fluid from the results of Green's-function Monte Carlo computations is considered. Use of the criterion of maximum overlap of the exact ground state with an extended Jastrow function leads to certain equalities for correlation functions. By using methods borrowed from theories of classical fluids various schemes are proposed that permit the determination of the "best" Jastrow function. The case of Fermi statistics is also considered.

I. INTRODUCTION AND SUMMARY

The Green's-function—Monte Carlo (GFMC) method[1] is a practical tool for obtaining exact information on the ground state of a many-body system with Bose statistics. The development of similar, exact methods in the case of Fermi statistics is now under active investigation.[2] Such an approach is based on statistical sampling of the configuration space and gives a set of configurations drawn from the exact ground-state wave function ψ_0 or from some related functions. This sampling is enough to compute exactly the expectation value of interesting observables such as energy, correlation functions, and the momentum distribution. However, one would also like to have information on the strucuture of ψ_0. For instance, one would like to know the role played in ψ_0 by Jastrow correlations, i.e., correlations between pairs of particles, by three-particle correlations, etc. In order to answer this question one has to introduce a criterion that selects in a suitable subspace of the Hilbert space of the system (for instance, the subspace of the Jastrow functions) the function that best reproduces some aspect of the system. An obvious requirement to the criterion is that one recovers the exact ψ_0 as the only answer when the subspace coincides with the full Hilbert space.

The first choice, of course, is to use the variational principle for the expectation value of the Hamiltonian, but in this way one is not making direct use of the configurations generated by the GFMC computation. Moreover, it is well known[1] that the energy is rather insensitive to the intermediate and long-range part of the correlations contained in the wave function, with only the short-range part being really important. The criterion we use is the maximum overlap, i.e., we ask for the maximum of the overlap integral $\langle \psi_{\text{mod}} | \psi_0 \rangle$ between the exact ground state and a model wave function ψ_{mod} that spans a certain subspace M of the full Hilbert space. This criterion selects the state in M that is closer to ψ_0 in a geometrical sense, and we call it $\overline{\psi}_{\text{mod}}$. Clearly the larger the subspace M, the closer is $\overline{\psi}_{\text{mod}}$ to ψ_0.

The maximum-overlap criterion offers various advantages over other criteria that one can think of, and it appears to be useful. In the first place it makes direct use of the properties of ψ_0, and not only indirectly through the Hamiltonian. Secondly, the extremum of $\langle \psi_{\text{mod}} | \psi_0 \rangle$ is obtained when certain equalities for correlation functions are satisfied. The larger the subspace M the more complex are the correlation functions involved, so one has a systematic way of improving our knowledge of ψ_0 starting from the simplest case where M is the subspace of the Jastrow functions. An additional bonus of this criterion is that the present GFMC computations that use the so-called importance sampling[1] already generate all the information needed to extract these correlation functions. Finally, the method is also sensitive to the intermediate and long-range part of the correlations contained in ψ_0. For instance, we find immediately that $\overline{\psi}_{\text{mod}}$ must contain the long-range r^{-2} correlations[3] present in ψ_0.

At first sight the equations that we obtain do not appear very practical because they require a GFMC computation that uses the unknown $\bar{\psi}_{\mathrm{mod}}$ as the importance-sampling function. We show, however, that by borrowing methods developed in the theory of classical liquids, one can set up methods to obtain $\bar{\psi}_{\mathrm{mod}}$ using only the result of a GFMC computation that has used a nonoptimum importance-sampling function. The case of Fermi statistics is, in general, much more complex but we find some simple results if we limit ourselves to extract the symmetric part of correlations contained in ψ_0.

The contents of the paper are the following. In Sec. II we present the basic results in the case of Bose statistics. In Sec. III we consider some methods to solve the equations of Sec. II with standard numerical algorithms. Finally the case of Fermi statistics is discussed in Sec. IV.

II. MAXIMUM-OVERLAP CRITERION

Let a system of N identical bosons have $\psi_0(\vec{r}_1, \ldots, \vec{r}_N)$ as the ground-state wave function. We consider the subspace of the Hilbert space of the system spanned by the extended Jastrow wave function, or Feenberg functions, which we write in the form

$$\psi_{\mathrm{mod}}(\{\vec{r}_i\} \mid \{u_\alpha\}) = (\langle \hat{\psi}_{\mathrm{mod}} \mid \hat{\psi}_{\mathrm{mod}} \rangle)^{-1/2} \times \hat{\psi}_{\mathrm{mod}}(\{\vec{r}_i\} \mid \{u_\alpha\}) , \tag{1}$$

where $\hat{\psi}$ is the unnormalized function

$$\hat{\psi}_{\mathrm{mod}}(\{\vec{r}_i\} \mid \{u_\alpha\}) = \exp\left[-\tfrac{1}{2}\sum_{\alpha=1}^{M}\sum_{a_\alpha} u_\alpha(R_{a_\alpha})\right] . \tag{2}$$

a_α indicates a set of α particles chosen between $1,2, \ldots, N$, R_{a_α} stands for the ensemble of the coordinates of these α particles, and $\sum_{a_\alpha}$ is the sum over all distinct sets a_α. The wave function ψ_{mod} is characterized by the M functions $u_1, u_2, \ldots, u_M$ that we call pseudopotentials, and M is the maximum order of correlations that we allow in ψ_{mod}. For $M=1$ one has a Hartree function, for $M=2$ one has a so-called Jastrow function, with $M=3$ one allows also three-particle correlations, etc. The one-particle term u_1 is zero unless the system is nonuniform because there is an external potential or because the system is in the solid phase. Since ψ_0 is real and symmetric, u_α also has these same properties. $\langle \hat{\psi}_{\mathrm{mod}} \mid \hat{\psi}_{\mathrm{mod}} \rangle$ is the normalization integral

$$\langle \hat{\psi}_{\mathrm{mod}} \mid \hat{\psi}_{\mathrm{mod}} \rangle = \int d^3r_1 \cdots d^3r_N \exp\left[-\sum_{\alpha=1}^{M}\sum_{a_\alpha} u_\alpha(R_{a_\alpha})\right] . \tag{3}$$

The extremum of the overlap integral $\langle \psi_{\mathrm{mod}} \mid \psi_0 \rangle$ with respect to the pseudopotentials gives the conditions

$$\frac{\delta\langle \psi_{\mathrm{mod}} \mid \psi_0 \rangle}{\delta u_\beta(R_\beta)} = (\langle \hat{\psi}_{\mathrm{mod}} \mid \hat{\psi}_{\mathrm{mod}} \rangle)^{-1/2} \left[\frac{\delta\langle \hat{\psi}_{\mathrm{mod}} \mid \psi_0 \rangle}{\delta u_\beta(R_\beta)} - \frac{1}{2} \frac{\langle \hat{\psi}_{\mathrm{mod}} \mid \psi_0 \rangle}{\langle \hat{\psi}_{\mathrm{mod}} \mid \hat{\psi}_{\mathrm{mod}} \rangle} \frac{\delta\langle \hat{\psi}_{\mathrm{mod}} \mid \hat{\psi}_{\mathrm{mod}} \rangle}{\delta u_\beta(R_\beta)} \right] = 0 . \tag{4}$$

The computation of the functional derivatives is simple, for instance

$$\begin{aligned} \frac{\delta\langle \hat{\psi}_{\mathrm{mod}} \mid \hat{\psi}_{\mathrm{mod}} \rangle}{\delta u_\beta(R_\beta)} &= -\int d^3r_1 \cdots d^3r_N \sum_{a_\beta} \delta(R_\beta - R_{a_\beta}) \hat{\psi}^2_{\mathrm{mod}}(\{\vec{r}_i\} \mid \{u_\alpha\}) \\ &= -\frac{N!}{(N-\beta)!} \int d^3r_{\beta+1} \cdots d^3r_N \hat{\psi}^2_{\mathrm{mod}}(\{\vec{r}_i\} \mid \{u_\alpha\}) , \end{aligned} \tag{5}$$

and a similar expression holds for the derivatives of $\langle \hat{\psi}_{\mathrm{mod}} \mid \psi_0 \rangle$ with $\hat{\psi}_{\mathrm{mod}}\psi_0$ replacing $\hat{\psi}^2_{\mathrm{mod}}$. One recognizes in (5) a reduced distribution function, a part from a constant. Given a probability distribution in configuration space one defines the reduced distribution function $n^{(\beta)}(\vec{r}_1, \ldots, \vec{r}_\beta)$ of order β as the probability density of finding the given number β of distinct particles at coordinates $R_\beta = (\vec{r}_1, \ldots, \vec{r}_\beta)$. If the probability distribution is taken as $\hat{\psi}^2_{\mathrm{mod}} / \langle \hat{\psi}_{\mathrm{mod}} \mid \hat{\psi}_{\mathrm{mod}} \rangle$, then

$$n^{(\beta)}_{\mathrm{mod}}(\vec{r}_1, \ldots, \vec{r}_\beta \mid \{u_\alpha\}) = \frac{N!}{(N-\beta)!} \int d^3r_{\beta+1} \cdots d^3r_N \hat{\psi}^2_{\mathrm{mod}}(\{\vec{r}_i\} \mid \{u_\alpha\}) / \langle \hat{\psi}_{\mathrm{mod}} \mid \hat{\psi}_{\mathrm{mod}} \rangle , \tag{6}$$

where for future use we have explicitly written the functional dependence of $n^{(\beta)}_{\mathrm{mod}}$ on the set of pseudopotentials u_α.

In a similar way we can consider $\hat{\psi}_{\mathrm{mod}}\psi_0 / \langle \hat{\psi}_{\mathrm{mod}} \mid \psi_0 \rangle$ as a probability distribution; this gives rise to the so-called mixed reduced distribution functions[1]:

$$n^{(\beta)}_{\mathrm{mxd}}(\vec{\mathrm{r}}_1,\ldots,\vec{\mathrm{r}}_\beta\,|\,\{u_\alpha\})=\frac{N!}{(N-\beta)!}\int d^3r_{\beta+1}\cdots d^3r_N\,\hat{\psi}_{\mathrm{mod}}(\{\vec{\mathrm{r}}_i\}\,|\,\{u_\alpha\})\psi_0(\{\vec{\mathrm{r}}_i\})/\langle\hat{\psi}_{\mathrm{mod}}\,|\,\psi_0\rangle\ . \tag{7}$$

Taking into account (5) – (7) the extremum conditions (4) can be written as

$$\frac{\delta\langle\psi_{\mathrm{mod}}\,|\,\psi_0\rangle}{\delta u_\beta(R_\beta)}=\tfrac{1}{2}\langle\psi_{\mathrm{mod}}\,|\,\psi_0\rangle[n^{(\beta)}_{\mathrm{mod}}(\vec{\mathrm{r}}_1,\ldots,\vec{\mathrm{r}}_\beta\,|\,\{u_\alpha\})-n^{(\beta)}_{\mathrm{mxd}}(\vec{\mathrm{r}}_1,\ldots,\vec{\mathrm{r}}_\beta\,|\,\{u_\alpha\})]=0\ . \tag{8}$$

We conclude that the maximum overlap is obtained for that set of pseudopotentials $\{\bar{u}_\alpha\}$ for which

$$n^{(\beta)}_{\mathrm{mod}}(\vec{\mathrm{r}}_1,\ldots,\vec{\mathrm{r}}_\beta\,|\,\{\bar{u}_\alpha\})=n^{(\beta)}_{\mathrm{mxd}}(\vec{\mathrm{r}}_1,\ldots,\vec{\mathrm{r}}_\beta\,|\,\{\bar{u}_\alpha\}),\quad \beta=1,\ldots,M \tag{9}$$

i.e., the mixed distribution functions must be equal to those for the model wave function up to an order equal to the maximum order of the pseudopotentials included in ψ_{mod}. These M functional equations represent the basic result of our paper. The correlation functions $n^{(\beta)}_{\mathrm{mod}}$ are those that can be obtained from a standard variational computation of the energy when ψ_{mod} is used as trial wave function. Moreover, the mixed correlation functions $n^{(\beta)}_{\mathrm{mxd}}$ can be obtained from a GFMC computation. In fact, such computation makes use of importance sampling,[1] i.e., one generates a sequence of configurations drawn from the product of ψ_0 and of an importance-sampling function, usually chosen as a Jastrow function. If this importance-sampling function is chosen as $\hat{\psi}_{\mathrm{mod}}$ then the configurations that are generated are exactly those required to construct $n^{(\beta)}_{\mathrm{mxd}}$, and the actual computation of $n^{(\beta)}_{\mathrm{mxd}}$ from a set of configurations is a standard part of the data analysis in Monte Carlo computations. However, Eqs. (9) as written are not very useful because by trial and error one should try to satisfy these equations by varying $\{u_\alpha\}$; for any change of the pseudopotential one should perform a new GFMC computation. In the next section we present methods to overcome this difficulty.

If ψ_{mod} represents a good approximation to ψ_0 so that one can treat the difference $\psi_0-\psi_{\mathrm{mod}}$ as a perturbation, then to first order in this difference one finds[1] a linear relation between exact and mixed averages. In our case it reads

$$n_0^{(\beta)}=2n^{(\beta)}_{\mathrm{mxd}}-n^{(\beta)}_{\mathrm{mod}}\ , \tag{10}$$

where $n_0^{(\beta)}$ is the exact distribution function.

From GFMC computations it is found[1] that such relations are reasonably well satisfied, and if we use (10) in (9), then the approximate form of the maximum-overlap conditions reads

$$n^{(\beta)}_{\mathrm{mod}}(\vec{\mathrm{r}}_1,\ldots,\vec{\mathrm{r}}_\beta\,|\,\{\bar{u}_\alpha\})=n_0^{(\beta)}(\vec{\mathrm{r}}_1,..,\vec{\mathrm{r}}_\beta),\quad \beta=1,\ldots,M\ . \tag{11}$$

If the system is in a fluid state and there is no external potential, then the density is constant, $n_0^{(1)}(\vec{\mathrm{r}})=\rho=N/V$, so that $u_1=0$. From variational computations of the energy[1] it is known that a Jastrow wave function, i.e., expression (2) with $M=2$, already represents a reasonable approximation to ψ_0, and inclusion of the three-particle term u_3 gives an excellent approximation.[4] In the case of a Jastrow function the maximum-overlap conditions (9) become a single equation[5]:

$$g_J(r\,|\,\bar{u}_2)=g_{\mathrm{mxd}}(r\,|\,\bar{u}_2)\ , \tag{12}$$

where we have replaced the subscript mod by J and the two-particle distribution functions by the radial distribution functions (RDF):

$$n_J^{(2)}(\vec{\mathrm{r}}_1,\vec{\mathrm{r}}_2\,|\,u_2)=\rho^2 g_J(\,|\,\vec{\mathrm{r}}_1-\vec{\mathrm{r}}_2\,|\,\,|\,u_2)$$

and similarly for $n^{(2)}_{\mathrm{mxd}}$. The approximate relations (11) in this case become

$$g_J(r\,|\,\bar{u}_2)=g_0(r)\ . \tag{13}$$

If we allow also three-particle terms in ψ_{mod} then the exact relations (9) can be written as

$$\begin{gathered}g_{\mathrm{mod}}(r\,|\,\bar{u}_2,\bar{u}_3)=g_{\mathrm{mxd}}(r\,|\,\bar{u}_2,\bar{u}_3),\\ g^{(3)}_{\mathrm{mod}}(\vec{\mathrm{r}}_1,\vec{\mathrm{r}}_2,\vec{\mathrm{r}}_3\,|\,\bar{u}_2,\bar{u}_3)=g^{(3)}_{\mathrm{mxd}}(\vec{\mathrm{r}}_1,\vec{\mathrm{r}}_2,\vec{\mathrm{r}}_3\,|\,\bar{u}_2,\bar{u}_3)\ ,\end{gathered} \tag{14}$$

where we have introduced the usual triplet distribution function $n^{(3)}=\rho^3 g^{(3)}$.

We are not able to make rigorous statements concerning the existence and uniqueness of a solution to Eqs. (9) or (11). This problem is related to a similar one in classical statistical mechanics, the uniqueness of the interatomic potential for given correlation functions, and also in this case nothing rigorous is known, apart from the low-density limit. Let us comment, however, that Monte Carlo computations with Jastrow functions indicate that an equation such as (13) can be solved.[5] In addition, the perturbation scheme developed in the next section gives a single solution.

The condition of maximum overlap should allow the determination of the pseudopotentials at intermediate or large distances with a precision that is better than that obtained with the energy criterion, because the value of the energy is rather insensitive to the precise form of the pseudopotentials outside the region of the core of the potential, whereas correlations are more sensitive. For instance, from a variational computation with Jastrow functions it is well known that pseudopotentials not giving a very good[6] or even giving a poor[7] radial distribution function, give a good energy value. On the other hand, complex pseudopotentials[5,8] that give an excellent $g(r)$ improve only marginally the energy value. Another indication in this respect comes from the GFMC computation for the Lennard-Jones fluid, which shows[9] that the fluctuations of the computation are drastically reduced if the pseudopotential u_2, used as the importance-sampling function, contains that intermediate-range structure that was shown[10,5] to give an improved g_J, thus coming close to satisfy (12). This implies that in this case the configurations sampled by $\psi_J \psi_0$ are closer to those configurations that would be sampled by ψ_0^2.

A significant element of the ground state of a neutral quantum Bose fluid is the presence of long-range correlations[3] due to the zero-point motion of phonon excitations. In a three-dimensional system ψ_0 contains a Jastrow component with

$$u_2(r) \underset{r\to\infty}{\sim} \chi_{\text{ph}}(r) = mc(\pi^2\rho\hbar)^{-1} r^{-2} ,$$

where m is the atomic mass and c the sound velocity. We find that the model wave function, in order to have maximum overlap with ψ_0, must have this behavior. In fact, by taking a Fourier transform Eq. (12) becomes a relation for structure factors,

$$S_J(k \mid \bar{u}_2) = S_{\text{mxd}}(k \mid \bar{u}_2) , \tag{15}$$

where the structure factor is related to a RDF by the usual relation

$$S(k) = 1 + \rho \int d^3r\, e^{i\vec{k}\cdot\vec{r}} [g(r) - 1] . \tag{16}$$

The small-k behavior of $S(k)$ is dominated by the large-distance behavior of $\bar{u}_2$ in the case of S_J and of $\bar{u}_2$ and χ_{ph} present in ψ_0 in the case of S_{mxd}. These behaviors are obtained correctly by the random-phase approximation,[3] and it is a simple matter to check that if we write

$$\bar{u}_2(r) \underset{r\to\infty}{\sim} A/r^a ,$$

Eq. (15) to leading order in k implies $a = 2$ and $A = mc(\pi^2\rho\hbar)^{-1}$.

III. METHODS OF SOLUTION

We suppose that for a certain quantum Bose fluid we have available three radial distribution functions: the exact $g_0(r)$, the mixed $g_{\text{mxd}}(r \mid u)$ from a GFMC computation that has used a generic pseudopotential $u(r)$ as the importance-sampling function, and the Jastrow $g_J(r \mid u)$ for this same pseudopotential. In addition the three corresponding structure factors are assumed to be known.[11] In this section we drop the index 2 in the Jastrow pseudopotential u_2. We want to determine the pseudopotential $\bar{u}(r)$ that has maximum overlap with ψ_0. The GFMC computations performed for a variety of pair interactions have shown[1] that the perturbative relation (10) is accurate so that we start with the approximate equation (13) for $\bar{u}$. This equation is exactly equal to the equation found in the theory of *classical* fluids with the inverse problem, i.e., the determination of the pair potential that gives an observed $g(r)$, because of the formal identity between the weight factor ψ_J^2 in the quantum case and the Boltzman factor

$$\exp\left[-\beta \sum_{i<j} v(r_i - r_j)\right]$$

in the classical case when $\beta v(r) = u(r)$. In the case of classical fluids this inverse problem[12] has been attacked by using the integral-equation approach, for instance, the Born-Green equation with superposition closure or the hypernetted chain equation. However, it is well established that none of these equations is accurate enough for this purpose. Since $u(r)$ for the physically interesting pair interactions has a shape that can be considered a respectable pair interaction for a *classical* system, we foresee that application of the integral-equation approach will not be more successful in the quantum case.

A simplifying feature of our problem is that the pseudopotential $u(r)$ used in a GFMC computation is obtained from a variational computation of the energy, so we expect it to be rather close to $\bar{u}(r)$ at least at short distances. Therefore, we can assume that the difference

$$\delta(r)=\bar{u}(r)-u(r) \tag{17}$$

is not large, and we need only a theory that gives the change of g_J due to a limited change in the pseudopotential. This is exactly the kind of problem that was confronted by the so-called perturbation theory of classical liquids[13] and successfully resolved: The properties of a system with pair interaction $v(r)$ are expressed in terms of the properties, assumed known, of a "reference" system and of the difference $v(r)-v_0(r)$ between the interactions of the two systems. In our case the pseudopotential $u(r)$ plays the role of "reference" potential and $\delta(r)$ that of perturbation.

As a first scheme we introduce a method based on the so-called modified hypernetted chain equation.[14] We start with the exact relation for any pseudopotential,

$$\begin{aligned}\ln g_J(r\mid u)=g_J(r\mid u)-1-c_J(r\mid u)\\ -u(r)+b(r\mid u)\,,\end{aligned} \tag{18}$$

which is just a standard relation[13] in the case of a classical fluid with $u(r)$ in place of βv. c_J is the direct correlation function corresponding to g_J as given implicitly by the Ornstein-Zernike relation

$$\begin{aligned}g_J(r\mid u)-1=c_J(r\mid u)+\rho\int d^3r'\,c_J(r'\mid u)\\ \times[g_J(\,|\vec{r}-\vec{r}\,'|\mid u)-1]\,,\end{aligned} \tag{19}$$

and b is the so-called bridge function,[13] whose density expansion is known. If g_J is known exactly for a certain u, then (18) and (19) can be used to deduce b. The study[14] of $b(r\mid u)$ in the case of a classical system for a variety of $u(r)$, from a hard core to a Coulomb potential, has presented a remarkable property of the bridge function: To a good approximation the shape of b is independent of $u(r)$, and at most there is a change in the length scale. In the present case we can neglect this change in length scale because, as we said, $u(r)$ and $\bar{u}(r)$ should be very similar at short distances, and we simply assume[15]

$$b(r\mid\bar{u})=b(r\mid u)\,. \tag{20}$$

By taking the difference between (18) and the similar relation for $g_J(r\mid\bar{u})$ and using (20) and the equality $g_J(r\mid u)=g_0(r)$ we arrive at the expression

$$\begin{aligned}\bar{u}^{(1)}(r)=u(r)+g_0(r)-g_J(r\mid u)-c_0(r)\\ +c_J(r\mid u)+\ln[g_J(r\mid u)/g_0(r)]\end{aligned} \tag{21}$$

for the "best" pseudopotential in terms of known quantities. Here c_0 is the direct correlation function that corresponds to g_0. In (21) we have only a first approximation to $\bar{u}$ [this is the reason for the index (1) on $\bar{u}$] because of the assumption (20). It is possible to improve on this result, however, by computing $g_J(r\mid\bar{u}^{(1)})$, for instance, by a standard Monte Carlo computation. In general, this g_J will not be equal to g_0 because of the approximate nature of (20), but now we can compute $b(r\mid\bar{u}^{(1)})$ and make the weaker assumption $b(r\mid\bar{u})=b(r\mid\bar{u}^{(1)})$. We can now proceed in a similar manner as done previously, and this produces a new estimate $\bar{u}^{(2)}$ given by (21) where u is replaced by $\bar{u}^{(1)}$. This procedure can be repeated until $g_J(r\mid\bar{u}^{(i)})-g_0(r)$ is smaller than the statistical errors, of g_0 and g_J.

We note that already the first approximation (21) gives the correct long-range behavior of $\bar{u}(r)$. In fact, from (21) and (19) one finds that the Fourier transform of $\delta^{(1)}(r)\equiv\bar{u}^{(1)}(r)-u(r)$ is

$$\begin{aligned}\delta^{(1)}(k)=\rho^{-1}[S_0(k)-S_J(k\mid u)+S_0^{-1}(k)\\ -S_J^{-1}(k\mid u)]+I(k)\,,\end{aligned} \tag{22}$$

where

$$I(k)=\int d^3r\,e^{i\vec{k}\cdot\vec{r}}\ln[g_J(r\mid u)/g_0(r)]\,. \tag{23}$$

If $u(r)$ is a short-range function, then all terms of (22) give contributions to $\delta^{(1)}(k)$ that are regular as $k\to 0$, apart from the term $S_0^{-1}(k)$. This gives the contribution $2mc/(\rho\hbar k)$ that brings in $\bar{u}^{(1)}(r)$, the correct long-range behavior. This behavior does not change under iteration of the procedure because of the cancellation of k^{-1} terms in $\delta^{(i)}(k)$ for $i>1$.

It is a typical case in GFMC computations that $u(r)$ is a short-range function; it should already reproduce rather well $\bar{u}(r)$ at short distances, i.e., in the region where $g_0(r)$ rapidly goes to zero. One is interested in finding $\bar{u}(r)$ at intermediate and large distances. In this case a simpler scheme can be used: the well-known optimized random-phase approximation[13] (ORPA) that is widely used for classical liquids and that we can also formulate in our case. The approximation is built in two stages. As a first step one approximates the reference $g_J(r\mid u)$ with the radial distribution function of *classical* hard spheres. Precisely, if we define the y function by

$$y_J(r\mid u)\equiv e^{u(r)}g_J(r\mid u)\,, \tag{24}$$

the approximation becomes

$$g_J(r\,|\,u)\approx e^{-u(r)}y_{\rm HS}(r,d) \tag{25}$$

where $y_{\rm HS}$ is the y function of classical hard spheres of diameter d, i.e., the function appropriate when $f(r)\equiv\exp[-u(r)]$ is $f(r,d)=0$ for $r<d$ and $f(r,d)=1$ for $r>d$. The diameter d must be chosen such that[13]

$$\int d^3r\, y_{\rm HS}(r,d)[e^{-u(r)}-f_{\rm HS}(r,d)]=0 \tag{26}$$

and in view of (25) this can be written in terms of structure factors at $k=0$:

$$S_J(0\,|\,u)=S_{\rm HS}(0,d)\ . \tag{27}$$

Let us note that the classical hard-sphere system enters here just because of the already-mentioned formal similarity between Jastrow pseudopotential and pair interaction in a classical system.

As a second step one computes the effect of $\delta(r)=\bar{u}-u$ on the RDF in the chain approximation (RPA) with a self-consistent condition (optimization) that takes into account the effect of the repulsive core of $u(r)$. This gives[13]

$$g_J(r\,|\,u+\delta)=g_J(r\,|\,u)+\mathscr{C}(r\,|\,\delta)\ , \tag{28}$$

$$\mathscr{C}(r\,|\,\delta)=-(2\pi)^{-3}\int d^3k\, e^{i\vec{k}\cdot\vec{r}}S_{\rm HS}^2(k,d)[\delta(k)+\Delta(k)]/\{1+\rho S_{\rm HS}(k,d)[\delta(k)+\Delta(k)]\}\ , \tag{29}$$

where $\delta(k)$ is the Fourier transform of $\delta(r)$ and $\Delta(k)$ is a function that implements the optimization condition: $\Delta(k)$ is such that $\mathscr{C}(r\,|\,\delta)=0$ for $r<d$ and, on the other hand, $\Delta(r)=0$ for $r>d$. From (28) and (29) one can extract $\delta(k)$ and $\Delta(k)$ by simple algebra after taking a Fourier integral. Going back in r space we find, in the physically interesting region $r>d$,

$$\delta(r)=(2\pi)^{-3}\rho^{-1}\int d^3k\frac{S_J(k\,|\,u)-S_0(k)}{S_{\rm HS}(k,d)[S_0(k)+S_{\rm HS}(k,d)-S_J(k\,|\,u)]}e^{-i\vec{k}\cdot\vec{r}}\ , \tag{30}$$

where we have taken into account that $g_J(r\,|\,u+\delta)=g_0(r)$ and that $\Delta(r)=0$ for $r>d$. Equations (30) and (27) represent an easily computable expression for $\delta(r)$ in terms of the variational S_J, of the exact S_0, and of the classical hard-sphere structure factor that is well known[13] in parametrized form from simulation work. Since this result relies on the approximation (25), this procedure is more appropriate in the case of systems with harsh repulsive forces such as the Lennard-Jones potential. We note that the approximation (30) also gives the correct r^{-2} long-range behavior of $\bar{u}(r)$.

Variational computations[4] of the energy for the Lennard-Jones potential have shown that the three-body term u_3 in the wave function has a significant role, and therefore one would like to obtain the "best" $\bar{u}_3$ by solving Eqs. (14). Perturbative methods similar to that previously mentioned can be devised in this case also, but the complexity of the full three-body correlation function $g^{(3)}$ will require an expansion of $g^{(3)}$ and of $u^{(3)}$ on a suitable basis set. This problem will be considered on another occasion.

Experience in dealing with the case of classical liquids and our expectation on the shape of $\bar{u}_2(r)$ make us confident that the methods we have proposed in this section will give a reliable estimate of the best pseudopotential. The accuracy of these methods however, depends very much on the accuracy with which $S_0(k)$ and $S_J(k\,|\,u)$ are known. We have assumed that these functions are known exactly, but in fact statistical errors are present due to the nature of the Monte Carlo method; these errors tend to be enhanced in $\delta(r)$. This indicates the need that in a GFMC computation as much attention should be given to extract the correlation functions as that to the computation of the energy. Another aspect that currently limits the accuracy with which $\bar{u}_2$ can be computed is the problem of extension[11] of the radial distribution functions. None of the methods[16,17] that have been used up to now to extend $g(r)$ outside the length of the simulation box is really satisfactory when fine details of the structure factor are needed. In fact, one[16] of the methods does not guarantee[17] the continuity of $g(r)$, and the other[17] is based on an *ad hoc* procedure.

Our discussion up to the present has been based on the approximate maximum-overlap equation (13). However, similar perturbative methods can be also developed for the exact equation (12). In this case one has to expand both sides of $g_J(r\,|\,u+\delta)=g_{\rm mxd}(r\,|\,u+\delta)$ with respect to δ. In the RPA approximation, for instance, one finds two chain functions, one like (29) and one similar, but with $\frac{1}{2}\delta(k)$ instead because in $g_{\rm mxd}$ the pseudopotential enters through ψ_J and not ψ_J^2. Since the equations become more complex and the present GFMC computations indicate that the perturbative relations (10) are adequate, we do not pursue the matter further.

IV. FERMI STATISTICS

The criterion of maximum overlap can be easily extended to the case of Fermi statistics if we consider as a model wave function a Slater-Jastrow function $\psi_{\rm SJ}$ as commonly used in variational computation of the energy.[1] In the case of the unpolarized state the most general $\psi_{\rm SJ}$ has a different pseudopotential for pairs of particles with parallel (u_p) or antiparallel (u_a) spins. The configurational part of the model function is

$$\hat{\psi}_{\rm SJ}(\{\vec{r}_i\}\,|\,u_p,u_a)=d_\uparrow d_\downarrow \prod_{i<j}\exp[\delta_{\sigma_i,\sigma_j}u_p(|\vec{r}_i-\vec{r}_j|)+(1-\delta_{\sigma_i,\sigma_j})u_a(|\vec{r}_i-\vec{r}_j|)]\,, \tag{31}$$

where $\delta_{\sigma,\sigma'}$ is the Kronecker symbol, σ_i indicates the spin projection of particle i, and $d_\uparrow$ and $d_\downarrow$ are the determinants of plane waves that fill the Fermi sphere for the $N/2$ particles with spin up or down, respectively.

The variation of the modulus square of the overlap integral $\langle\psi_{\rm SJ}|\psi_0\rangle$ between the exact ground state ψ_0 and the normalized model wave function, $\psi_{\rm SJ}=(\langle\hat{\psi}_{\rm SJ}|\hat{\psi}_{\rm SJ}\rangle)^{-1/2}\hat{\psi}_{\rm SJ}$, with respect to u_p gives

$$\frac{\delta|\langle\psi_{\rm SJ}|\psi_0\rangle|^2}{\delta u_p(r)}=\frac{\langle\psi_0|\hat{\psi}_{\rm SJ}\rangle}{\langle\hat{\psi}_{\rm SJ}|\hat{\psi}_{\rm SJ}\rangle}\frac{\delta\langle\hat{\psi}_{\rm SJ}|\psi_0\rangle}{\delta u_p(r)}+\frac{\langle\hat{\psi}_{\rm SJ}|\psi_0\rangle}{\langle\hat{\psi}_{\rm SJ}|\hat{\psi}_{\rm SJ}\rangle}\frac{\delta\langle\psi_0|\hat{\psi}_{\rm SJ}\rangle}{\delta u_p(r)}-\frac{|\langle\hat{\psi}_{\rm SJ}|\psi_0\rangle|^2}{\langle\hat{\psi}_{\rm SJ}|\hat{\psi}_{\rm SJ}\rangle^2}\frac{\delta\langle\hat{\psi}_{\rm SJ}|\hat{\psi}_{\rm SJ}\rangle}{\delta u_p(r)}\,, \tag{32}$$

and a similar equation holds for $u_a(r)$. As in the case of Bose statistics, these functional derivatives can be related to radial distribution functions, and in fact we find

$$\frac{\delta|\langle\psi_{\rm SJ}|\psi_0\rangle|^2}{\delta u_p(r)}=V\left[\frac{\rho}{2}\right]^2\frac{|\langle\hat{\psi}_{\rm SJ}|\psi_0\rangle|^2}{\langle\hat{\psi}_{\rm SJ}|\hat{\psi}_{\rm SJ}\rangle}[g_{\rm SJ}^{\uparrow\uparrow}(r\,|\,u_p,u_a)-g_{\rm mxd}^{\uparrow\uparrow}(r\,|\,u_p,u_a)]=0\,, \tag{33}$$

where $g_{\rm SJ}^{\uparrow\uparrow}$ is the RDF for particles with parallel spin for the model function (31) and $g_{\rm mxd}^{\uparrow\uparrow}$ is the mixed average. These RDF's are given by an obvious generalization of (6) and (7) with a normalization such that

$$g\underset{r\to\infty}{\longrightarrow}1\,.$$

$\rho=N/V$ is the *total* number density. Variation of $\langle\psi_{\rm SJ}|\psi_0\rangle$ with respect to u_a gives a similar result that involves RDF for particles with antiparallel spins. We conclude that maximum overlap obtains for the pseudopotentials $\bar{u}_p$ and $\bar{u}_a$ such that

$$\begin{aligned}&g_{\rm mxd}^{\uparrow\uparrow}(r\,|\,\bar{u}_p,\bar{u}_a)=g_{\rm SJ}^{\uparrow\uparrow}(r\,|\,\bar{u}_p,\bar{u}_a),\\&g_{\rm mxd}^{\uparrow\downarrow}(r\,|\,\bar{u}_p,\bar{u}_a)=g_{\rm SJ}^{\uparrow\downarrow}(r\,|\,\bar{u}_p,\bar{u}_a)\,.\end{aligned} \tag{34}$$

If we restrict pseudopotentials u_p and u_a to be equal, the maximum-overlap criterion implies only one equation, the equality of the mixed and of the model *total* RDF, $g=\frac{1}{2}(g^{\uparrow\uparrow}+g^{\uparrow\downarrow})$. This same equality is obtained in the case of a fully polarized state when $\psi_{\rm SJ}$ contains a single Slater determinant.

These results can be also generalized to the case of model wave functions that, in the symmetric part, contain many-particle pseudopotentials. The maximum-overlap equations again involve mixed and model many-particle distribution functions.

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[1] For a review, see D. M. Ceperley and M. H. Kalos, in *Monte Carlo Method in Statistical Physics,* edited by K. Binder (Springer, Berlin, 1979).

[2] D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. 45, 566 (1980); M. A. Lee, K. E. Schmidt, M. H. Kalos, and G. V. Chester. *ibid.* 46, 728 (1981).

[3] L. Reatto and G. V. Chester, Phys. Rev. 155, 88 (1967).

[4] K. Schmidt, M. H. Kalos, M. A. Lee, and G. V. Chester, Phys. Rev. Lett. 45, 573 (1980).

[5] G. Gaglione, G. L. Masserini, and L. Reatto, Phys. Rev. B 22, 1237 (1980).

[6] See, for instance, the old result for the Lennard-Jones potential: W. L. McMillan, Phys. Rev. 138, A442 (1965), compared to a recent computation (Ref. 5).

[7] Typical of this is the case of the Yukawa repulsive interaction, see D. M. Ceperley, G. V. Chester, and M. H. Kalos, Phys. Rev. B 17, 1070 (1978), and compared with the result of Ref. 8.

[8] L. Reatto and A. Scotti, Phys. Rev. D 19, 2304 (1979).

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

[10] C. De Michelis and L. Reatto, Phys. Lett. A 50, 275 (1974).

[11] This is not a trivial statement because the RDF given by numerical methods such as Monte Carlo or GFMC is defined up to $r = L/2$ where L is the length of the box of simulation. In order to obtain $S(k)$ one has to extend the RDF at larger distances because in a typical computation $g(r \sim L/2)$ has not yet reached its asymptotic value of unity.

[12] R. Taylor and R. O. Watts, Solid State Commun. 38, 965 (1981).

[13] See, for instance, J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids* (Academic, New York, 1976).

[14] Y. Rosenfeld and N. W. Ashcroft, Phys. Rev. A 20, 1208 (1979).

[15] L. Reatto, in *Recent Progress in Many Body Theories,* edited by J. G. Zabolitzky *et al.* (Springer, Berlin, 1981).

[16] L. Verlet, Phys. Rev. 165, 201 (1968).

[17] G. V. Chester and D. M. Ceperley, Phys. Rev. A 15, 755 (1977).