Fermionic Shadow Wave Function Variational Calculations of the Vacancy Formation Energy in ^{3}He

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We present a novel technique well suited for studying the ground state of inhomogeneous fermionic matter in a wide range of different systems. The system is described using a fermionic shadow wave function, and the energy is computed by means of the variational Monte Carlo technique. The general form of the fermionic shadow wave function is useful for describing many-body systems with the coexistence of different phases as well in the presence of defects or impurities, but it requires overcoming a significant sign problem. As an application, we studied the energy to activate vacancies in solid ^{3}He.

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The microscopic theoretical description of inhomogeneous Fermionic systems is a long-standing challenge. Among such systems we can include defective quantum crystals (e.g., ^{3}He crystals or electron Wigner crystals in the presence of vacancies or defects) or where an ordered and disordered phase coexist such as, for instance, a fluid or crystal. The main difficulty consists in the fact that one has to deal with a wave function that combines the antisymmetry required by the Pauli principle and the inhomogeneity of the system itself.

While mean field methods are very efficient in dealing with homogeneous phases (e.g., an extensive and perfect solid), the phase coexistence or the description of local defects presents difficulties. The main reason is the locality of the inhomogeneity. Therefore, an explicit description of the wave function seems a much better approach.

The rigorous microscopic evaluation of the vacancy-formation energy in ^{3}He is one of the problems that suffers most from the limitations of standard theoretical tools.

The problem was successfully solved for many-boson systems several years ago by means of the so-called shadow wave function (SWFs) [1–3]—a class of wave functions based on the introduction of auxiliary degrees of freedom, which was successfully applied to a variety of inhomogeneous phases of ^{4}He [4,5] and p-H$_2$ [6]:

$$\psi_{\mathrm{SWF}}(\mathbf{R}) = \phi_p(\mathbf{R}) \int \Xi(\mathbf{R},\mathbf{S})\phi_s(\mathbf{S})d\mathbf{S}, \qquad (1)$$

where $\mathbf{R} = \{\mathbf{r_1}, \ldots, \mathbf{r_N}\}$ are the coordinates of the N constituents of the system, and $\mathbf{S} = \{\mathbf{s_1}, \ldots, \mathbf{s_N}\}$ are auxiliary degrees of freedom called "shadows." ϕ_p and ϕ_s are two-body correlation factors (of the so-called Jastrow form) for particles and shadows, respectively, and $\Xi(\mathbf{R},\mathbf{S})$ is the kernel describing the correlations between particles and shadows. Here, as in most applications, we take the kernel to be a Gaussian:

$$\Xi(\mathbf{R},\mathbf{S}) = \exp[-c(\mathbf{R}-\mathbf{S})^2]. \qquad (2)$$

The main properties of the SWF are (i) the fact that it introduces correlations to all orders via the integration over the auxiliary degrees of freedom and (ii) the fact that despite its manifest translational invariance, it can describe phases in which the translational symmetry is broken (solids, interfaces, defects). However, the extension to many-Fermion systems is hard. A straightforward extension (which we term ASWF) based on the antisymmetrization of the particle degrees of freedom was proposed several years ago for the study of homogeneous ^{3}He [7], and later applied to the homogeneous electron gas [8]:

$$\psi_{\mathrm{ASWF}}(\mathbf{R}) = \prod_{l=\uparrow,\downarrow} D_l[\phi_k(\mathbf{r}_i)]\phi_p(\mathbf{R}) \times \int \exp[-c(\mathbf{R}-\mathbf{S})^2]\phi_s(\mathbf{S})d\mathbf{S}, \qquad (3)$$

where $D_l[\phi_k(\mathbf{r}_i)]$ is a Slater determinant of particle orbitals.

This form has an evident drawback. Once the orbitals are specified, as, e.g., plane waves satisfying the Born–von Kármán conditions for an extensive system, the nodal structure remains unchanged even if the auxiliary degrees of freedom provide the correlations necessary to break the symmetry so as to correctly describe a set of localized particles.

The only viable solution to the problem is to introduce an antisymmetric wave function in which crystallization can be described without explicit symmetry breaking, but that at the same time can develop a correct nodal structure according to the phase described. This goal can be achieved by writing a shadow wave function in which the antisymmetry is imposed on the auxiliary degrees of freedom, thereby maintaining explicit correlations among the particles only in the symmetric part of the function. The so-called fermion-shadow wave function (FSWF) assumes the following form:

$$\psi_{\mathrm{FSWF}}(\mathbf{R}) = \phi_p(\mathbf{R}) \int \exp[-c(\mathbf{R}-\mathbf{S})^2] \times \prod_{l=\uparrow,\downarrow} D_l[\phi_k(\mathbf{s}_i)]\phi_s(\mathbf{S})d\mathbf{S}. \tag{4}$$

It is possible to prove that ψ_{FSWF} is antisymmetric under the exchange of two particles of like spin [9]. The main difference between the ASWF and FSWF comes from the fact that the latter develops a nodal structure for the particle degrees of freedom that depends on the integration over the shadow degrees of freedom, and includes effects of correlations to all orders. In particular it is easily proved that when particles and shadows are strongly localized by the effect of the two-body correlations among the shadows themselves, the wave function is closely approximated by a determinant of Gaussians connecting each particle to each shadow, which is obviously closer to the structure of the wave function expected for a quantum crystal.

There is a very high technical price to pay in order to exploit the FSWF in computations. In a variational Monte Carlo calculation, the absolute square of the wave function is used as a probability density, $P(\mathbf{R})$, and the local energy is averaged over the sampled configurations. Thus

$$E = \frac{\int d\mathbf{R}\,\psi^*(\mathbf{R})\psi(\mathbf{R})E_L}{\int d\mathbf{R}\,\psi^*(\mathbf{R})\psi(\mathbf{R})} = \frac{\int d\mathbf{R}P(\mathbf{R})E_L}{\int d\mathbf{R}P(\mathbf{R})}, \tag{5}$$

where $E_L = \psi^{-1}H\psi$ is the local energy of the system. The integral is evaluated by generating configurations according to $P = |\psi|^2$ that are sampled using the Metropolis algorithm.

In using SWFs, one constructs $\psi^*(\mathbf{R})\psi(\mathbf{R})$ by integrating over two sets of shadow variables, $\mathbf{S}$ and $\mathbf{S}'$. The integrand of SWFs may be defined as

$$Z(\mathbf{R},\mathbf{S},\mathbf{S}') = \phi_p^2(\mathbf{R})\exp[-c(\mathbf{R}-\mathbf{S})^2 - c(\mathbf{R} - \mathbf{S}')^2]\phi_s(\mathbf{S})\phi_s(\mathbf{S}'), \tag{6}$$

and some probability density function may be chosen, $\tilde{P}(\mathbf{R},\mathbf{S},\mathbf{S}')$. Sampling in the usual way, a generic operator can be computed as

$$\langle O\rangle = \frac{\int d\mathbf{R}d\mathbf{S}d\mathbf{S}'\tilde{P}(\mathbf{R},\mathbf{S},\mathbf{S}')w(\mathbf{R},\mathbf{S},\mathbf{S}')O(\mathbf{R})}{\int d\mathbf{R}d\mathbf{S}d\mathbf{S}'\tilde{P}(\mathbf{R},\mathbf{S},\mathbf{S}')w(\mathbf{R},\mathbf{S},\mathbf{S}')}, \tag{7}$$

where

$$w(\mathbf{R},\mathbf{S},\mathbf{S}') = \frac{Z(\mathbf{R},\mathbf{S},\mathbf{S}')}{\tilde{P}(\mathbf{R},\mathbf{S},\mathbf{S}')}. \tag{8}$$

A reasonable choice for an ordinary SWF is the integrand itself:

$$P(\mathbf{R},\mathbf{S},\mathbf{S}') = Z(\mathbf{R},\mathbf{S},\mathbf{S}'), \tag{9}$$

with $w = 1$ and $\tilde{P} = P = Z$. Similarly in ψ_{ASWF} the integrand is positive, and can be used for $P(\mathbf{R},\mathbf{S},\mathbf{S}')$.

When using ψ_{FSWF}, the integrand is not positive definite, and sampling it is not possible. It is always possible, however, to sample a suitable probability distribution and compute a weighted average. The most straightforward choice in this case is the absolute value of the integrand. Let

$$Q(\mathbf{R},\mathbf{S},\mathbf{S}') = \phi_p^2(\mathbf{R})\exp[-c(\mathbf{R}-\mathbf{S})^2 - c(\mathbf{R}-\mathbf{S}')^2] \times \prod_{l=\uparrow,\downarrow} D_l[\phi_k(\mathbf{s}_i)] \prod_{l'=\uparrow,\downarrow} D_l[\phi_k(\mathbf{s}_i')]\phi_s(\mathbf{S})\phi_s(\mathbf{S}'), \tag{10}$$

$$\tilde{P}(\mathbf{R},\mathbf{S},\mathbf{S}') = |Q(\mathbf{R},\mathbf{S},\mathbf{S}')|, \tag{11}$$

$$w(\mathbf{R},\mathbf{S},\mathbf{S}') = \frac{Q(\mathbf{R},\mathbf{S},\mathbf{S}')}{|Q(\mathbf{R},\mathbf{S},\mathbf{S}')|} \equiv \pm 1. \tag{12}$$

It should be noted that the normalization integral, while containing positive and negative terms, is always positive by construction. However, the speed of convergence of the integral strongly depends on the fluctuations in sign of the integrand. In particular, the intrinsic variance of the integrand might become excessively large and prevent the computation of an average with acceptable statistical errors. This is particularly true for disordered systems, such as liquids or disordered solids, where the wave function has strong variations in space.

A simple reorganization of the calculation produces a dramatic improvement in the Monte Carlo efficiency. In applying the Metropolis method to shadow wave function, including the ASWF variant, the usual procedure is to sample new values of $\mathbf{R}$, $\mathbf{S}$, and $\mathbf{S}'$ in turn. It is always true that the integrals in Eq. (7) over $\mathbf{S}$ and $\mathbf{S}'$ for fixed $\mathbf{R}$ are positive. This suggests that a change in the order of summation might be useful for the FSWF class of functions, especially with disorder, by propagating the shadows $\mathbf{S}$ and $\mathbf{S}'$ for M steps (with M big enough) for fixed $\mathbf{R}$. That is, we expect that the sum of the ± 1 weight of M steps,

$$\left[\sum w_i\right]_S \times \left[\sum w_i\right]_{S'} = W_S W_{S'}, \tag{13}$$

will usually be positive. In fact, increasing M in the more difficult cases where exchanges of sign often appear, gives weights $W_S W_{S'}$ usually positive and significantly different from zero. The algorithm becomes (i) sample a configuration $\mathbf{R}$ of particles, (ii) sample M configurations of $\mathbf{S}$, (iii) sample M configurations of $\mathbf{S}'$, (iv) combine all the weight factors and accumulate the local energy for the average and variance, and iterate from (i) to (iv) until the convergence is reached and the variance is as low as desired. For a calculation of the crystalline phase with no empty sites we typically sampled configurations of particles, and using $M = 1$ or $M = 100$ does not significantly change the result. If a vacancy is present in the system and the sign frequently changes, we usually sampled 5×10^6 configurations and for each one $M = 1.5 \times 10^3$.

As an illustration of the capabilities of FSWFs, we studied the ground state of solid ^{3}He in the range of molar volumes between 20 and 24 cc/mol. A comparison with previous variational estimates based on standard antisymmetric wave functions is given below. As a next step, we studied the vacancy-formation energy by computing the energy in the presence of an empty site. As already pointed out, standard imaginary time projection calculations require that a wave function imposing crystallization be used, preventing one from taking properly into account all the phenomenology related to lattice relaxation and vacancy mobility. As a model He-He interaction we chose the Hartree-Fock dispersion HFDHE2 potential by Aziz *et al.* [10], which gives an overall description of the equation of state in good agreement with experiments, though it does not introduce explicit three-body terms. In the Jastrow functions ϕ_s the pseudopotential $u_s(r_{ij})$ was taken as the rescaled particle-pair potential, $v(r_{ij})$, namely, $u_s(r_{ij}) = \alpha v(\beta r_{ij})$ (α and β are additional variational parameters), while in the ϕ_p we used a McMillan form [7] combined with a summation over a basis as in Ref. [11]. All the variational parameters entering in the wave function were optimized at each density using an energy-variance minimization technique of C. J. Umrigar and M. P. Nightingale applied to the system with no defects.

We report the energy of 54 atoms in Table I. The energy per particle is also displayed in Fig. 1, where we compared our results (circles) (i) with those found in Ref. [7] computed using the ASWF starting from a normal antiferromagnetic order NAF (diamonds), and including exchanges (triangles), and (ii) with the more accurate diffusion Monte Carlo (DMC) results of Ref. [12] (squares). As can be seen the FSWF provides the lowest of the variational estimates of the energy. The DMC energies are lower at each density by a constant value of about 1 K.

TABLE I. Total and kinetic energy per particle at different densities in the solid bcc phase for the crystal with no defects (54 atoms) and with the presence of an empty site (53 atoms). All the energies are expressed in K.

$\rho\sigma^3$	$E/N(54)$	$T/N(54)$	$E/N(53)$	$T/N(53)$
0.419	0.422(1)	23.947(1)	0.69(1)	23.71(3)
0.427	0.548(2)	24.608(1)	0.78(8)	24.6(2)
0.438	0.955(1)	26.005(2)	1.26(1)	25.76(3)
0.457	1.556(1)	27.986(2)	1.844(8)	28.05(2)
0.479	2.455(1)	30.482(2)	2.801(7)	30.60(2)
0.503	3.481(1)	32.487(2)	4.127(7)	32.35(2)

The vacancy-formation energy at constant pressure for a system with N particles at a fixed density ρ can be computed as [6,13,14]

$$\Delta E_v = E(N-1, N_l = N) - \frac{N-1}{N} E(N, N_l = N), \quad (14)$$

where the number of lattice sites N_l is conserved and the density of the two systems is the same. The vacancy-formation energy includes contributions from lattice relaxation and tunneling that cannot be accounted for by a wave function with an underlying lattice structure (such as a Jastrow-Nosanow wave function). The computation of the energy for the system with $N - 1$ particles is performed by removing one particle and one shadow from the trial wave function. It has to be noted that dropping one shadow from the shadow determinant means having a hole state in one of the determinants of Eq. (4). In the case of an open-shell configuration where one or more single-particle states are not filled, one needs to perform the calculation using twist average boundary conditions [15,16] so that the total wave function has zero total momentum. Using FSWFs, we conjecture that it is not important which particular shadow orbital is omitted, because the total momentum of the system is always conserved.

We tested this by repeating the same calculation by removing different single-shadow states from the kernel. In particular the energy of the system where orbitals with different vector number **n** were removed is the same within statistical error. We stress that, by contrast, in using a normal many-body wave function with no shadows or using an ASWF the energy would depend upon the unfilled single-particle orbital. We assume for now that the system containing one empty site is well described by the same wave function of the system with the complete crystal. The modified structure of the system with a vacancy is modeled by the shadow extra variables. Therefore for 53 atoms we used the same parametrization of ϕ_p, ϕ_s and the coupling constant c entering in Gaussians of the system with 54 atoms.

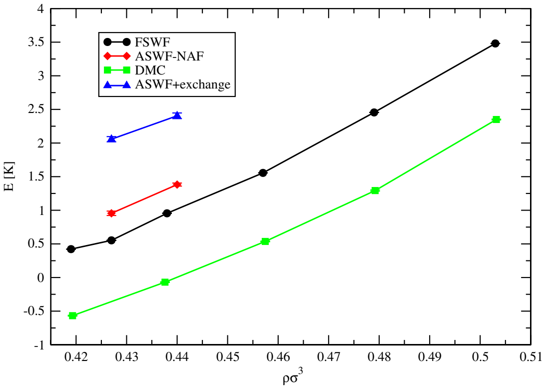

FIG. 1 (color online). The FSWF energy per particle (black circles) as a function of the density. The result is compared with the two results provided by the ASWF of Ref. [7] (blue triangles and red diamonds) and with the DMC results of Ref. [12] (green squares).

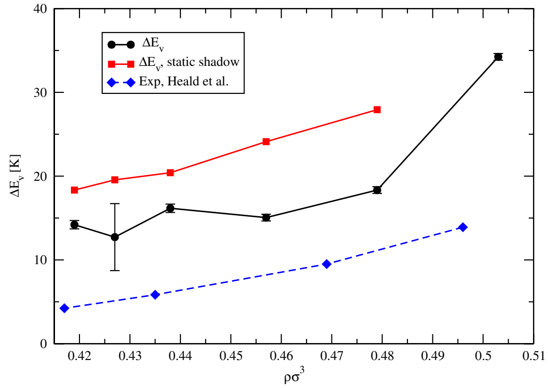

FIG. 2 (color online). The vacancy-formation energy ΔE_v as a function of the density using the FSWF (black circles) and by keeping the shadows fixed. Some experimental data from Ref. [17] is also reported for comparison. See the text for details.

The energies of the system with a vacancy are reported in Table I. The vacancy-formation energy obtained using Eq. (14) is given in Fig. 2, where we included the same calculation using the static shadows (red squares). In the latter case the shadow degrees of freedom are kept fixed on the lattice sites so their effect is switched off. This corresponds to using a variational wave function of the antisymmetric Jastrow-Nosanow type. The FSWF is more effective as is clear from the figure. The vacancy-formation energy computed by means of the FSWF is larger than the experimental data (blue diamonds) taken from Ref. [17] (see also Ref. [18] and references therein). The discrepancy can be attributed to several possible sources. First of all the calculation might be affected by strong finite-size effects. In fact the effective concentration of vacancies in the system is rather high (i.e., $1/N$), and this might imply a contribution to the vacancy-formation energy coming from a vacancy-vacancy interaction. There is also additional room for improvement in the overall variational description. For example, the parameters could be reoptimized in the presence of the vacancy, or a more sophisticated version of the wave function including a local-density dependence of the two-body correlations might be used [4].

In conclusion, in this Letter we present a novel variational wave function to study fermionic systems with impurities. We describe the fermionic shadow wave function that we used to compute the equation of state of solid ^{3}He in the bcc phase, and the vacancy-formation energy as a function of the density. We stress the fact that using standard wave functions it is not possible for correctly studying systems with the presence of defects or impurities such as a vacancy. In particular the theoretical study of ^{3}He with vacancies requires a correct description of relaxation and tunneling effects that cannot be addressed by using standard forms of wave functions. Within the variational framework we also computed the pair distribution functions between atoms and the density around a vacancy. The calculation of other properties is possible, but this, as well as the technical improvement of our present method, will be the subject of future work. Using a FSWF it is possible to study ^{3}He with the presence of impurities of ^{4}He as well as the mixture of the two gases, and to move near the region where the solid and liquid phases start to coexist. Work in these directions is in progress.

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