Pairing, Charge, and Spin Correlations in the Three-Band Hubbard Model

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Using the Constrained Path Monte Carlo (CPMC) method, we simulated the two-dimensional, three-band Hubbard model to study pairing, charge, and spin correlations as a function of electron and hole doping and the Coulomb repulsion $V_{pd}$ between charges on neighboring Cu and O lattice sites. As a function of distance, both the $d_{x^2−y^2}$-wave and extended s-wave pairing correlations decayed quickly. In the charge-transfer regime, increasing $V_{pd}$ decreased the long-range part of the correlation functions in both channels, while in the mixed-valent regime, it increased the long-range part of the s-wave behavior but decreased that of the d-wave behavior. Still the d-wave behavior dominated. At a given doping, increasing $V_{pd}$ increased the spin-spin correlations in the charge-transfer regime but decreased them in the mixed-valent regime. Also increasing $V_{pd}$ suppressed the charge-charge correlations between neighboring Cu and O sites. Electron and hole doping away from half-filling was accompanied by a rapid suppression of anti-ferromagnetic correlations.

I. INTRODUCTION

In this paper, we will report the results of a quantum Monte Carlo (QMC) study of the ground-state properties of the two-dimensional, three-band Hubbard model. Of the three simple electronic models commonly studied as possible models of the cuprate superconducting materials, the three-band Hubbard model has been the least intensively studied, partially because of the general belief that its low energy excitation spectrum is similar to the other two. Indeed in the strong coupling limit, both the one-band and three-band Hubbard models have the t-J model as an approximate limit. However, there still remains some controversy about whether one-band models, like the Hubbard and t-J models, are adequate to describe the low energy physical properties of the cuprate superconductors. One of our objectives was to study the possible existence of superconductivity in the three-band model in regions where model parameters are physical as opposed to regions where asymptotic models are clearly more appropriate. A focus of our ground state study is the effect of the inclusion of $V_{pd}$, a repulsive Coulomb interaction between charges on neighboring Cu and O lattice sites.

The most solid information about possible superconductivity in the one-band Hubbard model has come from a series of QMC calculations. For instance, using a finite temperature QMC method, White et al. found an attractive effective pairing interaction in the $d_{x^2−y^2}$ and extended s-wave channels. Moreo and Scalapino subsequently found pairing correlations but also found that they did not increase when the lattice size was increased. This result, suggesting the absence of off-diagonal long range order, was consistent with an earlier QMC study by Imada and Hatsugai.

The fermion sign problem limits almost all QMC calculations of the Hubbard model to small system sizes and finite temperature simulations to high temperatures. These limitations had left open the possibility that superconductivity still lurked at larger systems sizes and lower temperatures. Recently, a new zero temperature QMC method, the Constrained Path Monte Carlo (CPMC) method was developed to get around the sign problem. Using this method, Zhang et al. calculated ground-state pairing correlation functions for the Hubbard model as a function of the distance and found that as the system size or the interaction strength is increased the magnitude of the long-range part of the pairing correlation functions vanished for both the $d_{x^2−y^2}$ and extended s-wave channels. Although this method produces an approximate solution, its results, together with the null results from previous QMC studies, are very discouraging for finding superconductivity in the one-band Hubbard model.

At finite temperature, past numerical work on the Hubbard model is probably more severe than for the one-band and small systems. In fact the sign problem for the three-band model has included several sets of QMC simulations, focusing on the magnetic superconducting and insulating properties of the model. As for the QMC simulations of the Hubbard model, the sign problem limited these studies to relatively high temperatures and small systems. In fact the sign problem for the three-band model is probably more severe than for the one band model. At least the one band model lacks a sign problem at half filling. In general, an anti-ferromagnetic state is found at half-filling which is strongly suppressed upon doping. Attractive interactions between pairs were found with a spectrum of results: Dominance of extended s-wave and d-wave pairing have been separately

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reported, leading to claims of extended s-wave and d-wave ODLRO. These results remain controversial.

At zero temperature, past numerical work on the three-band model has mainly consisted of exact diagonalization computations where calculations of hole binding energies was emphasized, and several QMC computations where pairing calculations were emphasized. The exact diagonalization studies unequivocally established that holes can bind. The QMC studies, established the existence of an extended s-wave and d-wave attractive pairing interaction, with one claim of of no evidence of s-wave superconductivity. More recently, a CPMC study by Guerrero and Gubernatis confirmed the exact diagonalization result that holes bind but found that increasing system size tended to decrease the long range part of the pairing correlations. In contrast to the exact diagonalization work, this QMC study found hole binding in the absence of a Coulomb repulsion \( V_{pd} \) between charge on neighboring Cu and O sites. The exact diagonalization studies found that hole binding required an unphysically large value of \( V_{pd} \).

In the work reported here, we applied the CPMC method to the three-band Hubbard model and computed the static pairing, charge, and spin correlation functions for systems with \( 6 \times 6 \) unit cells. We set the hopping and on-site Coulomb parameters as expected physically relevant values and studied the properties of the systems as a function of charge-transfer energy, electron and hole hopping, and \( V_{pd} \) through a range of physically relevant values. The consequences of varying these parameters for the most part depended on whether the value of the charge-transfer energy placed the model in a charge-transfer or mixed valent regime. The cuprate superconductors are believed to be in the charge-transfer regime.

The remainder of our report is organized as follows: In Section II, we define the Hamiltonian and the physical quantities calculated and discuss the choice of model parameters. In Section III we briefly describe the CPMC method, and then in Section IV we present our numerical results. Finally in Section V we discuss in detail our main conclusions.

II. THREE-BAND HUBBARD HAMILTONIAN

As proposed by Emery, the three-band model mimics the CuO\(_2\) layer in the cuprate superconductors by having one Cu and two O atoms per unit cell, with the Cu atoms arranged on a square lattice and the O atoms centered on the edges of the square unit cells. In this layer, Emery assumed that the relevant orbitals are just those of copper 3d\(_{x^2−y^2}\) and oxygen 2p\(_x\) and 2p\(_y\).

The Hamiltonian has the form:

\[
H = \sum_{\langle j,k \rangle} t_{j \sigma}^{jk} (p_{j \sigma} p_{k \sigma} + p_{j \sigma}^\dagger p_{k \sigma}^\dagger) + \epsilon_p \sum_{j \sigma} n_{j \sigma}^p + U_p \sum_{j} n_{j \uparrow}^p n_{j \downarrow}^p
+ \epsilon_d \sum_{i \sigma} n_{i \sigma}^d + U_d \sum_i n_{i \uparrow}^d n_{i \downarrow}^d
+ V_{pd} \sum_{\langle i,j \rangle} n_{i \sigma}^d n_{j \sigma}^p + \sum_{\langle i,j \rangle \sigma} t_{pd}^{ij}(d_{i \sigma}^\dagger p_{j \sigma} + p_{j \sigma}^\dagger d_{i \sigma})
\]

In writing the Hamiltonian, we adopted the convention that the operator \( d_{i \sigma}^\dagger \) creates a hole with spin \( \sigma \) at a Cu 3d\(_{x^2−y^2}\) orbital and \( p_{j \sigma} \) creates a hole with spin \( \sigma \) in an O 2p\(_x\) or 2p\(_y\) orbital. \( U_d \) and \( U_p \) are the Coulomb repulsions at the Cu and O sites, \( \epsilon_d \) and \( \epsilon_p \) are the corresponding orbital energies, and \( V_{pd} \) is the nearest neighbor Coulomb repulsion. As written, the model has a Cu-O hybridization \( t_{pd}^{ij} = \pm t_{pd} \) with the minus sign occurring for \( j = i + \hat{x}/2 \) and \( j = i - \hat{y}/2 \) and also hybridization \( t_{pp}^{ij} = \pm t_{pp} \) between oxygen sites with the minus sign occurring for \( k = j - \hat{x}/2 - \hat{y}/2 \) and \( k = j + \hat{x}/2 + \hat{y}/2 \). These phase conventions are illustrated in Fig. 1.

The values of the parameters in the Hamiltonian have been estimated by a number of different constrained density functional and quantum cluster calculations. In electron-volts reasonable ranges for these values seem to be: \( t_{pd} = 1.3 - 1.6, U_d = 8.5 - 10.5, \epsilon_p - \epsilon_d = 3.6, U_p = 4.0 - 7.5, t_{pp} = 0.65, \) and \( V_{pd} = 0.6 - 1.2 \). Taken together, these estimates define a reasonably limited range of the parameters for the which the model might be labeled “physical.”

The Cu site Coulomb repulsion \( U_d \) is a large energy, making doubly occupancy of Cu sites by two holes very unfavorable. The next largest parameter, the charge transfer energy \( \epsilon_d = \epsilon_p - \epsilon_d > 0 \), plays a special role. Depending on the relative values of \( \epsilon, U_d \) and the bandwidth \( W \), the system can be classified in different regimes: the charge-transfer regime with \( U_d > \epsilon > W \) or the mixed-valent regime with \( U_d > W > \epsilon \), where \( W \) is some measure of the width of the lower band. Estimates place the cuprate superconductors in the charge-transfer regime. The role of the Cu-O hybridization \( t_{pd} \) is important. Through the super-exchange mechanism, this hybridization generates an antiferromagnetic exchange interaction between the spins in the Cu sites. The O-O hybridization \( t_{pp} \) and the O site Coulomb repulsion \( U_p \) are the two smallest energies. When \( t_{pp} \) is non-zero, the non-interacting band structure has features that seem to appear in the normal state properties of the cuprate materials. We were mainly interested in studying the consequences of \( V_{pd} \). These consequences were studied in part by previous QMC simulations of Dopf et al. and Scalettar et al. In what follows we will scale all the energies by \( t_{pd} \).

For the non-interacting case \( (U_p = U_d = V_{pd} = 0) \), the band structure is easily determined numerically and is illustrated in Fig. 2 for a set of parameters used. We will add and remove holes from lower band, and this band is said to be half-filled when there is one hole per unit cell. At half-filling, for a wide range of parameters, the ground-state is an anti-ferromagnetic insulator just like the one-band Hubbard model. This band gap can be estimated from Fig. 2. A better physical feel can be obtained from the exact expression easily obtained if \( t_{pp} = 0 \): It is simply \( \epsilon \). The band-width \( W = \sqrt{(\epsilon/2)^2 + 8 - \epsilon/2} \). It
varies monotonically from 8 to zero as ε varies from zero to infinity. ε = 2 marks a value for which W = ε. This picture does not change much for relatively small non-zero values of t_{pp}. As shown by Doye et al.\cite{12} for ε = 1 the charge transfer gap is vanishing small, whereas for ε = 3 a finite charge transfer gap arises in the strong-coupling region. ε = 1 is in the mixed valent regime, while ε = 3 is in the charge transfer regime. And we will see that ε = 2 behaves more like the charge-transfer than the mixed-valent regime. In Fig. 3, we show the Fermi surfaces for infinite systems at the various dopings studied.

If ε ≫ U_d, the three-band model maps into a one-band model with \( t_{e,f} \sim t_{pd}^2/\epsilon \) and U = U_d. For U_d ≫ t_{e,f}, the one-band model can in turn be mapped into the t-J model with \( J = 4t_{e,f}^2/U_d \). Zhang and Rice\cite{13} have argued that the t-J model can also be appropriate when 0 < t_{pd} < \epsilon, U_d, U_d - \epsilon, t_{pd} are real materials, \( t_{pd} \) is estimated to be \( \sim 2.7 - 3.7 \). Therefore, besides the lack of conclusive evidence that the one-band model superconducts, it is also unclear that the mapping among the most studied models is appropriate for physical values of the parameters.

With the numerical method used, a variety of expectation values can be computed. We focused on the pairing, spin, and charge correlation functions. More specifically we computed the extended s-wave and the \( d_{x^2-y^2} \) pairing correlations as functions of distance

\[
P_\alpha(\vec{R}) = \langle \Delta^\alpha_\downarrow(\vec{R})\Delta^\alpha_\downarrow(0) \rangle
\]

where

\[
\Delta^\alpha_\downarrow(\vec{R}) = \sum_{\delta} f_\delta(\vec{R}) \left[ \langle d_{\vec{R}+\delta\uparrow} d_{\vec{R}+\delta\downarrow} - d_{\vec{R}+\delta\downarrow} d_{\vec{R}+\delta\uparrow} \rangle \right] + [p_{\vec{R}+\delta\uparrow}^x p_{\vec{R}+\delta\downarrow}^x - p_{\vec{R}+\delta\downarrow}^x p_{\vec{R}+\delta\uparrow}^x] + [p_{\vec{R}+\delta\uparrow}^y p_{\vec{R}+\delta\downarrow}^y - p_{\vec{R}+\delta\downarrow}^y p_{\vec{R}+\delta\uparrow}^y]
\]

with \( \delta = \pm \hat{x}, \pm \hat{y} \). For the extended s-wave pairing \( f_\delta(\vec{R}) = 1 \) for all \( \delta \) and for the \( d_{x^2-y^2} \) pairing, \( f_\delta(\vec{R}) = 1 \) for \( \delta = \pm \hat{x} \) and \( f_\delta(\vec{R}) = -1 \) for \( \delta = \pm \hat{y} \). The magnitude of these quantities are dominated by a large peak in \( P_\alpha(\vec{R}) \) when \( \vec{R} = |\vec{R}| \) is less than a few nearest neighbor distances. Over these distances, \( P_\alpha \) measures local correlations among spin and charge, has little information about long-range pairing correlations, and may give a “false positive” indication of enhanced pairing. Because of this we will report neither the \( q = 0 \) spatial Fourier transformation nor the partial sums like \( S_\alpha(L) = \sum_{R \leq L} P_\alpha(\vec{R}) \) as done in some previous works\cite{12,13} instead we will report \( S_\alpha(L) = \sum_{R \geq L} P_\alpha(\vec{R}) \) where \( L \) is about two lattice spacings. We will also report the “vertex contribution” to the correlation functions (see, for example, White et. al.\cite{12}) defined as follows:

\[
V_\alpha(\vec{R}) = P_\alpha(\vec{R}) - \tilde{P}_\alpha(\vec{R}),
\]

where \( \tilde{P}_\alpha(\vec{R}) \) is the contribution of dressed non-interacting propagator: for each term in \( P_\alpha(\vec{R}) \) of the form \( \langle \phi_1^\dagger \phi_2 \rangle \), \( \tilde{P}_\alpha(\vec{R}) \) has a term like \( \langle \phi_1^\dagger \phi_2 \rangle \). We found that in most cases the conclusions remain the same no matter which quantity we look at.

For the static spin-spin correlation function we used the Fourier transform of the spin-spin correlation function for the spin on the Cu sites

\[
S(k) = \frac{1}{N} \sum_{lm} e^{i(k\cdot(l-m))} \langle (n_{l,\uparrow}^d - n_{l,\downarrow}^d)(n_{m,\uparrow}^d - n_{m,\downarrow}^d) \rangle,
\]

where \( l \) and \( m \) refers to the Cu sites and \( N \) is the number of unit cells. For charge-charge correlations we computed a charge-transfer correlation function involving the O sites neighboring a Cu site quantity:

\[
C(k) = \frac{1}{N} \sum_{ij} e^{i(k\cdot(i-j))} \langle \rho(i)\rho(j) \rangle,
\]

where \( j \) are the nearest-neighbors of \( i \), \( \rho(i) = n_{i,\uparrow}^d - n_{i,\uparrow}^p - n_{i,\downarrow}^d + n_{i,\downarrow}^p \) with \( n_{i,\uparrow}^d \), \( n_{i,\downarrow}^d \), \( n_{i,\uparrow}^p \), \( n_{i,\downarrow}^p \) being the charge-density operators on the Cu, x-axis O, and y-axis O in the unit cell \( i \).

### III. NUMERICAL METHOD

Our numerical method, the constrained path Monte Carlo (CPMC) method, is extensively described and benchmarked elsewhere.\cite{11} Here we only discuss its basic strategy and approximation. In the CPMC method, the ground-state wave function |ψ\rangle is projected from a known initial wave function |ψ(0)\rangle by a branching random walk in an over-complete space of Slater determinants |φ\rangle. In such a space, we can write |ψ(0)\rangle = \sum_{φ} χ(φ)|φ\rangle. The random walk produces an ensemble of |φ\rangle, called random walkers, which represent |ψ(0)\rangle in the sense that their distribution is a Monte Carlo sampling of χ(φ), that is, a sampling of the ground-state wave function. More specifically, starting with some trial state |ψ_T\rangle, we project out the ground state by iterating

\[
|ψ(0)\rangle = e^{-\Delta τ (H-E_T)} |ψ\rangle
\]

where \( E_T \) is some guess of the ground-state energy. Purposefully \( \Delta τ \) is a small parameter so for \( H = T + V \) we can write

\[
e^{-\Delta τ H} \approx e^{-\Delta τ T/2} e^{-\Delta τ V} e^{-\Delta τ T/2}
\]

where \( T \) and \( V \) are the kinetic and potential energies.

For the study at hand, the initial state |ψ_T\rangle is the direct product of two spin Slater determinants, i.e.,

\[
|ψ_T\rangle = \prod_{ω} |φ_T^{ω}\rangle
\]
Because the kinetic energy is a quadratic form in the creation and destruction operators for each spin, the action of its exponential on the trial state is simply to transform one direct product of Slater determinants into another. While the potential energy is not a quadratic form in the creation and destruction operators, its exponential is replaced by sum of exponentials of such forms via the discrete Hubbard-Stratonovich transformation. For the on-site Coulomb term, this transformation is

\[
e^{-\Delta \tau U_d n_i^d n_{i,-}\sigma} = \frac{1}{2} \sum_{x=\pm 1} e^{-x\Delta \tau J_d (n_i^d - n_{i,-}\sigma)}
\]

\[
e^{\Delta \tau U_d (n_i^d + n_{i,-}^d)}
\]

provided \(U_d \geq 0\) and \(\cosh \Delta \tau J_d = e^{-\Delta \tau U_d/2}\). For the nearest neighbor Coulomb repulsion term, we make the same type of transformation but we have to do it many more times: \(n_i^d n_j^d = n_i^d n_{j;\uparrow}^p + n_i^d n_{j;\downarrow}^p + n_i^d n_{j;\uparrow}^\downarrow + n_i^d n_{j;\downarrow}^\downarrow\). For each term and each \(j\) in the \(x\) and \(y\) directions, a Hubbard-Stratonovich transformation is required for a total of 8 such transformations. Because the computational time scales with the number of Hubbard-Stratonovich transformations, having a \(V_{pd} \neq 0\) increases the computational cost by a factor of 8.

One consequence of the Hubbard-Stratonovich transformation is the factorization of the projection into an up and down spin part. Accordingly we re-express the iteration step as

\[
\prod_\sigma |\phi_\sigma\rangle = \int d\vec{x} P(\vec{x}) \prod_\sigma B_\sigma(\vec{x}) |\phi_\sigma\rangle
\]

where \(\vec{x} = (x_1, x_2, \ldots, x_N)\) is the set of Hubbard-Stratonovich fields (one for each lattice site), \(N\) is the number of lattice sites, \(P(\vec{x}) = (\mathcal{Z}^N)\) is the probability distribution for these fields, and \(B_\sigma(\vec{x})\) is an operator function of these fields formed from the product of the exponentials of the kinetic and potential energies.

The Monte Carlo method is used to perform the multidimensional integration over the Hubbard-Stratonovich fields. It does so by generating a set of random walkers initialized by replicating \(|\psi_T\rangle\) many times. Each walker is then propagated independently by sampling a \(\vec{x}\) from \(P(\vec{x})\) and propagating it with \(B(\vec{x})\). After the propagation has “equilibrated,” the sum over the walkers provides an estimate of the ground-state wave function \(|\psi_0\rangle\).

We used two different estimators for the expectation values of some observable \(\mathcal{O}\). One is the mixed estimator

\[
\langle \mathcal{O} \rangle_{\text{mixed}} = \frac{\langle \psi_T | \mathcal{O} | \psi_0 \rangle}{\langle \psi_T | \psi_0 \rangle}
\]

and the other is the back-propagated estimator

\[
\langle \mathcal{O} \rangle_{\text{bp}} = \frac{\langle \psi_T | e^{-\Delta \tau H} \mathcal{O} | \psi_0 \rangle}{\langle \psi_T | e^{-\Delta \tau H} | \psi_0 \rangle}
\]

where \(|\psi_0\rangle\) is the QMC estimate of the ground state and \(\ell\) is typically in the range of 20 to 40. For observables that commute with the Hamiltonian, the mixed estimator is a very accurate one and converges to the exact answer as \(|\psi_0\rangle\) converges to exact ground state. For observables that do not commute with the Hamiltonian, like correlation functions, the back-propagated estimator has been found to give very accurate estimates of ground-state properties. Significant differences between the predictions of these two estimators often exist.

To completely specify the ground-state wave function for a system of interacting electrons, only determinants satisfying \(\langle \psi_0 | \phi \rangle > 0\) are needed because \(|\psi_0\rangle\) resides in either of two degenerate halves of the Slater determinant space, separated by a nodal surface \(N\) that is defined by \(\langle \psi_0 | \phi \rangle = 0\). The degeneracy is a consequence of both \(|\psi_0\rangle\) and \(-|\psi_0\rangle\) satisfying Schrödinger’s equation. The sign problem occurs because walkers can cross \(N\) as their orbitals evolve continuously in the random walk. Asymptotically they populate the two halves equally, leading to an ensemble that has zero overlap with \(|\psi_0\rangle\). If \(N\) were known, we would simply constrain the random walk to one half of the space and obtain an exact solution of Schrödinger’s equation. In the constrained-path QMC method, without \textit{a priori} knowledge of \(N\), we use a trial wave function \(|\psi_T\rangle\) and require \(\langle \psi_T | \phi \rangle > 0\). This is what is called the constrained-path approximation.

All the calculations reported here were done for copper-oxide planes with periodic boundary conditions. Mostly, we study closed shell cases, for which the corresponding free-electron wave function is non-degenerate and translationally invariant. For \(6 \times 6\) unit cells, the dopings, producing Fermi surfaces in Fig. 2, correspond to closed shell fillings. In these cases, the free-electron wave function, represented by a single Slater determinant, is used as the trial wave function \(|\psi_T\rangle\). The use of an unrestricted Hartree-Fock wave function as \(|\psi_T\rangle\) generally produced no significant improvement in the results. At half-filling, which is not a closed shell case, we used a linear combination of two degenerate \(Q = (\pi, \pi)\) spin-density wave states.

In a typical run, the average number of walkers was 600, and the time step was 0.03. We performed 1600 steps before we started taking measurements, and we did the measurements in 30 blocks of 320 steps each to ensure statistical independence. Back propagation measurements had 40 backward steps.

**IV. RESULTS**

As mentioned before, all our simulations were done on lattices of \(6 \times 6\) unit cells. For this size, 36 holes corresponds to a half-filled case. In units of \(t_{pd}\), we set \(U_d = 6, U_p = 0\), and \(t_{pp} = 0.3\) for most studied cases. We varied \(V_{pd}\) between 0 and 1 for several different hole fillings and values of the charge-transfer energy \(\epsilon\). We were mainly concerned with hole doped cases, number of holes.
A. Charge Correlation Functions

In Fig. 4 we show the expectation values of the charge on the Cu sites as a function of $V_{pd}$ for several band fillings and values of the charge-transfer energy $\epsilon$. When $V_{pd} = 0$, we see that for the half-filled case, even with a relatively large value of $\epsilon$, there are substantial holes distributed on the O sites. When doped to 42 and 46 holes, most of the added holes go to the O site. Except for the $\epsilon = 1$ case, increasing $V_{pd}$ from 0 transfers some of the O charge to the Cu. The transfer rate increases if $\epsilon$ is increased. These are expected results: in the charge-transfer regime, $U_d > \epsilon > W$, with a repulsive $V_{pd}$, it become energetically favorable for some charge to move from O to Cu even at the expense of some unfavorable double occupancy of the Cu site caused by a large $U_{d}$. On the other hand, in the mixed-valent regime, $U_d > W > \epsilon$, when $\epsilon = 1$, we see a movement of holes from the Cu site to the O sites. Here the energy difference between the Cu and O states is smaller, and a strong on-site repulsive $U_d$ favoring charge removable from the Cu sites dominates the smaller repulsive $V_{pd}$, opposing the movement of charge to the O sites. In general, the presence of $V_{pd}$ seems to expand the charge-transfer regime. Similar results have been seen in finite-temperature QMC and zero-temperature exact diagonalization studies.

Another effect of increasing $V_{pd}$ is the decreasing of the correlation between the charge on the Cu and the neighboring O sites. This is shown in Fig. 5. At a given band filling, increasing $\epsilon$ only has a little effect. Similar behavior was also seen in a finite-temperature QMC study. One also observes that in the charge-transfer regime the decreasing rate seems independent of the filling and $\epsilon$. Because $C(0) \approx N_h/N - \langle n_{Cu}n_O \rangle$, it is no surprise to observe an increase in $C(k = 0)$ with an increasing $V_{pd}$.

It is instructive to compare our findings with Stephan et al. results. Their exact diagonalization results showed that when $U_{Cu} = U_O = \infty$, doped holes make the hole on the Cu sites transfer to the O sites, and with increasing $V_{pd}$, the charge on the Cu site decreases continuously. They also found that the addition of a second hole produces a smaller additional change in the neighboring Cu-O charge correlation than the first one does. Both behaviors of the hole on the Cu site and neighboring Cu-O charge correlation indicate that a charge-transfer “bipolaron” forms in this system. Therefore they concluded that the binding energy is obtained from electronic polarization. From our simulation results, in the charge transfer region, the charge on the Cu site increases with hole doping and increasing $V_{pd}$, suggesting that electronic polarization has no effect in the physically relevant region. Hence we expect that the binding energy is mainly gained from magnetic mechanism.

B. Spin Correlation Functions

In Fig. 6 we show the behavior of the local magnetic moment on the Cu sites. First, we see that increasing the hole doping increases the moment. More specifically, at a given doping, increasing $\epsilon$ increases the moment. When $\epsilon > 1$, increasing $V_{pd}$ increases the moment, but when $\epsilon = 1$, increasing $V_{pd}$ decreases it. Clearly, the increase of the moment is strongly correlated with the increase and decrease of charges on the Cu sites.

In Figs. 7 and 8 we show the wavevector dependence of the Fourier transform of the static spin-spin correlation function for the Cu sites as a function of $V_{pd}$ for a doping to 42 holes. This function is plotted along high symmetry lines in the first Brillouin zone. The different figures correspond to different values of $\epsilon$. In mixed valent regime, Fig. 7, we see that increasing $V_{pd}$ suppress this function over the entire zone. This suppression is consistent with the suppression of the local moment seen in Fig. 6. On the other hand, in the charge-transfer regime, Fig. 8, increasing $V_{pd}$ enhances this function, again consistent with the enhancement of the local moment seen in Fig. 6. By comparing the two figures we see that for a given $V_{pd}$ increasing $\epsilon$ increases these correlations and sharpens the peaks in the functions. In each figure there are two principal peaks: One is connected with the displacement of the antiferromagnetic peak to $(\pi, \pi - \delta')$. The other is the appearance of an incommensurate structure at $(\pi - \delta', \pi - \delta')$. A weaker spin-density wave structure is at $(\pi, 0)$.

Previous QMC simulations of the one-band Hubbard model have seen a similar shifting (and splitting) of the peak in the static structure factor from the antiferromagnetic position $(\pi, \pi)$ to positions $(\pi, \pi - \delta)$ on the face of the Brillouin zone and $(\pi - \delta', \pi - \delta')$ along the diagonal direction. This behavior is in agreement with the experimental data for LSCO presented in Fig. 3 of Ref., where a minimum is observed at $(\pi, \pi)$ along the diagonal direction. Our CPMC simulations of $t - t' - U$ Hubbard model also found that for a large $t'$, a weak peak appears along the diagonal direction. We remark that we did not study the dependence of either of these peaks on lattice size.

To examine whether the incommensurate peak along the diagonal direction is produced by a finite O-O hopping $t_{pp}$, in Fig. 9 (a) and (b) we display the spin structure factor $S(k)$ as a function of $t_{pp}$ for different $\epsilon$. The parameters are the same as in Fig. 7. Here a nonzero $t_{pp}$ makes the hole filling correspond to a closed-shell case. From Fig. 9 (b), even for a very small $t_{pp}$, a weak peak at the $(\pi - \delta', \pi - \delta')$ still exists. With increasing $t_{pp}$, the spin-spin correlations are strongly suppressed near the AF wavevector $(\pi, \pi)$, and at the same time the amplitude of the incommensurate peak along the diagonal direction or tendency to this peak forming is enhanced. For the half-filling case (data not shown) we also observed that increasing $t_{pp}$ greatly suppresses AF order.
Finally, we report how the AF long range order in
the half-filling case is destroyed by the hole doping. In
Fig. 10(a) and (b), the spin structure factor is plotted for
different hole filling cases. From Fig. 10(a), it is clearly
seen that AF spin-spin correlation is strongly suppressed
by the hole doping. As shown in Fig. 10(b), in the light
hole doping region ($N_h = 42$), there exist two incommen-
surate peaks. When the system is doped to $N_h = 46$, the
incommensurate peak along the diagonal direction disap-
ppears, but the peak on the face of of the Brillouin zone is
robust. In the heavy doping region ($N_h = 54$), the spin
structure factor is featureless near ($\pi, \pi$), and the peak
occurs at ($\pi, 0$).

C. Pairing Correlation Functions

A typical pairing correlation function as a function of
distance and $V_{pd}$ is shown in Fig. 11. Here we show the
d-wave function and see that it is dominated by a large
peak at short distances ($R < 2$). At these distances, in-
creasing $V_{pd}$ increases the magnitudes of the correlations
slightly. At larger distances ($R > 2$), the trend reverses.
The dominance of the local peak is such that a measure
of pairing like the $k = 0$ dependence of the Fourier trans-
form of the pairing correlation function or the integral of
$P(R)$ with a large distance cut-off can exhibit behavior
indicative of the only the short-range behavior and hide
the more relevant long-range behavior.

The short-range behavior is illustrated in more detail
in Fig. 12. For two different values of $U_d$, we plot the
value of the $R = 0$ peak in the vertex contribution for
both extended s-wave and d-wave symmetries for several
values of $\epsilon$. In both the charge-transfer and mixed valent
regimes, the $R = 0$ value for both symmetries increases
monotonically with increasing $V_{pd}$.

For comparison, the long-range ($R > 2$) behavior is
illustrated in Fig. 13. In both the s and d-wave chan-
nels, the long-range vertex contributions in the charge-
transfer regime decrease with increasing $V_{pd}$ but in the
mixed-valent regime it increases. Over the range of $V_{pd}$
simulated, the long-range part of the d-wave contribution
is consistently larger than the s-wave contribution.

As a function of filling, the behavior is more complex.
In Fig. 14 is the short-range part of the vertex contribu-
tion. In the mixed valent regime, both the extended s-
wave and d-wave channels decrease rapidly with electron
and hole doping. In the charge-transfer regime, the d-
wave functions falls with doping but the extended s-wave
function initially increases. The long-range contribu-
tion, shown in Fig 15, shows the dominance of the d-wave
channel. In the mixed-valent regime it basically decreases
with doping, whereas in the charge-transfer regime, it ini-
tially increases but only to decrease rapidly for large hole
doping. Our findings suggest that the conclusions of Dopf
et al. reflect the behavior of local interaction vertex, not
the long range property.

V. SUMMARY AND CONCLUSIONS

We summarize our results as follows: Using the CPMC
method, we simulated the two-dimensional three-band
Hubbard model to study its charge, spin, and pairing
correlations as a function of electron and hole doping,
and the charge-transfer energy $\epsilon$ and the Coulomb re-
pulsion $V_{pd}$ between charges on neighboring Cu and O
lattice sites. We found that increasing $V_{pd}$ suppressed
the charge-charge correlations between neighboring Cu
and O sites. In the mixed-valent regime it had the effect
moving small amounts of charge from the Cu sites to the
O sites. In the charge-transfer regime, the effect was the
opposite. Upon hole doping, more of the extra holes went
to the O sites than to the Cu sites.

At a given doping, increasing $V_{pd}$ increased the spin-
spin correlations in the charge-transfer regime but de-
creased them in the mixed-valent regime. Also electron
and hole doping away from half-filling was accompanied
by a rapid suppression of anti-ferromagnetic correlations.
As a function of doping, $\epsilon$, and $V_{pd}$, the behavior of the
magnetic moment on the Cu sites was strongly correlated
with the behavior of the charge on the Cu sites.

As a function of distance, both the $d_x^2-y^2$-wave and
extended s-wave pairing correlations decayed quickly. In
the charge-transfer regime, increasing $V_{pd}$ decreased the
long-range part of the correlation functions in both chan-
nels, while in the mixed-valent regime, it increased the
long-range part of the s-wave behavior but decreased
that of the d-wave behavior decreased. Still the d-
wave behavior dominated. At a given doping, increasing
$V_{pd}$ increased the spin-spin correlations in the charge-
transfer regime but decreased them in the mixed-valent
regime. Also electron and hole doping away from half-
filling was accompanied by a rapid suppression of anti-
ferromagnetic correlations.

We presented a more extensive study of the effects of
$V_{pd}$ than previous QMC studies at zero and finite temper-
ature. Our results illustrate the presence of both s and
d-wave correlations in the charge-transfer regime, with
the d-wave correlations generally dominating. These re-
results highlight the difference in the behavior between the
short and long range part of these correlation function.
Figures of merits that include the short-range part are
dominated by the behavior of the short-range part. For
the system size studied the correlations are weak. We
did not study these correlations as function of system
size. We believe the size dependence will be the same as
previous studies.

Lastly, as a complementary part to results presented
so far, we briefly report the effects of $U_p$ on charge, mag-
etic and pairing correlations. In both the mixed valent
and charge-transfer regions, and for all band fillings, we
found that a finite $U_p$ ($U_p = 2.0$) moves some charge
from the oxygen sites to the copper sites, which causes
an increasing of magnetic moment at the copper sites.
Consistent with previous observations that $U_p$ has a
negative effect on the hole binding, the long-range part of the d-wave correlation functions is suppressed by $U_p$. Our simulation results also show that $U_p$ has a larger effect in the mixed valent region than that in the charge-transfer region.

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FIG. 9. Average static spin structure factor for Cu sites as a function of the wavevector $k$ and $t_{pp}$. (a) $\epsilon = 1$, (b) $\epsilon = 3$, and the number of holes equals 42.

FIG. 10. Average static spin structure factor for Cu sites as a function of the wavevector $k$ and $N_h$ with $\epsilon = 3$. (a) Half-filling and doped cases and (b) Doped cases.

FIG. 11. d-wave pairing correlation function as a function of distance $R$ for different values of $V_{pd}$. The number of holes equals 42.

FIG. 12. Local ($R = 0$) vertex contributions to the extended $s$ and d-wave pairing correlation function as a function of $V_{pd}$ for different values of $\epsilon$ and $V_{pd}$. The number of holes equals 42.

FIG. 13. Long-range (averaged for $R > 2$) part of the vertex contributions (averaged over $R > 2$) to the extended $s$ and d-wave pairing correlation function as a function of $V_{pd}$ for different values of $\epsilon$ and $V_{pd}$. The number of holes equals 42.

FIG. 14. Local part ($R = 0$) of the vertex contributions to the extended $s$ and d-wave pairing correlation function as a function of filling. $V_{pd} = 0$. The number of holes equals 42. (a) $\epsilon = 1$. (b) $\epsilon = 3$.

FIG. 15. Long-range part (averaged for $R > 2$) of the vertex contributions to the extended $s$ and d-wave pairing correlation function as a function of filling. $V_{pd} = 0$. The number of holes equals 42. (a) $\epsilon = 1$. (b) $\epsilon = 3$. 
$4 \langle (\bar{z}(i)\bar{z}(i)) \rangle$

- $N_h=42; \varepsilon=1.0$
- $N_h=42; \varepsilon=2.0$
- $N_h=46; \varepsilon=3.0$
- $N_h=42; \varepsilon=3.0$
- $N_h=36; \varepsilon=3.0$

$V_{pd}$
figure9(a) and figure9(b)
Spin structure factor $S(k)$

$Nh=36$
$Nh=42$
$Nh=46$
$Nh=54$

$\text{(a)}$ $\text{(b)}$

$\text{figure10(a) and figure10(b)}$
\[ P_d(R) \]

\[ V_{pd} = 0.0 \]
\[ V_{pd} = 0.2 \]
\[ V_{pd} = 0.5 \]
figure 12(a) and figure 12(b)
figure13(a) and figure13(b)

(a) (b)

$V_{\alpha \_ave \ (R>2.0)}$

$U_d = 4.0, U_d = 6.0$

$V_{pd} \rightarrow 0.0, 0.2, 0.4, 0.6, 0.8, 1.0$

$V_{pd} \rightarrow 0.0, 0.2, 0.4, 0.6, 0.8, 1.0$

$V_{d\_ave; \ \varepsilon=1.0}$

$V_{d\_ave; \ \varepsilon=2.0}$

$V_{s\_ave; \ \varepsilon=1.0}$

$V_{s\_ave; \ \varepsilon=2.0}$
figure14(a) and figure14(b)
figure15(a) and figure15(b)