Pairing and charge-density correlations in the three-dimensional negative-U Hubbard model on the fcc lattice

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Using symmetry considerations and exact-diagonalization techniques, we examine s-wave pairing and charge-density correlations in the three-dimensional negative-U Hubbard model on the fcc lattice. The correlations as functions of band filling and hopping and interaction parameters are studied. Results are presented for general cases. Implications for properties of alkali-metal-intercalated C_{60} materials are discussed.

The recent discovery[1] of superconductivity in alkali-metal-intercalated C_{60} solids, A_xC_{60} (A=alkali metals), has raised great interest in the nature of the superconductivity and other properties of these materials. Several authors have proposed[2,3] the negative-U Hubbard model for these systems. The on-site (i.e., on a single C_{60} molecule) attractive electron-electron interaction can be derived from eliminating electron-phonon[2,4] or electron-electron[3,5] degrees of freedom. It is emphasized that the band filling (half-filled) and the crystal lattice structure (fcc) play important roles in producing the superconductivity. While the specific microscopic mechanism responsible for the superconductivity observed in A_xC_{60} is still an open question,[6] it is instructive to study the negative-U Hubbard model on the fcc lattice to reveal its fundamental properties, regardless of the origin of the effective intramolecular attractive interactions. Earlier work[7] on the negative-U Hubbard model consists of mostly mean-field and perturbation theories. Recent Monte Carlo simulation and exact-diagonalization studies[8,9] have mainly focused on the two-dimensional Hubbard models, with both positive and negative U, on square lattices in connection with the high-T_c superconductivity in copper-oxide compounds. In this paper, we examine superconducting and charge-density correlations as functions of band filling and hopping and interaction parameters in the three-dimensional negative-U Hubbard model on the fcc lattice. We use symmetry considerations and exact-diagonalization techniques in the calculation. The results are presented for general cases. Implications for A_xC_{60} are discussed.

The negative-U Hubbard model is defined by the Hamiltonian

$$H=\sum_{i,j;\sigma} t_{ij}c_{i\sigma}^{\dagger}c_{j\sigma}-U\sum_{i} n_{i+}n_{i-} , \tag{1}$$

where $c_{i\sigma}^{\dagger}(c_{i\sigma})$ is the creation (annihilation) operator for electrons in the orbital at the site i with spin $\sigma(=+,-)$, $n_{i\sigma}=c_{i\sigma}^{\dagger}c_{i\sigma}$ the number operator, t_{ij} the hopping amplitude, and $-U(U>0)$ the on-site interaction. To perform the exact-diagonalization study, we choose an fcc cluster of eight sites as shown in Fig. 1. The periodic boundary conditions are chosen such that each site i has 12 nearest neighbors, two each of the other sites in the cluster except the site $i+4$, and six next-nearest neighbors, all the site $i+4$. With these periodic boundary conditions, this is equivalent to sampling eight points in the Brillouin zone (BZ): one at the center of BZ, $\Gamma=(0,0,0)$; three at the X points, $X_1=(2\pi,0,0)$, $X_2=(0,2\pi,0)$, and $X_3=(0,0,2\pi)$; and four at the L points, $L_1=(\pi,\pi,\pi)$, $L_2=(\pi,\pi,-\pi)$, $L_3=(\pi,-\pi,\pi)$, and $L_4=(\pi,-\pi,-\pi)$. The cubic lattice constant of the fcc structure $a=1$. In this eight-site cluster with periodic boundary conditions, electron hoppings to both first and second nearest neighbors, with hopping parameters $-t$ and $-s$ $(t,s>0)$, are allowed. In the following calculations the nearest-neighbor hopping parameter t is chosen as the energy unit. We study the system with one to eight electrons, i.e., up to the half-filled case. The Hamiltonian matrix is of order $4^8=65\,536$. Using particle number, spin and spatial symmetries, and group-theoretical techniques, the Hamiltonian matrix is first block diagonalized and the largest block is of order 98, a reduction of three orders of magnitude. Eigenvalues and eigenvectors are obtained by diagonalizing all the matrix blocks.

The ground states for one to eight electrons in the cluster are determined and then used to calculate the correla-

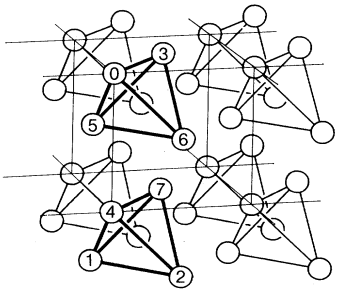

FIG. 1. The eight-site cluster of the fcc structure used in the calculation. Periodic boundary conditions are applied in all directions. Each site i has 12 nearest neighbors, two each of the other sites in the cluster except the site $i+4$, and six next-nearest neighbors, all the site $i+4$.

tion functions. It is found that for even number of electrons in the cluster, the ground state is always of symmetry $^1\Gamma_1$, i.e., a spin-zero fully symmetric state, as expected for the attractive Hubbard model. The increase of the interaction strength U/t and the next nearest-neighbor hopping amplitude s/t tend to stabilize the ground state. For odd number of electrons in the cluster, the increase of U/t also stabilizes the ground state, which is of spin one-half contributed by the unpaired electron. However, the ground-state symmetry crossover occurs as s/t changes. Some of its consequences will be discussed below.

There are two important types of correlations in the negative-U Hubbard model, namely, the charge-density and s-wave pairing. To characterize these correlations we study the $\mathbf{q}=0$ equal-time s-wave pair-field correlation function

$$\mathbf{P}_s=\langle \Delta^\dagger\Delta+\Delta\Delta^\dagger\rangle \ , \tag{2}$$

with

$$\Delta^\dagger=\left[\frac{1}{N}\right]^{1/2}\sum_j c_{j+}^{\dagger c}c_{j-}^\dagger \tag{3}$$

and the equal-time charge-density structure factor

$$\mathbf{C}(\mathbf{q})=\langle \rho_q\rho_q^\dagger\rangle \ , \tag{4}$$

with

$$\rho_{\mathbf{q}}^\dagger=\left[\frac{1}{N}\right]^{1/2}\sum_{j,\sigma}\exp(i\mathbf{q}\cdot\mathbf{l}_j)n_{j\sigma} \ , \tag{5}$$

where $\langle\cdots\rangle$ is the ground-state average, N is the number of the sites in the cluster, and $\mathbf{l}_j$ the position vector of the site j. In the above equations, the summation of j runs over the eight sites in the cluster and $\mathbf{q}$ takes one of the eight values sampled in the Brillouin zone.

Recent Monte Carlo simulation studies[9] of the negative-U Hubbard model on the square lattice have shown that the s-wave pair-field correlation is initially enhanced when doped away from half-filling before decreasing for larger dopings for moderate interaction parameters. In Fig. 2 we present the calculated s-wave pair-field correlation P_s as a function of the number of electron pairs in the bulk fcc system for various on-site attractive interaction strength. Results with odd number of electrons in the system (not shown here) follow the same trend, but with smaller magnitude, which is due to the contribution from the unpaired electron to the normalization factor. The interaction parameter U is varied from weak ($U/t=1.0$) to strong ($U/t=10.0$) interaction region. It is interesting to notice that there exists a "critical" value U_c that is approximately $6.0t$ for $s/t=0.1$ used in the calculation. For $U>U_c$ the P_s is suppressed away from half-filling, indicating that the s-wave superconductivity is mostly favored in the half-filled case. However, when $U<U_c$ the P_s is initially enhanced away from half-filling, suggesting that superconductivity is more favorable when the system is doped away from the half-filled case. Zhang and co-workers argued[2] for superconductivity in the half-filled case for

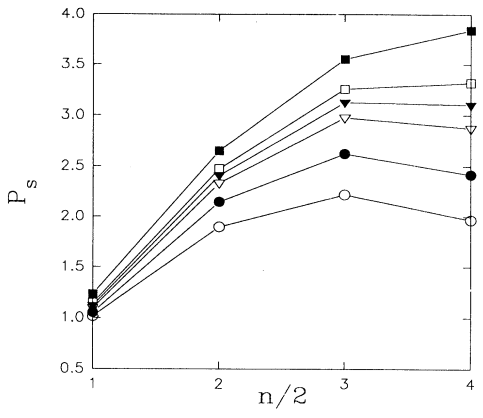

FIG. 2. The s-wave pair-field correlation P_s as a function of the number of electron pairs (n is the number of electrons) in the cluster for various on-site attractive interaction strength: $U/t=1.0$ (open circles), 3.0 (filled circles), 5.0 (open triangles), 6.0 (filled triangles), 7.0 (open squares), and 10.0 (filled squares). The value of s/t is fixed at 0.1.

K_3C_{60}, emphasizing that the fcc crystal structure will frustrate the charge-density wave state thus favoring the s-wave superconductivity. Our results show that whether the half-filled case is mostly favored for superconductivity also depends on the strength of the on-site attractive interaction. Although it has been estimated[2-6] that the on-site attraction in A_3C_{60} systems is only moderate, it is reasonable to expect that U/t is in the strong-interaction region and above the "critical" value, due to the small width of the conduction band,[10] thus the weak intermolecular hopping amplitude. Nevertheless, it is still of interest to investigate the possibility that with different doping and other physical conditions (e.g., pressure) the strength of the effective on-site attraction is below the "critical" value, thus superconductivity is favored in non-half-filled cases.

We also have investigated the dependence of the pair-field correlation P_s on the next-nearest-neighbor hopping amplitude s/t in this correlated electron system. Figure 3 shows the results for one to four pairs of electrons in the system with $U/$ 5.0 (results with other values of U/t are similar). It is seen that for a single pair of electrons in the system P_s is essentially s/t independent for up to $s/t=1.0$. For more electron pairs in the system, P_s becomes s/t dependent and a peak structure centered around $s/t=0.3$ develops with sharper structure for higher band fillings. This s/t dependence is the result of the competition between the kinetic energy effects and the many-body correlation in the system. It is worth noting that for given value of U/t (5.0 for results presented in Fig. 2) whether the half-filled case is the most favorable state for superconductivity depends on the value of s/t. For example, for $s/t=0.1$ (corresponding to the results shown in Fig. 2), P_s has a maximum value for three electron pairs in the system, i.e., away from half-filling; but with s/t between 0.13 and 0.44 the maximum value of P_s occurs at the half-filled case. Therefore, it is possible that the most favored superconducting state may be achieved at or away from the half-filled case in the same

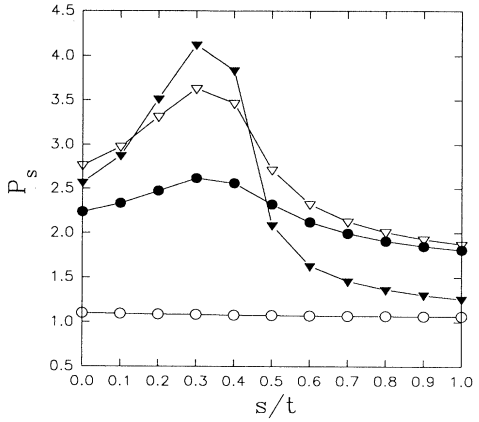

FIG. 3. The s-wave pair-field correlation P_s as a function of s/t for various number of electron pairs (n_p) in the cluster: $n_p=1$ (open circles), 2 (filled circles), 3 (open triangles), and 4 (filled triangles). The value of U/t is fixed at 5.0.

type of materials with different doping and other physical conditions (which in turn affects the ratio of s/t). It can also be seen that for large values of $s/t(>0.5$ for $U/t=5.0)$, s-wave pairing is always favored in lower-than-half-filled cases.

In the two-dimensional negative-U Hubbard model, it has been shown[9] that the $\mathbf{q}=(\pi,\pi)$ charge-density-wave and s-wave pair-field correlations have long-range order in the ground state, and $P_s=C(\pi,\pi)$ for the half-filled band. As the band filling decreases from half-filling, the charge-density-wave order is suppressed while the s-wave pair-field correlation is initially enhanced. In the three-dimensional fcc lattice, it is expected[2] that the charge-density-wave order will be frustrated, thus the s-wave pairing will be favored in the ground state. We have calculated the charge-density structure factor and indeed found that it is drastically suppressed from the value in an ideal charge-density wave state (for example, in a simple cubic lattice). Results of $C(\mathbf{q}=\mathbf{X})$ for various interaction strength but fixed s/t $(=0.1)$ are shown in Fig. 4; they follow the same trend. The value is initially suppressed and then enhanced at $n=6$ before being suppressed again for lower band fillings. For $\mathbf{q}=\mathbf{L}$ the situation is a little different. Figure 5(a) shows that $C(L_{1,2,4})$ is almost monotonically suppressed away from half-filling, while Fig. 5(b) shows that $C(L_3)$ is initially enhanced and then suppressed for lower band fillings. The two cases are different because with odd number of electrons in the system, the charge-density correlation is enhanced for a "preferred wave vector" (L_3 here) caused by the distribution of the unpaired electron. The detailed behavior of this distribution and its consequences is expected to depend on the choice of the cluster when its size is relatively small, as it is in the present work. Results from using larger clusters or other theoretical techniques are desirable to compare with those shown in this work.

The charge-density structure factor as a function of the hopping parameter s/t has been studied. As previously mentioned, for varying s/t the ground state of the system is stable for even number of electrons in the system and unstable, with symmetry crossovers, for odd number of electrons in the system. Therefore, we present the calculated results for the two cases separately.

Results for even number of electrons in the system are shown in Figs. 6(a) (for $\mathbf{q}=\mathbf{X}$) and 6(b) (for $\mathbf{q}=\mathbf{L}$). It is seen that $C(\mathbf{q})$ is s/t independent for one pair of elec-

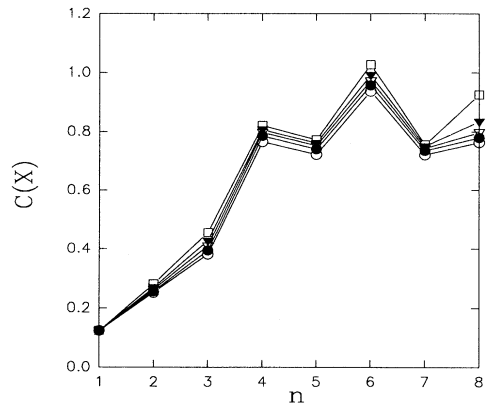

FIG. 4. The charge-density structure factor for the X points as a function of the number of electrons in the system for $s/t=0.1$ and $U/t=1.0$, 3.0, 5.0, 7.0, 10.0 (bottom to top curve).

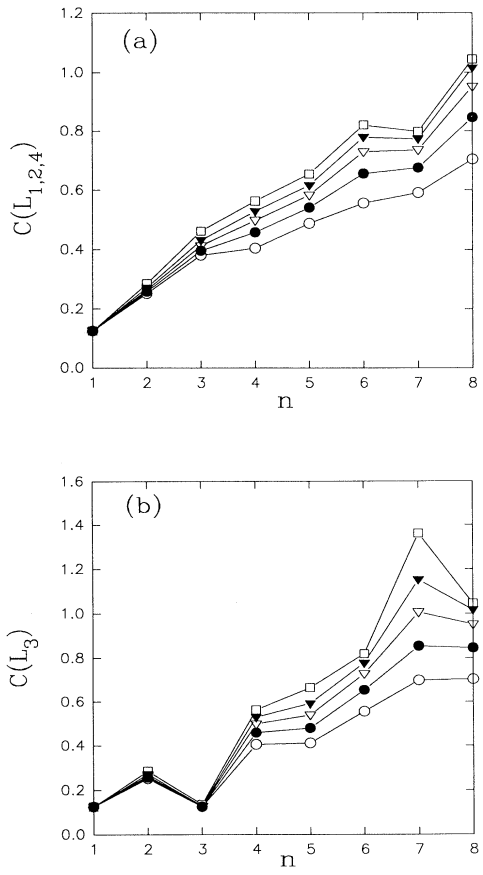

FIG. 5. Same as Fig. 3, but for (a) $L_{1,2,4}$ and (b) L_3.

trons in the system. For more electron pairs in the system, $C(\mathbf{q}=\mathbf{X})$ is a slowly decreasing function of s/t with the exception for the half-filled case where a peak develops around $s/t=0.3$ with a sharp decay to zero for larger s/t; meanwhile $C(\mathbf{q}=\mathbf{L})$ has a broad-peak structure with the peak position shifting from $s/t=0.4$ for two electron pairs to $s/t=0.5$ for three and four electron pairs in the system.

The behavior of $C(\mathbf{q})$ for odd number of electrons in the system is much more complex due to the ground-state symmetry crossover as s/t varies. In Figs. 7, 8, and 9, we present the results for $n=3$, 5, and 7, respectively, neglecting the trivial $n=1$ case. It can be seen in all three figures that the charge-density structure factor undergoes dramatic changes around $s/t=0.2$–0.4. It must be pointed out, however, that these changes are mainly caused by the ground-state symmetry crossover as a function of s/t. Again, it is highly desirable to further study this problem by using larger clusters or other theoretical techniques.

To summarize, we have presented the results of an exact-diagonalization study of the s-wave pair-field corre-

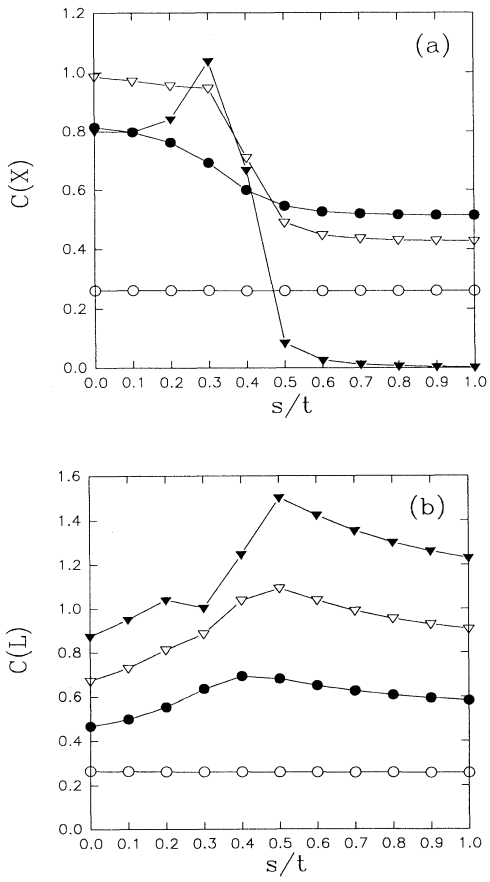

FIG. 6. The charge-density structure factor as a function of s/t for the (a) X points and (b) L points with various number of electron pairs (n_p) in the system: $n_p=1$ (open circles), 2 (filled circles), 3 (open triangles), and 4 (filled triangles). The value of U/t is fixed at 5.0.

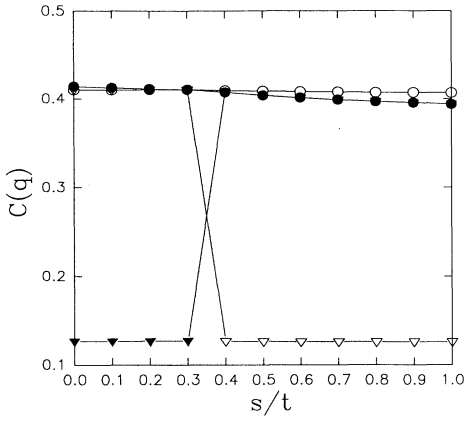

FIG. 7. The charge-density structure factor as a function of s/t for $n=3$ with $\mathbf{q}=X_{1,3}$ (open circles), $L_{1,2,4}$ (filled circles), X_2 (open triangles), and L_3 (filled triangles).

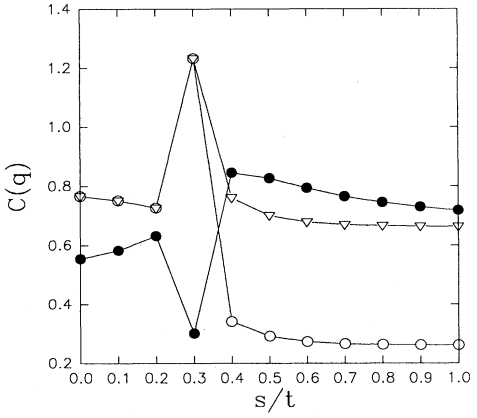

FIG. 8. Same as Fig. 7, but for $n=5$.

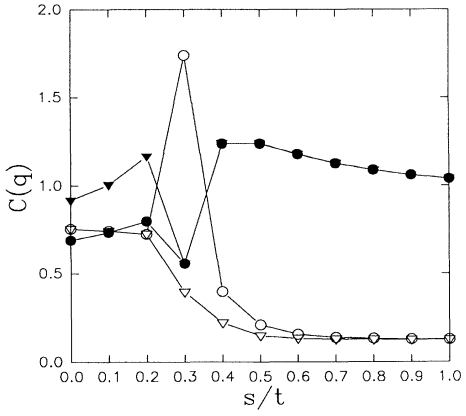

FIG. 9. Same as Fig. 7, but for $n=7$.

lation and charge-density structure factor in the three-dimensional negative-U Hubbard model on the fcc lattice. Their behavior as the function of the on-site attractive interaction strength, the second-nearest-neighbor hopping amplitude (all relative to the nearest-neighbor hopping amplitude), and the band filling has been systematically studied. It is found that s-wave superconductivity may be favored for the half-filled band or for doped, less-than-half-filled band, depending on the interaction strength and the second-nearest-neighbor hopping amplitude. The charge-density structure factor is drastically suppressed from the result for an ideal charge-density wave state (for example, in a simple cubic lattice). The value is initially enhanced for the three X points and one of the four L points sampled in the Brillouin zone when doped away from half-filling and then suppressed. For the other three L points, it is almost monotonically suppressed away from half-filling. As a function of the second-nearest-neighbor hopping amplitude, the charge-density structure factor behaves quite differently for even and odd number of electrons in the system, due to the contribution from the unpaired electron in the latter case. Implications of the calculated results for properties of alkali intercalated C_{60} solids have been discussed. It is suggested that under different doping and other physical conditions (e.g., pressure) the effective on-site attractive interaction strength as well as the second-nearest-neighbor hopping amplitude may fall into different regions studied in this work, yielding different superconducting and charge-density properties.

We recognize that the size of the cluster used in the present work is rather small and the finite-size effect is of some concern. However, the next smallest fcc cluster contains 16 sites and, in the half-filled case, yields 4^{16} many-body states. The task of exact diagonalizing such Hamiltonian matrices, even after the full use of symmetry reduction, certainly exceeds the capability of presently employed technique. Other theoretical methods, such as the Monte Carlo simulation, may be useful in providing further insight on this problem. The finite-size scaling behavior of the properties studied here remains an open question at this time.

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