Charge Transfer Excitons and Possible Exitonic Pairing in the Extended Three Band Hubbard Model.

C. Vermeulen\textsuperscript{1}, W. Barford\textsuperscript{1} and E. R. Gagliano\textsuperscript{2}

1. Department of Physics, The University of Sheffield, Sheffield, S3 7HR, United Kingdom.

2. Centro Atomico Bariloche, 8400 Bariloche, Argentina.

Abstract

Exact diagonalisations of the extended Hubbard model are performed. In the insulating regime it is shown that the nearest neighbour copper-oxygen repulsion, $V$, leads to Frenkel excitons in the charge transfer gap at values of $V$ of the order of copper-oxygen hybridisation, $t$. In the metallic regime it is shown that the static charge-transfer and density-density correlation functions diverge as a function of $V$, indicating a charge-transfer instability and phase separation. This is accompanied by a softening of the $q \to 0$ mode of the dynamic correlation functions which is associated with the excitonic excitations responsible for the superconducting correlations observed in the proximity of the phase separation boundary of ref. \textsuperscript{[15]}.\[E\]

PACS Numbers: 71.35.+z, 64.70, 74.72.-h

March, 1995.
The charge-transfer fluctuations $\text{Cu}^{2+} \rightarrow \text{Cu}^+ \text{ and } \text{O}^{2-} \rightarrow \text{O}^-$ coupled to the nearest neighbour copper-oxygen repulsion, $V$, leads to a variety of interesting phenomena. For example, in the insulating-stoichiometric limit it leads to the formation of charge-transfer excitons [1], [2], for which there is some experimental evidence from Raman [3] and optical [4] experiments. In the metallic regime the softening of the charge-transfer excitations leads to a charge-transfer instability and phase separation, which suggests the possibility of an excitonic pairing mechanism [5], [6]. This instability is also related to the pinning of the Fermi energy on hole doping, and to the creation of new states in the charge-transfer gap [7]. Such behaviour is qualitatively similar to the observations from photoemission [8] and O 1s spectroscopy [9].

The three band extended Hubbard model, which best describes this behaviour, has been studied by a number of authors. Littlewood et al. [10], following the initial suggestion of Varma et al. [5], studied the charge-transfer excitations in the weak coupling limit, via the RPA. This work was followed up by Bang et al. [11] in the weak coupling limit, and by Raimondi et al. [12] in the strong coupling limit. These analyses all indicated superconducting correlations, mediated by excitonic excitations, close to the charge-transfer instability. Barford and Long [13] performed a unitary transformation to second order in the copper-oxygen hybridisation and found superconductivity and phase separation. Finally, Sano and Ono [14], Vermeulen et al. [15] and Stechel et al. [16] used the mapping onto a Luttinger liquid to show that the one dimensional model exhibits superconducting correlations and anomalous flux quantisation in the proximity of the phase separation boundary.

It is the purpose of this letter to study in detail the dynamics of the charge-transfer excitations as a function of doping and $V$ by solving exactly finite size clusters in one di-
mension. We will study the charge-transfer excitons in the insulating regime. By performing finite size calculations we will compare the exact results to the predictions of the variational theory of Vermeulen and Barford [2]. Next, by studying the dynamic charge-transfer and density-density correlation functions in the metallic regime we will relate the softening of the \( q \to 0 \) mode and the divergence of the static correlation functions to the superconducting correlations and phase separation instabilities of the copper-oxide chain phase diagram of ref. [15].

Our model for the copper-oxide chain consists of two atoms per unit cell. Neglecting the oxygen-oxygen hybridisation and considering the Coulomb interaction up to first-nearest neighbours, the copper-oxide chain is described by the two band model Hamiltonian

\[
H = -t \sum_{<ij>\sigma} (d_{i\sigma}^{\dagger}p_{j\sigma} + \text{h.c.}) + \frac{\Delta}{2} \sum_{i\sigma} (p_{j\sigma}^{\dagger}p_{j\sigma} - d_{i\sigma}^{\dagger}d_{i\sigma}) \\
+ U_d \sum_i d_{i\sigma}^{\dagger}d_{i\sigma}^{\dagger}d_{i\sigma}d_{i\sigma} + U_p \sum_j p_{j\sigma}^{\dagger}p_{j\sigma}^{\dagger}p_{j\sigma}p_{j\sigma} + V \sum_{<ij>\sigma\sigma'} d_{i\sigma}^{\dagger}d_{i\sigma'}^{\dagger}p_{j\sigma}p_{j\sigma'},
\]

where \( i \) and \( j \) are copper and oxygen sites respectively, \( <ij> \) represents nearest neighbours and the operator \( d_{i\sigma}^{\dagger} (p_{j\sigma}^{\dagger}) \) creates a Cu (O) hole with spin \( \sigma \). \( \Delta \) is the charge-transfer energy, \( U_d \) (\( U_p \)) is the copper (oxygen) Coulomb repulsion and \( V \) and \( t \) are the copper-oxide Coulomb repulsion and hybridisation, respectively. We will denote \( N_p \) as the number of particles and \( N_s \) as the number of sites. Our choice of model parameters will be those relevant to the high temperature superconductors. Thus we take \( U_d = 8t \), \( \Delta = 2 - 4t \) and \( U_p = 0 - 4t \) where \( t \sim 1.5eV \) [7]. However, as we are interested in the rôle played by the nearest neighbour interaction, \( V \), this will be left as a free parameter.

Firstly we examine the model in the insulating phase at a hole density of \( n = 0.5 \). At
this density the system is a charge transfer insulator for all $\Delta \neq 0$, and the ground state is a spin density wave. The majority of the charge resides on the copper sites, forming a Néel state. The exciton is identified as the lowest frequency peak, $E_{\text{exc}}$, of the dynamical current-current correlation function, $J(w)$, when it appears inside the charge transfer gap, $E_{\text{gap}}$. $J(w)$ is defined by

$$J(w) = -\frac{1}{\pi} Im (G^R(w)),$$

where

$$G^R(w) = F.T. <\psi_0 | j^\dagger(t) j(0) | \psi_0 >$$

$$= <\psi_0 | j^\dagger \left( \frac{1}{H - (E_0 + w) + i\eta} \right) j | \psi_0 > \eta \to 0.$$ (2)

$G^R(w)$ is the retarded Green function and $j$ is the current operator defined as $j = -i \sum_{l,\sigma} (c^\dagger_{l\sigma} c_{l+1\sigma} - c^\dagger_{l+1\sigma} c_{l\sigma})$. $\{ | \psi_0 >, E_0 \}$ are the ground state eigensolutions. In practice we choose a finite value of $\eta$ to broaden the peaks. The Green function is calculated via the continued fraction technique [18]. The energy of the gap is defined by $E_{\text{gap}} = E(N_p + 1) + E(N_p - 1) - 2E(N_p)$. Figure 1 shows a typical profile for the excitonic spectrum using a 12 site chain, and the values of $U_d = 8t, U_p = 0, \Delta = 2t$ and $V = 2t$. The values of $V_{\text{crit}}$, the point at which $E_{\text{gap}} = E_{\text{exc}}$, are shown in tables (1) and (2) for 8, 12 and 16 site chains for $\Delta = 2t$ and $4t$, respectively. The values for $V_{\text{crit}}$ at $N = \infty$ are found by finite size scaling, whereby $E_{\text{gap}}^{N_s}(V)$ and $E_{\text{exc}}^{N_s}(V)$ are plotted against $\frac{1}{N^2}$ and the straights lines are extrapolated to $\frac{1}{N^2} = 0$. Notice that $V_{\text{crit}}$, which is of the order $t$, is a decreasing function of $\Delta$ and $U_p$. 
The exciton may be pictured as a hole that has been excited from the lower Hubbard band (or conduction band), which is predominately copper in character, to the valence band, which is predominately oxygen in character. The real space picture is therefore of a hole on a copper site hopping onto a neighbouring oxygen site. This effectively leaves an ‘electron’ on the copper site and a hole on the oxygen site, and due to the Coulomb repulsion between neighbouring sites this leads to an effective attraction between the electron and the hole. This attraction reduces the energy to a point below the charge transfer gap and causes the formation of a tightly bound ‘electron-hole’ pair, or a Frenkel exciton. The energy in forming the exciton is a balance between the Coulomb attraction of the ‘electron-hole’ pair and the kinetic energy loss. The former is driven by $V$, whereas the latter is determined by $t$. Hence, when $V$ is of the order of $t$ we expect excitons to exist within the charge transfer gap.

As a more quantitative study, we have extended the variational estimate by Vermeulen and Barford [2] of $V_{\text{crit}}$ for the two dimensional copper-oxide plane. This was performed via a canonical transformation up to $O(t^2)$ in the hopping $t$ of eqn(1), assuming strong coupling ($U_d \rightarrow \infty$). Figure 2 shows $\tilde{V}_{\text{crit}}$ against $\tilde{\Delta}$ for the one dimensional infinite chain and several values of $U_p$ (where $\tilde{V} = \frac{V}{\tilde{t}}$, $\tilde{\Delta} = \frac{\Delta}{\tilde{t}}$ and $\tilde{t} = \frac{t^2}{\Delta}$). Notice that for large $\tilde{\Delta}$ (where the calculation becomes asymptotically rigorous) $\tilde{V}_{\text{crit}}$ decreases as a function of $U_p$, and is a constant function of $\tilde{\Delta}$, i.e. $V_{\text{crit}}$ decreases with $\Delta$. This is in agreement with the numerical results of tables (1) and (2), and arises from the fact that increasing the oxygen repulsion increases the single-particle gap, but has little effect on the exciton energy. In contrast, the variational estimate of ref[2] indicates that in two dimensions $U_p$ has no effect on $V_{\text{crit}}$ for large $\tilde{\Delta}$. We also confirm the validity of the variational estimate by comparing $V_{\text{crit}}$ with the finite size numerical results in table (2), which indicates good agreement.
We now turn to the rôle that the charge transfer excitations may play in the doped phase of the cuprate superconductors. From previous work [15] this model is well known to undergo phase separation within a hole density range of \(0.5 < n < 1.0\) and large enough \(V\). There is also strong evidence that the system becomes superconducting in the proximity of the phase separation boundary. We intend to investigate the rôle played by correlated particle-hole excitations near the Fermi surface in these two physical effects.

It is difficult to identify excitonic peaks from the current-current correlation function in the metallic regime. Instead, it is more convenient to study the dynamic density-density and charge-transfer correlation functions (i.e. susceptibilities) at low momenta. The dynamic charge-transfer correlation function, in particular, focuses on local intra-cell charge fluctuations of copper and its surrounding oxygens. Such a local fluctuation in charge can be considered excitonic in character, and at low energy and momenta these will correspond to excitations near the Fermi surface. The dynamic charge-transfer correlation function is defined as

\[
\chi_q^\delta(w) = F.T. <\delta_q^\dagger(t)\delta_q(0)>,
\]

where

\[
\delta_q = \frac{1}{\sqrt{N_s}} \sum_l (-1)^l n_l e^{iqxl}.
\]

The dynamic density-density correlation function, \(\chi_q^n(w)\), is defined by replacing \(\delta_q\) by \(n_q = \sum_k c_{k+q}^\dagger c_k\). In terms of our lattice Hamiltonian \(n_q\) is defined as \(\frac{1}{\sqrt{N_s}} \sum_l (n_l - < n >) e^{-iqxl}\). This function examines charge fluctuations across the whole lattice. From a thermodynamical argument it can be shown that the compressibility, \(\kappa\), is related to the static density-density
correlation function in the long wavelength limit, $C_{q \to 0}^n$, by

$$\kappa = \frac{\beta}{V \rho^3} C_{q \to 0}^n. \quad (5)$$

$C_{q \to 0}^n$ is the integrated dynamic correlation function ($= \int \chi_{q \to 0}^n(\omega)d\omega$), $\rho$ is the density, $\beta$ is the inverse temperature and $V$ is the volume. So a divergence of the static density-density correlation function in the limit $q \to 0$ is directly related to a divergence of $\kappa$, and hence to phase separation. Moreover, the divergence of the static correlation function should be accompanied by a soft mode. Figures 3(a) and (b) show the position of the lowest peak in the dynamic charge-transfer correlation function and the integrated weight for $q = \frac{2\pi}{N_s}$ (i.e. the finite size $q \to 0$ limit) on a 12 site chain at a filling of 8/12 and 10/12, respectively. As the nearest neighbour repulsion is increased the static charge-transfer correlation function rapidly increases and diverges at about $V \sim 2.0t$ for 8 holes and $V \sim 1.5t$ for 10 holes. (The divergence is taken to be at the point of inflection, as a finite size system cannot have a truly diverging susceptibility.) This is accompanied by the softening of the diverging $q \to 0$, $\omega \to 0$ mode. (All other $q$ modes stiffen as $V$ is increased.) Likewise, the static density-density correlation function also diverges. The frequency of the density-density soft mode is identical to the charge-transfer soft mode, as charge-transfer and density fluctuations are coupled. This arises from the strong Coulomb interactions on copper which means that local charge fluctuations will tend not to conserve local charge and so these excitations are coupled to non-local charge fluctuations. The divergence of the static correlation functions is consistent with the divergence of the discrete compressibility at $V \simeq 2.0t$ and 1.6$t$ for 8 and 10 holes, respectively, as shown in the phase diagram of ref. [15]. Moreover, it is reasonable
to associate the softening of the \( q \rightarrow 0 \) charge-transfer excitations with the indications of superconducting correlations from both the Luttinger liquid charge exponent, \( K_p \), exceeding unity and to the onset of anomalous flux quantisation \[15\].

The effect of \( U_p \) is to suppress strongly both the static density-density and charge-transfer correlation functions. At \( n = \frac{8}{12} \) and \( V = 3t \ C_{q \rightarrow 0}^n \) drops from 0.22 at \( U_p = 0 \) to 0.09 at \( U_p = 2t \).

In conclusion, we have shown that the nearest neighbour repulsion leads naturally to Frenkel excitons in the charge-transfer gap at values of \( V_{\text{crit}} \) of the order of \( t \) in the insulating regime. Further, we have found that in one dimension increasing \( U_p \) has the effect of decreasing the value of \( V_{\text{crit}} \), and we have given a qualitative argument to explain this effect. These numerical results are in good agreement with the analytical results of \[2\].

In the metallic regime we have shown that the static charge-transfer and density-density correlation functions diverge as a function of \( V \), indicating a charge-transfer instability and phase separation. This is accompanied by a softening of the \( q \rightarrow 0 \) mode in the dynamic correlation functions which we associate with the excitonic excitations responsible for the superconducting correlations observed in the proximity of the phase separation boundary of ref. \[15\].

Acknowledgements

We thank the SERC (United Kingdom) for the provision of a Visiting Research Fellowship (ref. GR/H33091). W.B. also acknowledges a grant from the University of Sheffield research fund. C.J.V. is supported by a University of Sheffield scholarship. We thank R. Bursill and
M. Grilli for stimulating discussions.
References

[1] J. Lorenzana and L. Yu, Phys. Rev. B 43 11474 (1991).

[2] C. Vermeulen and W. Barford, J. Phys. (Condens. Matt.) in press (1995).

[3] Ran Liu et al, Phys. Rev. Lett. 71 3709 (1993).

[4] J. D. Perkins et al, Phys. Rev. Lett. 71 1621 (1993).

[5] C. M. Varma, S. Schmitt-Rink and E. Abrahams, Solid State Commun. 62 681 (1987).

[6] M. D. Nuñez Regueiro and A. A. Aligia, Phys. Rev. Lett. 61 1889 (1988).

[7] W. Barford, E. R. Gagliano and C. Vermeulen, Phys. Rev. B in press (1995).

[8] J. W. Allen et al., Phys. Rev. Lett. 64 595 (1990).

[9] H. Romberg, M. Alexander, N. Nucker, P. Alderman and J. Fink, Phys. Rev. B 42 8768 (1990).

[10] P. B. Littlewood, C. M. Varma and E. Abrahams, Phys. Rev. Lett. 63 2602 (1989).

[11] Yunkyu Bang, G. Kotliar, R. Raimondi C. Castellani and M. Grilli, Phys. Rev. B 47 3323 (1993).

[12] R. Raimondi, C. Castellani, M. Grilli, Y. Bang and G. Kotliar, Phys. Rev. B 47 3331 (1993).

[13] W. Barford and M. W. Long, J. Phys. (Condens. Matt.) 5 199 (1993).

[14] K. Sano and Y. Ono, Physica C 205 170 (1993).
[15] C. Vermeulen, W. Barford and E. R. Gagliano, Europhys. Lett. 28 653 (1994).

[16] E. B. Stechel, A. Sudbo, T. Giamarchi and C. M. Varma, Phys. Rev. B 51 553 (1995).

[17] G. A. Sawatzky. 1991, High Temperature Superconductivity. ed. D. P. Tunstall and W. Barford, Publishers: Adam Hilger. (Bristol)

[18] E. R. Gagliano, Phys. Rev. Lett. 62 1154 (1989).
| $\Delta = 2t$ | Number of lattice site, $N_s$ |
|-------------|-----------------------------|
| $U_d = 8t$  | 8  | 12 | 16 | $\infty$ |
| $U_p = 0$   | 2.06$t$ | 1.7$t$ | 1.54$t$ | $\ldots$ | 1.29$t$ |
| $U_p = 4t$  | 1.57$t$ | 1.22$t$ | 1.09$t$ | $\ldots$ | 0.88$t$ |

Table 1.

| $\Delta = 4t$ | Number of lattice site, $N_s$ |
|-------------|-----------------------------|
| $U_d = 8t$  | 8  | 12 | 16 | $\infty$ | Analytic |
| $U_p = 0$   | 2.02$t$ | 1.54$t$ | 1.38$t$ | $\ldots$ | 0.94$t$ | 1.22$t$ |
| $U_p = 4t$  | 1.82$t$ | 1.31$t$ | 1.16$t$ | $\ldots$ | 0.77$t$ | 1.05$t$ |

Table 2.
Figure Captions

Figure 1. The current-current response function at $U_d = 8t$, $U_p = 0t$, $\Delta = 2t$ and $V = 2t$ for the stoichiometric 12 site chain. $E_g$ is the charge transfer gap energy and $E_e$ identifies the exciton energy.

Figure 2. $\tilde{V}_{\text{crit}} (= V_{\text{crit}}/\tilde{t})$ versus $\tilde{\Delta} (= \Delta/\tilde{t})$, where $\tilde{t} = t^2/\Delta$, for the one dimensional chain, using the theory of ref. [2], in the $U_d = \infty$ limit. The exciton is a bound state above the lines.

Figure 3. (a) The $q = \frac{\pi}{6}$ static charge-transfer (diamonds) and density-density (solid squares) correlation functions, and the position of the lowest frequency mode of the dynamic correlation functions (open squares) as a function of $V/t$ for 8 holes in a 12 site chain. The frequency is in units of $t$. Notice the different normalisations for the correlation functions. $U_d = 9t$, $U_p = 0$ and $\Delta = 2t$. (b) The same as (a) with 10 holes.

Table 1. Values of $V_{\text{crit}}$ for various system sizes.

Table 2. Values of $V_{\text{crit}}$ for various system sizes. The analytic result is in the $U_d = \infty$ limit.