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# Nuclear relaxation in one-dimensional Hubbard systems

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Measurements of the proton nuclear relaxation time $T_1$ have been performed at room temperature in two conductive tetracyanoquinodimethane (TCNQ) salts: *N*-methylphenazinium-TCNQ and quinolinium-(TCNQ)$_2$. A frequency dependence of $T_1$ is reported, which provides evidence for a one-dimensional diffusive motion. In order to explain this result, the spin correlation function is calculated for the Hubbard chain model by explicitly taking into account the one-dimensional character of the system. A diffusive process is shown to arise from the scattering of the conduction electrons by the Coulomb repulsions.

## I. INTRODUCTION

Theoretical investigations of the Hubbard chain model have been stimulated recently by the experimental studies in one-dimensional (1D) conductors, in particular tetracyanoquinodimethane (TCNQ) salts. But whereas thermodynamic properties have been intensively studied, dynamic properties have received only little attention. This paper is concerned with both the experimental and the theoretical aspects of the spin dynamics in the Hubbard chain model. First we report a frequency dependence of the nuclear relaxation time $T_1$ in two conductive TCNQ salts: *N*-methylphenazinium (NMP)-TCNQ, and quinolinium-(TCNQ)$_2$. This fact is rather surprising since the observation frequencies (the electronic and the nuclear Larmor frequencies) are much smaller than the energies which characterize these quasimetallic systems. Actually no frequency dependence is expected from the current theories which were previously used to explain the nuclear relaxation in these compounds.[1-3] The experimental results provide evidence for a 1D diffusive motion of the electronic spins, as previously reported in other 1D systems, i.e., Heisenberg chains[4] and linear excitons.[5] Therefore, we present in Sec. III a calculation to obtain the low-frequency part of the spin correlation function, taking into account the 1D character of the system. It is shown that a diffusive behavior arises from the scattering of the electrons by the Coulomb repulsions.

## II. EXPERIMENTAL

The proton nuclear relaxation time has been measured in NMP-TCNQ and quinolinium-(TCNQ)$_2$ as a function of the nuclear Larmor frequency between 7 and 100 MHz, using a standard $\pi - \frac{1}{2}\pi$ pulse method. The recovery of the nuclear magnetization is exponential over about a decade. Measurements have been performed at room temperature on polycrystalline samples. The results are given in Figs. 1 and 2. The nuclear relaxation rate $T_1^{-1}$ is plotted against the inverse square root of the nuclear Larmor frequency $\nu_N^{-1/2}$ in order to make apparent the 1D diffusive behavior. One obtains a straight line in the entire frequency range (from 7 to 100 MHz) for quinolinium-(TCNQ)$_2$, and only from 40 to 100 MHz for NMP-TCNQ. Before we attempt to analyze these results, we present a few other experimental features. A change in the $T_1$ values, especially for NMP-TCNQ, was observed after the samples were exposed to open air for a few days. The increase in the relaxation rates was about 30%, and was frequency independent. A possible explanation is that the additional relaxation is induced by the surface-absorbed oxygen on the finely divided samples. Definitive measurements (Figs. 1 and 2) have been performed on vacuum-sealed samples. We have also measured $T_1$ as a function of the temperature at given frequencies. The temperature dependence of $T_1$ in quinolinium-(TCNQ)$_2$ is found to display a Korringa-like variation between 150 and 300 K as previously reported.[2] The NMP salt shows a rather small variation in the 100–300-K range. Our results at 25 MHz for vacuum-sealed samples agree with the results previously reported.[1]

As long as the electronic and nuclear Zeeman energies $\omega_e$ and $\omega_N = 2\pi\nu_N$ are much smaller than the thermal energy $kT$, the nuclear relaxation rate due to concentrated electronic spins is expressed for a polycrystalline sample as[6]

$$1/T_1 = \tfrac{1}{5}\pi\left[6\langle d^2\rangle\Phi^z(\omega_N) + (7\langle d^2\rangle + 5\langle a^2\rangle)\Phi^+(\omega_e)\right], \tag{1}$$

where $\langle a^2\rangle$ and $\langle d^2\rangle$ are the mean square of the scalar and dipolar parts of the hyperfine couplings (in $\hbar$ units). $\Phi^+(\omega)$ is the Fourier transform of the local electronic spin autocorrelation function:

$$\Phi^+(t) = \langle s_\lambda^+(t)s_\lambda^-(0)\rangle .$$

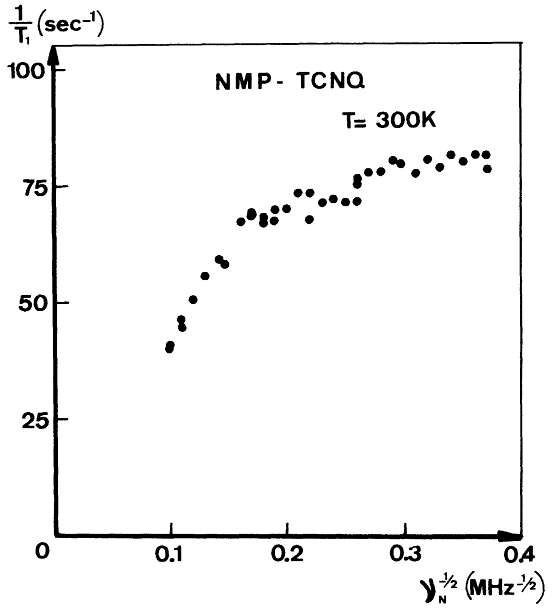

FIG. 1. Proton relaxation rate as a function of the inverse square root of the nuclear Larmor frequency in NMP-TCNQ.

Similarly we define:

$$\Phi^z(t)=\langle s^z_\lambda(t)s^z_\lambda(0)\rangle .$$

The time evolution of the electronic spin $s^+_\lambda$ at site $\lambda$ arises from the complete electronic Hamiltonian except the Zeeman term. For an isotropic Hamiltonian, one has in the paramagnetic region: $2\Phi^z(\omega)=\Phi^+(\omega)=\Phi(\omega)$. In the case of a 1D diffusive behavior, $\Phi(\omega)$ can be written as

$$\Phi(\omega)=(C/2\pi)[1/(2D\omega)^{1/2}], \qquad (2)$$

where $C$ is a normalizing constant and $D$ is the diffusion coefficient.

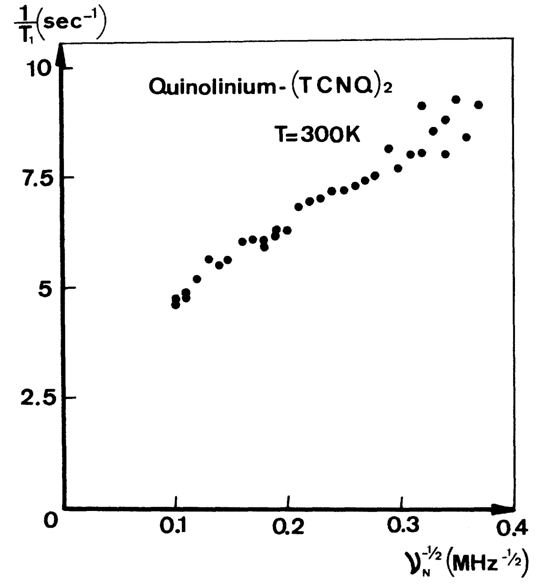

FIG. 2. Proton relaxation rate as a function of the inverse square root of the nuclear Larmor frequency in quinolinium-(TCNQ)$_2$.

In Eq. (1) we have neglected the crosscorrelation functions

$$\langle s^+_\lambda(t)s^-_{\lambda'}(0)\rangle \text{ with } \lambda\neq\lambda' .$$

As explained in Ref. 6, the contribution of these terms is expected to be rather small in polycrystalline samples, for geometrical reasons. Moreover, the cross correlation functions have the same low-frequency behavior as the autocorrelation function, so that the assumption made in Eq. (1) is not crucial.

A quantitative analysis of the experimental results requires some knowledge of the strength of the hyperfine couplings. As a first approximation the scalar part can be calculated from the hyperfine constant of TCNQ$^-$ in solution (1.5 G),[7] taking into account the average number of electrons per TCNQ site; this gives $\langle a^2\rangle=1.9\times10^{14}$ (rad/sec)$^2$ for NMP-TCNQ and $\langle a^2\rangle=0.9\times10^{14}$ (rad/sec)$^2$ for quinolinium-(TCNQ)$_2$. There are some experimental data available which show that in TCNQ salts the scalar coupling should be dominant (i.e., the observation of a *positive* Overhauser effect[8]). However, there is no reason to assert that the dipolar part of the coupling is quite negligible. Therefore, the first part of the right-hand side of Eq. (1) could give an appreciable contribution to the relaxation, especially because $\Phi(\omega_N)$ is expected to be greater than $\Phi(\omega_e)$. In the case of quinolinium-(TCNQ)$_2$, one can interpret the results in the following way: The $\omega_N$ contribution is assumed to be constant because $\omega_N$ is supposed to be lower than the cutoff frequency which limits the diffusion process (this assumption will be discussed in Sec. IV). The frequency dependence of $T_1$ thus only arises from the $\omega_e$ contribution ($\omega_e=660\omega_N$). Taking into account only the scalar part of the coefficient of $\Phi(\omega_e)$, the diffusion coefficient may be evaluated from the slope of $T_1^{-1}$ against $\nu_N^{-1/2}$ by means of Eqs. (1) and (2), and one obtains $D/C^2=0.6$ eV. For NMP-TCNQ (Fig. 1), the frequency variation of $T_1$ is more complicated. It consists of two parts; in the high-frequency region there is evidence for a 1D diffusive behavior but the slope is not accurately defined, at lower frequencies the variation of $T_1$ becomes smaller. A possible frequency dependence of $\Phi(\omega_N)$ or cutoff effects could be put forward to explain the experimental results. But it would be unrealistic to attempt such an explanation at the present stage of the theory.

## III. THEORETICAL

### A. Previous theories

Most electronic properties of NMP-TCNQ and quinolinium-(TCNQ)$_2$ can be described in terms of the linear Hubbard Hamiltonian

$$H = U + \Theta = u \sum_{\lambda} n_{\lambda\uparrow} n_{\lambda\downarrow} - \theta \sum_{\lambda\sigma} (c^{\dagger}_{\lambda\sigma} c_{\lambda+1\sigma} + c^{\dagger}_{\lambda+1\sigma} c_{\lambda\sigma}) , \qquad (3)$$

where $c^{\dagger}_{\lambda\sigma}$, $c_{\lambda\sigma}$, and $n_{\lambda\sigma}$ are, respectively, the creation, annihilation, and population operator for an electron of spin $\sigma$ in the Wannier state localized at site $\lambda$, $u$ is the one-site Coulomb repulsion, and $\theta$ is the nearest-neighbor transfer integral. We define $n$ as the average number of electrons per TCNQ site [$n=1$ for NMP-TCNQ and $n=\frac{1}{2}$ for quinolinium-(TCNQ)$_2$]. Orders of magnitude of $u$ and $\theta$ have been deduced from the analysis of transport and magnetic properties of NMP-TCNQ,[9] $u \simeq 0.15$–$0.18$ eV, and $\theta \simeq 0.04$–$0.05$ eV in the high-temperature region. Similar values are expected for quinolinium-(TCNQ)$_2$.

In the framework of this model, Ehrenfreund *et al.*[1] have attributed the unusually large value of $T_1^{-1}$ in NMP-TCNQ to an enhancement of the relaxation due to the Coulomb interactions. This interpretation is based upon the random-phase-approximation calculation of the dynamic susceptibility by Moriya[10] and Izuyama *et al.*[11] Hone and Pincus[3] have calculated the nuclear relaxation in the case of a half-filled band ($n=1$) with strong interactions ($u \gg \theta$) by using a high-temperature expansion ($kT \gg \theta$), but they assume a Gaussian line shape for the spin correlation function $\Phi(t)$, which is very dubious for 1D systems. Clearly the random-phase-approximation calculation and the Hone-Pincus theory cannot explain the frequency dependence of $T_1$, because they do not take into account the 1D dynamic properties of the system.

More recently, Villain[12] has considered the case of infinite Coulomb repulsion ($u \gg \theta, kT$) for a non-half-filled band ($n \neq 1$). The problem is then reduced to the calculation of the position correlation function for itinerant electrons. A 1D diffusive law is obtained, $\Phi(\omega) \propto \omega^{-1/2}$. On the other hand, the limit of electrons without interaction ($u=0$) can be solved exactly,[13] and for a narrow-band system, a logarithmic divergence takes place at low frequencies: $\Phi(\omega) \propto \ln \omega^{-1}$.

The purpose of the following calculation is to show how the Coulomb repulsions between electrons change the coherent motion into a diffusive (incoherent) process. The calculation is restricted to the high-temperature limit, $kT \gg \theta$. A possible extension will be discussed in Sec. IV. *A priori*, no conditions are imposed on the value of $u$ relative to $\theta$ or $kT$.

### B. Principle of the calculation

By performing the usual transformation,

$$c^{\dagger}_{\lambda\sigma} = N^{-1/2} \sum_{q} e^{-iq\lambda} c^{\dagger}_{q\sigma} ,$$

the spin correlation function is expressed in $Q$ space,

$$\Phi(t) = \sum_{Q} \Phi_Q(t) = \sum_{Q} \langle S^{+}_{Q}(t) S^{-}_{-Q}(0) \rangle ,$$

where the time evolution of the spin in $Q$ space

$$S^{+}_{Q} = N^{-1} \sum_{q} c^{\dagger}_{q\uparrow} c_{q+Q\downarrow}$$

comes from the Hubbard Hamiltonian [Eq. (3)]:

$$S^{+}_{Q}(t) = e^{iHt} S^{+}_{Q} e^{-iHt} .$$

Owing to the commutation rule $[S^{+}_{Q}, U] = 0$, the problem is somewhat similar to the exchange narrowing of the EPR line. It is therefore convenient to use the memory function formalism,[14] as recently applied to describe the EPR line shape in Heisenberg system.[15] The spin correlation function in $Q$ space is governed by the following equation:

$$\dot{\Phi}_Q(t) = -i\Omega\Phi_Q(t) - \int_0^t M_Q(\tau)\Phi_Q(t-\tau)\,d\tau , \qquad (4)$$

where $\Omega = \langle [S^{+}_{Q}, \Theta] S^{-}_{-Q} \rangle / \langle S^{+}_{Q} S^{-}_{-Q} \rangle$. In the high-temperature limit ($kT \gg \theta$), one has $\Omega = 0$. Furthermore, in the Markoffian approximation—the validity of which we shall justify later on—the memory function $M_Q(t)$ is assumed to decrease much more rapidly than the function $\Phi_Q(t)$ itself. Hence, Eq. (4) is integrated as

$$\Phi_Q(t) = \langle S^{+}_{Q} S^{-}_{-Q} \rangle e^{-\delta_Q |t|} , \qquad (5)$$

where

$$\delta_Q = \int_0^{+\infty} M_Q(t)\,d\tau . \qquad (6)$$

The Fourier transform of $\Phi_Q(t)$ has then a Lorentzian line shape, and the frequency correlation function in real space is given by

$$\Phi(\omega) = \sum_{Q} \frac{\langle S^{+}_{Q} S^{-}_{-Q} \rangle}{\pi} \frac{\delta_Q}{\omega^2 + \delta_Q^2} . \qquad (7)$$

As long as $\Omega = 0$ and the Markoffian assumption is valid, it can easily be shown from Eq. (4) that $M_Q(t)$ has the same short-time development as the second derivative of $\Phi_Q(t)$:

$$M_Q(t) = \langle [S^{+}_{Q}, \Theta](t) [\Theta, S^{-}_{-Q}] \rangle / \langle S^{+}_{Q} S^{-}_{-Q} \rangle . \qquad (8)$$

### C. Coherent case

Although this is not the main object of the present calculation, it is interesting to examine first the case of vanishing Coulomb interaction ($u = 0$). For small wave numbers $Q$ (whose contribution is preponderant at low frequencies), the short-time development of $M_Q(t)$ is written as

$$M_Q(t) = 2\theta^2 Q^2 (1 - \tfrac{3}{2}\theta^2 Q^2 t^2 + \cdots) . \tag{9}$$

Assuming a Gaussian line shape for $M_Q(t)$, it can be seen that the correlation times of $M_Q(t)$ and $\Phi_Q(t)$ are roughly equal [$\tau_c \simeq (\theta Q)^{-1}$]. Although the Markoffian hypothesis is no longer valid in this case, it is noteworthy that the present formalism leads to the correct frequency dependence of $\Phi(\omega)$; indeed with $\delta_Q = \sqrt{2}\,\theta Q$, Eq. (7) yields

$$\Phi(\omega) = \frac{n(2-n)}{4\sqrt{2}\,\pi^2\theta} \ln \frac{\sqrt{2}\,\pi\theta}{\omega} ,$$

while the exact result for the coherent motion is[13]:

$$\Phi(\omega) = [n(2-n)/4\pi^2\theta][1.39 + \ln(4\theta/\omega)] .$$

### D. Diffusive case

Let us now examine the case of interest for us: $u \neq 0$. Because of the condition $kT \gg \theta$, the density operator is reduced to $\rho = \exp[-\beta(U - \mu N)]$, where $\beta = 1/kT$, $\mu$ is the chemical potential and $N$ is the operator for the total number of electrons. In order to calculate $M_Q(t)$ in the site representation, it is convenient to characterize the thermodynamical state of the system by the parameter $x$, which is defined as

$$\langle n_{\lambda\uparrow} n_{\lambda\downarrow} \rangle = m^2 x ,$$

where $m = \langle n_{\lambda\uparrow} \rangle = \frac{1}{2} n$. It is straightforward to obtain the limits of $x$:

$$\beta u \ll 1 \rightarrow x = 1 ,$$

$$\beta u \gg 1 \rightarrow \begin{cases} x = 0 & \text{for } 2m < 1 , \\ x = (2m-1)/m^2 & \text{for } 2m > 1 . \end{cases}$$

The static correlation function can be expressed as

$$\langle S_Q^+ S_{-Q}^- \rangle = \frac{1}{N^2} \sum_{\lambda\lambda'} e^{iQ(\lambda' - \lambda)} \langle s_\lambda^+ s_{\lambda'}^- \rangle .$$

Since the density operator does not connect different sites, only the $\lambda = \lambda'$ term remains:

$$\langle S_Q^+ S_{-Q}^- \rangle = N^{-1} m (1 - mx) .$$

In order to evaluate $M_Q(t)$, a short-time expansion of the time evolution operator is performed:

$$A(t) = e^{i(U+\Theta)t} = e^{iUt} \left( 1 + i \int_0^t \Theta(t_1) dt - \int_0^t dt_1 \int_0^{t_1} dt_2 \Theta(t_1) \Theta(t_2) + \cdots \right) , \tag{10}$$

where $\Theta(t) = e^{-iUt} \Theta\, e^{iUt}$. The first term (Hamiltonian $U$ alone) causes an oscillation at frequency $u$, but no decrease of the memory function; for small $Q$, the contribution of this first term, which we denote $\tilde{M}_Q(t)$, is expressed as

$$\tilde{M}_Q(t) = 2\theta^2 Q^2 \{ (1 - 2m + 2m^2 x) + [m/(1 - mx)][(1 - mx)^2 e^{-iut} + x(1 - 2mx + m^2 x) e^{iut}] \} .$$

The decrease of $M_Q(t)$ therefore arises from the transfer term. The expression for $\Theta(t)$ can be calculated in the site representation

$$\Theta(t) = \Theta \cos ut + \overline{\Theta}(1 - \cos ut) + \Theta' \sin ut , \tag{11}$$

where

$$\overline{\Theta} = \theta \sum_{\lambda\sigma} (n_{\lambda+1\sigma} - n_{\lambda\sigma})^2 (c_{\lambda\sigma}^\dagger c_{\lambda+1\sigma} + c_{\lambda+1\sigma}^\dagger c_{\lambda\sigma}) ,$$

$$\Theta' = -i\theta \sum_{\lambda\sigma} (n_{\lambda+1\sigma} - n_{\lambda\sigma})(c_{\lambda\sigma}^\dagger c_{\lambda+1\sigma} - c_{\lambda+1\sigma}^\dagger c_{\lambda\sigma}) .$$

For times shorter than $1/u$, the leading term in Eq. (11) is $\Theta$; this would give a correlation time $\tau_c \simeq 1/\theta Q$ for $M_Q(t)$, as in the purely coherent case. But for $ut \gg 1$, one has

$$\int_0^t \Theta(\tau)\, d\tau = \overline{\Theta} t ,$$

which gives for the time evolution operator [Eq. (10)]

$$A(t) = e^{iUt}(1 + i\overline{\Theta} t - \tfrac{1}{2}\overline{\Theta}^2 t^2 + \cdots) , \tag{12}$$

where $\overline{\Theta}$ appears as an effective Hamiltonian which includes the scattering effects due to the Coulomb interactions,

$$\overline{\Theta} = \frac{1}{t} \int_0^t e^{-iU\tau} \Theta e^{iU\tau} d\tau \quad (ut \gg 1) .$$

Therefore, Eq. (12) applies if the scattering effects are effective within a time shorter than the correlation time for the coherent motion, i.e., if

$u \gg \theta Q$ .

Thus the short-wavelength functions ($Q \gg u/\theta$) display a coherent behavior, while for small $Q$ the memory function should be calculated from Eq. (12), and the calculation is performed in the site representation, and finally leads to

$$M_Q(t) = \tilde{M}_Q(t) - \tfrac{1}{2} t^2 \tilde{R}_Q(t) + \cdots ,$$

where $\tilde{R}_Q(t)$ is also an oscillating function,

$$\tilde{R}_Q(t) = 2\theta^4 Q^2 \left( 12m(1-mx)(1-2m+2m^2x) + \frac{m(3-4m+4m^2x)}{1-mx} \left[ (1-mx)^2 e^{-iut} + x(1-2m+m^2x) e^{iut} \right] \right) .$$

In order to evaluate the area under $M_Q(t)$ [Eq. (6)], we neglect the rapid oscillations at frequency $u$

$$M_Q(t) = 2\theta^2 Q^2 (1-2m+2m^2x) \times [1 - 6m(1-mx)\theta^2 t^2 + \cdots] . \tag{13}$$

Hence the Markoffian approximation is valid if $Q \ll 1$, which is the usual condition for the hydrodynamic limit. Assuming a Gaussian shape for $M_Q(t)$ (the explicit shape is of no consequence in a Markoffian approximation), we obtain for $\delta_Q$:

$$\delta_Q = \int_0^{+\infty} M_Q(t)\, d\tau = DQ^2 , \tag{14}$$

which defines the diffusion coefficient $D$:

$$D = \theta \left( \frac{\pi(1-2m+2m^2x)}{6m(1-mx)} \right)^{1/2} . \tag{15}$$

This $Q^2$ dependence of the linewidth of $\Phi_Q(\omega)$ is characteristic of a diffusive process. It is to be compared with the result of the coherent case $\delta_Q = \sqrt{2}\,\theta Q$. The difference arises from the substitution of $\bar{\Theta}$ for $\Theta$ in the time evolution operator [Eq. (12)]. This leads for the second derivative of $M_Q(t)$ to a term proportional to $\theta^4 Q^2$ [Eq. (13)] instead of $\theta^4 Q^4$ in the coherent case [Eq. (9)]. The physical meaning of this result is the following: The free mean path of the electrons is limited by the Coulomb interactions. For small $Q$, it is much shorter than the wavelength of the unperturbed transfer motion, and the coherency of this motion is therefore broken by the scattering of the electrons from a Bloch state to another one. This gives rise to a diffusion process.

In order to obtain the frequency correlation function in configuration space, we must perform the summation of the diffusive small-$Q$ modes ($Q \ll u/\theta$), and of the coherent large-$Q$ modes. As the contribution of the small $Q$ is dominant at low frequencies, we obtain from Eqs. (7) and (14)

$$\Phi(\omega) = [m(1-mx)/2\pi][1/(2D\omega)^{1/2}] . \tag{16}$$

The condition of application for this result is that the Coulomb interactions be strong enough to perturb an appreciable part of the $Q$ modes, i.e., $u \gtrsim \theta$. At this point it may be noted that the continuous transition from coherent to incoherent motion could be described by treating the complete Hamiltonian $\Theta(t)$ [Eq. (11)].

### E. Special case $n = 1$

The previous results are valid for any $n$ as long as $kT \gg \theta$ and $u \gtrsim \theta$. However, in the case of the half-filled band ($n = 2m = 1$) for $kT \ll u$ ($x \to 0$), Eq. (13) yields $M_Q(t) = 0$, and therefore $D = 0$. In this case, the hopping of the electrons from one site to another is no longer possible. As shown by Hone and Pincus,[3] the density operator should be expanded as a function of $\beta\theta$ in order to obtain the term of *virtual* hopping. In fact, in this case and for $\theta/u \ll 1$, the Hubbard Hamiltonian is reduced to the Heisenberg model with $J = 4\theta^2/u$,[16] and therefore one still expects a diffusive behavior for the spin correlation function with a diffusion constant $D = \sqrt{2\pi}\,\theta^2/u$.[17]

## IV. DISCUSSION

Although the condition $kT \gg \theta$ is not fulfilled in our $T_1$ measurements at room temperature in NMP-TCNQ and quinolinium-$(\text{TCNQ})_2$, the present theory is able to explain some experimental features. The most important is the $\omega^{-1/2}$ frequency dependence of the nuclear relaxation rate. Furthermore, a theoretical value of the diffusion coefficient can be evaluated from Eqs. (15) and (16). Taking $\theta = 0.05$ eV, one obtains for quinolinium-$(\text{TCNQ})_2$

$$D/C^2 \simeq \theta/m^2 = 0.8 \text{ eV}.$$

The agreement is quite good with the experimental value $D/C^2 = 0.6$ eV. Moreover, the low-frequency divergence of $\Phi(\omega)$ explains the large values of $T_1^{-1}$. For instance, at $\nu_N = 20$ MHz, the calculated scalar contribution $\pi\langle a^2\rangle \Phi(\omega_e)$ is 17 $\text{sec}^{-1}$ for NMP-TCNQ, and 4 $\text{sec}^{-1}$ for quinolinium-$(\text{TCNQ})_2$ [to be compared with the experimental values $T_1^{-1} = 70$ $\text{sec}^{-1}$ for NMP-TCNQ and 7 $\text{sec}^{-1}$ for quinolinium-$(\text{TCNQ})_2$].

Since we do observe a diffusive process at frequencies as low as $\nu_e \sim 10^{10}$ $\text{sec}^{-1}$, this value gives an upper bound for the frequency at which the $\omega^{-1/2}$ divergence is broken. The most efficient cutoff mechanism for the 1D diffusive motion is likely to be the interchain hopping of the electrons. Thus, the cutoff frequency $\omega_c$ should be of the same order of magnitude as the interchain transfer integral $\omega_c \sim \theta'$. From these considerations we may estimate that the anisotropy of the conductivity should be at least $10^3$ in NMP-TCNQ and quinolinium-$(\mathrm{TCNQ})_2$. To our knowledge the anisotropy of the conductivity has not been measured in these compounds, but such an order of magnitude has been reported for TTF-TCNQ.[18] This estimate of the anisotropy is based upon the assumption that the diffusive process $[\Phi(\omega) \propto \omega^{-1/2}]$ is observed at the *electronic* Larmor frequency $\omega_e$, while $\omega_N$ is less than the cutoff frequency, $\omega_N < \omega_c$. If this were not the case, that is, if the diffusive process at $\omega_N$ were also observed, the anisotropy of the conductivity would be as large as $10^6$. Because such a high value is unlikely for TCNQ salts, it is reasonable to rule out the $\omega_N$ contribution to the diffusion as we did here above.

The temperature variation expected from Eqs. (15) and (16) is rather small. It arises from the temperature dependence of the parameter $x$. The case of the half-filled band is somewhat special. At high temperature the diffusion coefficient is given by Eq. (15), $D \simeq \theta$, while at low temperature one has $D = \sqrt{2\pi}\,\theta^2/u$. Taking into account the value of the normalizing constant [$C = \frac{1}{4}$ in Eq. (16), and $C = \frac{1}{2}$ in the Heisenberg model], a slight enhancement is expected for the nuclear relaxation rate at the metal-Mott insulator transition,

$$\frac{1}{T_1}\bigg|_{\text{insulator}} = \left(\frac{u}{\theta}\right)^{1/2} \frac{1}{T_1}\bigg|_{\text{metal}} , \qquad (17)$$

while the enhancement factor given by the Hone-Pincus theory[3] is roughly $u/\theta$. Equation (17) allows a better fit of the small temperature variation of $T_1$ in NMP-TCNQ.[1]

However, the temperature dependence of $T_1$ in quinolinium-$(\mathrm{TCNQ})_2$ $(T_1^{-1} \propto T)$ provides a more serious challenge to our calculation. By anticipating a more complete theory, a qualitative explanation could be proposed: In quinolinium-$(\mathrm{TCNQ})_2$, the Coulomb interactions do not play a major role with regard to the thermodynamic properties because there is only one electron for two sites. Thus the density operator would be dominated by $\Theta$, although $u > \theta$, $\rho = \exp[-\beta(\Theta - \mu N)]$. For $kT < \theta$ the static correlation function thus yields

$$C = \langle S_Q^+ S_{-Q}^- \rangle \simeq kT\eta(\omega_F) ,$$

where $\eta(\omega_F)$ is the density of states at the Fermi level. In this way one can explain both the Korringa-like temperature dependence and the 1D diffusive frequency dependence with a diffusive constant which remains roughly equal to $\theta$.

So the main limitation of the present calculation is the high-temperature assumption. A more comprehensive theory should take into account the exact form for the density operator, $\rho = \exp[-\beta(U + \Theta - \mu N)]$. However, it is likely that our basic result—diffusive behavior of $\Phi(\omega)$—remains valid as long as an appreciable part of the energy levels in $Q$ space are thermally accessible, that is, down to $kT \lesssim \theta$. Finally it may be noted that other effects such as disorder and electron-phonon couplings, which actually exist in TCNQ salts, can contribute to the scattering of the electrons. The present theory can also be refined by taking into account the non-Markoffian effects which occur in 1D systems.[15]

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