Accurate Computation of the Magnetic Susceptibility for the Normal Phase of Organic Conductors

S. Moukouri
Department of physics, University of Cincinnati, Cincinnati, OH 45221
(January 12, 2022)

The magnetic susceptibility of the quarter-filled one-dimensional extended Hubbard model is calculated using the density-matrix renormalization group technique. It is found that in the charge gap regime of the model (\( U > 4t \) and \( V > 2t \)), or in the metallic region with important superconductive fluctuations (\( U < 4t \) and \( V > 2t \)), \( \chi(T) \) displays a singularity at \( T = 0 \) and an inflection point at low temperatures that are similar to what occurs in the spin-half quantum spin chain. These results, whose accuracy outdoes that of any other available technique, are useful data which allow a comparison between theory and experiment in the normal phase of the organic conductors.

During the last three decades, there has been an impressive collection of experimental results on organic conductors such as TTF-TCNQ, Bechgaard salts and their sulfur analogs. These materials display various low-temperature states including superconductivity, itinerant and localized spin magnetism, charge and spin density wave collective ordering, spin-Peierls instability, quantified nesting and quantum hall effects. It is suspected that this rich phenomenology is the consequence of the combined influence of low dimensionality and electron correlations. These materials are built from large planar molecules with \( \pi \)-orbitals that are oriented out of the molecular plane. Intersite hopping is favored along the stacking direction (\( t_a \)). The hopping integrals in the planar directions are respectively \( t_b = t_a/10 \) and \( t_c = t_a/500 \), which lead to strongly anisotropic electronic properties. It is generally believed that when \( T > T_X = t_b/\pi \), the physics of these materials is mainly one-dimensional. This stems from the fact that there is experimental evidence that above \( T_X \), these materials cannot be described by the Fermi liquid theory. In particular, it has been experimentally found that their magnetic susceptibility \( \chi(T) \) displays a temperature dependence which is not compatible with a Fermi liquid. Instead of the Pauli behavior of a Fermi liquid, a sizeable decrease is observed as \( T \) is lowered. The Luttinger liquid theory (LL), which plays in one dimension the role of the FL, has been proposed to interpret experimental results. Many of the available LL predictions are valid only at very low temperatures, but in this region, the 3D character reemerges. Thus, one resorts to the direct study of model Hamiltonians.

The 1D Hubbard model which belongs to the LL universality class is believed to be the appropriate model of organic compounds. Although the ground state properties of the basic Hubbard model (\( V = 0 \) in equation (3) below) were obtained long ago \(^2\), \(^1\), it was only recently that its thermodynamic properties were successfully calculated \(^1\). There are however experimental constraints which imply that the basic Hubbard model is not the appropriate model for the organic materials \(^8\). For instance, the observation of \( 4k_F \) fluctuations in TTF-TCNQ imply that the correlation function exponent \( K_F < 1/2 \). NMR measurements on the \((TMTSF)_2X\) materials predict that \( K_F = 0.15 \). These values are confirmed by photoemission measurements \(^3\). In the basic Hubbard model, however, \( K_F \) can not be less than \( 1/2 \) \(^3\).

The discrepancy between the prediction of the basic Hubbard model and the experiments, has led to the suggestion that dimerization and next nearest neighbor repulsion \( V \) may play a non-negligible role \(^7\), \(^8\). However, when these parameters are added, the model is not solvable. Knowledge of the strength of correlations is of central importance. The correlation parameters can be directly extracted from \( \chi(T) \). Fermi liquid theory and band structure calculations predict values that differ by an order of magnitude \(^8\). Current efforts are oriented towards the computation of more reliable values of \( \chi(T) \). This quantity is very useful to determine the correlation parameters. Bourbonnais \(^8\) applied a perturbative renormalization group (RG) to the g-ology Hamiltonian, which for an appropriate choice of parameters is a low energy limit of the Hubbard model. He computed \( \chi(T) \) and found that its \( T \) dependence was important down to \( T = 0 \). His results are, however, reliable only in the weak coupling regime and at low \( T \). Mila and Penc \(^8\) used the world-line quantum Monte Carlo algorithm to compute \( \chi(T) \) for the dimerized Hubbard model. Aside from the usual statistical errors that become important at low temperatures, another factor that reduced the quality of their calculation was that they had to perform three different extrapolations on momentum, imaginary time step and chain length. A recent analytical RG supplemented with a diagrammatic expansion and a QMC calculation predicted that \( \chi(T) \) would display a singularity at \( T = 0 \) and two inflection points at low \( T \) for the basic Hubbard model \(^8\). These features were first found in the susceptibility of the spin-half Heisenberg chain \(^3\). These fine structures are, however, overlooked by QMC. The reason is that besides the limited accuracy, the number of points computed in the low-temperature region remains
small to allow these structures to be resolved.

In this letter, we show that a thermodynamic density-matrix renormalization group (DMRG) algorithm presented in an earlier publication \cite{12} can lead to an accurate determination of \(\chi(T)\) for the extended Hubbard model. Our results are in excellent agreement with the exact results of Ref \cite{12} for \(V = 0\). We identify two sectors corresponding to the two regimes of the model. In the first, where the Hamiltonian is gapless in both charge and spin channels, \(\chi(T)\) increases moderately with \(V\). But in the charge gapped regime of the model we observe an important rise of \(\chi(T)\). We reach low enough temperatures to clearly see the appearance of an inflection point as soon as we enter the regime where the model presents a charge gap (\(V > 2t\)). At low \(T\), we find that the values of \(\chi(T)\) do not smoothly extrapolate to the zero temperature susceptibility \(\chi_0\). This lead us to conclude that a singularity exists at \(T = 0\).

We apply the thermodynamic DMRG algorithm of Ref \cite{12} \cite{16}. This algorithm is identical to the original \(T = 0\) DMRG algorithm \cite{13}. But the computation of the low-lying states which was the goal of the \(T = 0\) algorithm is now regarded as an intermediary step. In this step, we calculate as many target states as necessary to build a renormalized Hamiltonian which well describes higher energy states. For this, we target \(M\) states belonging to different spin sectors. The reduced density matrix may be written as follows,

\[
\rho = \sum_k \omega_k \rho_k, \quad (1)
\]

where \(\rho_k\) and \(\omega_k\) are respectively the reduced density matrix of the \(k\)th state and its weight. \(\rho_k\) is given by the wave function relation

\[
\rho_k(i_1, i_2; i'_1, i'_2) = \sum_{i_3, i_4} \Psi_k(i_1, i_2, i_3, i_4) \Psi_k^*(i'_1, i'_2, i_3, i_4). \quad (2)
\]

As usual, the four indices represent the different blocks forming the superblock. The main step of the algorithm is the exact diagonalization, by a dense matrix technique, of the reduced superblock Hamiltonian made of the two external blocks. The eigenvectors obtained this way are used for the computation of thermodynamic quantities. A systematic thermodynamic analysis is made in the following way. We start by fixing the temperature range, \(\chi(T)\) is calculated for initial values of block states \(m\) and target states \(M\). Then its dependence is analyzed by varying \(m\) and \(M\). We attribute the same weight to each target state, \(\omega = 1/M\). The importance of a target space in the reduced density matrix is thus given by the number of target states fixed for this space. We find that at the largest lattice size studied here, a good convergence is achieved by attributing 32 states to the \(S_T^z = 0\) sector and 4 states to each of the other sectors. We keep a total of 300 states in the two external blocks and the maximum truncation error is less than \(p(m, M) < 10^{-4}\).

A detailed analysis of the procedure has been given elsewhere \cite{16}. \(\chi_0 = \chi(T = 0)\) is calculated by the use of the LL relation \(\chi_0 = 2/(N\Delta_\sigma(N))\), where \(\Delta_\sigma(N)\) is the finite size gap defined as the energy difference between the lowest state with \(S_T = 1\) and the ground state, \(\Delta_\sigma(N) = E_1(N) - E_0(N)\). We find that the calculated \(\chi_0\) is in excellent agreement with Shiba’s exact result \cite{11}.

The thermodynamic equations of the basic Hubbard model were formulated long ago \cite{4}, but, it was only recently that Jüttner et al. succeeded in computing physical quantities at finite \(T\). In their study, these authors took a different approach which avoided the difficulties of the thermodynamic Bethe ansatz equations (BAE). These are an infinite set of coupled nonlinear integral equations that involve an infinite number of unknown functions. Actual calculations were possible with only a restricted basis \cite{4}. Jüttner et al. used the mapping of the Hubbard model to the two-dimensional classical Shastry model. They then applied the transfer matrix method to derive a set of BAE with a finite number of unknowns. The resulting nonlinear integral equations are solved numerically. The DMRG algorithm presented above provides a possibility of making an independent verification of their results. This algorithm has been quite successful in the study of quantum spin chains \cite{13} and of a magnetic impurity in spin chains \cite{17}. Its first application to fermion systems served for illustrative purposes and a detailed analysis of its convergence was made \cite{16}. In that study, it was mathematically shown that the finite-\(T\) algorithm is as rigorous as the \(T = 0\) algorithm. The only difference is that there are two control parameters, \(m\) and \(M\), instead of \(m\) only.

For a quantitative analysis with experimental results in the normal state of organic conductors, the effects of dimerization of the bond-length in the direction perpendicular to molecular planes should also be considered. In this study we consider the extended Hubbard model at quarter band-filling, which is the density of many organic compounds,

\[
H = -t \sum_i (c_{i\sigma}^+ c_{i+1\sigma} + \text{h.c.}) + U \sum_i n_{i\uparrow} n_{i\downarrow} + V \sum_i n_i n_{i+1}. \quad (3)
\]

The phase diagram of the model (3) has been obtained by Mila and coworkers \cite{5} \cite{4}. They applied the exact diagonalization on small clusters as well as analytical techniques in various limits to show that the model has two regimes. The first regime is a metallic Luttinger liquid phase that is gapless in both spin and charge channels. In the LL phase, the dominant fluctuations are spin density waves (SDW); in the strong \(V\) region they observed important superconductive fluctuations. The second regime is a charge density wave insulator characterized by an opening of the charge gap while the spin degrees of freedom remain gapless. The boundary between the two regimes is given by the line going from
(U, V) = (+∞, 2) to (4, +∞).

Fig. 1 shows that the excellent agreement with BAE results seen in the study of quantum spin chains [15] can also be achieved for the Hubbard model. Our results, for U = 1 to 16, were obtained by studying lattices of up to Nmax = 24 and then by extrapolating to N → +∞. They are in excellent agreement with the transfer matrix calculation of Jüttner et al. The maximum relative difference between the DMRG and the transfer matrix results is 0.05. This occurs at low temperatures where the quality of the DMRG calculations is affected by finite size effect. The lowest temperature reached in the transfer matrix calculation is T = 0.025. In the DMRG, the lowest T, which is roughly given by the finite size gap Δσ(Nmax) depends not only on the size of the system but also on the value of U. We find that paradoxically the strong coupling regime which is hard to study by analytical or QMC methods, is the most favorable since it has smaller Δσ for a fixed size. We performed an interpolation between T = 0 and T = Δσ(Nmax). We discuss below the reason of a particular choice of the interpolating function.

A recent study [3] has predicted that in the weak coupling regime, (i) the position of the maximum Tmax of χ(T) is interaction independent for 0 < U < 4, (ii) the inflection point at T = 0.1 of the non-interacting model will survive and will be interaction independent, (iii) the appearance of a new inflection point which is the consequence of the interaction at lower T, (iv) finally, the existence of a singularity at T = 0 in analogy with the antiferromagnetic Heisenberg spin-half chain. We find that the position of Tmax is gradually moved toward low T as the interaction increases. This DMRG result is more likely because in the Hubbard model, the weak coupling regime is qualitatively similar to the strong coupling regime. Thus one expects the same qualitative behavior in the two regions. We can not however directly verify the predictions (ii) and (iii) because in the weak coupling regime, the variations of χ(T) are so small that these possible features may be wiped away by extrapolation of the finite N results. In the strong coupling regime, the maximum is shifted to low T, a possible inflection point may appear at even lower T. It is thus possible that we have not reached the regime predicted by the analytical RG.

The inclusion of V in the strong coupling regime induces a clear appearance of the regime described by the RG study. In Fig. 2 we show χ(T) for U = 8 and V = 0 to V = 4. When U = 8 and V = 4, we have Δσ = 0.019. The inflection point, which is around 0.025, is clearly seen in our calculation. For the interpolation between T = 0 and T = Δσ(Nmax), we tried two techniques, polynomial and logarithmic. The latter has been tried in analogy with the study of the spin-half Heisenberg chain [16]. The conformal field theory has shown that at T = 0, χ(T) displays a logarithmic singularity [3]. Since adding V leads to an opening of the charge gap, in this regime the model bears some analogy with the spin-half Heisenberg chain. We find that the fit χ(T) = χ0 + A/LogT + BT is better than a simple polynomial fit. The polynomial fit introduces a cusp in χ(T). Indeed, we could also fit the V = 0 curves with a logarithmic function, but this seemed incorrect to us because we had not reached the inflection point Ti. The decrease of χ(T) for T > Ti is faster than for T < Ti; it is only in this latter regime that a logarithmic fit seems correct. From our calculation, at first sight one should relate this low T behavior of χ(T) to the onset of the insulating phase. But the analysis below of the weak U regime reveals that these features can exist even in a metallic phase. Hence, their occurrence in the case V = 0 is possible.

In the weak U regime, the model remains metallic for all values of V. The charge and spin degrees of freedom are both gapless. We observe in Fig. 3 that for U = 2, χ(T) increases with V, as for U = 8, although in this case the magnitude is smaller. For V = 4, we are in the region of the phase diagram where superconducting fluctuations are important. We find that at low T, the best fit to data is logarithmic. Hence, the RG predictions are also true in the metallic phase. We conclude by continuity that this is also valid when V = 0. We were unable to
and dominant superconductive fluctuations, found that in the insulating regime and in the region of longer publication. Our current effort is the calculation with experiment. This will be done in a cent RG study. Our results can be used for extensive chain. This is in conformity with the prediction of a re-behavior that is reminiscent of the spin-half Heisenberg optical conductivity by Vescoli et al. [21] lead to the optical conductivity. A recent reexamination of the dimerization found by Mila [7] from the analysis of the susceptibility comparison with that of another physi-cal quantity. The rough estimation made here is in good agreement with the values th of parameters renders any precise estimation of the dimerization in the Hamiltonian. This proliferation will provide a better estimation of the correlation parameters.

I wish to thank M. Jarrell for support and A. Klümper for sharing his transfer matrix data. This work started when I was at the University of Sherbrooke (Canada). I benefited from numerous exchanges with C. Bourbonnais, L. G. Caron and A.-M. S. Tremblay. This work was supported by the National Science Foundation grants DMR-0073308 and PHY94-07194.

FIG. 3. $\chi(T)$ for $U = 2$ and $V = 0, 1, 2, 3, 4$ from bottom to top.

see these features for $V = 0$, either because they occur at very low $T$ or they are wiped out by the extrapolation. The existence of the $T = 0$ singularity may be the consequence of the spin-charge separation. It is therefore a generic behavior of LL [10].

The magnetic susceptibility is a useful quantity for the extraction of correlation parameters $U$ and $V$ from experimental data. In Ref [3] it has been suggested that the ratio defined by $R = (\chi(T_{\text{max}}) - \chi(T_1))/\chi(T_{\text{max}})$ can be used to compare theory and experiment. While we will perform an extensive comparison in a longer publication, let us here look at the case of $(TMTSF)_2(PF)_6$. In this compound, $T_{\text{max}} = 275K$ and $T_1 = 150K$. A rough estimate of $R_{\text{exp}}$ is 0.22. It is also found that the resistivity displays insulating behavior. This implies that one necessarily has $U > 4$ and $V > 2t$. In this regime, the best match to the experimental value is obtained for $U = 8$ and $V = 4$. The corresponding estimate of the ratio is $R_{\text{th}} = 0.16$. This value can be improved either by increasing $U$ or $V$ slightly or by including the effect of the dimerization in the Hamiltonian. This proliferation of parameters renders any precise estimation of $U$ and $V$ very cumbersome. It will be necessary to supplement the susceptibility comparison with that of another physical quantity. The rough estimation made here is in good agreement with the values $U = 7$, $V = 2.8$ and 0.7 for the dimerization found by Mila [3] from the analysis of the optical conductivity. A recent reexamination of the optical conductivity by Vescoli et al. [21] lead to $U = 5$ and $V = 2$.

In this study, we have shown that using the finite $T$ DMRG algorithm, we can compute accurately the magnetic susceptibility of the extended Hubbard model. We found that in the insulating regime and in the region of dominant superconductive fluctuations, $\chi(T)$ displays a behavior that is reminiscent of the spin-half Heisenberg chain. This is in conformity with the prediction of a recent RG study. Our results can be used for extensive comparisons with experiment. This will be done in a longer publication. Our current effort is the calculation of the NMR relaxation factor $T_1$. A concurrent analysis of $\chi(T)$ and $T_1$ will provide a better estimation of the correlation parameters.

[1] C. Bourbonnais and D. Jérôme, science (1999). D. Jérôme, science 281, 1156 (1991). D. Jérôme and H. J. Schulz, Adv. in Phys. 31, 299 (1982).
[2] J. Voit, Rep. Prog. Phys. 58, 977 (1995).
[3] K. Penc and F. Mila, Phys. Rev. B 50, 11 429 (1994).
[4] F. Mila, Phys. Rev. B 49, 4788 (1994).
[5] F. Mila and X. Zotos, Europhys. Lett. 24, 133 (1993).
[6] H. J. Schulz, Phys. Rev. lett. 64, 2831 (1990); Int. J. Mod. Phys. B 5, 57 (1991).
[7] F. Mila and K. Penc, Phys. Rev. B 51, 1997 (1995).
[8] C. Bourbonnais, J. Phys. I (France) 3, 143 (1993).
[9] H. Néiisse et al., cond-mat 9903046, Eur. Phys. J. B (in press).
[10] C. Bourbonnais, private communication.
[11] H. Shiba, Phys. Rev. B 6, 930 (1972).
[12] G. Jüttner, A. Klümper and J. Suzuki, Nucl. Phys. B 522, 471 (1998).
[13] S. Eggert, I. Affleck and M. Takahashi, Phys. Rev. Lett. 73, 332 (1994).
[14] T. Usuki, N. Kawakami and A. Okiji, J. Phys. Soc. Jap. 59, 1357 (1990).
[15] S. Moukouri and L. G. Caron, Phys. Rev. Lett. 77, 4640 (1996).
[16] S. Moukouri and L. G. Caron in Density Matrix Renormalization , p. 329-336, I. Peschel, X. Wang M. Kaulke and K. Hallberg Eds., Springer (1999).
[17] W. Zhang, J. Igarashi and P. Fulde, J. Phys. Soc. Jap. 66, 1912 (1997).
[18] S. R. White, Phys. Rev. Lett. 69, 2863 (1992); Phys. Rev. B 48, 10345 (1993).
[19] M. Takahashi, Prog. Theor. Phys. 47, 69 (1972).
[20] E. H. Lieb and F. Y. Wu, Phys. Rev. Lett. 20, 1445 (1968).
[21] V. Vescoli, J. Favand, F. Mila, L. Degiorgi, Eur. Phys. J. B 3, 149 (1998).