Superconductivity and spin correlation in organic conductors: A quantum Monte Carlo study

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The *d*-wave pairing correlations along with spin correlation are calculated with the quantum Monte Carlo method for the two-dimensional Hubbard model on lattice structures representing organic superconductors κ-(BEDT-TTF)$_2$X and (TMTSF)$_2$X. In both cases the pairing correlations for superconducting order parameters with nodes are found to be enhanced. The symmetry and the enhancement of the pairing is systematically correlated with the spin structure factor, suggesting a spin-fluctuation mediated pairing. We have further found that, as we deform the Fermi surface to make the system approach the half-filled square lattice, the coherence of the pairing saturates while the local pairing amplitude continues to increase. [S0163-1829(99)10429-6]

It is a great theoretical challenge to explore whether the superconductivity in ''exotic materials'' such as the cuprates, heavy fermion systems, and (at least some) organic conductors can be encompassed into a single class, i.e., superconductivity mediated by spin fluctuations. For more than a decade, the possibility of spin-fluctuation-mediated pairings has in fact been investigated intensively both theoretically and experimentally for heavy fermion systems[1] and high-T_c cuprates.[2] There, one important sign of spin-fluctuation-mediated pairing has been the superconducting gap with nodes.

There is now a body of accumulating experimental evidence that organic superconductors[3] κ-(BEDT-TTF)$_2$X (Refs. 4–8) and (TMTSF)$_2$X (Ref. 9) also have non-*s*-wave gap like in heavy fermion or cuprate systems. The unconventional pairing, along with the proximity of superconductivity to the antiferromagnetic or spin-density wave state, suggests that pairing may be mediated by spin fluctuation. The pseudogap-like behavior of $1/(T_1T)$ above T_c in κ-(BEDT-TTF)$_2$X (Refs. 4,6,7,10) is also reminiscent of a similar behavior in the underdoped high-T_c cuprates, suggesting that electron correlation may play an important role there.[11]

Theoretically, one of the simplest many-body Hamiltonians to incorporate the electron correlation is the Hubbard model. Some analytical calculations using diagrammatical techniques have supported spin-fluctuation-mediated pairing in the Hubbard model on lattices representing κ-(BEDT-TTF)$_2$X (Refs. 12–16) or (TMTSF)$_2$X (Ref. 17). However, numerical evidence supporting such a possibility has yet to be discovered.

Thus the purpose of the present paper is to explore numerically the pairing correlation in the Hubbard model for lattices representing κ-(BEDT-TTF)$_2$X and (TMTSF)$_2$X, with special attention paid to whether the pairing is linked with the behavior of the spin correlation. Comparing the results for the two cases, we find that the symmetry of the pairing is indeed determined by the peak position of the spin structure factor, supporting spin-fluctuation-mediated pairing. We further deform the Fermi surface from the case corresponding to κ-(BEDT-TTF)$_2$X to find that the coherence of pairs saturates as the system approaches the half-filled square lattice (i.e., where, at least for large enough U, the system becomes a Mott insulator with antiferromagnetic order). Here we adopt the ground-state, canonical-ensemble quantum Monte Carlo (QMC) method.

We start from the Hubbard model on a two-dimensional lattice (Fig. 1),

$$\mathcal{H}=-\sum_{x,y,\sigma}[t_x(c^{\dagger}_{x,y,\sigma}c_{x+1,y,\sigma})+t_y(c^{\dagger}_{x,y,\sigma}c_{x,y+1,\sigma}) +t'_1(c^{\dagger}_{x,y,\sigma}c_{x-1,y+1,\sigma})+t'_2(c^{\dagger}_{x,y,\sigma}c_{x+1,y+1,\sigma})+\mathrm{H.c.}] +U\sum_{x,y} n_{x,y,\uparrow}n_{x,y,\downarrow}. \quad (1)$$

Here, (x,y) is the coordinate of a site with the lattice constant taken to be unity, and periodic boundary condition is assumed.

While the QMC method has been widely used to investigate the Hubbard model on the 2D square lattice, enhanced pairing correlation has eluded detection. Recently, however, the present authors identified this as coming from the fact that the pair-scattering processes that produce superconductivity have a very small energy scale of $O(0.01t)$ or less:[18,19] if one takes a closed-shell condition (a parameter set with no ground-state degeneracy for $U=0$), the energy gap between the highest occupied levels and the lowest unoccupied levels for $U=0$ is as large as $\sim O(0.1t)$ for tractable system sizes, so that the effect of the low-energy pair scatterings would be smeared out. On the other hand, QMC calculations with an open-shell condition, in which the effect of low-energy pair scatterings is expected to be incorporated, suffer from nu-

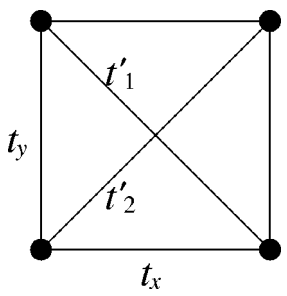

FIG. 1. The hopping parameters considered.

merical difficulties such as the negative-sign problem. An open-shell configuration is ill-conditioned also in the sense that there are a finite number of levels within an infinitesimal distance from the Fermi energy, so that one can suspect an enhancement of pairing correlations, if any, may be due to such an effect.

We have circumvented the problem by taking slightly different values of t_x and t_y to lift the degeneracy between wave numbers (k_1,k_2) and (k_2,k_1), and put the Fermi level in between those levels. This way we can prevent the low-energy pair scattering processes from being masked and at the same time take a closed-shell configuration. If we take typically $t_y/t_x=0.999$, which gives the gap between the highest occupied and the lowest unoccupied levels Δ of $<0.01t$, we can achieve for $U/t=1$ convergence with respect to the projection imaginary time τ in the QMC without running into a serious sign problem.[20]

We calculate the pairing correlation functions

$$P(r)=\sum_{|\Delta x|+|\Delta y|=r}\langle O^{\dagger}(x+\Delta x,y+\Delta y)O(x,y) + O(x+\Delta x,y+\Delta y)O^{\dagger}(x,y)\rangle \tag{2}$$

with

$$O(x,y)=\sum_{\delta_x,\delta_y,\sigma}\sigma(c_{x,y,\sigma}c_{x+\delta_x,y,-\sigma}-c_{x,y,\sigma}c_{x,y+\delta_y,-\sigma}), \tag{3}$$

which includes the conventional $d_{x^2-y^2}$ symmetry [with $\delta_x=\delta_y=1$, corresponding to the order parameter proportional to $f(\mathbf{k})\equiv\cos(k_x)-\cos(k_y)$ in k space], but written here in a general form. Hereafter we define $r\equiv|\Delta x|+|\Delta y|$ as the real-space distance. To give the above-mentioned insight, we also calculate the spin structure factor,

$$S(\mathbf{q})=\frac{1}{N}\sum_{i,j}e^{i\mathbf{q}\cdot(\mathbf{r}_i-\mathbf{r}_j)}\langle\mathbf{S}_i\cdot\mathbf{S}_j\rangle. \tag{4}$$

We first look into the case where the Fermi surface, represented by the highest occupied and the lowest unoccupied levels, resembles those of κ-(BEDT-TTF)$_2$X materials. It has been proposed that κ-(BEDT-TTF)$_2$X can be modeled by a single band Hamiltonian on a lattice with $t_x=t_y\gtrsim t_1'\gg t_2'$ and $n=1$ (half-filled).[21–23] This is because (i) the dimerization of the BEDT-TTF molecules is so strong that we can consider a dimer as a single site as far as the low-energy excitations are concerned, and (ii) the hopping parameter in the c direction alternates between two slightly different values, but the difference is small enough to be neglected as a first approximation.

First we take 134 electrons in a 12×12 (band filling $n=0.93$) lattice with $t_x=1$, $t_y=0.999$, $t_1'=0.70$, $t_2'=-0.11$. We have taken $t_y=0.999$ for the slight lift of degeneracy mentioned above. The reason for taking small but negative t_2' and the slight deviation from $n=1$ [to which the κ-(BEDT-TTF)$_2$X system corresponds] is to distribute the highest occupied and the lowest unoccupied levels on the Fermi surface as uniformly as possible (inset, Fig. 2). In Fig. 2, we show the result for the $d_{x^2-y^2}$ pairing correlation $P_{x^2-y^2}(r)$ as a function of the real-space distance r for $U=1$. It can be seen that the pairing correlation for $U=1$ is enhanced over that for $U=0$, especially at large distances.

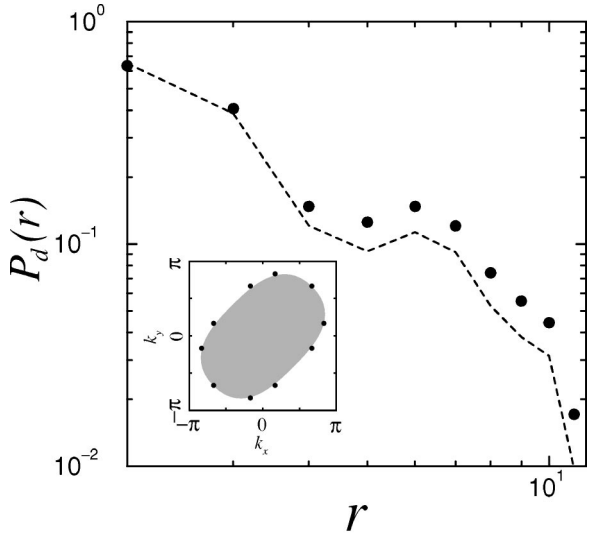

FIG. 2. QMC result for the $d_{x^2-y^2}$ pairing correlation as a function of the real-space distance for 134 electrons in 12×12 sites ($n=0.93$) with $t_x=1$, $t_y=0.999$, $t_1'=0.70$, $t_2'=-0.11$, $U=1$ (solid circles), and $U=0$ (dashed line). The oscillation in the correlation functions is a Fermi surface effect ($2k_F$ oscillation). The inset shows the highest occupied and the lowest unoccupied levels within 0.01 to the Fermi energy.

If we look at the spin structure factor in k space in Fig. 3, a broad peak around (π,π) is seen. Such an antiferromagnetic spin fluctuation enhances repulsive pair-scattering processes (in momentum-space) with momentum transfer (π,π). Repulsive pair-scattering processes from $\sim\pm(0,\pi)$ to $\sim\pm(\pi,0)$ (and vice versa) favor a superconducting order parameter that takes the maximum of its absolute value with opposite signs around these two areas. Thus, the enhancement of the $d_{x^2-y^2}$ pairing correlation along with the peak of $S(\mathbf{q})$ at (π,π) are consistent with the spin-fluctuation-mediated pairing.

We have further investigated the link between $d_{x^2-y^2}$ pairing correlation and the spin correlation systematically by deforming the Fermi surface. In Fig. 4, the enhancement of the pairing correlation is plotted against $S(\mathbf{Q})$ with $\mathbf{Q}=(\pi,\pi)$ for three cases I, II, and III. The main difference among the three cases is in the value of t_1' as given in the

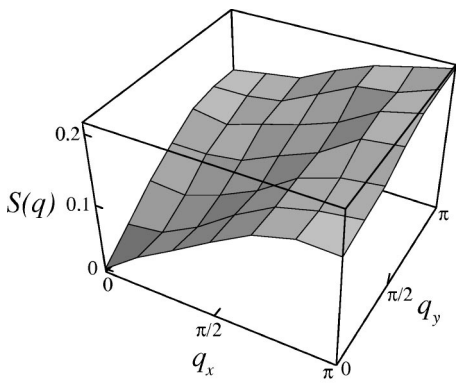

FIG. 3. QMC result for the spin structure factor as a function of the wave vector. The parameters are the same as in Fig. 2.

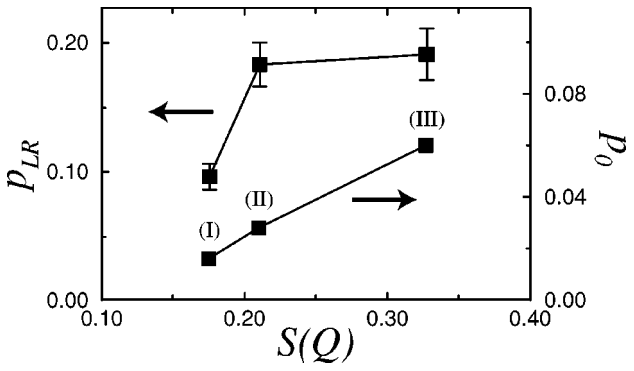

FIG. 4. A plot for p_{LR} and p_0 against $S(\mathbf{Q})$ with $\mathbf{Q}=(\pi,\pi)$ for parameter sets (I) $n=0.96$, $t_y=1.001$, $t_1'=1.00$, $t_2'=0$, (II) $n=0.93$, $t_y=0.999$, $t_1'=0.70$, $t_2'=-0.11$ (corresponding to Fig. 2), (III) $n=0.94$, $t_y=0.999$, $t_1'=0.20$, $t_2'=0$, all with 12×12 sites, $t_x=1$, and $U=1$.

caption, while other slight differences are due to technical reasons. Namely, we are going from the isotropic triangular lattice (I) to a case close the square lattice (III) via case (II) (corresponding to Fig. 2) for n fixed around unity. $S(\mathbf{Q})$ increases as we approach the half-filled square lattice. In Fig. 4, the pairing is probed from two quantities: the pairing correlation (measured from the noninteracting case) summed over large distances, $p_{\mathrm{LR}}\equiv\Sigma_{r\geq4}\{[P_d(r)]_{U=1}-[P_d(r)]_{U=0}\}$, and the local amplitude of pairing, $p_0\equiv[P_d(0)]_{U=1}-[P_d(0)]_{U=0}$.

Figure 4 shows that p_0 grows hand in hand with $S(\mathbf{Q})$, endorsing the spin-fluctuation-mediated formation of $d_{x^2-y^2}$ pairs. On the other hand, p_{LR}, the enhancement of the long-range part of $P_d(r)$, which measures the coherence of the pairs, also grows with $S(\mathbf{Q})$ as we go from (I) to (II), but it saturates between (II) and (III), suggesting that the coherence does not necessarily grow with the local pair amplitude.

To show that such a correlation between the d-wave pairing and the spin correlation is not accidental for the cases studied above, we move on to the square lattice ($t_1'=t_2'=0$) for various values of the band filling n. In Fig. 5, we show a plot similar to Fig. 4 for the square lattice, along with the plot against n in the inset. For intermediate densities, p_{LR}, p_0, and $S(\mathbf{Q})$ all grow as n approaches the half-filling ($n=1$). If we come too close to half-filling, however, p_{LR} becomes saturated, while $S(\mathbf{Q})$ and p_0 keeps growing. This is even more clearly seen at exactly half-filling, where p_{LR} is strongly suppressed (inset of Fig. 5), while p_0 continues to grow. The result that when $S(\mathbf{Q})$ becomes too large the pairs are formed but their coherence (p_{LR}) stops to grow, unlike their local amplitude p_0, might have some relevance to the normal-state pseudogap behavior observed close to the superconducting-antiferromagnetic boundary in κ-(BEDT-TTF)$_2$X as well as in the underdoped high-T_c cuprates.

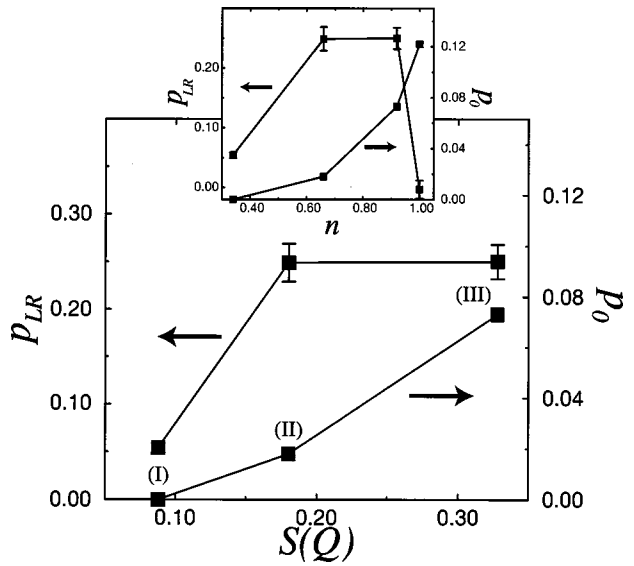

FIG. 5. A plot similar to Fig. 4 for a 10×10 square lattice with (I) 34 ($n=0.34$) (II) 66 ($n=0.66$) (III) 92 ($n=0.92$) electrons. The hopping parameters are fixed at $t_x=1$, $t_y=0.999$, $t_1'=t_2'=0$. The inset shows the band filling dependence of p_0 and p_{LR}, including the results for half-filling ($n=1$).

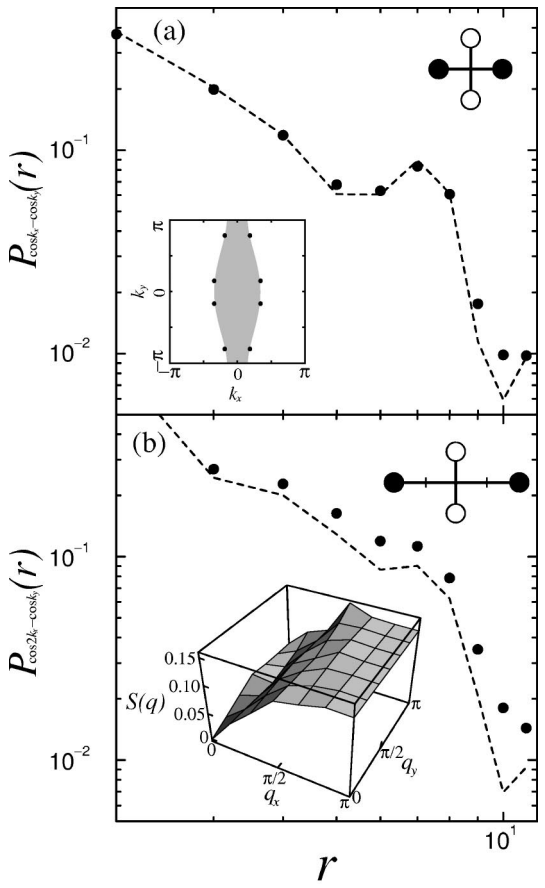

FIG. 6. A plot similar to Fig. 2 for 72 electrons in 12×12 sites ($n=0.5$) with $t_x=1$, $t_y=0.212$, $t_1'=t_2'=0$. Pairing correlations for $f(\mathbf{k})=\cos k_x-\cos k_y$ (a) (ordinary $d_{x^2-y^2}$), and for $f(\mathbf{k})=\cos 2k_x-\cos k_y$ (b). The upper inset in each figure schematically depicts the pairing (●: −, ○: +) in real space. The lower inset in (a) shows the highest occupied and the lowest unoccupied levels within 0.01 to the Fermi energy, while the spin structure factor is displayed in (b).

In order to confirm spin-fluctuation-mediated pairing to a wider extent, we next explore the case where the spin structure factor is not peaked around (π,π) by studying the case with a Fermi surface representing (TMTSF)$_2$X. If we neglect the weak dimerization along the stacking direction, these materials may be modeled by a single-band Hamiltonian on a strongly anisotropic two-dimensional lattice with t_y/t_x

$\sim O(0.1)(t_1'=t_2'=0)$ and $n=0.5$ (quarter-filled).[17,24] Here we take 72 particles in 12×12 ($n=0.5$), $t_x=1$, and $t_y=0.212$, for which the Fermi surface is as depicted in the lower inset of Fig. 6(a).

For this Fermi surface consisting of warped parallel lines around $k_x\pm\pi/4$, the nesting vector is $(\pi/2,\pi)$, so that the spin structure factor [lower inset of Fig. 6(b)] has a peak there.[25] Then, pair scattering processes from $\sim\pm(0,\pi)$ to $\sim\pm(\pi/2,0)$ (and vice versa) would be enhanced, which favors a superconducting order parameter proportional to $f(\mathbf{k})=\cos(2k_x)-\cos(k_y)$ [$\delta_x=2$, $\delta_y=1$ in Eq. (2)] rather than the ordinary $d_{x^2-y^2}$ pairing with $f(\mathbf{k})=\cos(k_x)-\cos(k_y)$. In fact, the possibility of such a pairing was pointed out in a random-phase approximation calculation.[17]

In Fig. 6, we can see that the pairing correlation for $f(\mathbf{k})=\cos(2k_x)-\cos(k_y)$ is indeed enhanced, while $d_{x^2-y^2}$ pairing correlation is not. The result provides another indication that the pairing symmetry is dictated by the dominant spin-fluctuation.

To summarize, the present result supports the spin-fluctuation-mediated anisotropic pairing scenario in organic superconductors, by the same token as in the high T_c cuprates discussed in Ref. 18,19. The enhancement of the local pair amplitude grows with $S(\mathbf{Q})$, while the off-diagonal long-range order (p_{LR}) stops to do so as the system approaches half-filled square lattice. It is an interesting future problem whether this is caused by the magnetic ordering or the metal-insulator transition, which is difficult to discern at present, since both of them occur at half-filled square lattice (at least for sufficiently large U). In the present study, we have worked at a small U due to technical reasons. It is also an important future problem to investigate whether the present conclusion is valid for more realistic values of U. The possibility of the triplet pairing, including an exotic possibility proposed in Ref. 15, also poses an intriguing issue.

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