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Chemical potential and order parameter of extended Hubbard model with strong intra-atomic attraction

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We provide here the numerical solutions for the quasiparticle chemical potential and for the order parameters of the singlet-superconducting, the charge-ordered, and the mixed phases in an extended Hubbard model with strong intra-atomic attraction, based on the analysis of our previous paper.

The conventional Hubbard model[1] has been modified along various directions. Due to the coupling between electrons and intramolecular vibrations or electronic excited states,[2–5] or between electrons in different bands in a chemical complex,[6] many authors have considered the Hubbard model with intra-atomic attractive interaction. A detail reference on such work was given in our recent paper.[7] After the interpretation of Anderson,[8] Street and Mott,[9] and Adler and Yoffa[10] on the electrical, magnetic, and optical properties of amorphous materials in term of the intra-atomic attraction, the Hubbard Hamiltonian with attractive intra-atomic correlation has emerged as a model not too unrealistic. Very lately Baraff *et al.*[11] studied the electron paramagnetic resonance[12] and the deep-level transient spectroscopy[13] with the conclusion that the vacancy in silicon is an attractive-correlation center.

Recently we have derived the phase diagram of the extended Hubbard model with intra-atomic attraction[7] (referred to as I). In that paper we could not obtain the analytical solutions for the order parameters and the chemical potential, even though these quantities are essential for the understanding of the physical properties. In this short paper, we will provide the numerical results and so make the investigation complete.

We first briefly summarize the analysis in I. Consider an extended Hubbard Hamiltonian

$$H=\sum_{ij\sigma}{}'t_{ij}c_{i\sigma}^{\dagger}c_{j\sigma}-\tfrac{1}{2}|U|\sum_{i\sigma}n_{i\sigma}n_{i-\sigma}+\frac{1}{2}\sum_{ij\sigma\sigma'}{}'W_{ij}n_{i\sigma}n_{j\sigma'}+\sum_{i\sigma}(E_i-\mu)n_{i\sigma}\ , \tag{1}$$

with an intra-atomic attraction energy $-|U|$ and a spin-independent interatomic interaction W_{ij}. Since the Hartree-band theory and the intra-atomic attraction do not yield any magnetic ordering, the ground state of the Hamiltonian must be nonmagnetic. In particular, we have the nonferromagnetic condition

$$\sum_i\frac{\langle\sigma_i^{\alpha}\rangle}{N}=0\ , \tag{2}$$

where σ_i^{α} is the $\alpha=+,-,z$ component of the spin operator $\vec{\sigma}_i$ for an electron at the lattice site $\vec{R}_i$, and N is the total number of sites.

We assume two interpenetrating sublattices A and B, and define a $\vec{Q}$ such that $\exp(i\vec{Q}\cdot\vec{R})=-1$ for any translation $\vec{R}$ which transforms one sublattice into the other. Let us construct a canonical transformation

$$\begin{aligned}c_{i\downarrow}^{\dagger}&=\exp(i\vec{Q}\cdot\vec{R}_i)b_{i\downarrow},\quad c_{i\uparrow}^{\dagger}=b_{i\uparrow}^{\dagger}\ ,\\ c_{i\downarrow}&=\exp(-i\vec{Q}\cdot\vec{R}_i)b_{i\downarrow}^{\dagger},\quad c_{i\uparrow}=b_{i\uparrow}\ ,\end{aligned} \tag{3}$$

and apply it to the charge operators to obtain

$$\begin{aligned}\rho_i^{+}&=(\rho_i^{-})^{\dagger}=c_{i\uparrow}^{\dagger}c_{i\downarrow}^{\dagger}=\exp(i\vec{Q}\cdot\vec{R}_i)\overline{\sigma}_i^{+}\ ,\\ \rho_i^{z}&=(n_{i\uparrow}+n_{i\downarrow}-1)/2=\overline{\sigma}_i^{z}\ ,\end{aligned} \tag{4}$$

where

$$\overline{\sigma}_i^{+}=b_{i\uparrow}^{\dagger}b_{i\downarrow}\ ,\quad \overline{\sigma}_i^{z}=(\overline{n}_{i\uparrow}-\overline{n}_{i\downarrow})/2\ , \tag{5}$$

with

$$\overline{n}_{i\sigma}=b_{i\sigma}^{\dagger}b_{i\sigma}\ . \tag{6}$$

It is easy to show that ρ_i^{+}, ρ_i^{-}, and ρ_i^{z} obey the same commutation rules as the spin operators. Therefore, within a phase factor $\exp(\pm i\vec{Q}\cdot\vec{R}_i)$ the spin operators $\overline{\sigma}_i^{\alpha}$ in the new representation play the roles of the charge operators ρ_i^{α} in the old representation, and vice versa.

We will retain only the nearest-neighbor interaction W and assume a constant one-site energy $E_i=E$. Then the canonical transformation transforms (1) and (2) into

$$H=\sum_{ij\sigma}{}' t_{ij}b_{i\sigma}^{\dagger}b_{j\sigma}+\tfrac{1}{2}|U|\sum_{i\sigma}\bar{n}_{i\sigma}\bar{n}_{i-\sigma}+2W\sum_{ij}\bar{\sigma}_i^z\bar{\sigma}_j^z+2\sum_i(E-\bar{\mu})\bar{\sigma}_i^z-\tfrac{1}{2}|U|\sum_{i\sigma}\bar{n}_{i\sigma}-(\bar{\mu}-\tfrac{1}{2}|U|+ZW/2)N\ , \tag{7}$$

$$\frac{2}{N}\sum_i\langle\bar{\sigma}_i^z\rangle=n-1\ , \tag{8}$$

$$\frac{1}{N}\sum_{i\sigma}\langle\bar{n}_{i\sigma}\rangle=1\ , \tag{9}$$

where

$$\bar{\mu}=\mu+|U|/2-ZW \tag{10}$$

and Z is the coordination number. Therefore, the extended Hubbard Hamiltonian of arbitrary electron density n with intra-atomic attraction and spin-independent interatomic interaction has been transformed into an extended Hubbard Hamiltonian of one electron per atom with intra-atomic repulsion and Ising-type interatomic exchange interaction in the effective external magnetic field $(E-\bar{\mu})$ along the z direction. The magnetization of the transformed system along the z direction has a fixed value given by (8).

From Eqs. (3)–(5) it is obvious that the magnetic order in the xy plane in the transformed Hamiltonian corresponds to the singlet-superconducting (SS) order in the original Hamiltonian. The nonuniform magnetic order along the z axis in the transformed Hamiltonian corresponds to the charge order (CO) in the original Hamiltonian. The intermediate state between these two magnetic orderings in the transformed Hamiltonian corresponds to the mixed (M) phase in the original Hamiltonian. Finally, the para- or the ferromagnetic state in the transformed Hamiltonian corresponds to the nonordered (NO) phase in the original Hamiltonian. We then only need to solve for the magnetic phase diagram of (7) in order to derive the phase diagram of (1).

Since the transformed Hamiltonian (7) describes a system of exactly one quasiparticle per atom, the degenerate perturbation theory can be applied at the strong coupling limit $|U|\gg t_{ij}$. For simplicity but without losing generality, we keep only the nearest-neighbor hopping t. An effective Hamiltonian to the second order in $|t/U|$ can be easily derived, and after transforming to the $c_{i\sigma}$-operator representation via (3) has the form

$$H=-J\sum_{ij}{}'(\rho_i^x\rho_j^x+\rho_i^y\rho_j^y)+K\sum_{ij}{}'\rho_i^z\rho_j^z-B\sum_i(2\rho_i^z+1)\ , \tag{11}$$

where $J=2t^2/|U|$, $K=J+2W$, and $B=\bar{\mu}-E=\mu+|U|/2-ZW-E$. This effective Hamiltonian is subject to the condition corresponding to (8) as

$$\frac{1}{N}\sum_i\langle\rho_i^z\rangle=\frac{(n-1)}{2}\ . \tag{12}$$

We should mention that in deriving (11), we have dropped some constant-energy terms. ρ_i^α can be treated as pseudospins because they obey the same commutation rules as the spin operators. Consequently, we call (11) the effective pseudospin Hamiltonian.

This effective pseudospin Hamiltonian is solved with the mean-field approximation following the Bogoliubov variational principle.[14] The reader is referred to Sec. III of I for details, while here we only present the final results obtained by solving numerically the coupled Eqs. (3.9), (3.10a), (3.10b), and (3.11) of I. Since the direction of pseudospin in the xy plane is not specified, it is sufficient to consider the possible magnetic ordering in the xz plane. If we define $X_A=\langle\rho_A^x\rangle$, $X_B=\langle\rho_B^x\rangle$, $Z_A=\langle\rho_A^z\rangle$, and $Z_B=\langle\rho_B^z\rangle$ for the two sublattices A and B, then the order parameters are X_A+X_B, X_A-X_B, and Z_A-Z_B which specify the various phases as follow. NO phase: $X_A+X_B=0$, $X_A-X_B=0$, $Z_A-Z_B=0$. SS phase: $X_A+X_B\neq0$, $X_A-X_B=0$, $Z_A-Z_B=0$. CO phase: $X_A+X_B=0$, $X_A-X_B=0$, $Z_A-Z_B\neq0$. M phase: $X_A+X_B\neq0$, $X_A-X_B\neq0$, $Z_A-Z_B\neq0$.

While solving the coupled equations numerically, we found four possible cases: (1) Only the NO solution exists; (2) either the NO and the SS solutions exist, or the NO and the CO solutions exist; (3) either the NO, the SS, and the M solutions exist, or the NO, the SS, and the CO solutions exist; and (4) for $W=0$ and $n=1$ only, all the NO, SS, M, and CO solutions exist. When there are solutions for more than one phase, we compute the free energies for different phases in order to determine which one is stable. It is discovered that as long as the CO (or the M) phase has solution, it is always the stable one. However, for $W=0$ and $n=1$, all the three SS, M, and CO phases are degenerate. We should mention that the so-obtained phase boundary agrees with the one derived in I via the Landau expansion.

We have proved in I that for $W<0$ as well as for $W=0$ and $n\neq1$, the only transition is from the SS phase to the NO phase. It is also proved there that the SS→NO transition temperature does not depend on the value of W. Hence, the SS order parameter X_A+X_B shown in Fig. 1 (in all figures $\tau=k_BT/ZJ$) is for any value of K/J. Since at $W=0$ and $n=1$ the three SS, M, and CO phases are degenerate, the curve for $n=1$ also represents the CO order parameter Z_A-Z_B.

For $K/J>0$, the CO and the M phases begin to appear in the phase diagram. In Fig. 2 we show the order parameters Z_A-Z_B (heavy solid curves), X_A+X_B (heavy dashed curve), and X_B-X_A (heavy

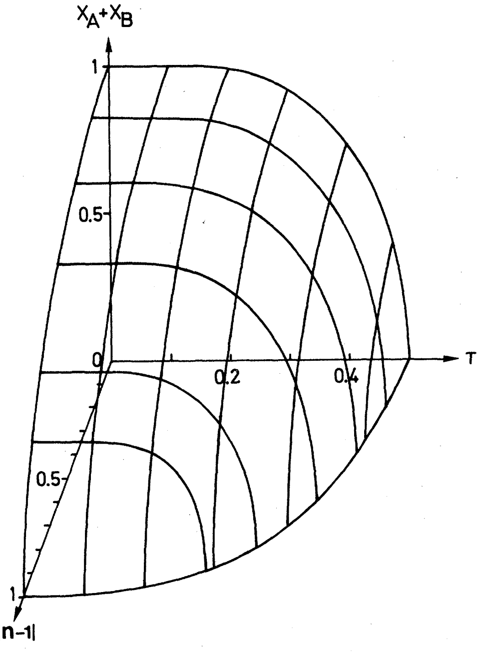

FIG. 1. Order parameter of the pure SS phase for any value of K/J.

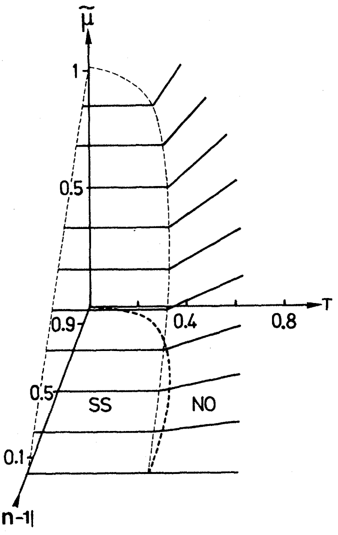

FIG. 3. Normalized quasiparticle chemical potential for $K/J = 1$.

dotted curves). Projecting on the plane of T and $|n-1|$, we see the pure CO phase existing between the thin solid curve and the thin dashed curve, the M phase existing between the thin dashed curve and the thin dotted curve, and the pure SS phase existing below the thin dotted curve. In the pure SS phase region, we did not plot the SS order parameter $X_A + X_B$ since it is the same as that given in Fig. 1. The characteristic features of the order parameters clearly demonstrate that all transitions are second order.

Equation (11) is essentially an effective Hamiltonian for pseudospins in a magnetic field $B = \tilde{\mu} - E = \mu + |U|/2 - ZW - E$ which should be determined self-consistently by the condition Eq. (12). Hence,

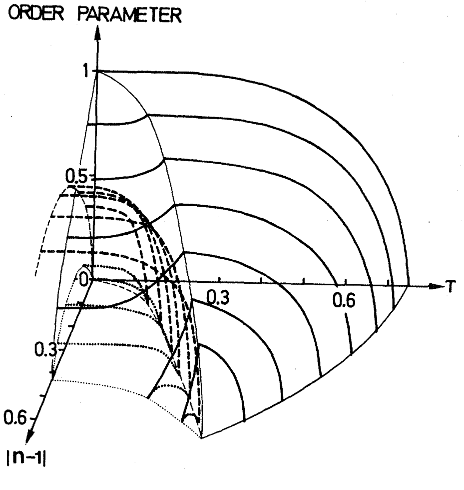

FIG. 2. Order parameters for $K/J = 1.5$: heavy solid curves for $Z_A - Z_B$; heavy dashed curves for $X_A + X_B$; and heavy dotted curves for $X_B - X_A$.

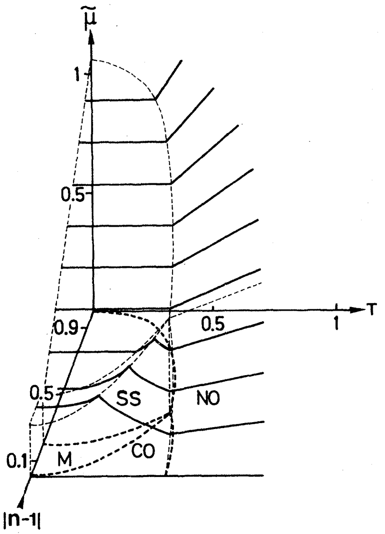

FIG. 4. Normalized quasiparticle chemical potential for $K/J = 1.1$.

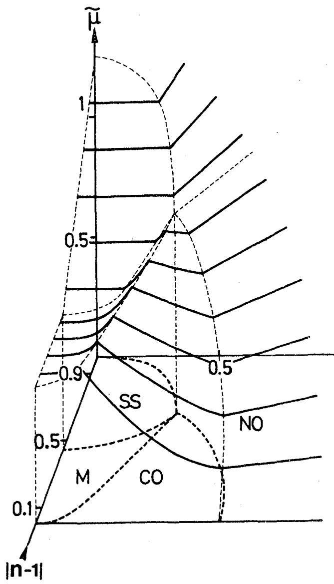

FIG. 5. Normalized quasiparticle chemical potential for $K/J = 1.5$.

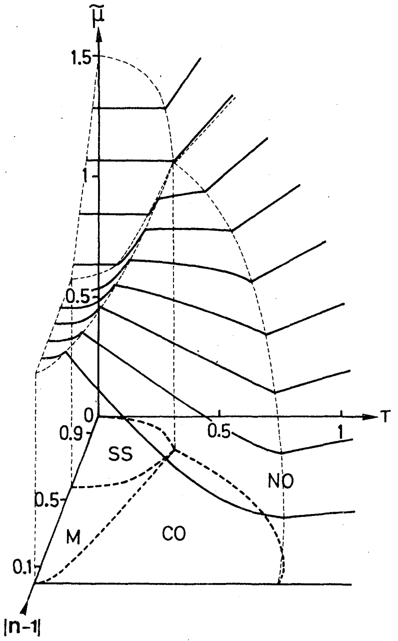

FIG. 6. Normalized quasiparticle chemical potential for $K/J = 2$.

the chemical potential can be computed. The normalized chemical potentials $\tilde{\mu} = (\bar{\mu} - E)/ZJ$ are given as heavy solid curves in Fig. 3 for $K/J = 1$ ($W = 0$), in Fig. 4 for $K/J = 1.1$, in Fig. 5 for $K/J = 1.5$, and in Fig. 6 for $K/J = 2$. Since the stable phase has the largest chemical potential, we can also determine the phase diagram from such analysis of the $\tilde{\mu}$. The so-derived phase boundaries, shown as heavy dashed curves in the plane of T and $|n-1|$, agree exactly with those given in I.

We would like to emphasize a few points concerning to the chemical potential. All the $\tilde{\mu}$ curves are continuous as should be for systems exhibiting second-order phase transition. For the pure SS phase, $\tilde{\mu}$ is temperature independent and linear in $|n-1|$. For given value of n, chemical potentials for different phases meet at the phase boundary in the form of a downward cusp. However, it is not so along the CO-M phase boundary where the cusp points upward. This is because the solution for the CO phase and the solution for the M phase do not coexist, and so the upward cusp does not violate the rule of largest chemical potential for stable phase.

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