ELECTRONIC CORRELATIONS IN ONE-DIMENSIONAL CONDUCTORS

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ABSTRACT-In this paper we use the variational Gutzwiller wave function to study the effects of the Coulomb electronic repulsive correlations on the plasma frequency and spin magnetic susceptibility of the Hubbard chain.

Our results agree with experimental data for quasi-one-dimensional conductors: on the one hand the plasma frequency is reduced by the electronic correlations and on the other hand these correlations lead to an enhancement of the spin magnetic susceptibility.

1. INTRODUCTION

The strong interest in synthetic metals started in the early seventies with the advent of TTF-TCNQ [1].

Many of these materials are highly anisotropic in their electrical properties and thus often referred to as "quasi-one-dimensional electronic systems". Such quasi-one-dimensionality follows from their structure, which is typically an array of rather weakly interacting metallic chains.

In the case of the organic crystals [2], [3], the electronic conduction takes place along stacks of planar organic molecules. These molecules, which are the elementary units of the linear chains, have a π-electron orbital which is oriented in the direction perpendicular to the plane of the molecule and allows for overlap between π-orbitals of adjacent molecules and thus for electrical transport.

The π-orbitals of the linear chains can either receive electrons from donor molecules or give electrons to acceptor molecules. These processes allow changing of the electronic density $n=N/N_a$ where N and N_a are the numbers of conducting electrons and sites of the linear chain.

When the electronic band, formed through the overlap between π-orbitals, is partially filled, the organic crystals behave as narrow band one-dimensional conductors.

The electronic structure of simple metals and alloys is in most cases well described by effective one-electron models where electron-electron interactions are taken into account through a self consistent field. This leads to the well-known model of Bloch for the conduction bands of metals and alloys.

Nonetheless, there is experimental evidence that in the case of the novel non-

trivial conductors and superconductors, as for example the just mentioned synthetic metals and the high T_c superconductors [4], the simple one-electron models are not sufficient to explain the electronic structure. These novel materials have in common the occurrence of low-dimensional effects (one and two dimensional) which imply a much more important role for the electron-electron interactions.

In the case of the organic quasi-one-dimensional metals the experimental values of the inverse of the plasma frequency and of the spin magnetic susceptibility, for example, are clearly enhanced in relation to those predicted by the model of Bloch [2],[3].

In this paper we use the one-dimensional Hubbard model [5] to describe the conducting π-electrons of the linear chains. The model is presented in Section 2. In Section 3 we apply the Gutzwiller variational scheme [6] (which was recently extended to the case of attractive correlations by one of us [7]) to evaluate the plasma frequency and spin magnetic susceptibility expressions. Section 4 gives a brief summary.

While the results concerning the spin magnetic susceptibility have not been published elsewhere, a previous study about the correlation effects on the oscillator strength of optical absorption was presented in Reference [8].

2. THE ONE-DIMENSIONAL HUBBARD MODEL

The structure of many synthetic metals can be represented by an array of weakly interacting chains. In the present work we neglect the interaction between the chains, which can be introduced as a small perturbation.

We consider N_a identical molecules at positions $x_j = j\,a = j$, $j = 1, \ldots\ldots\ldots, N_a$ (we use units such that the lattice constant $a = 1$). The molecular Wannier wave function for a conducting electron at site x_j and with spin σ ($\sigma = \pm\frac{1}{2}$) is denoted by $\phi_\sigma(x - x_j)$. We restrict our study to electronic densities such that $n \leq 1$ (the results for $n>1$ are readily obtained if one replaces electrons by holes). Moreover we only take into account the overlap between nearest neighbours electronic wave functions $\phi_\sigma(x - x_j)$ and $\phi_\sigma(x - x_{j+1})$. The hopping or transfer integral is given by:

$$t_{j,j+1} = t_{j+1,j} = t = \int dx\, \phi^*(x - x_j)\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\right]\phi(x - x_{j+1}) \quad (1)$$

where m is the electronic mass and V(x) is the lattice potential.

The square of the transfer integral (1) is related to the probability for electronic hopping between nearest neighbour sites.

The one-particle model obtained by the choice $t_{j,j+1} = t$ = constant, can be easily diagonalized, describing N conducting electrons in a band of width 4 t given by:

$$E(k) = -2\,t\cos(k) \qquad (2)$$

where the k momentum values are restricted to the first Brillouin zone, $|k| < \pi$. In the ground state only the orbitals with $|k| < k_F$ and spin projections $\sigma = \pm\frac{1}{2}$ are occupied (the one-dimensional Fermi surface is reduced to the two points $\pm k_F = \pm(\pi n)/2$).

The Hubbard model [5] contains, besides the hopping-term corresponding to the one-particle Hamiltonian described above, a many-body electronic potential which takes into account the Coulomb repulsive interaction between electrons on the same lattice site. Despite the drastic assumptions involved neglecting the long-range forces of the Coulomb repulsion, the Hubbard Hamiltonian has been quite successful in describing essential features of interacting electrons. The success of this model in describing, for example, some of the aspects of the physics of the novel synthetic metals is partially due to the screening of the long-range forces [9].

Besides the transfer integral (1), the Hubbard model includes the onsite repulsion parameter U,

$$U = \int dx\,dx' \phi^*_\sigma(x-x_j)\phi^*_{-\sigma}(x'-x_j)\frac{e^2}{|x-x'|}\phi_\sigma(x-x_j)\phi_{-\sigma}(x'-x_j) \qquad (3)$$

which is positive and measures the energy required to have two electrons of opposite spin projection on the same site.

The Hubbard model can describe two limiting situations. On the one hand for $U = 0$, the electrons are delocalized and have band-like behaviour. On the other hand for $U \gg t$, the weight of the electronic configurations showing double occupancy is drastically reduced, which implies a tendency for localization and antiferromagnetism if the density n is close to 1. In fact, in the particular case of the half-filled band, $n = 1$, the number of electrons N equals the number of lattice-sites N_a, and no double occupancy implies the full localization of the electrons.

In the intermediate regions ($U \simeq t$) we expect a cross-over from band-like to localized behaviour. This is the most interesting regime for the physics of the synthetic crystals, which show simultaneously metallic behaviour and properties which indicate a clear tendency for localization.

In second quantization the Hubbard model reads:

$$\hat{H} = -t\sum_{j,\sigma}[c^+_{j\sigma}c_{j+1\sigma} + c^+_{j+1\sigma}c_{j\sigma}] + U\hat{D} \qquad (4)$$

where $c^+_{j\sigma}$ ($c_{j\sigma}$) is the creation (annihilation) operator for an electron with spin σ at site j, which is described by the wave function $\phi(x - x_j)$ and $\hat{D}$ is the double occupancy operator given by:

$$\hat{D} = \sum_j n_{j\uparrow} n_{j\downarrow}; \quad n_{j\sigma} = c^{+}_{j\sigma} c_{j\sigma} \qquad (5)$$

3. VARIATIONAL STUDY OF THE PLASMA FREQUENCY AND SPIN MAGNETIC SUSCEPTIBILITY FOR ARBITRARY ELECTRON DENSITY.

The Hubbard Hamiltonian is a many-body model which is easier to handle than the complete Hamiltonian including the long-range forces of the Coulomb interactions, but still very difficult to diagonalize. In fact, this has only been achieved for a half-filled one-dimensional lattice [10]. For $n \neq 1$ the one-dimensional model was not fully solved but reduced to a system of coupled integral equations [10].

The variational ansatz introduced by Gutzwiller [6] is defined by:

$$|\phi> = e^{-[\eta \hat{D}]/2} |\phi_{SL}> \qquad (6)$$

where $|\phi_{SL}>$ is the Slater determinant which describes the ground state of (4) for $U = 0$ and η is a variational parameter.

The application of the exponential operator of the r.h.s. of Eq. (6) on the ground state wave function $|\phi_{SL}>$ reduces the weight of the configurations having doubly occupied sites.

According to the variational principle of quantum mechanics, the best approximation for the ground state energy is obtained by minimizing the functional

$$E = \frac{<\phi|\hat{H}|\phi>}{<\phi|\phi>} \qquad (7)$$

which leads to $\eta = 0$ for $U = 0$ and $\eta \to \infty$ for $U \to \infty$. We restrict the present study to the small U regime, i.e. $u = U/4t \leq 1$. The use of the quantum mechanics machinery allows the evaluation of a small η expansion of the energy (7). The detailed calculation is presented in reference [11]. After energy minimization we arrive at:

$$E = E_{HF} + E_{corr}$$

$$E_{HF}/\, t\, N_a = -\frac{4}{\pi} \sin k_F + u\left[\frac{2 k_F}{\pi}\right]^2 \qquad (8)$$

where E_{HF} denotes the energy obtained by the usual Hartree-Fock approximation and the correlation energy E_{corr} reads:

$$E_{corr}/t\, N_a = -u^2 \frac{4 k_F^4}{\pi} \frac{(1 - \frac{4 k_F}{3\pi})^2}{(\sin k_F)[k_F(\pi - k_F) + \sin^2 k_F]} \qquad (9)$$

As the kinetic energy T is related to the ground state energy (7) by $T = t\, dE/dt$ [8], we obtain:

$$|T|/t\, Na = \frac{4}{\pi} \sin k_F \left[1 - u^2 \frac{k_F^4 (1 - \frac{4 k_F}{3\pi})^2}{(\sin^2 k_F)[k_F(\pi - k_F) + \sin^2 k_F]}\right] \qquad (10)$$

The function (10) decreases monotonically with U for all densities. For the half-filled band case Eq. (10) reads:

$$|T| / t N_a = \frac{4}{\pi} [1 - 0.1951 u^2] \qquad (11)$$

This result is in good agreement with the Bethe ansatz expansion of Reference [12], covering 91.4% of the exact coefficient.

As we have already mentioned, experimental data show that the plasma frequency as determined by the partial sum rule (involving all intraband transitions) [2] is rather sensitive to correlation effects, decreasing for increasing values of the Coulomb effective repulsion.The square of the plasma frequency is proportional to the f-sum rule, which for the one-dimensional Hubbard model is simply proportional to the absolute value of the mean kinetic energy [8]. Thus the variational result (10) supports the experimental evidence that the oscillator strength of optical absorption of the synthetic quasi-one-dimensional metals is depressed by correlations. On the other hand, experimental data indicate an enhancement of the magnetic susceptibility for increasing values of the effective Coulomb repulsion [2], [3].

The magnetic susceptibility for the one-dimensional Hamiltonian (4) has been calculated exactly for the half-filled band case [13].

The main purpose of the present paper is to use the variational wave function (6) to derive a small U expansion for the spin magnetic susceptibility when $n \neq 1$. Applying a magnetic field to the electronic system described by (4), a small U energy expansion of the r.h.s. of Eq. (7) can be evaluated by the method described in [11] for zero magnetic field.

We omit here the details of the calculations, which are more involved than the ones of Reference [11] because of the magnetization dependence of the energy. Nevertheless, although the free propagators depend now on the spin indices, the diagrams which contribute to the correlation energy are the same as in the zero magnetic case.

The small U spin magnetic susceptibility expansion derived from the variational wave function (6) reads:

$$\chi = \chi_0 \{ 1 + u_F^2 + u_F [1 - J(k_F) [1 - J(k_F) G(k_F)]] \} \qquad (12)$$

where $\chi_0 = \mu_0^2 / (\pi t \sin(k_F))$ is the Pauli susceptibility of the non interacting system, $u_F = U/(2\pi t \sin(k_F)) < 1$ and

$$J(x) = \frac{(x\pi)^2 \ (1 - \frac{4x}{3\pi})}{\sin^2 (x) + x (\pi - x)} \qquad (13)$$

$$\pi^2 G(x) = 1 + \frac{1}{4} [\sin^2 (x) + x(\pi - x)] + (\frac{\pi}{2} - x) \cot (x) \qquad (14)$$

The magnetic susceptibility (12) is represented in figure 1 as a function of u for

fixed values of carrier density. χ is enhanced by correlation effects, and this effect is more pronounced for smaller values of band filling. A detailed comparison with the numerical results of Shiba [14] is difficult because our results are restricted to small u values. Nonetheless the curves of the figure agree qualitatively with his results. As expected, the magnetic susceptibility is enhanced by correlations for all carrier densities.

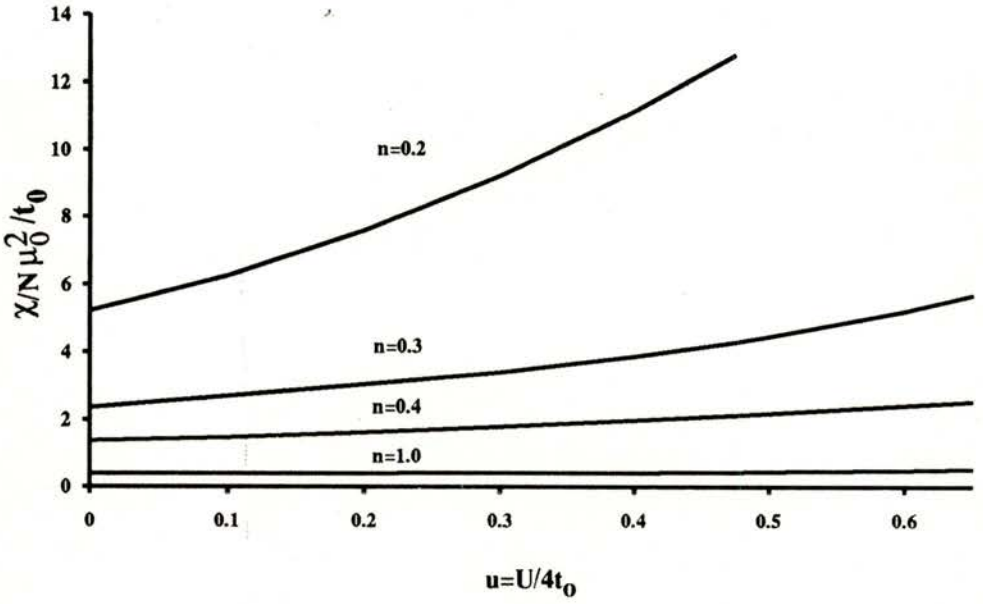

Fig.1:Magnetic Susceptibility as a function of u for different values of the electronic density as given by the Gutzwiller wave function.

4. CONCLUSION

In this paper we have studied the ground state properties of the Hubbard chain by means of the variational Gutzwiller ansatz. Our results are restricted to the small U regime, but arbitrary density n. The main aim of the paper is to show that, in addition to a decrease of the plasma frequency as determined from the

partial sum rule [8], the Gutzwiller wave function predicts that the electronic correlations lead to an enhancement of the magnetic susceptibility for all densities n>0, in agreement with the experimental data for organic synthetic metals [2], [3].

Another typical effect of the electronic correlations in these materials, which has also been detected experimentally [15], is the occurrence of phonon diffuse X-ray scattering at $4\,k_F$.

The study of this problem requires the introduction of the electron-phonon coupling, which is out of the scope of the present work. A generalization of the present variational method to the study of the effects of the electronic correlations on the electron-phonon interaction is in preparation.

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REFERENCES

[1] Ferraris, J., Cowan, D., Walatka, V. and Perlstein, J., J. Am. Chem. Soc. 95, 948 (1973).

[2] Jacobsen, C., Johannsen, I. and Bechgaard, K., Phys. Rev. Lett. 53, 194 (1984).

[3] Jérome, D. and Schultz, H. J., Adv. Phys. 31, 299 (1982).

[4] Bednorz, J. G. and Müller, K. A., Z. Phys. B, 64, 189 (1986).

[5] Hubbard, J., Proc. Roy. Soc. London, sec A 276, 238(1963); 277, 237 (1964).

[6] Gutzwiller, M., Phys. Rev. Lett. 10, 159 (1963); Phys. Rev. 134, A923 (1964); 137, A1726 (1965).

[7] Carmelo, J. and Micnas,R., J. Phys.: Cond. Matter 2, 6981 (1990).

[8] Baeriswyl, D., Carmelo, J. and Luther,A., Phys. Rev. B 33, 7247 (1986); 34, 8976 (1986).

[9] Mazundar, S. and Bloch, A., Phys. Rev. Lett. 50, 207 (1983).

[10] Lieb, E. and Wu, F., Phys. Rev. Lett. 20, 1445 (1968).

[11] Carmelo, J., Dzierzawa, M., Zotos, X. and Baeriswyl, D., Phys. Rev. B 43, 598 (1991).

[12] Carmelo, J. and Baeriswyl, D., Phys. Rev. B 37, 7541 (1988).

[13] Takahashi, M., Progr. Theor. Phys. 42, 1098 (1969); 43, 1619 (1970).

[14] Shiba, H., Phys. Rev. B 6, 930 (1972).

[15] Pouget, J. P., Khanna, S. K., Denoyer, F. and Comès, R., Phys. Rev. Lett. 37,437 (1976).