Quantum Monte Carlo evidence for superconductivity in the
develop three-band Hubbard model in two dimensions

Kazuhiko Kuroki and Hideo Aoki

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

**Abstract**

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 Cu3$d_{x^2−y^2}$ and O2$p_σ$ 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 off-set $Δε$, where the 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 $Δε >$ bare band width).
The high-temperature superconductivity in cuprates harbors some of the most fascinating aspects of strongly-correlated electron systems, but, despite a body of theoretical works on possible electronic mechanisms of superconductivity, we are still someway 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 3$d$ and oxygen 2$p_x$ and 2$p_y$ 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 $\Delta \varepsilon$ (Cu3$d$-O2$p$ level offset), where the energies are measured in units of the $d$-$p$ hybridization, $t_{dp}$. The presence of both parameters makes the physics richer. Specifically, 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

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

(1)

where $d_{i\sigma}^\dagger$ creates a Cu3$d_{x^2-y^2}$ hole and $p_{j\sigma}^\dagger$ an O2$p_{\sigma}$ 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 [3-6], but indications of the off-diagonal long-range order have not been detected so far. There is also a variational Monte Carlo study [7], but the justification of the variational wave functions remains somewhat open.

Subsequently reductions to effective Hamiltonians as certain limits of the original three-band model 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 with the on-site interaction $U_d$ and the effective nearest-neighbor hopping $t_{\text{eff}} = t_{dp}^2/\Delta \varepsilon$. If we further put $U \gg t_{\text{eff}}$, the system...
reduces to the \( t-J \) model with excluded double occupancies and \( J = 4t_{\text{eff}}^2/U \). Thus the \( t-J \) model is a natural limit of the three-band model in the Mott-Hubbard regime.

However, the real cuprates lie in the charge-transfer regime. Zhang and Rice [8] have proposed that even in this case, the low-lying states of the three-band model may be essentially 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. The \( t-J \) model thus picks up spin-singlet \( d-p \) molecular orbitals (or bonding Kondo states), which are envisaged to experience a superexchange interaction \( J \) while moving around with an effective transfer \( t \) with double occupancies avoided. The superexchange provides a natural source of an effective attraction among the molecular orbitals, and extensive theoretical works have indeed indicated that the \( t-J \) model superconducts for a certain range of \( J/t \). In one dimension (1D) this is shown clearly from a phase diagram having a finite pairing-dominated region around \( J \sim 2t \) [9]. In 2D, exact diagonalization results [10] 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 [11–13].

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 \( t_{dp}/\Delta \varepsilon, t_{dp}/U_d \rightarrow 0 \) remain valid for finite, realistic values of parameters? In real materials \( \Delta \varepsilon \sim 2.5t_{dp} \) [14] 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 a nontrivial question.

(iii) Would there be a qualitative difference 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 \( t-J \) 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, 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. 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 unfathomed 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 (Cu3d-O2p$_\sigma$ anti-bonding) 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 $\text{Min}\{\Delta\varepsilon, U_d\}$, 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 $\Delta\varepsilon = 3.6\text{eV}$ and $U_d = 10.5\text{eV}$ are best-fit to those of the single-band Hubbard model with $U \sim 5\text{eV}$. 

(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 of at least $12t_{dp}$ to ensure convergence.

(iv) The sample-size dependence is studied for lattice sizes up to $8 \times 8$ 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. For the largest $\Delta\varepsilon$ and $U_d$ considered here, the CPU time required was typically 50 hours on HITAC S-3800 supercomputer.

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

We first focus on the hole doping. We go from 18 holes for $4 \times 4$ unit cells (doping $\delta = 0.125$), 42 for $6 \times 6$ ($\delta = 0.166$), to 74 for $8 \times 8$ ($\delta = 0.156$). These fillings are chosen so as to satisfy (i) the proximity to $\delta \sim 0.15$, and (ii) the closed-shell condition (with a non-degenerate one-electron ground state) to ensure the stability of the QMC calculation. We have set $t_{pp} = -0.4t_{dp}$.

In Fig. 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 $\Delta\varepsilon$ and $U_d$. An increase in $\Delta\varepsilon$ or $U_d$ implies an increased ratio (electron-electron repulsion)/(band width), and the result in the weakly correlated regime shows that this works unfavorably for superconductivity as naively expected. 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 band width $W$ of the anti-bonding $d$-$p$ band ($W \sim 2.33t_{dp}$ for $\Delta\varepsilon = 2.7t_{dp}$ and $t_{pp} = -0.4t_{dp}$).

Right above the strong-correlation regime the pairing correlation starts to grow with the system size, which can be interpreted as a tendency toward the formation of off-diagonal long-range order. This is in sharp contrast with the weak-correlation regime, where $S_d$ has a small, 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 $S_\alpha$ into a sum over the real space distance $\Delta r$, $S_\alpha = \sum_{\Delta r} s_\alpha(\Delta r)$ with $s_\alpha(\Delta r)$ being the correlation function in real space. In Fig. we represent $s_d(\Delta r)$ 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 $\Delta r = (\Delta x, \Delta y)$. We
can see that $S_d(R)$ monotonically increases as we include more and more distant correlations, which implies that the growth of the $k = 0$ component, $S_d$, is indeed caused by the extension of the pairing correlation beyond the system size.

An indication that this kind of caution is indeed necessary is shown in the inset of Fig.2. Namely, although the extended $s$-wave pairing correlation, $S_s$, also increases with the system size, its real-space behavior, $S_s(R)$, is almost a constant, indicating that the size dependence only signifies a short-range correlation.

Now, despite the absence of electron-hole symmetry in the three-band Hubbard model, the electron-doped materials such as Nd$_{1-x}$Ce$_x$CuO$_4$ have been shown to superconduct as well. Quite apart from this, the electron-doped case is of another theoretical interest in the following sense. In the limit of $\Delta \varepsilon \to \infty$, $U_d \to \infty$ the electrons are doped to (i.e., holes are taken out from) the Cu3$d$ orbital, with only small amount of carriers left in O2$p$. This should make the system closer to the single-band Hubbard model than in the hole-doped case.

In doping electrons (or in taking out holes in the hole picture) the best choice of the band filling satisfying the above conditions are 58 holes $/8 \times 8$ (with the doping level $\delta = 0.1$) and 26 holes $/6 \times 6$ ($\delta = 0.26$). Thus, the band fillings are unfortunately not so close for the two sizes, which makes the analysis less conclusive.

Nevertheless, $S_d$ does again become an increasing function of $\Delta \varepsilon$ and $U_d$ for $\Delta \varepsilon \sim 2.5t_{dp}$ and $U_d \sim 3.0t_{dp}$, where $S_d$ grows as the size becomes $8 \times 8$ from $6 \times 6$, indicating a tendency toward $d_{x^2-y^2}$ electron-pairing in the strongly-correlated regime.

Encouraged by the electron-doped result, we move on to our final motivation. Namely we go back to the hole-doped case to investigate the Mott-Hubbard regime ($U_d < \Delta \varepsilon$) with large $\Delta \varepsilon$, which leaves few O2$p$ holes to give another 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.2. Strikingly enough, the system size dependence does appear as well for larger $\Delta \varepsilon$ and $U$ just like in Fig.2.
If we now combine this result with that in the hole-doped charge-transfer regime, the following picture emerges. Suppose we compare the relevant energy in the Mott-Hubbard regime, \( \text{Min}\{\Delta \varepsilon, U_d\} = U_d \), with the width of the anti-bonding 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 which 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. In principle we can thus envisage a superconductivity phase diagram against \( \Delta \varepsilon \) and \( U_d \), something like \( U\Delta \varepsilon > 8t^2_{dp} \) if we use the perturbative expression for \( W \).

If we now recall our reasoning, the result summarized above amounts that either (i) the single-band Hubbard model with \( U/t \) as large as the bare band width should concomitantly exhibit superconductivity, or (ii) we are looking at a regime where the finiteness of \( \Delta \varepsilon \) makes 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 3.6\( t_{dp} \) does not contradict with the previous one-band QMC results, where the largest \( U \) so far studied is only half the band width, 4\( t \). \( U = \frac{1}{2}W \) is mimicked by the three-band model with \( U_d \sim t_{pd} \) for \( \Delta \varepsilon = 3.6t_{dp} \), for which the sign of pairing is certainly absent in the present result as well. We believe this problem deserves further investigations.

Finally we comment on the possible relevance of our result in the charge-transfer regime to the high \( T_C \) materials. The value of \( \Delta \varepsilon \sim 2.5t_{dp} \) where \( S_d \) grows with system size is remarkably close to the value \( (\Delta \varepsilon = 2.7t_{dp}) \) obtained from a first-principles calculation for \( \text{La}_2\text{CuO}_4 \) [14]. As for the value of \( U_d \), the maximum value tractable with the QMC \( (U_d/t_{dp} = 3 \sim 3.5) \) happens to be smaller than realistic values \( (U_d/t_{dp} = 6 \sim 8) \), but even for these small values the tendency for superconductivity already emerges. We expect that the tendency can become stronger for larger values of \( U_d \).

In summary, we have detected an indication of superconductivity in the three-band Hubbard model without reducing it into some effective model. Strikingly, this indication
emerges in both of the charge-transfer and Mott-Hubbard regimes, and in both of the hole-doped and electron-doped cases as long as we are sitting in the strong-correlation regime. 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 Prof. Y. Kanada, and also by Grant No. 07237209 from the Ministry of Education, Science, and Culture, Japan.
REFERENCES

[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] M. Imada, J. Phys. Soc. Jpn. 57, 3128 (1988).
[4] R.T. Scalettar, S.R. White, D.J. Scalapino, and R.L. Sugar, Phys. Rev. B 44, 770 (1991).
[5] G. Dopf, A. Muramatsu, and W. Hanke, Phys. Rev. Lett. 68, 353 (1992).
[6] F.F. Assaad, W. Hanke, and D.J. Scalapino, Phys. Rev. B 50, 12835 (1994).
[7] S.N. Coppersmith, Phys. Rev. B 42, 2259 (1990).
[8] F.C. Zhang and T.M. Rice, Phys. Rev. B 37, 3759 (1989).
[9] M. Ogata, M.U. Luccini, S. Sorella, and F.F. Assaad, Phys. Rev. Lett. 66, 2388 (1991).
[10] E.Dagotto and J.Riera, Phys. Rev. Lett. 70, 682 (1993).
[11] C. Gros, Phys. Rev. B 38, 931 (1988).
[12] H. Yokoyama, J. Phys. Soc. Jpn. 57, 2482 (1988).
[13] T. Giamarchi and C. Lhuillier, Phys. Rev. B 43, 12943 (1991).
[14] M.S. Hybertsen, E.B. Stechel, M. Schlüter, and D.R. Jennison, Phys. Rev. B 41, 11068 (1990).
[15] H.J. Schulz, Phys. Rev. Lett. 64, 2831 (1990).
[16] N. Kawakami and S.-K. Yang, Phys. Lett. A 148, 359 (1990).
[17] N. Furukawa and M. Imada, J. Phys. Soc. Jpn. 61, 3331 (1992).
FIGURES

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 $\times$ 4 unit cells ($\triangle$), 42 /6 $\times$ 6 (○), and 74 /8 $\times$ 8 (□). For 8 $\times$ 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.

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

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 $t_{dp} = 1$, $t_{pp} = -0.3$. 