

Magnetic susceptibility of a two-site extended Hubbard Hamiltonian with arbitrary electron density

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The eigenvalue problem of a two-site extended Hubbard Hamiltonian, which contains the intra-atomic repulsive term U , the nearest-neighbor repulsive term V , and the hopping term t is solved exactly and the grand partition function is obtained. The magnetic susceptibility per site is calculated for arbitrary electron density $n \leq 2$. For the half-filled case ($n = 1$), it is found that the magnetic susceptibility approaches zero exponentially as the temperature goes to zero when V is comparable or larger than U . For the non-half-filled case ($n \neq 1$), the magnetic susceptibility is of Curie form for $kT \ll t$, and is of Curie-Weiss form for $U \gg kT \gg t$ when $|U - V| \ll 4t$. The corresponding Curie constants are considerably smaller than those of the predictions of a simple Hubbard Hamiltonian ($V = 0$). This may suggest that both V and t are important in the understanding of the smallness of the Curie constant in the magnetic susceptibility of the organic salt NMP-TCNQ (N-methylphenazinium-tetracyanoquinodimethanide).

I. INTRODUCTION

In a previous paper¹ we have used a two-site model to study the thermodynamic properties of a Hubbard linear chain with arbitrary electron density. A two-site model is used because, when the number of electrons per site n is not equal to one, the chemical potential (of a Hubbard model) as a function of temperature is a complicated problem² and can be solved for simple models only. The purpose of Ref. 1 is to explain the experimental measurement of the magnetic susceptibility of the organic salt NMP-TCNQ (N-methylphenazinium-tetracyanoquinodimethanide) reported by Epstein *et al.*³ The magnetic susceptibility is of the Curie-Weiss form for some temperature range that can be explained by the Hubbard model.⁴ But the Curie constant is much smaller than the theoretical prediction of the widely used half-filled-band model.⁵ Since NMP-TCNQ salt is believed to have 0.9 electrons per molecule, extension of the analysis to the non-half-filled case is important and desirable.⁶ This is what we have done in Ref. 1.

Unfortunately, the two-site model cannot explain the smallness of the Curie constant C either, even when $n = 0.9$ is used. Modification of the model is needed if one tries to give a better theoretical explanation. Since the nearest-neighbor repulsive interaction V is important in some TCNQ salts,⁷ we extend the two-site model to include this term in this paper. This is the so-called extended Hubbard model. Our purpose is to find how the interaction V can affect the magnitude of C for any given electron density.

We find that when V is small in comparison with the intramolecular repulsive interaction U , there is essentially no change in the value of C for all

$n \leq 2$. But when V is comparable to U , a big change occurs and C is reduced to a smaller value for some range of n . The big change of the magnetic susceptibility at low temperatures is due to the fact that the ground states are different for the two cases $V < U$ and $V > U$ for $\frac{1}{2} < n < \frac{3}{2}$. The difference is most easily seen for the special case when $n = 1$ and the transfer integral $t = 0$ in a long linear chain [see Eq. (1) below]. For $V < \frac{1}{2}U$ the ground state consists of one electron at each site,⁸ while for $V > \frac{1}{2}U$ the ground state consists of paired electrons at the alternating sites. The magnetic susceptibility of this special case has been studied by Beni and Pincus⁹ and by Tu and Kaplan.¹⁰ They found that for $V < \frac{1}{2}U$ the magnetic susceptibility is almost the same as that of the case $V = 0$, while for $V > \frac{1}{2}U$ the magnetic susceptibility approaches zero exponentially as the temperature goes to zero, because of complete cancellation of the magnetic moments of the paired electrons. The situation is somewhat different for the non-half-filled case. Because there is only partial cancellation of the magnetic moments, the magnetic susceptibility retains a Curie form at very low temperatures with a much smaller Curie constant. We also find that the nonzero transfer integral t has some effects on the reduction of the Curie constant.

Physically the two-site Hubbard model is more appropriate a model for dimerized salts, in which the electron-transfer amplitude is larger between molecules within a dimer and smaller between molecules on adjacent dimers. Therefore it is natural for us to apply our model to dimerized salts. However, none of the presently available susceptibility data of dimerized salts seems to be of our interest: Li-TCNQ (see Ref. 11) can be described well by a dimerized tight-band model

($U = V = 0$); and diethylthiocarbocyanine-TCNQ (DTC-TCNQ) (see Ref. 12) indicates one electron per molecule which has been studied by some authors.^{13,14} Beni *et al.*,¹⁵ based on a comparison between theory and experiment of thermopower, predict that the dimerized triethylammonium-(TCNQ)₂ [TEA-(TCNQ)₂] (see Ref. 16) should have a nearly quarter-filled band, i.e., $n = \frac{1}{2}$, which is not easy to be measured directly. A comparison between the susceptibility data and our results would provide another means for determining n . Unfortunately, those data are not available. Therefore, while our results may be applicable to future investigations of dimerized salts, we shall not discuss dimerized salts in this paper any further.

The eigenvalue problem of the two-site extended Hubbard Hamiltonian can be solved exactly. The grand partition function is then obtained, and the magnetic susceptibility is calculated for several ranges of V with n as a parameter. This is done in Sec. II followed by a discussion in Sec. III.

II. MAGNETIC SUSCEPTIBILITY

The extended Hubbard Hamiltonian is usually written in the form

$$H = t \sum_{\langle ij \rangle} \sum_{\sigma} c_{i\sigma}^{\dagger} c_{j\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow} + V \sum_{\langle ij \rangle} n_i n_j, \quad (1)$$

where $\langle ij \rangle$ indicates sum over nearest neighbors only, $c_{i\sigma}^{\dagger}$ creates an electron in site i with spin σ ,

and $n_{i\sigma} = c_{i\sigma}^{\dagger} c_{i\sigma}$, $n_i = \sum_{\sigma} n_{i\sigma}$. U is the intramolecular Coulomb interaction, V is the nearest-neighbor Coulomb interaction, and t is the transfer integral. For the two-site model we consider two particular neighboring sites and allow the number of electrons to vary by introducing the chemical potential μ in the Hamiltonian. In the presence of an external uniform magnetic field B , the Hamiltonian of a two-site model is

$$H_{ts} = t \sum_{\sigma} (c_{1\sigma}^{\dagger} c_{2\sigma} + c_{2\sigma}^{\dagger} c_{1\sigma}) + U \sum_{i=1}^2 n_{i\uparrow} n_{i\downarrow} + V n_1 n_2 - \gamma B \sum_{i=1}^2 (n_{i\uparrow} - n_{i\downarrow}) - \mu \sum_{i=1}^2 n_i, \quad (2)$$

where γ is the magnetic moment of an electron. The eigenvalue problem of Eq. (2) can be solved exactly, and there are 16 nondegenerate eigenvalues: $0, \pm t \pm \gamma B - \mu, U - 2\mu, V - 2\mu, V \mp 2\gamma B - 2\mu, \lambda_{\pm} - 2\mu, U + 2V \pm t \pm \gamma B - 3\mu$, and $2U + 4V - 4\mu$, where $\lambda_{\pm} = \frac{1}{2}(U + V) \pm \frac{1}{2}[(U - V)^2 + 16t^2]^{1/2}$. The grand partition function is easily found as

$$Z \equiv \sum_{\epsilon_s} e^{-\beta \epsilon_s} = 1 + 4e^{\beta \mu} (1 + e^{\beta(2\mu - U - 2V)}) \cosh(\beta \gamma B) \cosh \beta t + e^{2\beta \mu} \{ e^{-\beta U} + e^{-\beta V} [1 + 2 \cosh(2\beta \gamma B)] + e^{-\beta \lambda_+} + e^{-\beta \lambda_-} \} + e^{2\beta(2\mu - U - 2V)}, \quad (3)$$

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

$$n = \frac{1}{2} \frac{1}{\beta} \left(\frac{\partial \ln Z}{\partial \mu} \right)_{\beta, B=0} = 2e^{\beta \mu} (e^{3\beta \mu - 2\beta U - 4\beta V} + 3e^{2\beta \mu - \beta U - 2\beta V} \cosh \beta t + A e^{\beta \mu} + \cosh \beta t) \times (e^{4\beta \mu - 2\beta U - 4\beta V} + 4e^{3\beta \mu - \beta U - 2\beta V} \cosh \beta t + 2A e^{2\beta \mu} + 4e^{\beta \mu} \cosh \beta t + 1)^{-1}, \quad (4)$$

where

$$A = \frac{1}{2} (e^{-\beta U} + 3e^{-\beta V} + e^{-\beta \lambda_+} + e^{-\beta \lambda_-}).$$

By introducing the fractional band occupancy $f = \frac{1}{2}n$, we rewrite Eq. (4) as

$$e^{4\beta \mu} e^{-2\beta U - 4\beta V} (1 - f) + e^{3\beta \mu} e^{-\beta U - 2\beta V} (3 - 4f) \cosh \beta t + e^{2\beta \mu} A (1 - 2f) + e^{\beta \mu} (1 - 4f) \cosh \beta t - f = 0. \quad (5)$$

Equation (5) determines μ as a function of T (with fixed U, V , and t) for a given f . It is easily seen that for the half-filled-band case, $f = \frac{1}{2}$, $\mu = \frac{1}{2}U + V$ for all T . For other values of f , μ is a function of T which is plotted in Fig. 1 for three different values of f . We have limited ourself in the narrow-bandwidth limit $t/U \ll 1$. We see that

μ approaches a constant for large values of βU . When T is fixed, Eq. (5) gives μ as a function of f which is plotted in Fig. 2 for $\beta U = 5$ and 15. We see that for large values of βU , μ is a slowly varying function of f , except at $f = \frac{1}{4}, \frac{1}{2}$, and $\frac{3}{4}$. This picture would help us in determining the magnetic susceptibility analytically in the limit $\beta U \gg 1$. The magnetic susceptibility per site is given by

$$\chi = \frac{1}{2\beta} \left(\frac{\partial^2 \ln Z}{\partial B^2} \right)_{\mu, B=0} = \frac{2\beta \gamma^2 e^{\beta \mu} [(1 + e^{\beta(2\mu - U - 2V)}) \cosh \beta t + 2e^{\beta \mu - \beta V}]}{1 + 4e^{\beta \mu} (1 + e^{\beta(2\mu - U - 2V)}) \cosh \beta t + 2A e^{2\beta \mu} + e^{2\beta(2\mu - U - 2V)}}. \quad (6)$$

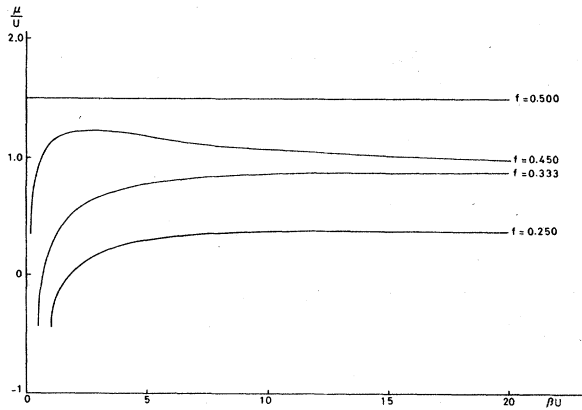


FIG. 1. Chemical potential as a function of temperature (μ/U vs βU) for $f=0.25, 0.33, 0.45,$ and 0.5 . $U/t=8, \alpha=1$.

From Eqs. (5) and (6), we plotted $\gamma^2/k\chi$ vs T in Fig. 3 for several values of $\alpha = V/U$ with $f = 0.45$. We see that for $\alpha > 1$, there are two portions of the plot that are approximately straight lines. The slopes (proportional to inverse of Curie constant) are different for the two portions corresponding to different electron distributions mentioned in the Introduction. In fact, from Eqs. (5) and (6) one can solve χ analytically in the limit $\beta U \gg 1$ for certain ranges of V . The results are listed in Tables I-III. The magnetic susceptibility is of the Curie-Weiss (or Curie) form for most of the cases, except for the half-filled case ($n=1$), whose magnetic susceptibility approaches zero

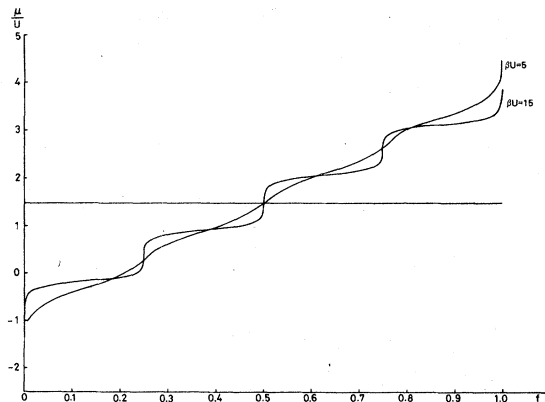


FIG. 2. Chemical potential as a function of fractional filling of band (μ/U vs f) for $\beta U=5$ and 15 . $U/t=8, \alpha=1$.

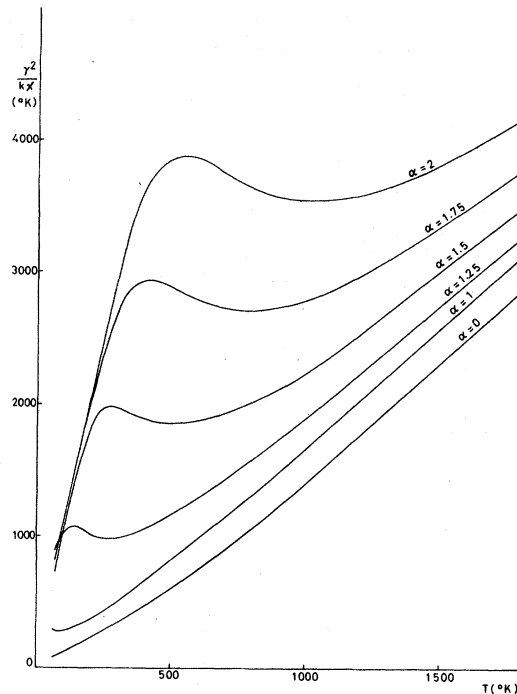


FIG. 3. Inverse magnetic susceptibility per site versus temperature for $\alpha=0, 1, 1.25, 1.5, 1.75,$ and 2 . $f=0.45, U=0.17$ eV.

exponentially as T goes to zero for $|U - V| \ll 4t$ and $V - U \gg 4t$ (Tables II and III).

III. DISCUSSION

From Tables I-III, it is easily seen that when $U - V \gg 4t$, the magnetic susceptibility is essentially the same as that of the case $V=0$. Therefore it is not of our interest. In the other extreme case $V - U \gg 4t$ (including $t=0, V > U$), the magnetic susceptibility is of the Curie form with Curie constant $C = (1-n)\gamma^2/k$ for $\frac{1}{2} \leq n < 1$. Therefore C is greatly reduced when n is close to 1 ($C = n\gamma^2/k$ for $V=0$). But this requires a large value of V which may not be realizable in the real physical system; therefore we shall not discuss this case any further.

A more interesting case is when $|U - V| \ll 4t$. Under this condition the magnetic susceptibility can also be greatly reduced, which we will discuss in a moment. The above condition is much easier to be satisfied in real physical systems. For a long linear chain we would expect the condition to become¹⁷ $U - 2V \ll 4\sqrt{2}t$. Since there are two nearest neighbors in the long chain, we have to replace V by $2V$ and t by $\sqrt{2}t$. If we take $U/t=8$

TABLE I. Magnetic susceptibility for $\beta t \ll 1 \ll \beta U$.

χ , range of n	χ , range of V		
	$U-V \gg 4t$ (small V)	$ U-V \ll 4t$	$V-U \gg 4t$ (large V)
$0 < n \leq \frac{1}{2}$	$n\beta\gamma^2 / \left(1 + n \frac{\beta t^2}{U-V}\right)$	$n\beta\gamma^2$	$n\beta\gamma^2$
$\frac{1}{2} \leq n < 1$	$n\beta\gamma^2 / \left(1 + n \frac{\beta t^2}{U-V}\right)$	$\frac{[(1+n)/3]\beta\gamma^2}{1 + \frac{4(2n-1)}{3(1+n)}[\beta^2 t^2 - \frac{1}{2}\beta(U-V)]}$	$(1-n)\beta\gamma^2$
$n = 1$	$\beta\gamma^2 / \left(1 + \frac{\beta t^2}{U-V}\right)$	$\frac{\frac{2}{3}\beta\gamma^2}{1 + \frac{2}{3}\beta^2 t^2 - \frac{1}{3}\beta(U-V)}$	$2\beta\gamma^2 \left(1 - \beta \frac{t^2}{U-V}\right) e^{-\beta(V-U)}$
$1 < n \leq \frac{3}{2}$	$(2-n)\beta\gamma^2 / \left(1 + (2-n) \frac{\beta t^2}{U-V}\right)$	$\frac{[(3-n)/3]\beta\gamma^2}{1 + \frac{4(3-2n)}{3(3-n)}[\beta^2 t^2 - \frac{1}{2}\beta(U-V)]}$	$(n-1)\beta\gamma^2$
$\frac{3}{2} \leq n < 2$	$(2-n)\beta\gamma^2 / \left(1 + (2-n) \frac{\beta t^2}{U-V}\right)$	$(2-n)\beta\gamma^2$	$(2-n)\beta\gamma^2$

as in the case of NMP-TCNQ, the condition can be satisfied if $V > \frac{1}{3}U$. Thus for the case of NMP-TCNQ, if the nearest-neighbor repulsive interaction is greater than one-third of the intramolecular repulsion, the magnetic susceptibility could be reduced to a smaller value. We have seen that the larger the value t is, the looser the condition on V . Therefore a nonzero t would help the reduction of the magnetic susceptibility.

When the condition $|U-V| \ll 4t$ is satisfied, the magnetic susceptibility is of the Curie form in the low-temperature limit $kT \ll t$ (Table II). The Curie constant $C = (1-n)\gamma^2/k$ is reduced by a factor of 12 in comparison with the case $V=0$ (cf.

Table II, $U-V \gg 4t$) when $n=0.9$ is used. (Note that when $n=1$, C equals zero in this case). When $n=0.9$ is used, we find that the theoretical value of C ($=0.62 \times 10^{-25}$ K) is just a little more than one-third of the experimental value (1.7×10^{-25} K) of NMP-TCNQ. On the other hand if we match the value of C with the experiment, we would predict $n=0.73$, which is not too far apart from $n=0.9$. We note that relative change of C is large when n is close to 1. There is also an encouraging sign that the Curie-Weiss region of NMP-TCNQ (50–200 K) is approximately in the region $kT \ll t$ ($t = 240$ K). At a higher temperature limit $U \gg kT \gg t$, the magnetic susceptibility is of the Curie-

TABLE II. Magnetic susceptibility for $1 \ll \beta t \ll \beta U$.

χ , range of n	χ , range of V		
	$U-V \gg 4t$ (small V)	$ U-V \ll 4t$	$V-U \gg 4t$ (large V)
$0 < n \leq \frac{1}{2}$	$n\beta\gamma^2$	$n\beta\gamma^2$	$n\beta\gamma^2$
$\frac{1}{2} \leq n < 1$	$\frac{1}{3}(5n-1)\beta\gamma^2$	$(1-n)\beta\gamma^2$	$(1-n)\beta\gamma^2$
$n = 1$	$\left. \begin{array}{l} \frac{1}{3}(5n-1)\beta\gamma^2 \\ \frac{1}{3}(9-5n)\beta\gamma^2 \end{array} \right\} = \frac{4}{3}\beta\gamma^2$	$4\beta\gamma^2 e^{-\beta[2t-(U-V)/2]}$	$4\beta\gamma^2 e^{-\beta(V-U)}$
$1 < n \leq \frac{3}{2}$	$\frac{1}{3}(9-5n)\beta\gamma^2$	$(n-1)\beta\gamma^2$	$(n-1)\beta\gamma^2$
$\frac{3}{2} \leq n < 2$	$(2-n)\beta\gamma^2$	$(2-n)\beta\gamma^2$	$(2-n)\beta\gamma^2$

TABLE III. Magnetic susceptibility for $t=0$ and $\beta U \rightarrow \infty$.

χ , range of n	χ , range of V		
	$U-V > 0$ (small V)	$U=V$	$U-V < 0$ (large V)
$0 < n \leq \frac{1}{2}$	$n\beta\gamma^2$	$n\beta\gamma^2$	$n\beta\gamma^2$
$\frac{1}{2} \leq n < 1$	$n\beta\gamma^2$	$\frac{1}{3}(n+1)\beta\gamma^2$	$(1-n)\beta\gamma^2$
$n = 1$	$n\beta\gamma^2$ $(2-n)\beta\gamma^2 = \beta\gamma^2$	$\frac{1}{3}(n+1)\beta\gamma^2$ $\frac{1}{3}(3-n)\beta\gamma^2 = \frac{2}{3}\beta\gamma^2$	$2\beta\gamma^2 e^{-\beta(V-U)}$
$1 < n \leq \frac{3}{2}$	$(2-n)\beta\gamma^2$	$\frac{1}{3}(3-n)\beta\gamma^2$	$(n-1)\beta\gamma^2$
$\frac{3}{2} \leq n < 0$	$(2-n)\beta\gamma^2$	$(2-n)\beta\gamma^2$	$(2-n)\beta\gamma^2$

Weiss form with a much larger $C = (1+n)\gamma^2/3k$ for $\frac{1}{2} \leq n \leq 1$ (Table I). (Note that $C \neq 0$ for $n=1$, and this is entirely due to the effect of $t \neq 0$.) If $n=0.9$ is used, we find that $C = 4.0 \times 10^{-25}$ K, which is more than twice of the experimental value. But this is a significant improvement over the case $V=0$, which predicts $C = 5.6 \times 10^{-25}$ K.

It seems that numerical comparison between theory and experiment does not agree well. But this may be partly due to the fact that a two-site

model is too simple a model to describe the real physical system. However, we do have an important conclusion that with some physically realizable values of V/U and t/U , the Curie constant can be reduced to a smaller value than that of the prediction of a simple Hubbard model. This may suggest that both V and t are important in the understanding of the smallness of the Curie constant in the magnetic susceptibility of the salt NMP-TCNQ.

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²For $n=1$, known as half-filled-band case, the chemical potential is known to be a constant independent of temperature. Almost all previous calculations of thermodynamic properties of the Hubbard model are limited to this special case because of the simplicity of the chemical potential.

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⁸The critical value of V is $\frac{1}{2}U$ in the long linear chain, because there are two nearest neighbors in the long chain, while there is only one in the two-site model.

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¹⁷Actually the original condition should be written $(U-V)^2 \ll 16t^2$. In the long linear chain this becomes $(U-2V)^2 \ll 32t^2$.