PHYSICAL REVIEW B VOLUME 7, NUMBER 11 1 JUNE 1973

High-Temperature Properties of the Half-Filled-Band Hubbard Model

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(Received 2 November 1972)

Some important thermodynamic (specific-heat and magnetic-susceptibility) and dynamic (nuclear-spin–lattice relaxation) properties of the half-filled-band Hubbard model are calculated by a high-temperature expansion. In the strong-correlation limit $U/t \gg 1$, the expansion remains useful through the metal-insulator transition, breaking down only when βt becomes of order unity. Excellent agreement is found with exact calculations for finite linear chains and qualitative agreement is obtained with nuclear T_1 measurements in N-methylphenazinium–tetracyanoquinodimethan (NMP–TCNQ). Although these comparisons are made for linear chains, the theoretical predictions are made for three- as well as for one-dimensional systems.

I. INTRODUCTION

Continued interest in the Hubbard Hamiltonian[1] stems from its simplicity as a physically reasonable model for exploring the consequences of short-range Coulomb correlations between electrons in a crystal. Growing attention has been paid to its thermodynamic and transport properties, in anticipation of meaningful comparisons with experiment. Indeed, it has recently been suggested[2] that the organic charge transfer salt N-methylphenazinium tetracyanoquinodimethan (NMP-TCNQ) is a realization of the half-filled-band (one electron per site) case for this model, with the electron dynamics further confined to well-separated linear chains. The present study is partially motivated by a desire to make some well-defined predictions of temperature-dependent quantities with which comparisons with experiment can be made. It appears in this context that the nuclear-spin–lattice relaxation time T_1 is a sensitive function of the localized versus delocalized electronic behavior,[3] which is temperature dependent in the Hubbard model. In this paper we shall restrict ourselves to the half-filled-band systems of a uniform linear chain (suggestive of NMP-TCNQ) and of simple three-dimensional lattices. The extension to arbitrary electron densities is currently under investigation.

In its simplest form the Hubbard Hamiltonian can be written

$$H = t \sum C^\dagger_{i+\Delta,\sigma} C_{i\sigma} + U \sum n_{i\uparrow} n_{i\downarrow} \equiv H_t + H_U \ , \qquad (1.1)$$

where $C^\dagger_{i\sigma}$ creates an electron in the (orbitally nondegenerate) state at lattice site i, Δ is summed over nearest-neighbor vectors, and $n_{i\sigma} = C^\dagger_{i\sigma} C_{i\sigma}$. Since we are mainly concerned with strong correlation effects, we shall only consider this limit; in fact our method is to include the intra-atomic Coulomb repulsion U exactly and treat the transfer integral t by perturbation theory (with smallness parameters t/U and $t/k_B T$) in calculations of the grand partition function and local electron-spin-correlation function. We are thus working in the regime of strong correlations and temperatures, high compared to the electronic bandwidth. The "fully atomic limit" $t=0$ is, of course, exactly soluble for its thermodynamics[4] and, because it is a purely static situation, it does not exhibit any interesting spin dynamics of relevance to nuclear relaxation. Earlier calculations of thermodynamic properties include exact calculations of finite rings and chains in the canonical[5] and grand canonical ensembles,[6] and also include an approach based on the functional integral method for infinite systems.[7] In Sec. II we shall compare our well-defined perturbation results for infinite systems with these previous studies. For our high-temperature studies, the basic quantities available to us are (a) the high-temperature peak in the specific heat near $U/4k_B$ when the electrons begin to delocalize,[5] and (b) the leading term in the Curie–Weiss expansion for the spin susceptibility. The low-temperature ($k_B T \ll U$) properties of the half-filled-band Hubbard model are known[8] to be equivalent to those of a Heisenberg antiferromagnet. Thus, because our expansion is good until $k_B T \sim t \ll U$, the results should overlap into the paramagnetic regime of the antiferromagnetic system.

The transport properties of the Hubbard model have been rather less studied. Brinkman and Rice[9] have investigated the mobility of a hole in an otherwise half-filled band in the limit $t/U \to 0$. Bari and Kaplan[10] treat the finite bandwidth by high-temperature perturbation theory to lowest order in a calculation of the conductivity. In this work, we have decided to concentrate on the nuclear-spin–lattice relaxation rate, which is a microscopic probe of the electron dynamics and is furthermore experimentally less sensitive to structural defects than are resistivity measurements. Again the interesting observed[11] behavior of T_1 in NMP-TCNQ motivated our interest in this regard. The physical behavior which we expect for the local electron-spin-correlation time τ_c is (a) at high temperatures $k_B T \gg \frac{1}{4} U$, the system is a nondegenerate electron gas with a hopping rate of $\tau_c \sim \hbar/t$, and (b) for $k_B T \ll \frac{1}{4} U$, the electrons condense onto the lattice sites and only spin fluctuations occur with $\tau_c \sim \hbar/J$, where J is the Heisenberg exchange energy which in the Hubbard model is $J \sim t^2/U$. Thus we expect a shortening of the relaxation time T_1 below the localization temperature $U/4k_B$, which is indeed observed.[11] Section III is devoted to a justification of these physical arguments.

II. THERMODYNAMICS

The simplest application of our methods is to the thermodynamic properties of the Hubbard model. In particular, the magnetic susceptibility χ and the specific heat C are obtained directly from the partition function Z, for which we can obtain directly a high-temperature expansion. As the unperturbed Hamiltonian we choose

$$\mathcal{H}_0 = \mathcal{H}_U - \mu N - \gamma B \sum (n_{i\uparrow} - n_{i\downarrow}), \tag{2.1}$$

where B is an external uniform magnetic field and $\mathcal{H}_0$ is diagonal in the lattice-site representation. Although the chemical potential μ can be determined in the usual manner by fixing the average number of particles, we can set it immediately at $\frac{1}{2} U$ for the present case of the half-filled band. Particle-hole symmetry implies that μ is independent of temperature, and it is clear both physically and by direct calculation in the high-temperature limit $\beta t \ll 1$ that $\mu = \frac{1}{2} U$. The density operator is expanded in the standard way:

$$e^{-\beta(\mathcal{H} - \mu N)} = e^{-\beta\mathcal{H}_0} T_\lambda \exp\left[- \int_0^\beta d\lambda\, \mathcal{H}_t(\lambda)\right], \tag{2.2}$$

where

$$\begin{aligned}\mathcal{H}_t(\lambda) &\equiv e^{\lambda\mathcal{H}_0}\mathcal{H}_t e^{-\lambda\mathcal{H}_0} \\ &\equiv t \sum \exp[\lambda U(n_{l,-\sigma} - n_{l+\Delta,-\sigma})] C^\dagger_{l\sigma} C_{l+\Delta\sigma} \, .\end{aligned} \tag{2.3}$$

Then the logarithm of the partition function can be written as a sum of cumulant averages of successively higher order in t (see Appendix). The necessary traces are readily calculated in the representation with $n_{i\sigma}$ diagonal, and the integrals over λ involve only low-order polynomials and exponentials. We find to lowest nonvanishing order

$$\begin{aligned}\ln \frac{Z}{Z_0} \approx N \left(\frac{z}{2}\right)\left(\frac{t}{U}\right)^2 (1 + e^{x/2}\cosh\beta\gamma B)^{-2}(x) \\ \times (x e^{x/2}\cosh\beta\gamma B + e^x - 1),\end{aligned} \tag{2.4}$$

where z is the number of nearest neighbors to a site and $x = \beta U$. The unperturbed partition function Z_0 is

$$Z_0 = (2 + 2 e^{x/2}\cosh\beta\gamma B)^N \; . \tag{2.5}$$

We have immediately the magnetic susceptibility per particle,

$$\begin{aligned}\chi = \frac{1}{\beta N}\frac{\partial^2}{\partial B^2}\ln Z \Big|_{B=0} \approx \beta\gamma^2(1 + e^{-x/2})^{-1} \\ \times\left[1 - \left(\frac{z}{2}\right)\left(\frac{t}{U}\right)^2\left(x \tanh\frac{x}{4}\right)\left(2 + \frac{x}{1 + e^{x/2}}\right)\right]\end{aligned} \tag{2.6}$$

At very high temperatures, $kT > U$ or $x < 1$, the corrections to a simple Curie law are small. The system is metallic and the temperature is well above the chemical potential $\mu = \frac{1}{2} U$, so the electrons are nondegenerate and the Curie law is to be expected. In fact, since we are in the narrow-band regime $(t/U)^2 \ll 1$, the conduction electrons remain nondegenerate as the temperature is reduced and there is no Pauli behavior in the susceptibility. At lower temperatures, where the system becomes an insulator, approximately described by a Heisenberg Hamiltonian with exchange constant $J \approx 2t^2/U$, we expect to find a Curie–Weiss susceptibility, and for $x \gg 1$ Eq. (2.6) does indeed take the form

$$\chi \approx \beta\gamma^2(1 - \Theta/T) \approx \gamma^2/(T + \Theta), \tag{2.7}$$

where the Weiss temperature Θ has the expected value

$$\Theta = z t^2/U \; . \tag{2.8}$$

In Fig. 1 these predictions are compared with the results of exact calculations for finite linear chains which have been extrapolated to chains of infinite length. The agreement is excellent for $k_B T > t$, where our expansions are expected to be useful. This is so even for U/t as small as 4, where we might have anticipated some difficulty with the assumption of small t/U. Our expansion breaks down completely at temperatures of order Θ, where there develops long-range antiferromagnetic order in three-dimensional systems and short-range order in lower-dimensional structures. To second order in t our calculation can take into account hopping only to nearest neighbors and back, and the crystal geometry therefore appears only trivially in the factor of z in the $(t/U)^2$ term. This is clearly insufficient to describe the onset of any collective phenomena involving long-range order, or even to account for the essential topological differences between one- and three-dimensional crystals. For comparison the results of the functional averaging approach of Kimball and Schrieffer[7] are also shown in Fig. 1. Although those results clearly seem worse for larger values of U/t the comparison is more easily made for the specific heat, which we discuss next.

From Eqs. (2.4) – and (2.5) we have for the specific heat

$$\frac{C}{Nk_B}=\frac{x^2}{N}\frac{\partial^2}{\partial x^2}\ln Z\approx w^2\cosh^{-2}w\left[1+4z\left(\frac{t}{U}\right)^2(2-5w\tanh w-3w^2\cosh^{-2}w+2w^2)\right], \quad (2.9)$$

where $w=\frac{1}{4}x=\frac{1}{4}\beta U$. The leading term is just the Schottky anomaly to be expected in the limit $t\rightarrow 0$, where the bands collapse into two sharp energy levels separated by an energy U. The peak occurs roughly at a temperature $\frac{1}{4}U$, where the metal-insulator transition takes place for small t/U. As $z(t/U)^2$ increases the peak position shifts to higher temperatures and the shape of the peak is modified. When the temperature is reduced below $\Theta\sim Jz$, virtual hopping processes give spin-wave-like excitations which should contribute another low-temperature peak to the specific heat, as was pointed out in Ref. 5. We should not expect to see evidence of this collective behavior in our treatment, since to

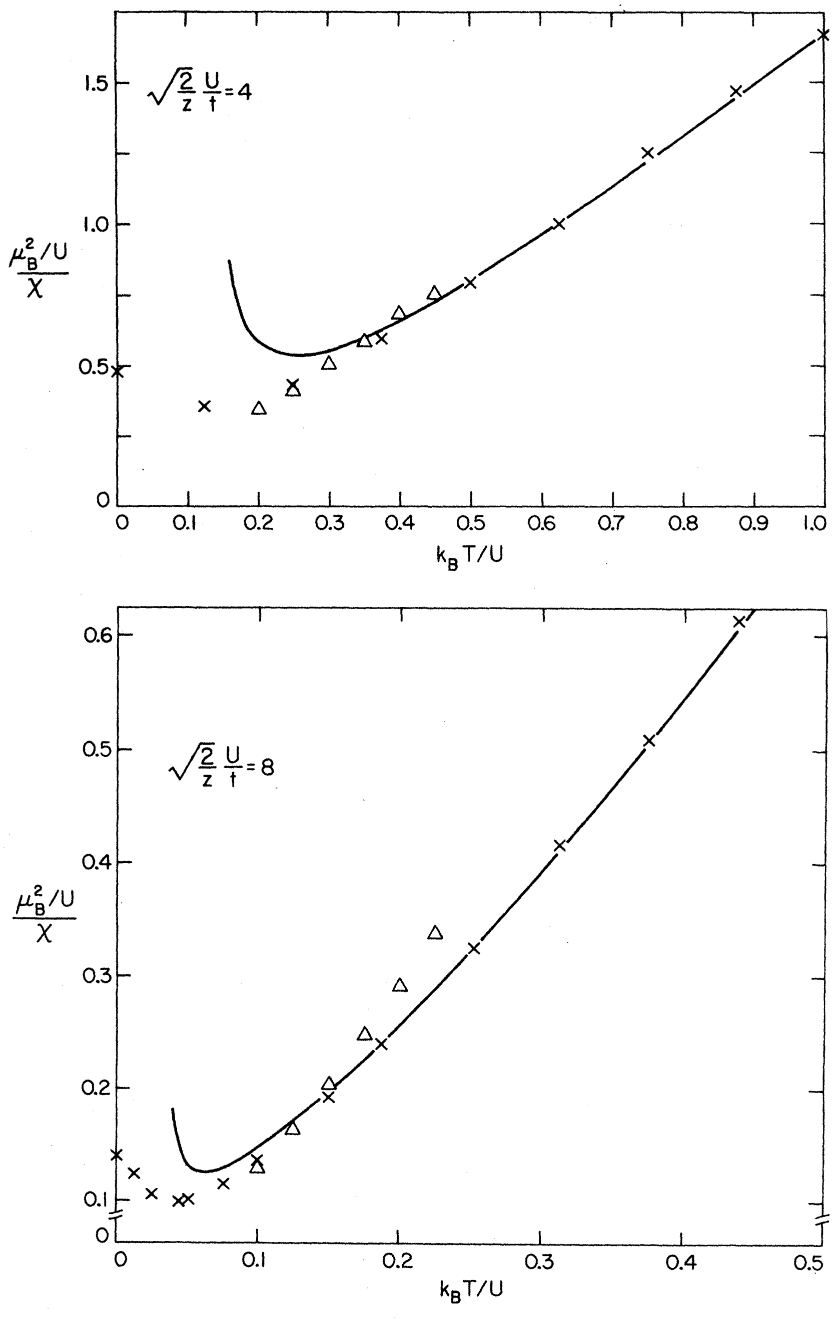

FIG. 1. Inverse susceptibility for values of $(2/z)^{1/2}(U/t)$ of 4, 6, 8, and 12. The curves represent the predictions of Eq. (2.6), the crosses are the finite linear-chain extrapolations of Ref. 6, and the triangles are the linear-chain predictions of the functional average approach of Ref. 7.

order $(t/U)^2$ only exchange between a single pair of spins is included. The shoulder which appears in our specific-heat curve (Fig. 2) for $U/t=6$, and which develops into separated peaks for $U/t=4$, is associated with a breakdown of the expansion rather than with the spin-wave peak. Certainly the very-

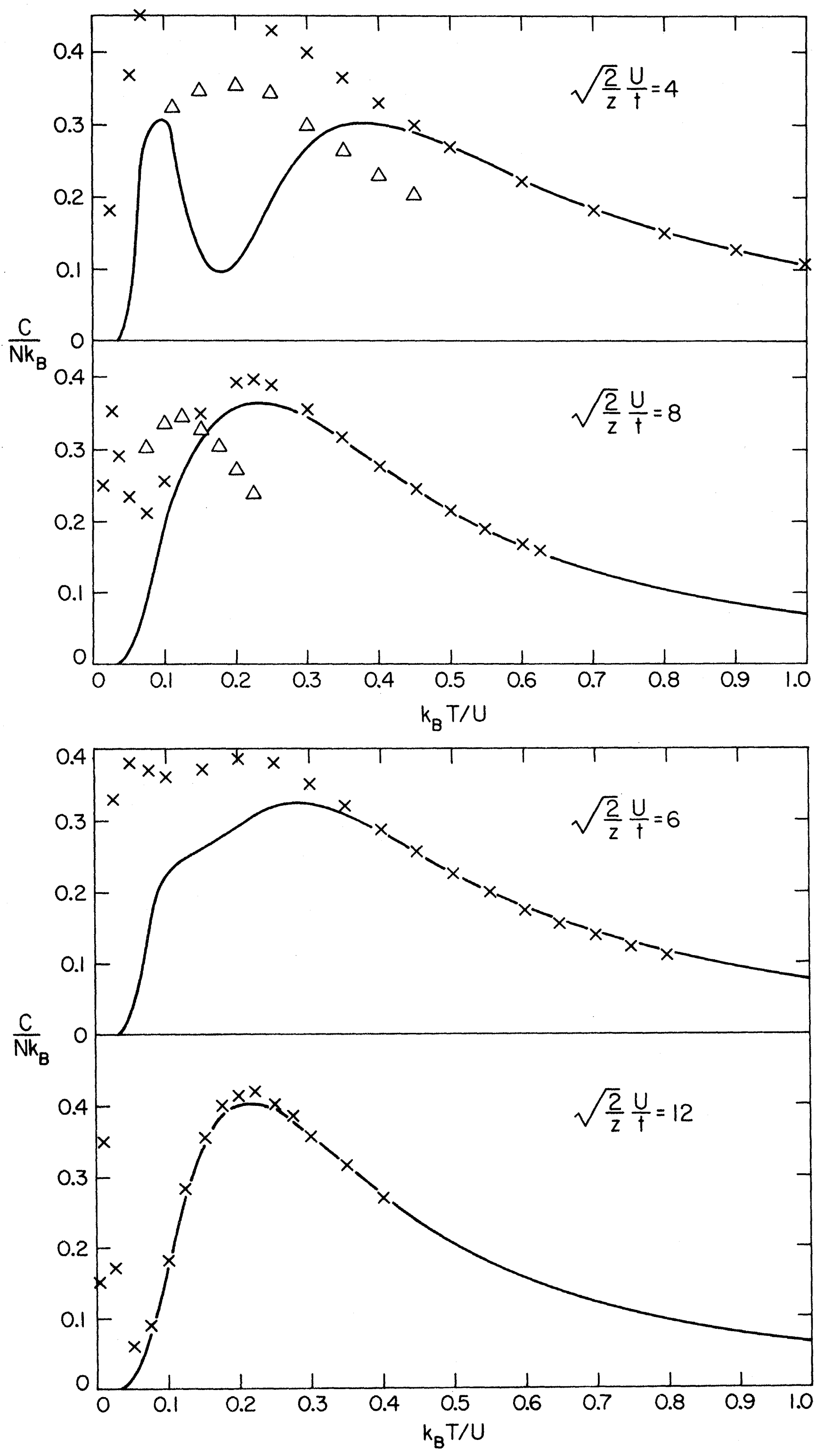

FIG. 2. Specific heat C/Nk_B for values of $(2/z)^{1/2}(U/t)$ of 4, 6, 8, and 12. The curves represent the predictions of Eq. (2.9), the crosses are the finite linear-chain extrapolations of Ref. 6, and the triangles are the linear chain predictions of the functional average approach of Ref. 7.

low-temperature exponentially small specific heat predicted by Eq. (2.9) is grossly incorrect. There can be no evidence of the power-law behavior (linear in one dimension) expected from long-wavelength spin waves. Again the good agreement at high temperatures of our results with exact calculations for finite linear chains is shown in Fig. 2. Also shown are the results of the functional averaging scheme employed by Kimball and Schrieffer.[7] The failure of this approach in the atomic limit $t=0$ has been discussed by Bari,[12] and for $U/t=8$ we see the shift of the peak from the correct value by about a factor of 2, characteristic of that limit.

III. DYNAMICS: NUCLEAR-SPIN–LATTICE RELAXATION

Although the high-temperature peak in the specific heat found in Sec. II can be viewed as a reflection of the metal-insulator transition, we would expect the most dramatic manifestations of that transition to be found in the dynamical properties of the system. In particular, as behavior characteristic of a metal changes to that of a Heisenberg paramagnet with decreasing temperature, we can anticipate drastic changes in the spin dynamics. These will be observed most simply and directly in the nuclear-spin–lattice relaxation rate $1/T_1$. In fact, there already exist experimental results for T_1 of protons in the organic linear chain crystal NMP-TCNQ which exhibit the expected structure somewhat below the metal-insulator transition temperature.

We assume that the nuclei (of spin I) relax to the lattice primarily via an isotropic hyperfine interaction $\mathcal{H}_{\rm hf}=A\sum\vec{I}_l\cdot\vec{S}_l$, each nucleus interacting only with electrons in the Wannier states at its own site. In the interaction picture the z component of nuclear spin $\tilde{I}^z(\tau)$ satisfies the integral equation

$$\tilde{I}^z(\tau)=\tilde{I}^z(0)+i\int_0^\tau d\tau'\,[\tilde{\mathcal{H}}_{\rm hf}(\tau'),\tilde{I}^z(\tau')]\,, \qquad (3.1)$$

where the time dependence of the operators is governed by the Hubbard plus Zeeman Hamiltonians. Iterating this equation once we find for the longitudinal nuclear-spin-correlation function

$$\begin{aligned}\langle\tilde{I}^z(\tau)\tilde{I}^z(0)\rangle&=\langle(I^z)^2\rangle-\int_0^\tau d\tau'\int_0^{\tau'}d\tau''\\&\quad\times\langle\{[\tilde{I}^z(\tau''),\,\tilde{\mathcal{H}}_{\rm hf}(\tau'')],\mathcal{H}_{\rm hf}(\tau')\}I^z\rangle\\&=\langle(I^z)^2\rangle-\int_0^\tau d\tau'(\tau-\tau')\\&\quad\times\langle[(I^z,\mathcal{H}_{\rm hf}),\tilde{\mathcal{H}}_{\rm hf}(\tau')]I^z\rangle\;,\end{aligned} \qquad (3.2)$$

where we have used the fact that the correlation function under the integral depends on τ' and τ'' only through their difference, $\tau'-\tau''$, in order to obtain the final equality. After doing the indicated commutations explicitly we replace Eq. (3.2) by an approximate exponential form,

$$\begin{aligned}\langle\tilde{I}^z(\tau)I^z(0)\rangle&\approx\langle(I^z)^2\rangle\exp[-\tfrac{1}{2}A^2\\&\quad\times\int_0^\tau d\tau'(\tau-\tau')\langle S_l^+\tilde{S}_l^-(\tau')+S_l^-\tilde{S}_l^+(\tau')\rangle]\,,\end{aligned} \qquad (3.3)$$

which is equivalent to Eq. (3.2) to second order in A [note that to this order $\tilde{I}^z(\tau')=I^z$ in the commutator]. In fact, the argument of the exponential in Eq. (3.3) is the first nonvanishing term in an exact cumulant series, and all higher-order terms vanish if the fluctuating hyperfine field at the nucleus corresponds to a Gaussian random process.[13] The electron-spin-correlation function in Eq. (3.3) decays in a time set by the electronic interactions, so that for the much longer times τ, of interest for nuclear spin decay, we can replace $\tau-\tau'$ by τ in the integrand and we can let the upper limit on the integral go to infinity. This is just the standard technique for treating strongly narrowed resonance systems; here the narrowing arises from the rapid fluctuations of the electron spin on a site. The resulting exponential decay then corresponds to the relaxation rate

$$\begin{aligned}(T_1)^{-1}&=A^2\int_0^\infty d\tau\langle C_{l\uparrow}^\dagger C_{l\downarrow}C_{l\downarrow}^\dagger(\tau)C_{l\uparrow}(\tau)\cos\omega_e\tau\\&=A^2\int_0^\infty d\tau\psi(\tau)\cos\omega_e\tau\;,\end{aligned} \qquad (3.4)$$

where we have explicitly extracted the Zeeman time dependence in the final $\cos\omega_e$ factor (ω_e is the electron Zeeman frequency), so that the remaining time dependence of the operators is given by the Hubbard Hamiltonian alone. We have also written the spin operators in terms of electron creation and destruction operators C_l and $C_l^\dagger$, and we have used time-reversal symmetry to arrive at the final simple form of Eq. (3.4). The approximations necessary to give the simple exponential decay are equivalent to the assumption of the validity of a spin-temperature description for the nonequilibrium spin system, and the final result for T_1 agrees with the result of calculations by this latter approach.

Although we are unable to calculate the electron correlation function $\psi(\tau)$ exactly, we can make a short-time expansion to determine its initial decay rate. Making the standard assumption that this decay is approximately Gaussian,

$$\begin{aligned}\psi(\tau)&\approx\psi(0)\exp[-\tfrac{1}{2}\tau^2|\ddot{\psi}(0)|/\psi(0)]\\&\equiv\psi(0)\,e^{-\tau^2/\tau_c^2}\,,\end{aligned} \qquad (3.5)$$

and taking $\cos\omega_e\tau\approx1$ for these short times, we obtain an explicit expression for T_1 as a function of temperature:

$$(T_1)^{-1}=A^2\psi(0)\,[\tfrac{1}{2}\psi(0)/|\ddot{\psi}(0)|]^{1/2}\,. \qquad (3.6)$$

The Gaussian assumption is expected to lead only to small errors which will be of particularly minor importance in the temperature dependence of T_1 if the shape of $\psi(\tau)$, Gaussian or not, is relatively insensitive to temperature. As we will show below, $\ddot{\psi}(0)$ contains rapid modulations at frequencies of order U which are not characteristic of the decay rate of ψ. so that $\ddot{\psi}(0)$ in Eq. (3.5) must be interpreted as an average of $\ddot{\psi}(\tau)$ over times long compared with $1/U$.

Thus the calculation has been reduced essentially to the determination of two static correlation functions, $\psi(0)$ and $\ddot{\psi}(0)$. These still cannot be found exactly at finite temperatures, because we cannot diagonalize the density matrix appropriate to the Hubbard Hamiltonian, but we can make use of the methods of Sec. II employed under similar circumstances to make a second expansion in the small parameter t/U. The results are easily interpreted. Static effects are contained in $\psi(0)=\langle S_l^+S_l^-\rangle = 2\langle (S_l^z)^2\rangle$ in a convenient spin notation. The relaxation rate is naturally proportional to the mean-square electron-spin density at the nucleus, as reflected in the factor $\psi(0)$ in Eq. (3.6). To lowest (zeroth) order in t/U we calculate directly

$$\psi(0)=\langle n_l(1-n_l)\rangle$$
$$\approx \frac{1}{2(1+e^{-x/2})}-\frac{z(t/U)^2}{4(1+e^{-x/2})^3}$$
$$\times[2+e^{-x/2}(x^2-2x+2)$$
$$-e^{-x}(x^2+2x+2)-2e^{-3x/2}] \quad , \qquad (3.7)$$

where we have continued to use the notation $x=\beta U$. For large U/t the contribution of the second term in (3.7) is negligible at all temperatures (e.g., a maximum of a few percent for $k_BT/U<0.2$ when $U/t=8$). The dominant first term directly reflects the simple essential physics of the static correlations. At high temperatures ($x\ll 1$), well into the metallic region, the up- and down-spin occupancies at a lattice site are effectively uncorrelated; $\langle n_{l\sigma}\rangle \approx \frac{1}{2}$ and $\psi(0)\approx\frac{1}{4}$. With the onset of insulating behavior ($x\gg 1$) each site is restricted by Coulomb correlations to single-electron occupancy and $\psi(0)\approx\frac{1}{2}$. The $(t/U)^2$ corrections reflect the development of coherent admixtures of up- and down-spin states in a site with the establishment of short-range antiferromagnetic order. The expansion to this order does not exhibit the shallow maximum in $\psi(0)$ at small but finite temperature discussed in Ref. 5. However, Eq. (3.7) agrees very well with the finite-chain results[6] above the temperature of this maximum.

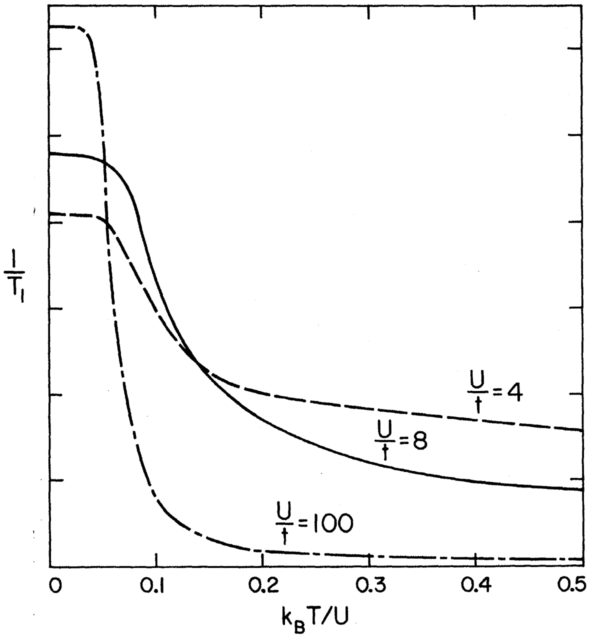

FIG. 3. Nuclear-spin–lattice relaxation rate $1/T_1$, as given by Eq. (3.6), (3.7), and (3.11), for values of $U/t=4$, 8, and 100 and $z=2$. As discussed in the text the curves are also appropriate for larger z with a suitable choice of U/t in each case.

The dynamical effects are contained in the final factor of Eq. (3.6). In fact, from Eq. (3.5) we see that $[2\psi(0)/|\ddot{\psi}(0)|]^{1/2}$ is the electron-spin correlation time τ_c. We expect, and we will find below, that τ_c goes from an electronic hopping time $\tau_c\sim\hbar/t$ in the high-temperature metallic region to the much longer exchange, or spin-flip, time $\tau_c\sim\hbar U/zt^2$ in the lower-temperature paramagnetic insulator phase. To calculate τ_c we require

$$\ddot{\psi}(\tau)=-\langle[C_{l\uparrow}^\dagger(\tau)C_{l\downarrow}(\tau),\mathcal{H}(\tau)][\mathcal{H},C_{l\downarrow}^\dagger C_{l\uparrow}]\rangle$$
$$=-t^2\sum_{\Delta'\Delta'}\langle[C_{l\uparrow}^\dagger(\tau)C_{l+\Delta\downarrow}(\tau)-C_{l+\Delta\uparrow}^\dagger(\tau)C_{l\downarrow}(\tau)]$$
$$\times(C_{l+\Delta'\downarrow}^\dagger C_{l\uparrow}-C_{l\downarrow}^\dagger C_{l+\Delta'\uparrow})\rangle \ , \qquad (3.8)$$

where Δ and Δ' are to be summed over nearest-neighbor vectors. It is now important to examine the time dependence of these operators a little more closely before simply setting τ equal to zero, as our formula for T_1 would suggest. Again we expand the time development operator $\exp[-i(\mathcal{H}_u+\mathcal{H}_t)\tau]$ in powers of $\mathcal{H}_t$ as an ordered exponential. On the very-short-time scale of order $\hbar/U$, only the leading term is important and we have

$$\ddot{\psi}(\tau)\approx-2t^2\sum_{\Delta'\Delta'}\langle e^{iU(n_{l\uparrow}-n_{l+\Delta\downarrow})\tau}C_{l\downarrow}^\dagger C_{l+\Delta\uparrow}$$
$$\times(C_{l+\Delta'\uparrow}^\dagger C_{l\downarrow}-C_{l\uparrow}^\dagger C_{l+\Delta'\downarrow})\rangle \ , \qquad (3.9)$$

where we have used particle-hole symmetry to combine some of the terms. Thus we see that for $(n_{l\uparrow}-n_{l+\Delta\downarrow})\neq 0$ there is a rapid oscillation at the frequency U modulating the decay of $\psi(\tau)$. Since it is the over-all decay rate rather than these oscillations in which we are interested, we want to average over times long compared to $1/U$ (but still short compared to the decay time). The net effect is clearly just to eliminate from the average those states for which $(n_{l\uparrow}-n_{l+\Delta\downarrow})\neq 0$, which we can do by writing the short-time average of Eq. (3.9) as

$$\ddot{\psi}(0) \to \langle \ddot{\psi}(\tau) \rangle_{\text{av}} = -2t^2 \sum_{\Delta, \Delta'} \langle (1 - n_{l\uparrow} - n_{l+\Delta\downarrow})^2 n_{l\downarrow} C_{l+\Delta\uparrow} C^\dagger_{l+\Delta'\uparrow} - n_{l+\Delta\downarrow} C^\dagger_{l\downarrow} C_{l+\Delta\uparrow} C^\dagger_{l\uparrow} C_{l+\Delta'\downarrow} \rangle \,. \tag{3.10}$$

It is this quantity which must be used for $\ddot{\psi}(0)$ in the expression for τ_c to get a meaningful result for the decay rate. The calculation of this static correlation function as a power series in t/U now proceeds exactly as before: We expand the density operator to second order in $\mathcal{H}_t$ and compute the traces directly in the representation with $n_{i\sigma}$ diagonal. The number of different terms which arise in this expression is large, but one can devise suitable diagrammatic or other means to account for them systematically. Then the calculation is lengthy, but straightforward. Because the result here contains terms of fourth order in the hopping Hamiltonian $\mathcal{H}_t$, it can be affected by more of the topology than the simple number of nearest neighbors z. However, if no two nearest neighbors to a site are also nearest neighbors of one another (which excludes the fcc lattice, for example) then the answer can be expressed in terms of z alone:

$$\ddot{\psi}(0) \to \langle \ddot{\psi}(\tau) \rangle_{\text{av}} = -\frac{zt^2}{4\cosh^2 \frac{1}{4}x} - \frac{zt^4/U^2}{8(1+e^{-x/2})^4} \{ 9z - 10 + e^{-x/2}[(4.5z-1)x^2 - (5z+2)x - 4z + 4] + e^{-x}[(8-7z)x^2 + (3z-2)x - 22z + 24] + e^{-3x/2}[(6.5z-3)x^2 + (9z-2)x + 4z - 4] + e^{-2x}[(z-2)x + 13z - 14] \} , \tag{3.11}$$

where, as before, $x = \beta U$. We then have directly as the correlation time τ_c in the limits of low and high temperatures

$$\begin{aligned} \tau_c &= [2\psi(0)/|\ddot{\psi}(0)|]^{1/2} \\ &\approx (2/z)^{1/2} t^{-1} \qquad (\beta U \ll 1) \\ &\approx \left(\frac{8(1 - zt^2/U^2)}{z(9z-10)} \right)^{1/2} \frac{U}{t^2} \qquad (\beta U \gg 1) \,. \end{aligned} \tag{3.12}$$

As was anticipated above, τ_c is set by a hopping time of order t^{-1} at high temperatures. As the temperature is reduced Coulomb correlations exponentially diminish the hopping rate, so that for $\beta U \gg 1$ the first term in Eq. (3.11) becomes damped by a factor $e^{\beta U/2}$, whereas the second term, which is associated with virtual hopping or exchange-induced spin fluctuations, approaches a constant. In this limit τ_c is set by an exchange time of order U/zt^2, again as anticipated above on physical grounds.

The full temperature dependence of the nuclear-spin-lattice relaxation rate $1/T_1$ for the cases $U/t = 4$, 8, and 100 for $z = 2$, appropriate to a one-dimensional system, is given in Fig. 3. Of course we must again recognize that the expansion breaks down at sufficiently low temperatures; certainly the results can no longer be trusted by the time $\beta z t^2/U = 1$. At lower temperatures the reduction in exchange-induced spin fluctuations is expected to lead to a reduction in the relaxation rate, leaving a peak in $1/T_1$ at a temperature of the order of $J = zt^2/U$. These effects can perhaps be treated most readily by direct consideration of the effective Heisenberg Hamiltonian. However, for large U/t our results do remain valid well below the metal-insulator transition, and the nuclear-spin-lattice relaxation is sensitive to that transition. We have seen that there is a sharp rise in $1/T_1$ as the dominant electron dynamics change from hopping in the metallic to Heisenberg exchange in the insulating phase. This rise does not occur at quite the same temperature as that at which the electrical conductivity changes from characteristically metallic to insulating behavior.[14] For linear chains in the large U/t limit the latter occurs at $T_{\text{MI}} \approx \frac{1}{4}U$. From Eq. (3.11) we see that for $z = 2$ the exchange contribution to the inverse correlation time τ_c^{-1} becomes comparable to the hopping contribution at

$$T_c \approx \frac{U}{4\ln(U/t)} \,. \tag{3.13}$$

This reduction from T_{MI} is relatively weak, and it has a simple physical origin. There are very few effective carriers at these low temperatures, but they contribute an anomalously large amount—t, rather than t^2/U—to τ^{-1} as compared with localized exchange-coupled electrons.

Although the curves of Fig. 3 are explicitly drawn for the linear chain ($z = 2$), they reflect very accurately the T_1 predictions for suitably chosen three-dimensional crystals. For $zt^2/U \ll 1$ we can neglect the z dependence of $\psi(0)$ and from Eq. (3.12) we find that the ratio of high- to low-temperature asymptotic values of $1/T_1$ depends on z only through the combination $(9z-10)t^2/U^2$. Similarly, we find from Eq. (3.11) that for general z Eq. (3.13) must be modified to give

$$T_c \approx -\frac{U}{2\ln[(9z-10)t^2/8U^2]} \,. \tag{3.14}$$

As this suggests, the T_1 predictions for $z = 8$ and $U/t = (496)^{1/2}$, for example, are virtually indistinguishable from those for $z = 2$ and $U/t = 8$.

From Fig. 3 we see that the sharpness of the rise in T_1^{-1} near T_c increases with U/t. One might

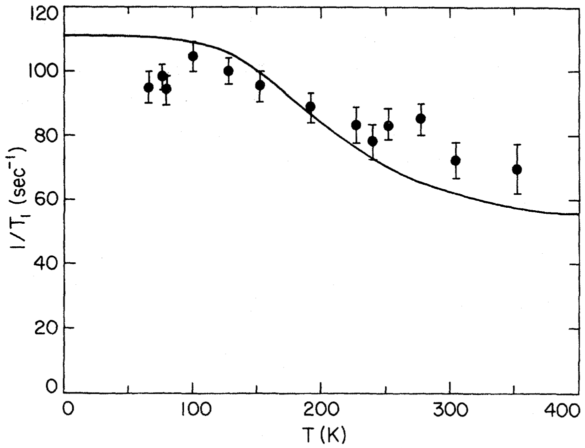

FIG. 4. Comparison of the nuclear-spin–lattice relaxation data (Ref. 11) for NMP-TCNQ with the predictions of the present theory (solid line). The vertical scale factor has been fitted, as described in the text.

anticipate a similar sharpening with increasing dimensionality of the system, a familiar feature of many phase transitions. However, we have just seen that for a fixed value of $(9z-10)t^2/U^2$ the form of T_1^{-1} is practically identical in one and three dimensions. In this regard, the important physical feature of the metal-insulator transition associated with the Hubbard model is that it represents a local ordering, and as such is not expected to be sharp even in three dimensions. As we discussed earlier, we cannot expect to predict actual cooperative phenomena, such as true phase transitions, by our technique, whose validity through the metal-insulator transition region then rests on the recognition of the local character of this phenomenon.

Finally we compare our results with the T_1 measurements on protons in NMP-TCNQ. The experiments suggest that the electronic properties of this material may be well described by a one-dimensional Hubbard Hamiltonian with $U/t \approx 4$ ($U \approx 0.18$ eV, $t \approx 0.05$ eV), at least in the metallic-temperature range. This value is rather small for our expansion in t/U to be trusted, but if we compare our predictions with the experiment, we find the excellent agreement indicated in Fig. 4. We point out that the low-temperature decrease in the relaxation rate anticipated above seems to be indicated by the experimental data. However, the value of the hyperfine constant $A/g\mu_B$ required for this quantitative agreement is about a factor of 3 larger than the 1.57 G obtained[15] from hyperfine splittings for TCNQ$^-$ in solution. We must view the agreement with the present theory as only qualitative, and this is hardly surprising in view of the marginal nature of this system as a candidate for comparison with the present theory. We have already mentioned the smallness of the value of U/t required, and we must also point out that the temperatures available are all less than t (≈ 575 °K), and even for the most part less than $2t^2/U$, where we know that the theory can no longer be trusted. Furthermore, the experimental evidence leaves some question as to the usefulness of the simple Hubbard Hamiltonian in describing NMP-TCNQ. The low-temperature data are best fitted by a value of $U/t \simeq 8$ rather than 4; the high-temperature susceptibility is approximately constant rather than taking the Curie form predicted by Eq. (2.6). But the system does undergo a metal-insulator transition, and we believe that the change in correlation time on passing through this transition as described above contains the important physics of the temperature dependence of T_1.

Finally, we point out that there exists recent independent work[16] on a high-temperature expansion of the partition function to study the thermodynanic properties of the Hubbard model.

APPENDIX: CUMULANT EXPANSION THEOREM

We are interested in thermodynamic averages of operators in a system governed by the general Hamiltonian

$$\mathcal{H} - \mu N = \mathcal{H}_0 + \mathcal{H}' . \tag{A1}$$

We write the desired average in the form

$$\langle A\rangle = \frac{\partial}{\partial\eta} \ln \mathrm{Tr}\left(e^{-\beta(\mathcal{H}-\mu N)} e^{\eta A}\right)\Big|_{\eta=0} , \tag{A2}$$

and make use of standard cumulant expansion theorems.[17] Thus we write

$$e^{\eta A} e^{-\beta(\mathcal{H}-\mu N)} = \langle\langle e^{\eta A}\rangle\rangle \rho\, T_\lambda \exp\left[-\textstyle\int_0^\beta d\lambda \mathcal{H}'(\lambda)\right] , \tag{A3}$$

where we have defined

$$\langle\langle X\rangle\rangle \equiv \mathrm{Tr}\, e^{-\beta\mathcal{H}_0} X , \tag{A4}$$

so that ρ is a normalized density operator, T_λ denotes the usual ordered exponential, and

$$\mathcal{H}'(\lambda) = e^{\lambda\mathcal{H}_0} \mathcal{H}' e^{-\lambda\mathcal{H}_0} . \tag{A5}$$

Then we have

$$\langle A\rangle = \frac{\partial}{\partial\eta}\left(\ln\langle\langle e^{\eta A}\rangle\rangle + \sum_{n=1}^{\infty} \left\langle \int_0^\beta d\lambda_1 \cdots \times \int_0^{\lambda_{n-1}} d\lambda_n \mathcal{H}'(\lambda_1)\cdots\mathcal{H}'(\lambda_n) e^{\eta A} \right\rangle_{\mathrm{cum}} \right)\Bigg|_{\eta=0} , \tag{A6}$$

where the first few terms in the large parentheses are given explicitly as

$$\ln\langle\langle e^{\eta A}\rangle\rangle + \frac{\int_0^\beta d\lambda \langle\langle \mathcal{H}'(\lambda) e^{\eta A}\rangle\rangle}{\langle\langle e^{\eta A}\rangle\rangle} + \int_0^\beta d\lambda \int_0^\lambda d\lambda' \left[\frac{\langle\langle \mathcal{H}'(\lambda)\mathcal{H}'(\lambda') e^{\eta A}\rangle\rangle}{\langle\langle e^{\eta A}\rangle\rangle} - \left| \frac{\langle\langle \mathcal{H}'(\lambda) e^{\eta A}\rangle\rangle}{\langle\langle e^{\eta A}\rangle\rangle} \right|^2 \right] . \tag{A7}$$

In the examples discussed in this paper we frequently have $\langle\langle \mathcal{H}'(\lambda)\rangle\rangle = \langle\langle \mathcal{H}'(\lambda)A\rangle\rangle = 0$. Under these circumstances the result to second order in $\mathcal{H}'$ is

$$\langle A\rangle \approx \langle A\rangle_0 + \int_0^\beta d\lambda \int_0^\lambda d\lambda' [\langle \mathcal{H}'(\lambda)\mathcal{H}'(\lambda')A\rangle_0 - \langle \mathcal{H}'(\lambda)\mathcal{H}'(\lambda')\rangle_0 \langle A\rangle_0] , \quad \text{(A8)}$$

where we have employed the standard notation for averages with respect to the unperturbed Hamiltonian:

$$\langle X\rangle_0 \equiv \mathrm{Tr}\,(e^{-\beta\mathcal{H}_0} X)/\mathrm{Tr}\, e^{-\beta\mathcal{H}_0} . \quad \text{(A9)}$$

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*Supported in part by the National Science Foundation.

†Supported in part by the Office of Naval Research.

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PHYSICAL REVIEW B VOLUME 7, NUMBER 11 1 JUNE 1973

High-Spin Expansion for Heisenberg Spin Systems

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(Received 3 November 1972)

It is known that in a well-defined high-spin limit, the properties of systems of quantum spins approach those of a corresponding system of classical spins. In this paper we give a method for computing corrections to this limit. We give the first nontrivial corrections to the partition function and spin-spin correlation function for a linear chain of Heisenberg-coupled spins. We briefly discuss possible comparisons with experiment.

I. INTRODUCTION

Several materials have been found in recent years which behave magnetically like one-dimensional crystals.[1-10] These crystals consist of chains of strongly coupled spins with a much weaker interchain coupling. At low enough temperatures the weak interchain coupling produces a phase transition to a state with three-dimensional long-range order, but above this temperature these systems appear one-dimensional in character.

One such material is $(CH_3)_4NMnCl_3$ known as TMMC. There is experimental[4,7] evidence that TMMC behaves as a one-dimensional system down to 1 °K. This system appears to be an isotropic spin-$\frac{5}{2}$ Heisenberg antiferromagnet. Birgeneau *et al.*[7] have found that Fisher's[11] solution of the classical Heisenberg chain fits the measured staggered susceptibility of TMMC from $T = 1$ °K to $T = 40$ °K. This classical model was also used by Dingle *et al.*[4] to fit susceptibility data for TMMC.

It is surprising that a classical spin model can be used at low temperatures. One might expect quantum effects to be important when kT is smaller than the energy required to change the state of a single spin, that is, when $JS/kT > 1$, where J is the Heisenberg coupling constant and S is the magnitude of the spin. This parameter ranges between 1 and 50 for TMMC at temperatures between 40 and 1 °K.

In this paper we describe a calculation of the first nontrivial quantum correction to the classical Heisenberg model. The method we describe is a general one, suitable for high-spin systems, and