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任意電子密度兩原子哈伯模式的費米能階及磁感性
Chemical Potential and Magnetic Susceptibility of a Two-Site Hubbard Hamiltonian with Arbitrary Electron Density

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ABSTRACT — The eigenvalue problem of a two-site Hubbard Hamiltonian, which contains both the correlation term U and the hopping term t, is solved exactly and the grand partition function of the system is obtained. The chemical potential as a function of temperature for a given number of electrons per site n is numerically calculated for several values of n. The chemical potential as a function of n at absolute zero is shown to have three discontinuities at $n=\frac{1}{2}$, 1, and $\frac{3}{2}$. The magnetic susceptibility per site is shown to be of the Curie-Weiss form for the temperature range $t \ll kT \ll U$. Both the Curie constant and the Weiss temperature are proportional to n (if $0<n\leq 1$) or to (2-n) (if $1<n\leq 2$). The Curie constant is independent of any parameter of the model and would predict n=0.27 for N-methyl-phenazinium-tetracyanoquinodimethane (NMP-TCNQ) which is not close to the experimental value of n=0.9.

I. Introduction

The narrow-band Hubbard Hamiltonian [1] has been widely used as a theoretical model for the quasi-one-dimensional organic crystal tetracyanoquinodimethane (TCNQ), especially for N-methylphenazinium-TCNQ [2] (NMP-TCNQ). But there are some discrepancies between the theoretical predictions and the experimental results. Notably the theory can not explain the smallness of the Curie constant of the magnetic susceptibility [3] of NMP-TCNQ reported in Ref. 2. There have been some attempts [4,5] by adding a nearest-neighbor Coulomb interaction term to the original Hubbard Hamiltonian in order to bring the theoretical prediction closer to the experimental data. But the results were negative.

It should be noted that almost all the previous calculations of the thermodynamic properties of the model have been limited to the half-filled-band case (one electron per molecule). But the experimental evidence and the theoretical calculations [6,7] of the thermoelectric power indicate that the number of electrons per molecule is less than one for many TCNQ salts. For example, the salt NMP-TCNQ may have a filling factor of 0.9 electrons per molecule. It is therefore important and desirable to do some thermodynamic calculations for the non-half-filled case [8]. It is the purpose of the present paper to do this kind of calculations by using a simple and soluble model. We restrict ourself to the calculations of the chemical potential and the magnetic susceptibility of the system.

For the half-filled case, the chemical potential of the Hubbard Hamiltonian is known to be a constant and independent of temperature. But for the non-half-filled case, the chemical potential is a complicated function of temperature which should be obtained before any thermodynamic calculations can be performed. Therefore for the non-half-filler case, the important task is to find the chemical potential as a function of temperature for a given electron density. Yoffa and Adler [9] have done this calculation in the atomic limit ($t=0$ in Eq. (1) below). In this paper we want to extend the analysis to the case of nonzero transfer integral t. We use a soluble two-site model [10] to achieve our purpose. Once the chemical potential is obtained as a function of temperature, the magnetic susceptibility can be easily calculated. We find that, for a certain range of temperatures, the magnetic susceptibility is of the Curie-Weiss form with both the Curie constant and the Weiss temperature as functions of the number of electrons per site.

The procedure to evaluate the chemical potential and the magnetic susceptibility is a standard one. We first solve the eigenvalue problem of the two-site model and then obtain the grand partition function of the system. From the grand partition function we easily obtain the chemical potential and the magnetic susceptibility of the system which are discussed in Sec. II and Sec. III respectively.

II. Chemical Potential

The Hubbard Hamiltonian is usually written in the form

$$H=t\sum_{<ij>}\sum_{\sigma} C^{+}_{i\sigma} C_{j\sigma} + U\sum_{i} n_{i\uparrow} n_{i\downarrow} , \tag{1}$$

where $<ij>$ indicates sum over nearest neighbors only; $C^{+}_{i\sigma}$ creates an electron in the lattice site i with spin σ; and $n_{i\sigma}=C^{+}_{i\sigma}C_{i\sigma}$. U is the intra-atomic Coulomb interaction (correlation energy) and t is the transfer integral (hopping energy). For the two-site model we consider two particular neighboring sites and allow the number of electrons to vary in the system by introducing the chemical potential μ in the Hamiltonian. Therefore in the presence of an external uniform magnetic field B, the Hamiltonian of a two-site model is

$$H_{t.s.}=t\sum_{\sigma}(C^{+}_{1\sigma}C_{2\sigma}+C^{+}_{2\sigma}C_{1\sigma})+U\sum_{i=1}^{2} n_{i\uparrow}n_{i\downarrow}$$

$$-\gamma B\sum_{i=1}^{2}(n_{i\uparrow}-n_{i\downarrow})-\mu\sum_{i=1}^{2}\sum_{\sigma} n_{i\sigma} , \tag{2}$$

where γ is the magnetic moment of an electron. The eigenvalue problem of Eq. (2) can be solved exactly, and there are 16 non-degenerate eigenvalues: $0, \pm t \pm \gamma B-\mu$, -2μ, $\pm 2\gamma B-2\mu$, $U-2\mu$, $2t\lambda_{\pm}-2\mu$, $U\pm t\pm\gamma\beta-3\mu$, and $2U-4\mu$, where $\lambda_{\pm}=\frac{U}{4t}\pm[(U/4t)^2$

$+1]^{\frac{1}{2}}$.

The grand partition function is defined as

$$Z \equiv \sum_{s} e^{-\beta\varepsilon_s}$$

$$=1+4e^{\beta\mu}[1+e^{\beta(2\mu-U)}]\cosh(\beta\gamma B)\cosh\beta t$$

$$+e^{2\beta\mu}[1+2\cosh(2\beta\gamma B)+e^{-\beta U}+e^{-2\beta t\lambda_+}+e^{-2\beta t\lambda_-}] \qquad (3)$$

$$+e^{2\beta(2\mu-U)} ,$$

where $\beta=1/kT$, and k is the Boltzmann's constant and T the temperature. The chemical potential μ is determined by fixing the number of electrons per site n which is given by

$$n=\frac{1}{2}\frac{1}{\beta}\left(\frac{\partial \ln Z}{\partial\mu}\right)_{\beta,\,B=0} \qquad (4)$$

$$=2e^{\beta\mu}\frac{e^{3\beta\mu}\,e^{-2\beta U}+3e^{2\beta\mu}e^{-\beta U}\cosh\beta t+Ae^{\beta\mu}+\cosh\beta t}{e^{4\beta\mu}e^{-2\beta U}+4e^{3\beta\mu}e^{-\beta U}\cosh\beta t+2Ae^{2\beta\mu}+4e^{\beta\mu}\cosh\beta t+1}$$

where $A=\frac{1}{2}\,[3+e^{-\beta U}+e^{-2\beta t\lambda_+}+e^{-2\beta t\lambda_-}]$.

Because we need the chemical potential for B=0 only, we have set B=0 in(4). Since n is twice the fractional band occupancy f(i.e. n=2f), we can rewrite (4) as

$$e^{4\beta\mu}e^{-2\beta U}(1-f)+e^{3\beta\mu}e^{-\beta U}(3-4f)\cosh\beta t$$

$$+e^{2\beta\mu}A(1-2f)+e^{\beta\mu}(1-4f)\cosh\beta t-f=0 \ . \qquad (5)$$

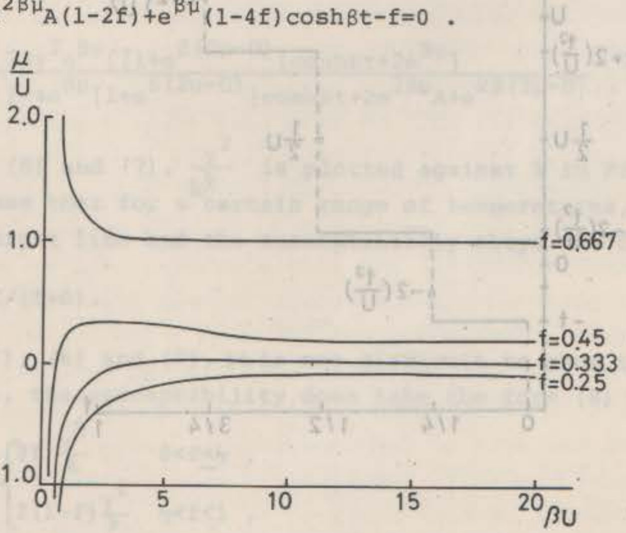

Fig.1 Chemical potential as a function of temperature (μ/U vs. βU) for f=0.25, 0.333, 0.45 and 0.667; U/t=8.

Equation (5) determines μ as a function of T for a given f, which is plotted in Fig. 1 for four different values of f. Here we have limited ourself in the narrow-bandwidth limit $t/U \ll 1$. It is easily seen that μ approaches slowly to a constant in the low-temperature region $\beta U \gg 1$ for a given f. As has been pointed out by Yoffa and Adler [9] that for f=1/3 and 2/3, μ approaches to a constant with a relatively small βU. For other values of f, the approach to a constant is much slower. In the zero-temperature limit $(\rho \to \infty)$, we find that

$$\mu = \begin{cases} -t & 0<f<1/4\ , \\ -2(\frac{t^2}{U}) & f=1/4\ , \\ t-4(\frac{t^2}{U}) & 1/4<f<1/2, \\ 1/2\ U & f=1/2 \\ U-t+4(\frac{t^2}{U}) & 1/2<f<3/4, \\ U+2(\frac{t^2}{U}) & f=3/4, \\ U+t & 3/4<f<1 \end{cases} \tag{6}$$

Equation (6) is plotted in Fig. 2.

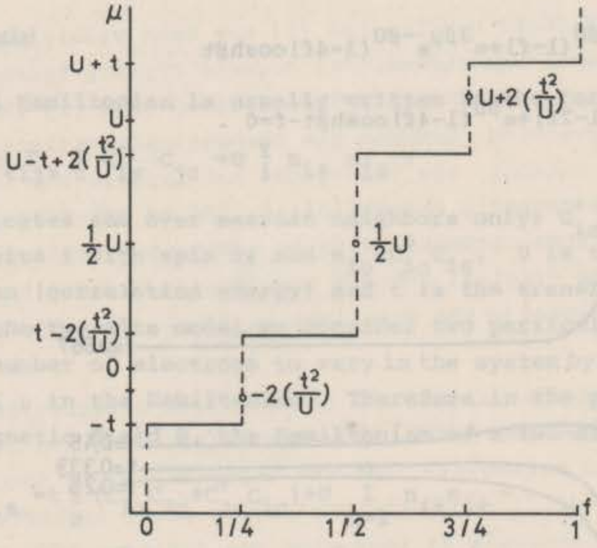

Fig. 2. Chemical potential as a function of fractional filling of band at T=0.

There are three discontinuities at $f=\frac{1}{4}$, $\frac{1}{2}$, and 3/4. At higher temperatures the discontinuities disappear but, in the low-temperature limit $\beta U >> 1$, the change of μ/U with respect to f is still large in the vicinity of $f=\frac{1}{2}$ (Fig. 3).

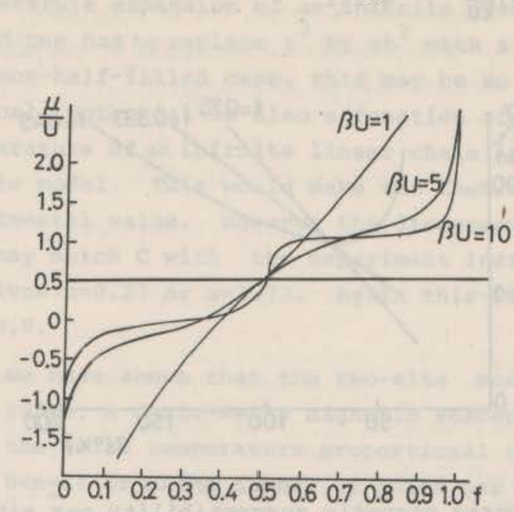

Fig. 3. Chemical potential as a function of fractional filling of band at three different temperatures $\beta U=1$, 5, and 10; $U/t=8$.

III. Magnetic Susceptibility

The magnetic susceptibility per site is given by

$$\chi=\frac{1}{2\beta}\left(\frac{\partial^2 \ln Z}{\partial B^2}\right)_{\mu,\,B=0}$$

$$=\frac{2\beta\gamma^2 e^{\beta\mu}\{[1+e^{\beta(2\mu-U)}]\cosh\beta t+2e^{\beta\mu}\}}{1+4e^{\beta\mu}[1+e^{\beta(2\mu-U)}]\cosh\beta t+2e^{2\beta\mu}A+e^{2\beta(2\mu-U)}} \,. \tag{7}$$

Combining Eqs. (5) and (7), $\frac{\gamma^2}{k\chi}$ is plotted against T in Fi. 4 for f=0.25, 0.33 and 0.45. We see that for a certain range of temperatures, the plot is approximately a straight line and the susceptibility obeys the Curie-Weiss Law

$$\chi=C/(T+\Theta) \,. \tag{8}$$

In fact from (5), (6) and (7), it is not difficult to show that, in the limits $\beta U>>1$ and $\beta t<<1$, the susceptibility does take the form (8) with

$$C=\begin{cases} 2f\,\frac{\gamma^2}{k} & 0<f\leq\frac{1}{2}\,, \\ 2(1-f)\frac{\gamma^2}{k} & \frac{1}{2}<f\leq 1\,, \end{cases} \tag{9}$$

and

$$\Theta = \begin{cases} 2f\frac{t^2}{kU} & 0<f\leq\frac{1}{2} \\ 2(1-f)\frac{t^2}{kU} & \frac{1}{2}<f\leq 1 \end{cases} \qquad (10)$$

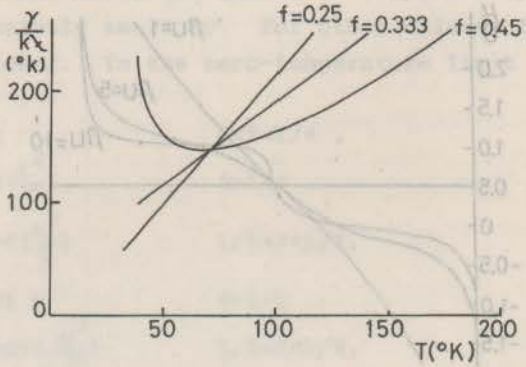

Fig. 4. Inverse magnetic susceptibility per site vs. temperature for f=0.25, 0.333 and 0.45; U=0.17 eV and t=0.021 eV.

Therefore both the Curie constant C and the Weiss temperature Θ depend on the number of electrons per site n=2f. For f<½, the band is less than half-filled, both C and Θ are proportional to the electron density n. While for f>½ , the band is more than half-filled, both constants are proportional to the hole density (2-n).

IV. Discussion

In order to compare the theory with the experiment, we outline the experimental results of Ref. 2 for NMP-TCNQ: The magnetic susceptibility obeys the Curie-Weiss law (8) in the temperature range between 50 and 200 K, $C=1.7\times10^{-25}$ K, Θ=61K, and U=0.17eV, t=0.021 eV. We have used these experimental values of U and t in the plotting of Fig. 4. Although in the temperature range between 50 and 200 K, the condition βt<<1 is not satisfied, Fig. 4 suggests that the Curie-Weiss law is still a good approximation in this temperature range. The constants C and Θ deviate from (9) and (10) slightly. But we can take (9) and (10) as our starting point for the comparison between the theory and the experiment. It is apparent that we can not fit both C and Θ with a single value of f. If we take the experimental value of n=0.9, we have $C=5.6\times10^{-25}$ K and Θ=27 K. We see that C is more than three times of the experimental value, while Θ is only about one half of the experimental value. The discrepancies may be due to the use of a two-site model rather than an infinite linear chain. But since C is independent of both U and t, it seems that the number of sites is not an important factor for the determination of C. While Θ is both U and t dependent, we may expect the value of Θ to depend on the number of sites included in the model. In fact, it is easy to show [11] that for the half-filled case, the thermodynamic properties of a two-site model is exactly the same as those of high-temperature expansion of an infinite system [12] up the second order in t, provided one has to replace t^2 by zt^2 with z the number of nearest neighbors. For the non-half-filled case, this may be no longer true, since in this case the chemical potential is also a function of t. But we may expect that the Weiss temperature of an infinite linear chain is about twice as large as that of a two-site model. This would make the theoretical prediction of θ close to the experimental value. However the disagreement in C remains. On the other hand, we may match C with the experiment instead of matching n. In this case Eq. (9) gives $n=0.27$ or $n=1.73$. Again this is quite different from the known value of 0.9.

In conclusion, we have shown that the two-site model does predict, in a certain temperature range, a Curie-Weiss magnetic susceptibility with both the Curie constant and the Weiss temperature proportional to the number of electrons per site n (if $0<n\leq 1$) or to the number of holes per site $(2-n)$ (if$<1<n\leq 2$). The Curie constant is independent of any parameter of the model and would predict a value of $n=0.27$ for NMP-TCNQ. It is apparent that a better theory is needed for the interpretation of the smallness of the Curie constant. Since the Coulomb interaction between the electrons in the neighboring sites may be important in the TCNQ salts, it is natural to extend the two-site model to include that term. The results of this investigation will be reported elsewhere.

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