Quantum Monte Carlo Evidence for Superconductivity in the Three-Band Hubbard Model in Two Dimensions

Kazuhiko Kuroki and Hideo Aoki

Department of Physics, University of Tokyo, Hongo, Tokyo 113, Japan

(Received 6 December 1995)

A possibility of the electronic origin of the high-temperature superconductivity in cuprates is probed with the quantum Monte Carlo method by revisiting the three-band Hubbard model comprising Cu $3d_{x^2-y^2}$ and O $2p_\sigma$ orbitals. The $d_{x^2-y^2}$ pairing correlation is found to turn into an increasing function of the repulsion U_d within the d orbitals or the d-p level offset $\Delta\varepsilon$, where the normalized correlation grows with the system size. We have detected this in both the charge-transfer and Mott-Hubbard regimes upon entering the strong-correlation region (U_d or $\Delta\varepsilon >$ bare bandwidth). [S0031-9007(96)00358-4]

PACS numbers: 74.25.Dw, 74.20.Mn

The discovery of high T_c superconductivity has kicked off intensive theoretical studies, but we are still some way from a complete understanding of what happens in the realistic parameter range. Experimental and theoretical studies have indicated that the essence of the cuprates lies in the two-dimensional CuO_2 plane, for which it is generally recognized that Emery's three-band Hubbard model [1] is the basic, starting model that describes both the copper $3d$ and oxygen $2p_x$ and $2p_y$ orbitals.

The model captures the essential feature of the system with two key parameters: U_d (the on-site Coulomb repulsion between copper d holes) and $\Delta\varepsilon$ (Cu $3d$–O $2p$ level offset), where the energies are measured in units of the d-p hybridization, t_{dp}. The inequality $\Delta\varepsilon < U_d$ is usually used to identify the insulating host material as a charge-transfer insulator, as opposed to the Mott-Hubbard insulator with $\Delta\varepsilon > U_d$ [2]. Here we shall extend this terminology into the doped case. The three-band Hubbard Hamiltonian is given in standard notations as

$$\mathcal{H} = t_{dp} \sum_{\langle i,j\rangle\sigma} (d_{i\sigma}^\dagger p_{j\sigma} + \text{H.c.}) + t_{pp} \times \sum_{\langle j,j'\rangle\sigma} (p_{j\sigma}^\dagger p_{j'\sigma} + \text{H.c.}) + \Delta\varepsilon \sum_{j\sigma} n_{j\sigma}^p + U_d \sum_i n_{i\uparrow}^d n_{i\downarrow}^d, \tag{1}$$

where $d^\dagger$ creates a Cu $3d_{x^2-y^2}$ hole and $p^\dagger$ an O $2p_\sigma$ hole, $t_{dp}(t_{pp})$ is the nearest-neighbor d-p (p-p) transfer. Here the repulsion within the p orbitals and the repulsion between d and p orbitals have been neglected for simplicity.

Great efforts have been made to search for superconductivity in this model [3–7], but indications of the off-diagonal long-range order have not been detected so far. There is also a variational Monte Carlo study [8], but the justification of the variational wave functions remains somewhat open.

Subsequently, reductions of the original three-band model into effective Hamiltonians in some limits have been attempted. In the limit of large level offset ($\Delta\varepsilon \gg U_d, t_{dp}$), the system is equivalent to the *single-band* Hubbard model described by the on-site interaction U_d and the effective hopping $t_{\text{eff}} = t_{dp}^2/\Delta\varepsilon$. If we further consider a limit $U_d \gg t_{\text{eff}}$, the system reduces to the *t-J* model where electrons, with double occupancies completely inhibited, experience an exchange interaction $J = 4t_{\text{eff}}^2/U_d$. Thus the *t-J* model is a natural limiting form of the three-band model in the Mott-Hubbard regime.

However, the real cuprates lie in the charge-transfer regime. Zhang and Rice [9] have proposed that even in this case, the low-lying states of the three-band model may be represented by the *t-J* model, at least in the limit of $U_d \gg \Delta\varepsilon \gg t_{dp}$, and provided that the spin-triplet d-p molecular orbitals may be neglected. In the *t-J* model the superexchange J provides a natural source of an effective attraction, and extensive theoretical works have indeed indicated that the *t-J* model superconducts for a certain range of J/t: In one dimension (1D) the phase diagram has a finite pairing-dominated region around $J \sim 2t$ [10]. In 2D, exact diagonalization results [11] indicate that the $d_{x^2-y^2}$-wave pairing correlation function is long tailed for sufficiently large $J \sim t$, which is also supported from variational Monte Carlo studies [12–14].

Now, even if the *t-J* model can be superconductive, the following fundamental questions do remain for the original three-band Hubbard model: (i) Does the perturbative picture that maps the three-band model into *t-J* model in the limit of $t_{dp}/\Delta\varepsilon, t_{dp}/U_d \to 0$ remain valid for finite, realistic values of parameters? In real materials $\Delta\varepsilon \sim 2.5t_{dp}$ [15] is only moderate, where the validity of the perturbation is not at all clear. (ii) Even if the perturbation is to remain valid through, e.g., renormalizations, whether the resultant J/t can become large enough to guarantee a high T_c is also highly nontrivial. (iii) Does a qualitative difference exist between the Mott-Hubbard and charge-transfer regimes concerning the appearance of superconductivity via, e.g., different effective J/t mentioned in (ii)?

All these points evoke another basic question; i.e., does the *single-band* Hubbard model, which shares the

 0031-9007/96/76(23)/4400(4)$10.00

t-J model as an effective Hamiltonian in the strong-correlation limit, have a superconducting phase? In 1D, the conformal field theory indicates that no matter how U/t is increased, the superconducting correlation fails to become dominant [16,17], indicating a behavior distinct from the situation when we let $J \sim t$ in the t-J model. In the 2D Hubbard model, quantum Monte Carlo calculations up to $U = 4t$ still show no sign of the off-diagonal long-range order [18]. To reconcile this, we have to consider a possibility that either the effective J/t is small, or $U = 4t$ is already outside the perturbative region. If the single-band Hubbard model remains normal for the whole range of parameters, while the three-band Hubbard model with finite, realistic values of parameters does superconduct, the Mott-Hubbard and charge-transfer regimes may possibly belong to different universality classes.

These problems have remained a long-standing puzzle, which is exactly our motivation to revisit the three-band Hubbard model, where we cover a hitherto unexplored range of parameters. If the answer is positive, we will have a stronger ground to consider the superconductivity in cuprates to be of electronic origin.

We employ the quantum Monte Carlo (QMC) method, where our motivation described above calls for special emphasis upon the following. (i) We consider the range of $\Delta\varepsilon$ and U_d extending to the bare width, W, of the most relevant (Cu $3d$–O $2p_\sigma$ antibonding) band. We define the case where both $\Delta\varepsilon$ and U_d are comparable with W to be the strong-correlation regime in the following sense. The relevant energy to be compared with W should be the effective repulsion within the d-p Wannier orbital, which should be greater than $\mathrm{Min}\{\Delta\varepsilon, U_d\}$, the minimum cost of energy for two holes occupying the same Wannier orbital. This is, in fact, illustrated in the low-lying spectra of finite systems, where the levels of the three-band model with $\Delta\varepsilon = 3.6$ eV and $U_d = 10.5$ eV are best fit with those of the single-band Hubbard model with $U \sim 5$ eV [15]. (ii) The carrier doping is kept close to the experimentally known optimum value ($\delta \sim 0.15$) for the superconductivity. (iii) Since a reliable detection of the pairing correlation is required, we adopt the ground-state (or projector) QMC formalism with the projection imaginary time (τ) of at least $12/t_{dp}$ to ensure convergence. (iv) The sample-size dependence is studied for lattice sizes up to 8×8 unit cells (192 atoms), which is combined with a real-space analysis to probe the range of the pairing correlation. To our knowledge, previous calculations do not satisfy all of these conditions simultaneously.

The details of the QMC calculation are the following. We have employed the discrete Hubbard-Stratonovich transformation introduced by Hirsch [19]. We have used the Trotter decomposition, where the imaginary time increment [$\Delta\tau = \tau/$(number of Trotter slices)] is taken to be ≤ 0.05. The systematic errors due to the decomposition, which should be smaller than $O(\Delta\tau^2)$ [20], is negligible compared with the system-size dependences of the correlation functions shown below. We have also adopted the stabilization algorithm used by several authors to investigate ground-state and low-temperature properties [21]. Finally, the so-called negative-sign problem makes the statistical errors large for large interactions. Here we have increased the strength of the interactions up to the point where the ratio of the total sign to the total number of samples decreases to 0.5. When all these conditions are satisfied, the CPU time required was typically 50 hours on HITAC S-3800 supercomputer for the largest $\Delta\varepsilon$ and U_d considered here.

As for the symmetry of the pairing, we have considered $d_{x^2-y^2}$-wave ($f_d = \cos q_x - \cos q_y$) and extended s-wave ($f_s = \cos q_x + \cos q_y$) pairing, for which we have calculated the $k = 0$ Fourier component of the real-space correlation function, $S_\alpha = (1/2N)\langle \Delta_\alpha^\dagger \Delta_\alpha + \Delta_\alpha \Delta_\alpha^\dagger \rangle$, with $\Delta_\alpha = \sum_{\mathbf{q}} f_\alpha(\mathbf{q}) (d_{\mathbf{q}\uparrow} d_{-\mathbf{q}\downarrow} + p^x_{\mathbf{q}\uparrow} p^x_{-\mathbf{q}\downarrow} + p^y_{\mathbf{q}\uparrow} p^y_{-\mathbf{q}\downarrow})$.

In this Letter we focus on the hole doping case [22], and go from 18 holes for 4×4 unit cells ($\delta = 0.125$), 42 for 6×6 ($\delta = 0.166$), to 74 for 8×8 ($\delta = 0.156$). Here the doping concentration δ is defined by $\delta = [$(number of holes)/(number of unit cells)$] - 1$. These fillings are chosen so as to satisfy (i) the proximity to $\delta \sim 0.15$, and (ii) the closed-shell condition (with a nondegenerate one-electron ground state) to ensure that the negative sign problem becomes less serious [23]. We have set $t_{pp} = -0.4 t_{dp}$ [15].

In Fig. 1 the dependence of S_d on $\Delta\varepsilon$ (a) or U_d (b) is shown. For small $\Delta\varepsilon$ and/or U_d, S_d decreases with $\Delta\varepsilon$ or U_d. An increase in $\Delta\varepsilon$ or U_d implies an increased ratio (electron-electron repulsion)/(bandwidth), which will indeed work unfavorably for superconductivity in the weak-correlation regime. However, S_d dramatically begins to increase with these parameters for larger values of $\Delta\varepsilon$ and/or U_d. The crossover to this behavior occurs in the "strong-correlation" regime where both $\Delta\varepsilon$ and U_d exceed the bandwidth W of the antibonding d-p band ($W \sim 2.33 t_{dp}$ for $\Delta\varepsilon = 2.7 t_{dp}$ and $t_{pp} = -0.4 t_{dp}$).

At the same time, the pairing correlation starts to *grow* with the system size right above the strong-correlation regime. Although this does not guarantee an off-diagonal long-range order, it can be interpreted as a tendency toward the formation of such order. This is in sharp contrast with the weak-correlation regime, where S_d has an inverse size dependence.

To check that we are really looking at the long-range part of the pairing correlation, we have looked into their behavior in a real space. If we decompose S_α into a sum over the real-space distance $\Delta\mathbf{r}$, $S_\alpha = \sum_{\Delta\mathbf{r}} s_\alpha(\Delta\mathbf{r})$ with $s_\alpha(\Delta\mathbf{r})$ being the correlation function in real space. In Fig. 2 we represent $s_d(\Delta\mathbf{r})$ by $S_d(R)$ defined by restricting the sum in the above formula to $|\Delta x|, |\Delta y| \leq R$ (in the periodic boundary condition), where $\Delta\mathbf{r} = (\Delta x, \Delta y)$. We can see that $S_d(R)$ monotonically increases as we include more distant correlations, which implies that the growth of the $k = 0$ component, S_d, is indeed caused

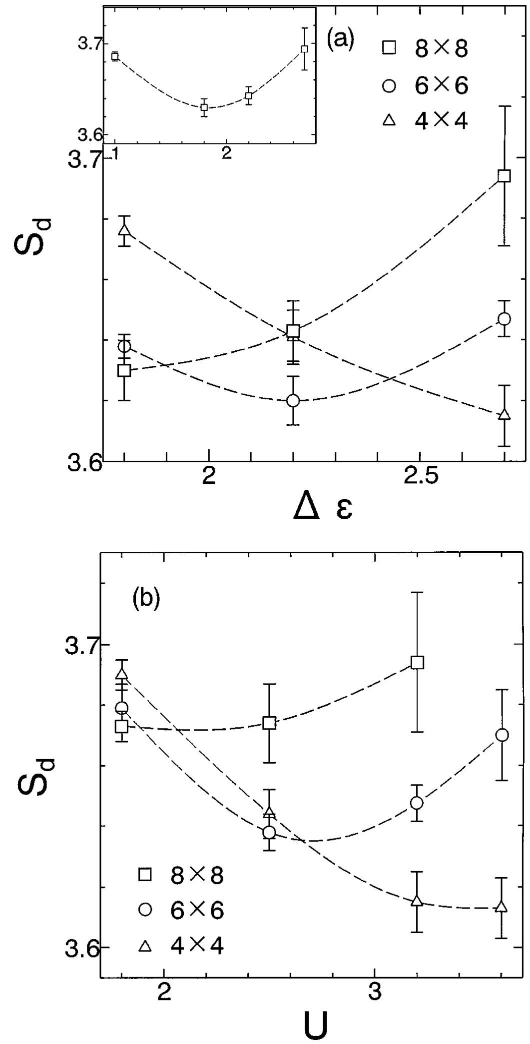

FIG. 1. The $d_{x^2-y^2}$-wave pairing correlation, S_d, is plotted (a) against $\Delta\varepsilon$ for a fixed $U_d = 3.2$, and (b) against U_d for a fixed $\Delta\varepsilon = 2.7$. We assume the hopping integrals $t_{dp} = 1$, $t_{pp} = -0.4$. Number of holes and the sizes of the system are 18 holes/(4 × 4) unit cells (△), 42/(6 × 6) (○), and 74/(8 × 8) (□). For 8 × 8 a wider range is displayed in the inset of (a) to show the change in sign of the gradient. The dashed lines are guide for the eye.

by the extension of the pairing correlation beyond the system size.

An indication that this kind of caution is really necessary is shown in inset (a) of Fig. 2. Namely, although the extended s-wave pairing correlation, S_s, also increases with the system size, its real-space behavior, $S_s(R)$, remains almost a constant, indicating that the size dependence only signifies a short-range correlation. We have also made a similar real-space analysis for the staggered magnetic correlation function $S(\pi,\pi) = \sum_{i,j}\langle (S_i^d)_z(S_j^d)_z + (S_i^{p^x})_z(S_j^{p^x})_z + (S_i^{p^y})_z(S_j^{p^y})_z\rangle(-1)^{(j_x-i_x)+(j_y-i_y)}$. The result [inset (b) of Fig. 2] shows a behavior similar to that for the extended s-wave pairing, indicating a short-range spin-spin correlation [24]. There is some possibility that

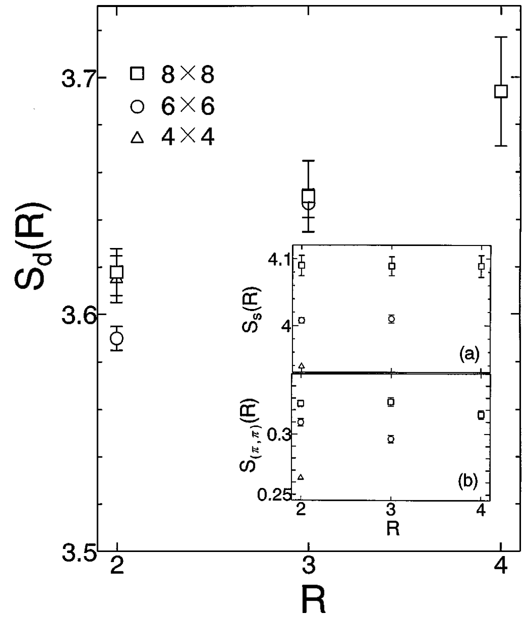

FIG. 2. The $d_{x^2-y^2}$-wave pairing correlation, $S_d(R)$, the extended s-wave pairing correlation, $S_s(R)$ [inset (a)], and the staggered magnetic correlation, $S_{(\pi,\pi)}(R)$ [inset (b)] are plotted as a function of the range, R, in real space.

the increase of S_d with system size might be due to the variations in δ mentioned ealier. Nonetheless, in any case, we see a clear difference between the size dependence of $S_d(R)$ and that of $S_s(R)$ or $S_{(\pi,\pi)}(R)$.

We now move on to the Mott-Hubbard regime ($U_d < \Delta\varepsilon$) with *large* $\Delta\varepsilon$, which leaves few O $2p$ holes to give a natural way to approach the *single-band* Hubbard model as mentioned earlier. In Fig. 3, we show the dependence of S_d on $\Delta\varepsilon$ with a fixed $U_d = 1.8t_{dp}$ (a) or on U_d with a fixed $\Delta\varepsilon = 3.6t_{dp}$ (b) with the same system sizes and band fillings as in Fig. 1. Strikingly enough, a positive dependence on the system size does appear as well for larger $\Delta\varepsilon$ and U just as in Fig. 1.

If we now combine these results in the Mott-Hubbard and charge-transfer regimes, the following picture emerges. Suppose we compare the relevant energy in the Mott-Hubbard regime, $\mathrm{Min}\{\Delta\varepsilon, U_d\} = U_d$, with the width of the antibonding band, which is $W = 1.87t_{dp}$ for $\Delta\varepsilon = 3.6t_{dp}$ (and $t_{pp} = -0.3t_{dp}$ which we have assumed here). The region at which the pairing correlation emerges is precisely $U_d \sim W$, which is a counterpart to $\Delta\varepsilon \sim W$ in the charge-transfer regime. Hence, *no matter what the regime in the three-band model,* a tendency toward $d_{x^2-y^2}$-wave pairing superconductivity emerges when the relevant energy (U_d or $\Delta\varepsilon$) exceeds W, i.e., when our definition of the strong-correlation criterion is met.

If we now recall our initial reasoning, the result summarized above amounts to either (i) the single-band Hubbard model with U/t as large as the bare bandwidth should concomitantly exhibit superconductivity or (ii) we are looking at a regime where the finiteness of $\Delta\varepsilon$ makes

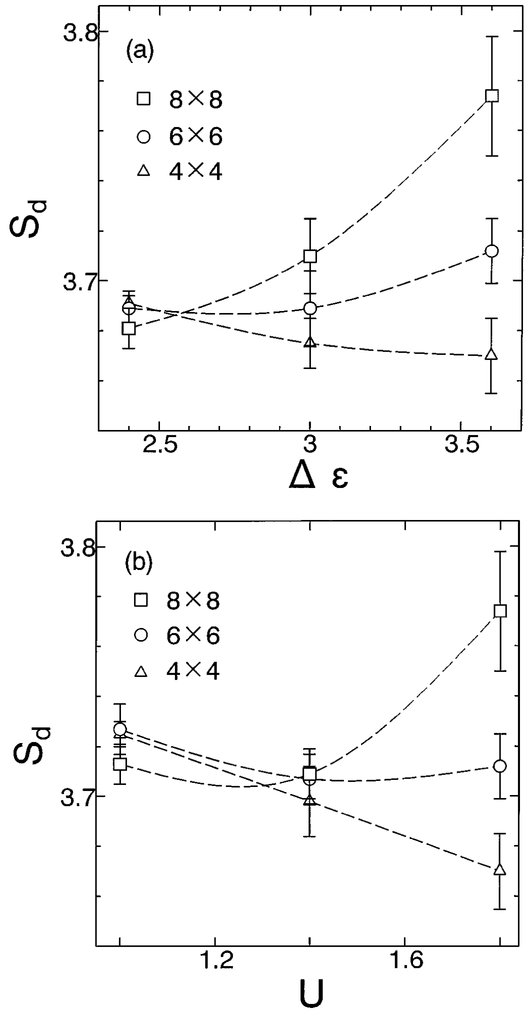

FIG. 3. Similar plot for S_d as in Fig. 1 in the Mott-Hubbard regime, $U < \Delta\varepsilon$. S_d is plotted (a) against $\Delta\varepsilon$ for a fixed $U_d = 1.8$, and (b) against U_d for a fixed $\Delta\varepsilon = 3.6$ for $t_{dp} = 1$, $t_{pp} = -0.3$.

the universality class of the three-band model distinct from that of the single-band Hubbard model through, e.g., different ranges of the effective J/t. The former possibility that the three-band model already resembles the one-band Hubbard model when $\Delta\varepsilon$ is increased up to $3.6t_{dp}$ does not contradict the previous one-band QMC results [18], where the largest U so far studied is only half the bandwidth, $4t$. $U = \frac{1}{2}W$ can be mimicked by the three-band model with $U_d \sim t_{pd}$ for $\Delta\varepsilon = 3.6t_{dp}$, which belongs to the region where the sign of pairing is absent in the present result as well. We believe this problem deserves further investigations.

In summary, we have detected a possible indication of superconductivity in the strong-correlation region of the three-band Hubbard model in both of the charge-transfer and Mott-Hubbard regimes, and in both of the hole-doped and electron-doped cases [22]. Since all of these regimes and cases share the t-J model as some limiting cases, this might suggest a scenario in which the superconductivity as conceived in the t-J limit extends well into the realistic parameter regime.

Numerical calculations were done on HITAC S3800/280 at the Computer Center of the University of Tokyo, and FACOM VPP 500/40 at the Supercomputer Center, Institute for Solid State Physics, University of Tokyo. This work was supported by "Project for Parallel Processing and Super Computing" at Computer Centre, University of Tokyo, arranged by Professor Y. Kanada, and also by Grant No. 07237209 from the Ministry of Education, Science, and Culture, Japan.

[1] V. J. Emery, Phys. Rev. Lett. **58**, 2794 (1987).
[2] J. Zaanen, G. A. Sawatzky, and J. W. Allen, Phys. Rev. Lett. **55**, 418 (1985).
[3] J. E. Hirsch, S. Tang, E. Loh, Jr., and D. J. Scalapino, Phys. Rev. Lett. **60**, 1668 (1988).
[4] M. Imada, J. Phys. Soc. Jpn. **57**, 3128 (1988).
[5] R. T. Scalettar, S. R. White, D. J. Scalapino, and R. L. Sugar, Phys. Rev. B **44**, 770 (1991).
[6] G. Dopf, A. Muramatsu, and W. Hanke, Phys. Rev. Lett. **68**, 353 (1992).
[7] F. F. Assaad, W. Hanke, and D. J. Scalapino, Phys. Rev. B **50**, 12 835 (1994).
[8] S. N. Coppersmith, Phys. Rev. B **42**, 2259 (1990).
[9] F. C. Zhang and T. M. Rice, Phys. Rev. B **37**, 3759 (1988).
[10] M. Ogata, M. U. Luccini, S. Sorella, and F. F. Assaad, Phys. Rev. Lett. **66**, 2388 (1991).
[11] E. Dagotto and J. Riera, Phys. Rev. Lett. **70**, 682 (1993).
[12] C. Gros, Phys. Rev. B **38**, 931 (1988).
[13] H. Yokoyama, J. Phys. Soc. Jpn. **57**, 2482 (1988).
[14] T. Giamarchi and C. Lhuillier, Phys. Rev. B **43**, 12 943 (1991).
[15] M. S. Hybertsen, E. B. Stechel, M. Schlüter, and D. R. Jennison, Phys. Rev. B **41**, 11 068 (1990).
[16] H. J. Schulz, Phys. Rev. Lett. **64**, 2831 (1990).
[17] N. Kawakami and S.-K. Yang, Phys. Lett. A **148**, 359 (1990).
[18] N. Furukawa and M. Imada, J. Phys. Soc. Jpn. **61**, 3331 (1992).
[19] J. E. Hirsch, Phys. Rev. B **28**, 4059 (1983).
[20] R. M. Fye, Phys. Rev. B **33**, 6271 (1986).
[21] G. Sugiyama and S. E. Koonin, Ann. Phys. (N.Y.) **168**, 1 (1986); S. Sorella *et al.,* Int. J. Mod. Phys. B **1**, 993 (1988); S. R. White *et al.*, Phys. Rev. B **40**, 506 (1989); M. Imada and Y. Hatsugai, J. Phys. Soc. Jpn. **58**, 3752 (1989).
[22] Similar results have been obtained for the electron-doped case [K. Kuroki and H. Aoki (unpublished)].
[23] E. Y. Loh, J. E. Gubernatis, R. T. Scalettar, S. R. White, D. J. Scalapino, and R. L. Sugar, Phys. Rev. B **41**, 9301 (1990).
[24] The short-ranged behaviors of S_s and $S(\pi,\pi)$ are already seen in the single-band Hubbard model. We have checked this for lattices up to 12×12 sites [K. Kuroki and H. Aoki (unpublished)].