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A variational estimate of the binding energy of charge transfer excitons in the cuprate superconductors

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Abstract. We present a variational estimate for the binding energy of a Frenkel exciton in the insulating cuprate superconductors. Starting from the three-band Hubbard model we perform a canonical transformation to $O(t^2)$, where t is the bare nearest-neighbour copper–oxygen hopping integral. An effective Hamiltonian is then derived to describe the hopping of the exciton through the copper oxide plane. The critical parameter in the model is the nearest-neighbour copper–oxygen Coulomb repulsion, V . It is found that a critical value of V is needed to observe bound Frenkel excitons, and that these excitons have the same symmetry as the parent copper orbital, $d_{x^2-y^2}$. We determine the critical value of V using a variational approach, and attempt to fit the parameters of the model to known experimental results.

1. Introduction

Various optical and Raman experiments [1–3] have indicated that charge transfer excitons of the interatomic kind ($d_{x^2-y^2} \rightarrow p_x, p_y$) may be the lowest-lying excitations of the insulating cuprate superconductors [4]. There are also theoretical predictions that charge transfer fluctuations play a crucial rôle in determining the superconducting and anomalous normal state properties of the doped compounds [5–10] although experimental evidence for these excitations in the doped phase is less clear. Recent numerical work on the three-band Hubbard model with the nearest-neighbour copper–oxygen repulsion, V , has shown that charge transfer excitations are indeed the lowest-lying excitations for a critical value of V [11].

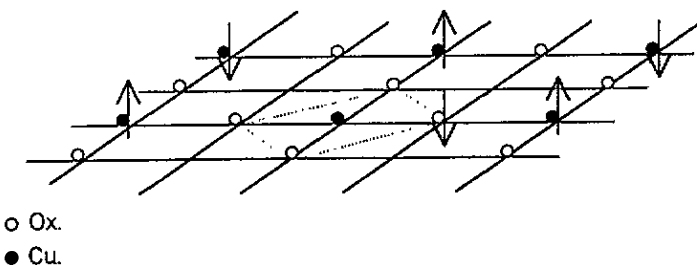


Figure 1. An exciton in a Néel background, moving in the copper oxide plane of a cuprate superconductor.

We envisage the charge transfer exciton as a localized Frenkel exciton consisting of a copper hole excited onto its neighbouring oxygen sites, leaving behind a vacant copper site.

The resultant bound particle-hole pair then delocalizes through the lattice, as illustrated in figure 1. The potential energy of the exciton is the nearest-neighbour Coulomb repulsion, V , as the oxygen hole has only one neighbouring copper hole. This compares to the potential energy $2V$ for an oxygen hole located amongst occupied copper sites. Thus the condition for the exciton to lie in the charge transfer gap is that the potential energy gained in forming an exciton must compensate the kinetic energy loss of binding the particle-hole pair.

In this paper we present a variational estimate for the binding energy of a charge transfer exciton in the insulating state of the cuprate superconductors. Starting from the three-band model, which treats the copper and oxygen orbitals on an equal footing, we perform a canonical transformation to $O(t^2)$, where t is the copper-oxygen hybridization integral. We thus derive an effective low-energy Hamiltonian which describes the charge dynamics of the copper oxide planes. However, since we do not consider terms of $O(t^4)$ we neglect superexchange effects. The possible consequences of superexchange are discussed in the conclusions. By keeping terms in the Hamiltonian which describe the motion of the exciton we derive its energy in both a Néel and a ferromagnetic background. This is therefore a variational estimate of the exciton energy. To calculate the exciton binding energy (i.e. the energy from the bottom of the conduction band) we compare the exciton energy to the minimum energy of the 'single'-particle-hole excitation energy. That is, the energy difference from the top of the valence band to the bottom of the conduction band.

The plan of this paper is as follows. In the next section we perform the canonical transformation on the three-band model. In section 3 we use this to derive the excitonic Hamiltonian and calculate the energy of the exciton in the insulating phase. Section 4 discusses the 'single'-particle Hamiltonians and calculates the free particle-hole gap. In section 5 we calculate the condition for obtaining excitons in the charge transfer gap. Finally, in section 6 we attempt to fit our model to the experimental results, and conclude.

2. The canonical transformation

Our starting point for the expansion is the unperturbed Hamiltonian

$$H = H_0 + H_t \quad (1)$$

where

$$H_0 = \frac{\Delta}{2} \sum_{ij\sigma} (p_{j\sigma}^\dagger p_{j\sigma} - d_{i\sigma}^\dagger d_{i\sigma}) + U_d \sum_i d_{i\uparrow}^\dagger d_{i\uparrow} d_{i\downarrow}^\dagger d_{i\downarrow} + U_p \sum_j p_{j\uparrow}^\dagger p_{j\uparrow} p_{j\downarrow}^\dagger p_{j\downarrow} + V \sum_{\langle ij \rangle \sigma \sigma'} (d_{i\sigma}^\dagger d_{i\sigma} p_{j\sigma'}^\dagger p_{j\sigma'}). \quad (2)$$

The perturbative part H_t is defined as

$$H_t = - \sum_{\langle ij \rangle \sigma} (t_{ij} d_{i\sigma}^\dagger p_{j\sigma} + \text{HC}) \quad (3)$$

where i and j are copper and oxygen sites respectively, $\langle ij \rangle$ represents nearest neighbours and the operator $d_{i\sigma}^\dagger$ ($p_{j\sigma}^\dagger$) creates a copper (oxygen) hole with spin σ . Δ is the charge transfer energy, U_d (U_p) is the copper (oxygen) Coulomb repulsion, and V is the copper oxide Coulomb repulsion. t_{ij} incorporates the phase of the atomic orbitals, and is defined as $t_{ij} = (-1)^{m_j} t$, where $m_1 = m_2 = 1$, $m_3 = m_4 = 2$ and j labels the oxygen orbitals neighbouring the i th copper orbital, as shown in figure 2. t is the bare nearest-neighbour copper-oxygen hybridization. It is convenient to absorb this phase factor explicitly into the

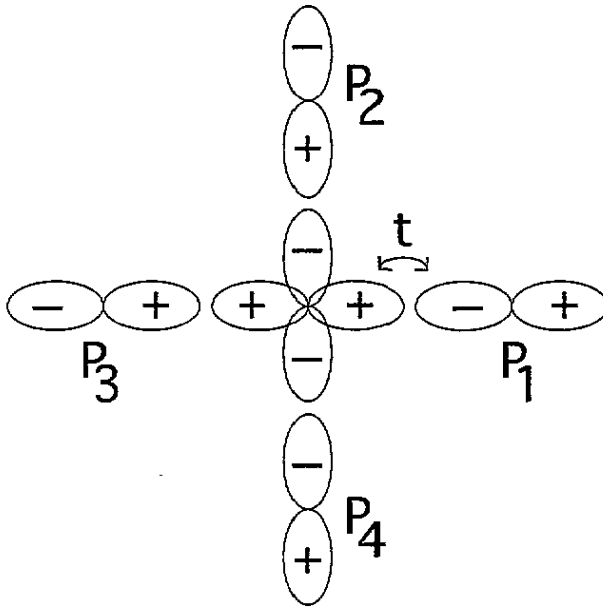


Figure 2. The $d_{x^2-y^2}$ bonding orbital of copper with its four neighbouring p_x, p_y bonding oxygen orbitals. t is the bare hopping integral between them.

oxygen orbitals, and hence we set $p_1 \rightarrow -p_1$ and $p_2 \rightarrow -p_2$. The copper-copper distance sets the length scale.

The effective low-energy Hamiltonian is formed using the unitary transformation $\tilde{H} = e^S H e^{-S}$, where $S^\dagger = -S$ [12]. By expanding in e^S it is trivial to show that

$$\tilde{H} = H_0 + H_t + [S, H_0] + [S, H_t] + \frac{1}{2}[S, [S, H_0]] + O(t^3). \tag{4}$$

To eliminate terms of order t we define S such that $H_t + [S, H_0] = 0$. The new Hamiltonian is then found by truncating the series at terms greater than $O(t^2)$. Thus $\tilde{H} = H_0 + H_{t^2}$, where $H_{t^2} = \frac{1}{2}[S, H_t]$. \tilde{H} acts on the Hilbert space of $|\tilde{n}\rangle$ where $|\tilde{n}\rangle = e^S |n\rangle$ and $|n\rangle$ is the basis of our original Hamiltonian.

By inspection we note that

$$\left[H_0, t \sum_{(ij)\sigma} (p_{j\sigma}^\dagger d_{i\sigma} - \text{HC}) \right] = -t \sum_{(ij)\sigma} f_{ij\sigma} (d_{i\sigma}^\dagger p_{j\sigma} + \text{HC}) \tag{5}$$

where

$$f_{ij\sigma} = \Delta + (V - U_d) d_{i\bar{\sigma}}^\dagger d_{i\bar{\sigma}} + (U_p - V) p_{j\bar{\sigma}}^\dagger p_{j\bar{\sigma}} + V \sum_{(jj')\sigma' j \neq j'} p_{j'\sigma'}^\dagger p_{j\sigma'} - V \sum_{(ii')\sigma' i \neq i'} d_{i'\sigma'}^\dagger d_{i\sigma'} \tag{6}$$

and j and j' neighbour i , and i' neighbours j .

It is relatively straightforward to show that

$$S = t \sum_{(ij)\sigma} (f_{ij\sigma})^{-1} (p_{j\sigma}^\dagger d_{i\sigma} - \text{HC}). \tag{7}$$

Using the fact that $[f_{ij\sigma}, d_{i\sigma}^\dagger p_{j\sigma}] = [f_{ij\sigma}, p_{j\sigma}^\dagger d_{i\sigma}] = 0$, H_{t^2} can be written as

$$H_{t^2} = \frac{t^2}{2} \sum_{\langle ij \rangle \sigma} \sum_{\langle kl \rangle, \sigma'} (f_{ij\sigma})^{-1} \left[p_{j\sigma}^\dagger d_{i\sigma} d_{k\sigma'}^\dagger p_{l\sigma'} + p_{j\sigma}^\dagger d_{i\sigma} p_{l\sigma'}^\dagger d_{k\sigma'} - d_{i\sigma}^\dagger p_{j\sigma} d_{k\sigma'}^\dagger p_{l\sigma'} - d_{i\sigma}^\dagger p_{j\sigma} p_{l\sigma'}^\dagger d_{k\sigma'} + \text{HC} \right]. \quad (8)$$

The terms in equation (8) which change the number of oxygen or copper holes are eliminated to yield

$$H_{t^2} = \frac{t^2}{2} \sum_{\langle ij \rangle \sigma} \sum_{\langle kl \rangle, \sigma'} (f_{ij\sigma})^{-1} [p_{j\sigma}^\dagger d_{i\sigma} d_{k\sigma'}^\dagger p_{l\sigma'} - d_{i\sigma}^\dagger p_{j\sigma} p_{l\sigma'}^\dagger d_{k\sigma'} + \text{HC}]. \quad (9)$$

Although our Hamiltonian has been simplified it is still very complicated, containing residual many-body effects resulting from copper–oxygen Coulomb repulsion and the effects of on-site copper and oxygen Coulomb repulsion.

3. The excitonic Hamiltonian

In constructing the excitonic Hamiltonian we first consider the part of equation (9) which hops the oxygen hole around a single copper–oxygen plaquette. This may be written in the form

$$H = \sum_i h_i \quad (10)$$

where

$$h_i = \frac{t^2}{(\Delta + V)} \sum_{\langle jj' \rangle \sigma} p_{j'\sigma}^\dagger p_{j\sigma}. \quad (11)$$

Thus when the hole hops to a neighbouring oxygen site via an empty copper site it costs an energy $t^2/(\Delta + V)$. The symmetry of this Hamiltonian is exploited by noting that the only non-zero solution of h_i is the constant-phase solution $P_{i\sigma} = \frac{1}{2}(p_{1\sigma}^\dagger + p_{2\sigma}^\dagger + p_{3\sigma}^\dagger + p_{4\sigma}^\dagger)$, where the indices on the oxygen operators stand for the four neighbours of the copper site at i . From this it can be inferred that our exciton has the same symmetry as the parent copper site, $d_{x^2-y^2}$, which is the A_{1g} symmetry in Raman notation. h_i can be rearranged into the more compact form, $h_i = [t^2/(\Delta + V)] P_{i\sigma}^\dagger P_{i\sigma}$. The full Hamiltonian is then derived by only keeping terms in equation (9) which hop this entity through the 'sea' of Cu^{2+} copper sites. We then arrive at the final Hamiltonian

$$H_e = \sum_{\langle ik \rangle \sigma \sigma'} \alpha_{\sigma \sigma'} E_{i\sigma}^\dagger E_{k\sigma'} + \sum_{\langle ik \rangle \sigma} \beta e_{i\sigma}^\dagger e_{k\sigma} + \sum_{i\sigma} \gamma E_{i\sigma}^\dagger E_{i\sigma} + \sum_{\langle ik \rangle \sigma} \delta E_{i\sigma}^\dagger E_{i\sigma} d_{k\bar{\sigma}}^\dagger d_{k\bar{\sigma}} + \sum_{\langle ik \rangle \sigma} \epsilon e_{i\bar{\sigma}}^\dagger E_{i\sigma} d_{k\sigma}^\dagger d_{k\bar{\sigma}} + (V + \Delta) \quad (12)$$

where the zero-point energy is given as the spin degenerate ground state of one hole per copper site, defined by $E(N_{\text{Cu}}) = -N_{\text{Cu}}\Delta/2 - 4t^2 N_{\text{Cu}}/(\Delta + V)$.

The operator $E_{i\sigma}^\dagger = P_{i\sigma}^\dagger d_{i\sigma}$ creates a spin 0 exciton on site i , while $e_{i\sigma}^\dagger = P_{i\sigma}^\dagger d_{i\bar{\sigma}}$ spin flips and creates a spin 1 exciton on site i . The first two terms in H_e hop these excitons through the lattice. The remaining terms in H_e are self-energy terms, which include spin

flips. i and k are nearest neighbour copper sites. The coefficients are

$$\begin{aligned} \alpha_{\sigma\sigma} &= \frac{t^2(\Delta - 3V)}{4\Delta(\Delta + V)} & \alpha_{\sigma\bar{\sigma}} &= \frac{t^2[V(3V - 5\Delta) + U_p(\Delta - 3V)]}{4\Delta(\Delta + V)(\Delta + U_p - V)} \\ \beta &= \frac{t^2}{4(\Delta + U_p - V)} & \gamma &= \frac{t^2(9\Delta - 6V)}{\Delta(\Delta + V)} \\ \delta = -\epsilon &= \frac{t^2(U_p + U_d - 2V)}{4(\Delta + V - U_d)(\Delta + U_p - V)}. \end{aligned} \tag{13}$$

The fact that $\delta = -\epsilon$ is due to the effects of exchange.

With this Hamiltonian we now wish to construct a variational estimate for the energy of the exciton. This is done by considering the dispersion of the exciton through either a ferromagnetic or a Néel background. In the ferromagnetic case we set $\alpha_{\sigma\sigma'} = \alpha_{\sigma\sigma}$ and $\beta = \delta = \epsilon = 0$. The variational wave function is then

$$|\phi_F\rangle = \frac{1}{\sqrt{N_{Cu}}} \sum_l e^{ik \cdot l} E_{l\uparrow}^\dagger \prod_j a_{j\uparrow}^\dagger |0\rangle \tag{14}$$

with an energy

$$E_c^F(\mathbf{k}) = (V + \Delta) + \frac{t^2(\Delta - 3V)}{2\Delta(\Delta + V)} [\cos k_x + \cos k_y] + \frac{t^2(9\Delta - 6V)}{\Delta(\Delta + V)}. \tag{15}$$

Similarly, the variational energy of an exciton in the Néel background is found by setting $\alpha_{\sigma\sigma'} = \alpha_{\sigma\bar{\sigma}}$ and $\beta = \epsilon = 0$. Thus,

$$|\phi_N\rangle = \frac{1}{\sqrt{N_{Cu}}} \sum_{l\sigma} e^{ik \cdot l} E_{l\sigma}^\dagger |\text{Néel}\rangle \tag{16}$$

with

$$\begin{aligned} E_c^N(\mathbf{k}) &= (V + \Delta) + \frac{t^2[V(3V - 5\Delta) + U_p(\Delta - 3V)]}{2\Delta(\Delta + V)(\Delta + U_p - V)} [\cos(k_x) + \cos(k_y)] \\ &+ \frac{t^2(U_p + U_d - 2V)}{(\Delta + V - U_d)(\Delta + U_p - V)} + \frac{t^2(9\Delta - 6V)}{\Delta(\Delta + V)}. \end{aligned} \tag{17}$$

In the limit of $U_p = \infty$, $E_c^N(\mathbf{k}) = E_c^F(\mathbf{k})$, and for $U_p < \infty$, $E_c^N(\min) < E_c^F(\min)$ in our allowed parameter range of $0 < V < (\Delta + U_p)$. It is therefore our intention to consider the scenario of an exciton moving in the Néel background, which is also the experimentally relevant case. The minimum energy of the exciton can be expressed in terms of the potential energy and an effective kinetic energy. For the case of $U_d = \infty$ this is written as

$$E_{exc}^N = (V + \Delta) - \frac{t^2}{\Delta} f_{exc}^N(V, U_p, \Delta) \tag{18}$$

where

$$f_{exc}^N(V, U_p, \Delta) = - \left(\frac{V(9V - 21\Delta) + U_p(10\Delta - 9V) + 8\Delta^2}{(\Delta + V)(\Delta + U_p - V)} \right) \tag{19}$$

using $\mathbf{k} = (0, 0)$ in equation (17).

4. Single-particle-hole Hamiltonian

As we wish to determine the condition for a bound exciton in the charge transfer gap, we need to consider the motion of an unbound particle-hole pair in order to find the single-particle gap energy. In determining the energy of the gap for a free-particle-hole pair excitation we intend to study separately the energies of an added hole and a removed hole from the insulating phase. The gap energy is then given as $E_{\text{gap}} = E(N_{\text{Cu}} + 1) + E(N_{\text{Cu}} - 1) - 2E(N_{\text{Cu}})$ where N_{Cu} is the number of copper sites. We start by considering the energy of a removed hole, and then consider the more complicated scenario of an added hole.

4.1. Removed hole

The Hamiltonian which describes the motion of a removed hole amongst $N_{\text{Cu}} - 1$ occupied copper sites is [13]

$$H_v = \frac{\Delta}{2} - \frac{4t^2}{\Delta} \sum_{i\sigma} \tilde{c}_{i\sigma}^\dagger \tilde{c}_{i\sigma} + \frac{t^2}{\Delta} \sum_{\langle ik \rangle \sigma} \tilde{c}_{k\sigma}^\dagger \tilde{c}_{i\sigma} + \sum_i \frac{4t^2}{(\Delta + V)} \quad (20)$$

where $\tilde{c}_{i\sigma}^\dagger$ creates a particle (destroys a hole i.e. $\tilde{c}_{i\sigma}^\dagger = d_{i\sigma}$) on site i . $\tilde{c}_{i\sigma}$ only acts on single occupied sites and the zero-point energy is as before, $E(N_{\text{Cu}})$. The Nagaoka theorem [14] informs us that in the strong-coupling limit the maximum bandwidth for the dispersion of the empty site is obtained in a ferromagnetic background. The $S = (N_{\text{Cu}} - 1)$ branch of the spectrum is then

$$E^v(k) = \frac{\Delta}{2} + \frac{2t^2}{\Delta} [\cos(k_x) + \cos(k_y)] - \frac{4t^2}{\Delta} + \frac{8t^2}{(\Delta + V)} + E(N_{\text{Cu}}). \quad (21)$$

The *minimum* energy of the empty site, at $k = (\pi, \pi)$, is the *top* of the valence band.

4.2. Added hole

The Hamiltonian for the added hole follows the analysis of Barford [15]. In that paper the same canonical transformation, equation (4), was performed on the Hamiltonian and the effective Hamiltonian was then diagonalized for the i th plaquette of one hole on the oxygen sites. This was done for the case $U_p = 0$. For a general U_p the Hamiltonian is given as

$$H_c = \left(2V + \frac{\Delta}{2}\right) - (t_1 - t_2) \sum_i S_{i0}^\dagger S_{i0} + t_3 \sum_{ik} S_{ik}^\dagger S_{ik} + t_1 \sum_{i\delta} T_{i\delta}^\dagger T_{i\delta} - \sum_i \left(\frac{4t^2}{\Delta} - \frac{4t^2}{(\Delta + V)} \right). \quad (22)$$

The zero-point energy is again that of a half-filled plane, $E(N_{\text{Cu}})$. $t_1 = 4t^2/\Delta$, $t_2 = 8t^2/(\Delta + 2V - U_d)$ and $t_3 = 2t^2 U_p / \Delta(\Delta + U_p)$. i represents all the plaquettes with an added hole. The operators are defined as

$$S_{ik}^\dagger = \frac{1}{\sqrt{2}} (P_{ik\uparrow}^\dagger d_{i\downarrow}^\dagger - P_{ik\downarrow}^\dagger d_{i\uparrow}^\dagger) \quad k = 0, \pm \frac{\pi}{2}, \pi \quad (23)$$

$$P_{ik\sigma}^\dagger = \frac{1}{2} \sum_{l=1}^4 e^{ikl} p_{l\sigma}^\dagger \quad (24)$$

$$T_{i0} = \frac{1}{\sqrt{2}}(P_{i\uparrow}^\dagger d_{i\downarrow}^\dagger + P_{i\downarrow}^\dagger d_{i\uparrow}^\dagger) \tag{25}$$

$$T_{i+} = P_{i\uparrow}^\dagger d_{i\uparrow}^\dagger \tag{26}$$

$$T_{i-} = P_{i\downarrow}^\dagger d_{i\downarrow}^\dagger. \tag{27}$$

S_{i0} is the ‘Zhang–Rice’ singlet operator. The factor $8t^2/(\Delta + 2V - U_d)$ arises from virtual Cu^+ hopping, while the remaining terms are accounted for by virtual Cu^{3+} hopping. The additional complication to the $U_p = 0$ case is the existence of non-zero antisymmetric eigenvalues for the singlet Cu^{2+}O^- pair. The oxygen hole can bond in a singlet configuration with its neighbouring copper hole and pick up a phase change as it hops around the plaquette. The motion of the added hole is complicated because a triplet state on the i th site is, in general, not orthogonal to a singlet or triplet state on the neighbours of i . It is also unclear how the antisymmetric singlet states hybridize with neighbouring sites. It is clear, however, that their bands are relatively flat and lie between the singlet and triplet symmetric states. Consequently we do not intend to consider these states in our equation.

We now wish to construct a variational estimate for the minimum energy of this Hamiltonian. To do this we again invoke the Nagaoka theorem [14] which tells us that the maximum bandwidth for the doped hole occurs in a ferromagnetic background. Given this the most obvious choice of variational wave function is that of a singlet moving in a ferromagnetic background. This has the Bloch wave function

$$|\alpha_k\rangle = \frac{1}{\sqrt{N_{\text{Cu}}}} \sum_l e^{ik \cdot l} S_{l0}^\dagger d_{l\uparrow}^\dagger \prod_j d_{j\uparrow}^\dagger |0\rangle. \tag{28}$$

This can scatter into a triplet $S_z = 0$ state of the form

$$|\beta_k\rangle = \frac{1}{\sqrt{N_{\text{Cu}}}} \sum_l e^{ik \cdot l} T_{l0}^\dagger d_{l\uparrow}^\dagger \prod_j d_{j\uparrow}^\dagger |0\rangle \tag{29}$$

and into a triplet $S_z = 1$ state of the form

$$|\gamma_k\rangle = \frac{1}{2\sqrt{N_{\text{Cu}}}} \sum_{(ll')} e^{ik \cdot l} T_{l'+}^\dagger d_{l'\uparrow}^\dagger d_{l\downarrow}^\dagger d_{l\uparrow}^\dagger \prod_j d_{j\uparrow}^\dagger |0\rangle. \tag{30}$$

These three wave functions give the following overlaps:

$$\langle \alpha_{k'} | \beta_k \rangle = -\delta_{kk'} \frac{1}{4} [\cos(k_x) + \cos(k_y)] \tag{31}$$

$$\langle \alpha_{k'} | \alpha_k \rangle = \delta_{kk'} (1 + \frac{1}{4} [\cos(k_x) + \cos(k_y)]) \tag{32}$$

$$\langle \beta_{k'} | \beta_k \rangle = \delta_{kk'} (1 + \frac{1}{4} [\cos(k_x) + \cos(k_y)]) \tag{33}$$

$$\langle \beta_{k'} | \gamma_k \rangle = -\langle \alpha_{k'} | \gamma_{k0} \rangle = \frac{1}{\sqrt{2}} \delta_{kk'}. \tag{34}$$

The variational energy is given by $E_c = \langle \alpha_k | H_c | \alpha_k \rangle / \langle \alpha_k | \alpha_k \rangle$.

Now, the Hamiltonian acting on the state $|\alpha_k\rangle$ gives

$$\begin{aligned} H_c |\alpha_k\rangle &= -(t_1 - t_2 - t_3) |\alpha_k\rangle - (t_1 - t_2 - t_3) \frac{1}{4} (\cos k_x + \cos k_y) |\alpha_k\rangle \\ &\quad + \frac{t_1}{4} (\cos k_x + \cos k_y) |\beta_k\rangle - \frac{t_1}{\sqrt{2}} |\gamma_k\rangle \end{aligned} \tag{35}$$

so using the overlaps, equations (31) to (34), E_c is given by

$$\begin{aligned} E_c &= \left(2V + \frac{\Delta}{2} \right) + \frac{-(t_1 - t_2 - t_3) - (t_1 - t_2 - t_3)e_k/4)(1 + e_k/4) + t_1 e_k^2/4^2 + t_1/2}{(1 + e_k/4)} \\ &\quad - \frac{8t^2}{\Delta} + \frac{8t^2}{(\Delta + V)} + E(N_{\text{Cu}}) \end{aligned} \tag{36}$$

where $e_k = [\cos(k_x) + \cos(k_y)]$. This value of the energy agrees very well with numerical calculations on 4×4 clusters [13].

In what now follows we will assume that only Cu^+ virtual excitations are present. This is achieved by setting U_d to infinity, i.e. $t_2 = 0$. U_d is known to be large in the cuprates so this assumption has physical validity. The energy of the excitation gap is then simply the distance between the top of the valence band and the bottom of the conduction band. The top of the valence band is at $\mathbf{k} = (\pi, \pi)$ and the bottom of the conduction band is given at $\mathbf{k} = (0, 0)$. Thus the minimum gap energy is given as $E_{\text{gap}} = E^c(0, 0) + E^v(\pi, \pi) - 2E(N_{\text{Cu}})$. Although this is not a momentum conserving transition, we take this as the gap energy as we require an upper bound on the value of V for obtaining a bound exciton. The gap energy can be rewritten in the form

$$E_{\text{gap}} = (2V + \Delta) - \frac{t^2}{\Delta} f_{\text{gap}}(V, U_p, \Delta) \quad (37)$$

where

$$f_{\text{gap}}(V, U_p, \Delta) = 5 + \frac{16V}{(\Delta + V)} - \frac{3U_p}{(\Delta + U_p)}. \quad (38)$$

5. Exciton binding energy

Having calculated the minimum energy of the exciton in the antiferromagnetic phase, and the minimum distance between the top of the valence band and the bottom of the conduction band we can now calculate the binding energy of the exciton. This is defined as

$$E_{\text{bind}} = E_{\text{gap}} - E_{\text{exc}} = V - \frac{t^2}{\Delta} (f_{\text{gap}} - f_{\text{exc}}). \quad (39)$$

The condition $E_{\text{bind}} = 0$ determines the critical value of V for there to be an exciton in the charge transfer gap. This is illustrated in figure 3 where the critical value of \tilde{V} is plotted against $\tilde{\Delta}$ (where $\tilde{V} = V/\tilde{t}$, $\tilde{\Delta} = \Delta/\tilde{t}$ and $\tilde{t} = t^2/\Delta$) for various values of U_p . We emphasize that this is an *upper* bound on the critical value of V , as we have underestimated the gap expected from an optical transition, and the energy of the exciton is variational. Equation (39) illustrates the competing effects of the potential energy gain (V) and the kinetic energy loss $t^2/\Delta(f_{\text{gap}} - f_{\text{exc}})$ in forming a bound exciton. Notice that the kinetic energy scale is $\tilde{t} = t^2/\Delta$. In figure 4 we plot the binding energy E_{bind} against \tilde{V} for $\tilde{\Delta} = 9\tilde{t}$ which can be interpreted as a Δ of 3 eV and $t = 1.0$ eV.

The effective mass is defined as $1/m^* = (1/\hbar^2) \partial^2 E / \partial k^2$. Thus, the ratio of the effective masses of the exciton is given as

$$\frac{m_{\text{ex}}}{m_{\text{hole}}} = \frac{\partial^2 E_{\text{hole}}}{\partial k^2} / \frac{\partial^2 E_{\text{ex}}}{\partial k^2} \quad (40)$$

i.e. their mass ratio is essentially just the ratio of their band widths. The free-hole band width is given as $E_c(\pi, \pi) - E_c(0, 0)$. The exciton band width is $E_{\text{exc}}(\pi, \pi) - E_{\text{exc}}(0, 0)$. This gives a mass ratio of

$$\frac{m_{\text{ex}}}{m_{\text{hole}}} = - \frac{(4\Delta + 2U_p)(\Delta + U_p - V)(\Delta + V)}{2(\Delta + U_p)[(V(3V - 5\Delta) + U_p(\Delta - 3V))]} \quad (41)$$

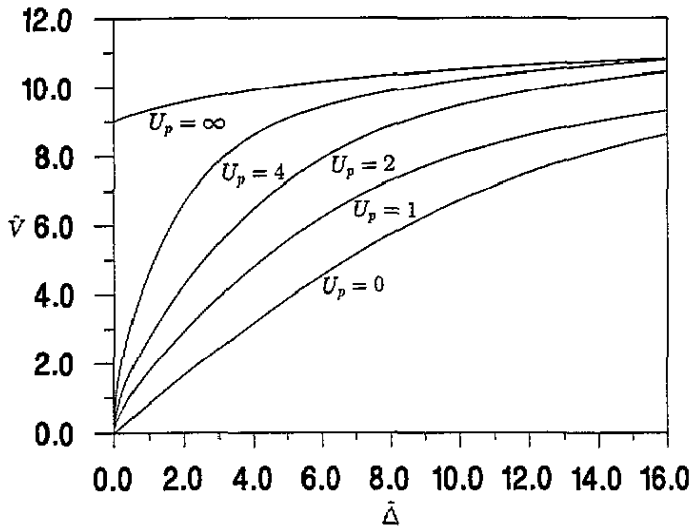


Figure 3. These curves show the boundary between a bound exciton moving in the Néel background and a free particle-hole pair for several values of U_p (U_p is given in terms of t). Above the line a bound exciton has the lower energy.

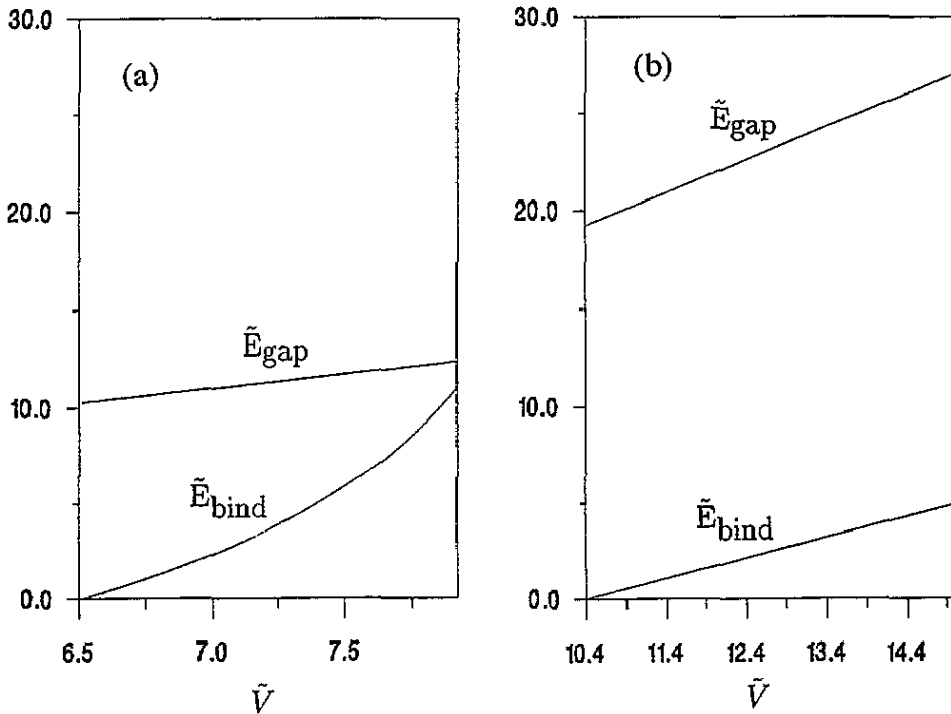


Figure 4. The binding energy of the exciton and gap energy for (a) $U_p = 0$ and (b) $U_p = \infty$, in units of \tilde{t} , as a function of \tilde{V} .

6. Discussions and conclusions

The theory presented in this paper predicts the binding energy of a charge transfer exciton with $d_{x^2-y^2}$ symmetry (A_{1g} in Raman notation) as a function of V , Δ , and U_p . We now

compare these predictions to the experimental data. Recent optical absorption experiments [3] give a value of the gap energy as $E_{\text{gap}} \sim 1.7$ eV, and a recent Raman scattering study of insulating cuprates [1] gives the binding energy of the A_{1g} exciton as $E_{\text{bind}} \sim 0.2$ eV. The value of the effective hopping amplitude \tilde{t} may be estimated from measurements of the superexchange interaction [16, 17], J , since $J = 4\tilde{t}^2/U_d \sim 0.13$ eV and $U_d \sim 10$ eV from photoemission data. This gives us an estimate for $\tilde{t} \sim 0.6$ eV. For fixed U_p we therefore have two equations (18) and (37) with two unknowns and so V and Δ can be evaluated. This proceeds as follows. Firstly \tilde{t} is eliminated from equations (18) and (37) to give the relation

$$(E_{\text{exc}}^{\text{N}} - (V + \Delta))f_{\text{gap}}(V, U_p) = (E_{\text{gap}} - (2V + \Delta))f_{\text{exc}}^{\text{N}}(V, U_p). \quad (42)$$

This gives an expression for V and Δ which can then be reinserted into the expressions for the energy of the gap to give the value of \tilde{t} .

For the case of $U_p = 0$ equation (42) is a quintic polynomial in V and Δ . This is solved using the bisection method to give $V \sim 2.7$ eV and $\Delta \sim 3.5$ eV. This gives the bare hopping matrix element as $t \sim 1.4$ eV. Although these parameters are quite reasonable the disappointing feature is that the value of V is large, and greater than U_p . This is probably unphysical, although direct oxygen–oxygen hopping would be expected to screen U_p . It should also be remembered that this calculation predicts an upper bound on the value of V required for excitons. The mass of the exciton is calculated to be $m_{\text{exc}} = 0.39m_{\text{hole}}$.

For the case $U_p = \infty$ equation (42) is a quadratic in Δ which can be solved using the usual quadratic formula. This gives a value of $V \sim 5.7$ eV, $\Delta \sim 0.4$ eV, and $t = 0.5$ eV. This time *all* the parameters are inconsistent with the values currently accepted by most to be those of the cuprate superconductors, i.e. $V \sim 1$ eV, $\Delta \sim 3$ eV, $t \sim 1.5$ eV [18]. The exciton mass is $m_{\text{exc}} = 0.36m_{\text{hole}}$.

In conclusion, we have performed a canonical transformation of the three-band Hubbard model up to $O(t^2)$ in the bare hopping amplitude and derived a variational estimate for the energy of an exciton and that of a free particle–hole pair moving through the copper oxide plane. We find that the kinetic energies of our particles are rescaled by an effective hopping amplitude $\tilde{t} = t^2/\Delta$, and that a critical value of the nearest-neighbour Coulomb repulsion is required to observe bound excitons. This critical value of V is also strongly dependent on the value of U_p , the oxygen–oxygen Coulomb repulsion. The exciton consists of an oxygen hole in a constant-phase sum of the orbitals tied to an empty copper site. It therefore has $d_{x^2-y^2}$ symmetry. Such an excitation is electric dipole forbidden, but an electric-field-induced dipole transition is allowed if the polarized light is parallel to the electric field [2]. Unfortunately such an experiment has not yet been performed.

In the Raman spectroscopy terminology the exciton has A_{1g} symmetry and is Raman active. These excitations have been observed, and by fitting the experimental data to our theory we have found an upper bound for V of 2.7 eV assuming $U_p = 0$, or 5.7 eV assuming $U_p = \infty$. The latter result is undoubtedly unrealistic.

In this paper we have not considered the effects of direct oxygen–oxygen hopping, t_{pp} . Including this would have two effects. Firstly it would screen U_p . Secondly it would render a non-bonding orbital with $d_{3z^2-r^2}$ symmetry bonding. The energy of this exciton is lowered while the $d_{x^2-y^2}$ symmetry state is raised. An exciton with $d_{3z^2-r^2}$ symmetry is observed in both optical and Raman spectroscopy with a binding energy of about 1.7 eV. In addition to neglecting t_{pp} we have also neglected the superexchange interaction. This interaction would be expected to narrow the valence and conduction bands and hence widen the single-particle energy gap. However, it is unlikely to effect our estimate of the exciton energy, as we assume that it propagates through a Néel background. Consequently we expect that

the superexchange term would *reduce* the value of V required for bound excitons from the value calculated by this theory.

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