Close Relation between Localized-Electron Magnetism and the Paramagnetic Wave Function of Completely Itinerant Electrons

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What is commonly called the Gutzwiller wave function ψ, an approximate ground state of the single-band Hubbard Hamiltonian, is considered here for N-site N-electron rings, when the number D of doubly occupied sites is small ($N = 6$, 10, 14, 18). For $D \to 0$ spin correlations in ψ surprisingly close to the exact values at zero bandwidth are found (i.e., those of the antiferromagnetic Heisenberg-model ground state). But the energy is grossly in error. A simple modification of ψ reproduces the exact energy with remarkable accuracy.

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The single-parameter correlated-electron ground state due to Gutzwiller,[1] and appropriate to the single-band Hubbard model,[1,2] is

$$\psi = \prod_{i=1}^{N} [1 - (1 - \eta) n_{i\uparrow} n_{i\downarrow}] \varphi. \tag{1}$$

Here φ is the familiar Slater determinant which is the ground state of the electrons when noninteracting and moving in a single tight-binding band, $n_{i\sigma}$ is the occupation-number operator for site i and spin σ, N is the number of sites, and η is the variational parameter. For $\eta = 1$, ψ is of course the ground state for zero interactions. In the case of the half-filled band $\eta = 0$ leads to the correct ground-state energy in the zero-bandwidth or atomic limit,[1] namely, zero, since when $\eta = 0$, ψ has only singly occupied sites. But this knowledge that the energy of ψ is zero tells one only that ψ is somewhere in the 2^N-dimensional space of states in which only singly occupied sites occur, and therefore gives no hint as to how close ψ is to the exact ground state, within this space. In this Letter we report the results of what we believe is the first calculation of the kind needed to answer this question. We also consider the approach of the energy to zero as well as the corresponding wave-function behavior.

For simplicity we consider the half-filled-band case of linear chains with nearest-neighbor hopping and periodic boundary conditions and compare our results with the corresponding exactly known quantities. We find excellent agreement for the spin correlations for small $x \equiv |t|/U$, where t and U are the hopping integral and interaction strength, respectively. This is surprising since ψ is firmly based only on the opposite case $x \to \infty$. The energy, on the other hand, is grossly in error for small x. We uncover the reason for this error, introduce a new wave function Ψ which is a simple modification of ψ, and show that its energy is in very close and, again, surprising agreement with the exact energy.

It is convenient to consider the expansion of φ in the basis of Slater determinants with Wannier functions occupied (localized basis).[1] It is then clear that φ has a unique expansion

$$\varphi = \varphi_0 + \varphi_1 + \varphi_2 + \cdots, \tag{2}$$

where φ_D is an eigenstate of

$$\hat{D} = \sum_{i=1}^{N} n_{i\uparrow} n_{i\downarrow} \tag{3}$$

with eigenvalue D. Equation (1) becomes

$$\psi = \varphi_0 + \eta \varphi_1 + \eta^2 \varphi_2 + \cdots. \tag{4}$$

We shall calculate the spin-spin correlation function

$$q_l = \langle s_{iz} s_{i+l\,z} \rangle, \tag{5}$$

where $s_{iz} = \frac{1}{2}(n_{i\uparrow} - n_{i\downarrow})$, and the energy $E = \langle H \rangle$; the angular brackets signify the expectation value in ψ. We limit ourselves to rings with odd $N/2$ to avoid degeneracy[3] of φ.

Consider now the atomic limit, where

$$q_l = (\varphi_0, s_{iz} s_{i+l\,z} \varphi_0)/(\varphi_0, \varphi_0). \tag{6}$$

Although we will skip the details[4] here, it is worth mentioning that for $N = 6$ the explicit calculation of (6) is very simple. Of the $6!/(3!)^2 = 20$ states in the expansion of φ_0 in the localized basis, symmetry reduces the number with different coefficients to only 3, and these coefficients are easily computed. We find $q_1 = -\frac{7}{45}$, $q_2 = \frac{1}{15}$, $q_3 = -\frac{1}{180}$ for the correlation function. It is already quite interesting to compare these with the exact results, namely[5] the correlations in the antiferromagnetic (AF) Heisenberg-spin-model ground state. The latter were obtained by Bonner and Fisher[6] (BF). The small percentage differences which we find are shown in parenthe-

TABLE I. Spin-spin correlation function q_l in the atomic limit of the Gutzwiller wave function. Numbers in parentheses give a comparison, as percentage errors, with the corresponding values in the Hubbard-model ground state.

l \ N	6	10	14	18
1	−0.1555... (0.10)	−0.15025 (0.18)	−0.14883	−0.14825
2	0.0666... (−3.9)	0.05985 (−5.8)	0.05814	0.05746
3	−0.0722... (6.5)	−0.05229 (9.5)	−0.04821	−0.04666
4		0.03856 (−11)	0.03381	0.03209
5		−0.04175 (11)	−0.03269	−0.02979
6			0.02744	0.02417
7			−0.02932	−0.02409
8				0.02136
9				−0.02259

ses next to the respective q values in the $N = 6$ column of Table I.

The remainder of our results for the spin correlations are also shown in this table. The nearest-neighbor correlation q_1 is seen to be amazingly close to the exact value in those finite-N cases where a comparison is possible. To compare with the exact value[7] for $N \to \infty$, we extrapolated by using a refinement[8] of the $1/N^2$ fit used by BF, obtaining the estimate

$$\lim_{N\to\infty} q_1 = -0.1474 \text{ (Gutzwiller)}, \tag{7}$$

with an estimated uncertainty of a few parts in the last figure. This value is about 0.2% higher than the exact value. That it is higher satisfies the check that for any N, the nearest-neighbor correlation is not less than that in the Heisenberg ground state, i.e.,

$$q_1 \geq q_{1\,\mathrm{Heis}}, \tag{8}$$

by the variational principle plus the symmetry under translation and spin rotations.

The errors in the more-distant-neighbor correlations are much larger, but are still small. In particular, the value of q_2 extrapolated to $N \to \infty$ is about 7% lower than the exact value quoted by Takahashi.[5] Thus one might worry that the large-l behavior will be badly approximated by the Gutzwiller ψ. To check this we followed BF and calculated $q_{\min}(N)$, namely, the average of $|q_{N/2}|$ and $|q_{N/2-1}|$, plotting it versus $1/N$ as shown in Fig. 1, where it is compared with the known exact values.[6] It is seen that the extrapolation

$$q_{\min}(N) \to 0 \tag{9}$$

as $N \to \infty$ is at least as secure as the identical extrapolation[6] for the Heisenberg ground state. According to Bonner,[9] the latter was proved later, rigorously, by Baxter.[10]

We also note that the various detailed qualitative idiosynchrasies of the correlation function noted by BF, namely, the oscillation of $|q_l|$ about a smooth function and the fact that $|q_{N/2}| > |q_{N/2-1}|$ even though $|q_l|$ monotonically decreases for $l = 1, 2, \ldots, N/2 - 1$, are also reproduced by ψ. Thus we conclude that the spin-spin correlation function given by ψ is an excellent approximation to the exact results.

We use Eq. (4) to calculate the energy E, choose η to minimize it, and expand the result in powers of η. We thus find the leading behavior for small

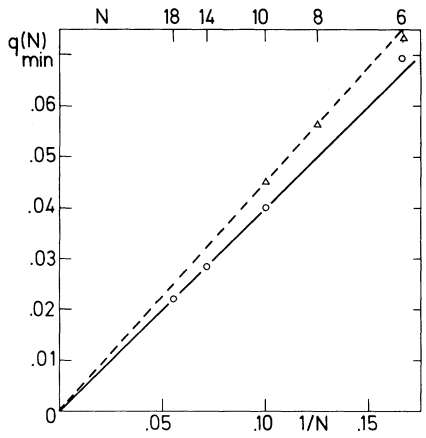

FIG. 1. Plot of $q_{\min}(N)$ vs $1/N$. The atomic limit of the Gutzwiller wave function (circles) is compared with the Heisenberg ground state from Ref. 6 (triangles). Extrapolation yields an estimate of the long-range order.

t/U to be

$$E = -N\alpha t^2/U, \tag{10}$$

where

$$\alpha = (\varphi_1, \hat{k}\,\varphi_0)^2/N(\varphi_0, \varphi_0)(\varphi_1, \varphi_1) \tag{11}$$

and $\hat{k}$ is the kinetic energy operator divided by t (so the Hubbard Hamiltonian is $t\hat{k} + U\hat{D}$). Calculations involving φ_1 are much more complicated than those of φ_0 since many more states appear when φ_1 is expanded in the localized basis. Nevertheless, they have been made for the same set of N values. We find that the energies are grossly in error, α being roughly one-half the exact value[6] for $N = 6$ and 10. The source of this error can be found on examination of the wave functions,[4] namely, the average distance between the doubly occupied site d and the empty site e in φ_1 is considerably larger than the exact value of one lattice spacing,[4] which is the value in $\hat{k}\varphi_0$.

This finding plus recognition of the fact[1,11] that (1) may be written $\psi = \eta^{\hat{D}}\varphi$ naturally lead us to define a new wave function

$$\Psi = h^{\hat{Q}}\psi = h^{\hat{Q}}\eta^{\hat{D}}\varphi, \tag{12}$$

where h is a variational parameter and $\hat{Q}$ is the number of d sites which do not have an e neighbor; a formal expression for $\hat{Q}$ can be found.[4] In the limit $h \to 0$, Ψ is the wave function of Eq. (1) modified by eliminating all terms in which the d and e sites do not occur in nearest-neighbor pairs. It belongs to the more general class of wave functions introduced in Gutzwiller's third paper.[1] The energy of this new state Ψ is extremely close to being exact; the corresponding α coefficient α_Ψ has errors of only about 0.5% for the cases $N = 6$, 10, which can be checked. The excellence of this result is again surprising in view of the fact that enough structure remains in the $h = 0$ limit of $h^{\hat{Q}}\varphi_1$ to make a much smaller value of α possible, consistent with the symmetry of Ψ.

Our α values can be extrapolated to $N \to \infty$ rather comfortably. The energy coefficient α_Ψ varies very nearly linearly[4] in N^{-2} (as does the exact energy[6]) leading to

$$\lim_{N\to\infty} \alpha_\Psi = 2.750 \tag{13}$$

with an uncertainty of a few parts in the last figure. This differs from the exact value by only -0.83%. The coefficient α corresponding to the Gutzwiller wave function, however, varies nearly linear in $1/N$ giving an extrapolation[4] of $\alpha \to 0.70 \pm 0.01$, an error of almost a factor of 4.

Since the modification in ψ affects φ_1, and not φ_0, the corresponding modification in q_l is of higher order in $|t|/U$ than the zeroth-order results obtained above.

While the relation of our results to the literature[1,11-21] will be discussed in detail elsewhere,[4] we comment briefly here. In their related work on the metal-insulator transition, Brinkman and Rice[12] used the Gutzwiller state ψ *plus* an approximation, due also to Gutzwiller,[1] needed to calculate the average energy of ψ. They found that minimization of this energy led to $E = 0$ for all $x < x_c$ (a positive number). As they were aware,[12] this indicates an error in view of the expectation that the ground-state energy for the Hubbard model $\sim t^2/U$ for small enough x.[5] Whether this error was due to the form of ψ, or to the approximation used to calculate the energy, could not be answered from the considerations made at that time. Our present results shed some light on this question. In one dimension the situation is clear: We found, for small x, that while E is proportional to t^2/U the coefficient α is far too small, an error due to the form of ψ; but α extrapolated to $N \to \infty$ is not zero, suggesting that the approximation used to calculate E is also in error. We expect that the main deficiency found in ψ, too weak d-e binding, will remain in higher dimensions. It is not clear if α will be zero in two or three dimensions (for $N \to \infty$).

There have been some attempts[11,13,19] to improve upon the work of Brinkman and Rice[12] by generalizing the wave function of Eq. (1) to "allow for" antiferromagnetism. The implicit assumption is thereby that ψ is paramagnetic. In view of the results obtained above, it is quite possible that ψ is AF in higher dimensions. Thus the assumption[11,13,19] that ψ is not AF is called into question.

The approach of the present paper has potential applicability to a variety of problems in the magnetism of strongly correlated electrons. For example, a moment's reflection shows how to modify φ in order to introduce into the spin Hamiltonian anisotropy or competing interactions such as first- and second-neighbor antiferromagnetic interactions (problems of current interest). The large-l behavior of q_l for linear chains could be studied and compared with recent results of a different approach.[21] The treatment of excited states along lines similar to that of the present paper appears promising. The present approach applied directly to the *non*-half-filled single-band Hubbard model with small t/U (although here allowing nonzero values of the total z component

of spin in φ should be considered). The final potential application we mentioned is the two-band Hubbard model called the Anderson-lattice model, currently the vogue in the mixed-valence problem.

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Image of the Electron Energy-Loss Function in Light Emitted from Tunnel Junctions

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Tunnel junctions of the type Al-I-M ($M \equiv$ Au, Cu, Ag) prepared on CaF_2-roughened substrates emit broadband visible light. It is found that the light intensity variation with wavelength in the range 350 to 700 nm images the electron energy-loss function, $\mathrm{Im}(-1/\epsilon)$, of each metal M as calculated from its optical constants. It is concluded that surface plasmons are damped above the interband transition in Au at 2.5 V and in Cu at 2.25 V. The findings are in harmony with data from surface-enhanced Raman spectroscopy.

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Tunnel junctions with randomly rough metal surfaces emit broadband visible light when they are subjected to a voltage bias.[1] The maximum energy of the emitted photons, $h\nu_{max}$, is determined by the applied bias, V_a, according to the quantum condition $h\nu_{max} = eV_a$. Initially[1] it was thought that the tunneling electrons excite slow junction plasmon modes which then decay by photon emission. More recent studies,[2] particularly on junctions with sinusoidal surface profiles,[3,4] point to fast surface-plasmon polaritons (SPP) as the intermediate state. Possible effects due to local plasmon modes excited in small particles also have been reported.[5] A theoretical description of these processes has been developed by Laks and Mills (LM).[6]

As yet, however, there is no satisfactory explanation of the spectral form of the light emitted

