Electronic and magnetic properties of the ionic Hubbard model on the striped triangular lattice at 3/4 filling

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We report a detailed study of a model Hamiltonian which exhibits a rich interplay of geometrical spin frustration, strong electronic correlations, and charge ordering. The character of the insulating phase depends on the magnitude of $\Delta/|t|$ and on the sign of $t$. We find a Mott insulator for $\Delta \gg U \gg |t|$; a charge transfer insulator for $U \gg \Delta \gg |t|$; and a correlated coherent insulator for $U \gg \Delta \sim |t|$. The charge transfer insulating state is investigated using a strong coupling expansion. The frustration of the triangular lattice can lead to antiferromagnetism or ferromagnetism depending on the sign of the hopping matrix element, $t$. We identify the "ring" exchange process around a triangular plaquette which determines the sign of the magnetic interactions. Exact diagonalization calculations are performed on the model for a wide range of parameters and compared to the strong coupling expansion. The regime $U \gg \Delta \sim |t|$ and $t < 0$ is relevant to Na$_{0.5}$CoO$_2$. The calculated optical conductivity and the spectral density are discussed in the light of recent experiments on Na$_{0.5}$CoO$_2$.

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I. INTRODUCTION

Many strongly correlated electron materials exhibit a subtle competition between different magnetic and charge ordered states, and between metallic, insulating, and superconducting phases. Widely studied (and poorly understood) materials include cuprate superconductors, organic charge transfer salts, manganites with colossal magnetoresistance, heavy fermion compounds and the iron pnictide superconductors. A fundamental theoretical challenge is explaining the hierarchy of energy scales and competing phases in these materials. The energy scales (such as the bandwidth and Coulomb repulsion) associated with the relevant electronic orbitals (and microscopic Hamiltonians such as Hubbard models) are typically of the order of eV. In contrast, the energy scales associated with the temperature and magnetic field dependences of transport properties and energy differences between competing phases are often several orders of magnitude smaller. Frustration of spin or charge ordering by competing interactions due to the geometry of the crystal lattice can enhance these effects. In addition, it is not clear what physical changes are produced by chemical doping. For example, does adding charge carriers just change the band filling or are there significant effects due to the associated disorder and changes in the electronic structure?

Here we report a detailed study of a specific strongly correlated electron model, the ionic Hubbard model on the triangular lattice at 3/4 filling with a stripe potential. The model illustrates how the interplay of geometric frustration and strong correlations lead to competition between different magnetic orders, charge ordering, metallic, and insulating behaviours. One concrete realisation of the model is that it may be the simplest many-body Hamiltonian that can describe Na$_{0.5}$CoO$_2$. Elsewhere we have reviewed experimental results on this material and described recent theoretical attempts to describe its unusual properties. When the filling $x$ in Na$_{x}$CoO$_2$ is close to other commensurate values, such as 1/3, 2/3, or 3/4, the system is still described by an ionic Hubbard model but the on-site potential has a different form and commensurability, depending on the ordering arrangement of the sodium ions. At incommensurate values of $x$ one expects phase coexistence of multiple Na-ordering phases.

The rest of the paper is organized as follows. In Sec. II we introduce an ionic Hubbard model on a triangular lattice including a discussion of its phase diagram. In Sec. III we analyse the model’s ground state properties using the Lanczos exact diagonalization technique on finite-size clusters. Dynamical properties such as the spectral density and optical conductivity are discussed in Sec. IV. Finally, a summary of the main results and their relevance to Na$_{0.5}$CoO$_2$ is given in Sec. V. We have also studied the same model using a complementary method, mean-field slave bosons. At appropriate places in the paper we compare and contrast the results.

II. THE IONIC HUBBARD MODEL ON A TRIANGULAR LATTICE

The Hamiltonian of the ionic Hubbard model is

$$H = -t \sum_{<ij>\sigma} (c_{i\sigma}^+ c_{j\sigma} + c_{j\sigma}^+ c_{i\sigma}) + U \sum_i n_{i\uparrow} n_{i\downarrow} + \sum_i \epsilon_i n_{i\sigma},$$

(1)
where $c^\dagger_{i\sigma}$ creates an electron with spin $\sigma$ at site $i$, $t$ is the hopping amplitude between neighbouring sites and $U$ is the effective on-site Coulomb repulsion energy between two electrons. We set $\epsilon_i = \Delta/2$ for the A-sites and $\epsilon_i = -\Delta/2$ for B-sites (cf. Fig. 1). The A-sites form rows which alternate with the B-sites of the triangular lattice. By a particle-hole transformation: $c^\dagger_{i\sigma} \rightarrow h_{i\sigma}$ model becomes a 1/4-filled (with holes) ionic Hubbard model with the sign transformation: $t \rightarrow -t$ and $\Delta \rightarrow -\Delta$.

In what follows we will discuss the charge gap which is defined for the model on a finite lattice with $N$ electrons and $2N/3$ lattice sites by

$$\Delta_e \equiv E_0(N+1) + E_0(N-1) - 2E_0(N), \quad (2)$$

where $E_0(M)$ is the ground state energy of the system with $M$ electrons.

### A. Previous theories of the ionic Hubbard model

The ionic Hubbard model (1) considered here contains geometrical frustration. This is in contrast to most previous work which has focused on bipartite, i.e., unfrustrated, lattices with different site energies, $\Delta$, on each of the bipartite sublattices and at half-filling. Some of the interest in this model can be appreciated from the half-filled atomic limit ($t = 0$). For $U > \Delta$ the charge gap for the addition of particles defined in Eq. (2), $\Delta_e = U - \Delta$, thus the system is a Mott insulator. But, for $U < \Delta$, $\Delta_e = \Delta - U$; and the system is a band insulator. At the point $U = \Delta$ this gap vanishes. Therefore a key question is what happens at the band to Mott insulator transition away from the atomic limit; in particular what happens to the gapless point - does it expand give a metallic phase? Further impetus comes from the proposals that the ionic Hubbard model is important for understanding ferroelectric perovskites\cite{15} organic charge transfer salts\cite{16,17} transition metal oxide heterostructures\cite{18} and non-linear electronic polarizability in transition metal oxides\cite{19} and, as discussed below the rich electronic phases observed in $A_xCoO_2$ [$A$=Na, K, Rb] (Ref. [3]).

The most studied case is the half filled one-dimensional chain with different site energies for odd and even numbered sites. This model shows three distinct insulating phases: a band insulator; a (ferroelectric) bond order wave insulator; and a Mott insulator.\cite{20} Metallic behaviour appears to be limited to the point in the phase diagram where band insulator gives way to the bond order wave insulator. Continuum limit bosonization calculations suggest that adding a next nearest neighbour hopping, $t'$, (which is equivalent to studying the zigzag chain) induces a large metallic region in the phase diagram,\cite{21} suggesting that even in one-dimension frustration already plays an important role in the ionic Hubbard model.

The infinite-dimensional ionic Hubbard model has been studied using dynamical mean-field theory (DMFT)\cite{22,23} which treats the on-site quantum dynamics exactly but ignores spatial correlations such as those associated with antiferromagnetic exchange. These papers studied the bipartite, Bethe lattice and found that a metallic phase separates the band insulating phase from the Mott insulating phases, in, at least, some parts of the phase diagram.

In two-dimensions most previous work has focused on the half-filled square lattice with site energies alternating in a checkerboard pattern. This model has been studied using both cluster DMFT\cite{24,25} and determinant quantum Monte Carlo (DQMC).\cite{26,27} These studies all suggested that a phase with non-zero spectral weight at the Fermi energy exists between the band insulator and Mott insulator phases, at least in some of the phase diagram. However, the has been some debate over whether this phase is metallic\cite{28} or bond ordered\cite{29}.

There has been far less work on the ionic Hubbard model away from half-filling. However, Penc \textit{et al}.\cite{30} studied the quarter-filled ionic Hubbard model on the zigzag ladder and found a competition between ferromagnetism and a paramagnetic phase with strong antiferromagnetic correlations. Bouadim \textit{et al}.\cite{31} studied the ionic Hubbard model on a square lattice with a checkerboard potential across all possible fillings with DQMC. The most interesting features they found, away from half filling, were Mott insulation at quarter and three quarters filling (which are related by the particle-hole symmetry of this model). Bouadim \textit{et al}. did not find any evidence of magnetic order in this phase. However, as the magnetic interactions are $O(t^4/U^2\Delta^2)$ the absence of magnetic order may be due to non-zero value of the temperatures they studied.

As well as bipartite arrangements of the different site energies there has also been considerable interest in random arrangements of site energies. Laad \textit{et al}.\cite{32} studied a system with a gaussian density of states and a bi-
modal distribution of site energies in infinite dimensions for various impurity concentrations, \( n \), and fillings, \( 1 - \delta \). They found insulating states for \( \delta = 1 - n \) and sufficiently large \( \Delta \) and \( U \). Byczuk et al. have used DMFT to study the (frustrated) for \( n = 1/8 \) and (bipartite) Bethe lattices in infinite dimensions with a bimodal distribution of site energies and half the sites taking each value of the site energy. At one-quarter filling they found that metal insulator transitions occur on both lattices when both \( U \) and \( \Delta \) are sufficiently large. They also noted that DMFT does not capture some of the possible effects of the disorder, such as Anderson insulating phases. In two dimensions Paris et al.\(^{22}\) used DQMC to study the square lattice at a range of fillings with 1/8 of the sites randomly chosen to have a different site energy than the rest of the lattice. They found that this model displayed Mott insulating, band insulating, Anderson insulating, and metallic phases.

Marianetti and Kotliar\(^{26}\) simplified our suggestion\(^{21}\) of that Eq. (1) is the appropriate effective low Hamiltonian for \( \text{Na}_2\text{CoO}_2 \) by further assuming that Na-ordering is of secondary importance and hence treated the potential due to the Na ions as random. They then used density functional theory to show that the distribution of Co site energies is bimodal and to parameterise the Hamiltonian (1) for \( x = 0.3 \) and 0.7. Finally they calculated the high temperature (\( T \gtrsim 100 \text{ K} \)) susceptibility for these dopings and found them to be in qualitative agreement with experiment. We deal here with the case \( x = 0.5 \) for which Na-ordering of the stripe-type (cf. Fig. 1) has been observed in experiments.\(^{27,28}\)

**B. The non-interacting model (\( U = 0 \))**

For \( U = 0 \) model (1) can be diagonalized straightforwardly leading to two bands, denoted \( \pm \). We introduce creation and destruction operators:

\[
e_{k\pm}(\epsilon^+_{Ak\sigma} + A_{k\pm}e^+_{Bk\sigma}), \quad (3)
\]

where \( e^+_{Ak\sigma} \) and \( e^+_{Bk\sigma} \) act on the Bloch states associated with the \( A \) and \( B \) sublattices, respectively, and

\[
A_{k\pm} = \frac{\Delta/2 \pm \sqrt{\Delta^2/4 + (4t \cos(k_x/2) \cos(k_y \sqrt{3}/2))^2}}{4t \cos(k_x/2) \cos(k_y \sqrt{3}/2)}, \quad (4)
\]

with the normalization constant: \( \alpha_{k\pm} = 1/\sqrt{1 + |A_{k\pm}|^2} \).

The energy dispersion of the two bands is:

\[
\epsilon_{\pm}(k) = -2t \cos k_x \pm \sqrt{\Delta^2/4 + (4t \cos(k_x/2) \cos(k_y \sqrt{3}/2))^2}, \quad (5)
\]

where \( k_x \) and \( k_y \) defined in the reduced \( (1 \times \sqrt{3}) \) Brillouin zone with lattice parameter \( a = 1 \). At 3/4-filling and for any \( \Delta \), there is always at least one band crossing the Fermi energy and so the system is metallic. The \( + \) band is half-filled and the \( - \) band filled for \( t > 0 \) and \( \Delta > 0 \), whereas for \( t < 0 \) this only occurs for \( \Delta > 0.64|t| \). For \( \Delta = 0 \) there is only one band, which has a width of \( W = 9|t| \).
C. Phase diagram

The ionic Hubbard model Ω on a triangular lattice contains a rich phase diagram resulting from the interplay between geometrical frustration, strong Coulomb repulsion and charge ordering phenomena. A schematic phase diagram can be constructed by first considering some simple limits:

(i) \( t = 0 \) (atomic limit): all A sites are singly occupied while B sites are doubly occupied. The system is insulating with a charge gap: \( \Delta_c = \min(\Delta, U) \). For \( \Delta > U \) it is a Mott insulator (MI) with \( \Delta_c = U \), whereas for \( \Delta < U \) it is a charge transfer insulator (CTI) with \( \Delta_c = \Delta \).

(ii) \( U = 0 \) (non-interacting limit): As discussed above the model is always metallic regardless the value of \( \Delta \).

(iii) \( \Delta = 0 \): For any \( U \) the model reduces to the regular Hubbard model on the isotropic triangular lattice at 3/4 filling. For large \( U/|t| \), it is equivalent to the \( t - J \) model on the triangular lattice. Dynamical mean-field theory calculations\(^{22a}\) give a ground state that is metallic. DMFT\(^{6,29}\) calculations on the Hubbard model for large \( U \) and variational Monte Carlo calculations on the \( t - J \) model give this metallic ground state as paramagnetic (ferromagnetic) for \( t < 0 \) (\( t > 0 \))\(^{20}\).

(iv) \( \Delta = \infty \): As the B-sites can be completely projected out from the Hilbert space, the model is mapped onto decoupled half-filled Hubbard chains. Hence, the system is (Mott) insulating for any non-zero positive \( U \); i.e., there is a charge gap \( \Delta_c \neq 0 \), and there are antiferromagnetic correlations (with power law decay) and no spin gap.

(v) \( U >> \Delta >> |t| \neq 0 \): For finite but small \( t \), virtual hopping processes lead to effective magnetic exchange couplings between the A sites. The effective low-energy \( t - J - J_{\text{diag}} - J_{\perp} \) Hamiltonian for the holes is

\[
H = t \sum_{ij} P(h_{i\sigma}^+ h_{j\sigma} + h_{j\sigma}^+ h_{i\sigma}) + J \sum_{\{ij\}} \left[ S_i \cdot S_j - \frac{n_i n_j}{4} \right]
+ J_{\text{diag}} \sum_{\{ij\}} \left[ S_i \cdot S_j - \frac{n_i n_j}{4} \right]
+ J_{\perp} \sum_{\{ij\}} \left[ S_i \cdot S_j - \frac{n_i n_j}{4} \right] - \sum_{i\sigma} \epsilon_i h_{i\sigma}^+ h_{i\sigma},
\]

where \{\...,\} and \[\...,\] denote sums over intra-A-chain, inter-A-chain sites, respectively. The sum over (\...\) is between an A and nearest-neighbour B-sites. The projector \( P = \Pi_i [1 - n_i n_{i\uparrow}] \) forbids double occupation of holes on any lattice site. The dynamics of the electron-doped system relevant to Na\(_x\)CoO\(_2\) with electron occupation 1 + \( x \) is related to the hole-doped system, with filling 1 - \( x \), through the replacement: \( t \rightarrow -t \) and \( \epsilon_i \rightarrow -\epsilon_i \) leaving the exchange parameters unchanged.

The exchange couplings \( J, J_{\perp} \) and \( J_{\text{diag}} \) can be obtained through a strong coupling expansion using Raleigh-Schrödinger perturbation theory on the hopping term around the configuration in which all B sites are doubly occupied and A-sites singly occupied (see Appendix A). This leads to an effective exchange coupling between electrons in A-sites in the horizontal direction:

\[
J = \frac{4t^2}{U} - \frac{8t^3}{\Delta^2} - \frac{16t^3}{\Delta U} + O(t^4), \tag{7}
\]

and in the perpendicular direction

\[
J_{\perp} = \frac{16t^4}{\Delta^2} \left[ \frac{1}{U + \Delta} + \frac{1}{U - \Delta} \right] + O(t^5). \tag{8}
\]

The exchange coupling \( J_{\text{diag}} \) between A and B sites is

\[
J_{\text{diag}} = 2t^2 \left[ \frac{1}{U + \Delta} + \frac{1}{U - \Delta} \right] + O(t^3), \tag{9}
\]

which is blocked if the B sites are doubly occupied but recovers the correct \( 4t^2/U \) exchange interaction as \( \Delta \rightarrow 0 \).

The second and third terms in \( J \) are antiferromagnetic (AFM) for \( t < 0 \) and ferromagnetic (FM) for \( t > 0 \). Higher order contributions to \( J \) are AF and can be found in Appendix A.

A schematic phase diagram of the 3/4-filled ionic Hubbard model on a triangular lattice (\( \Omega \)) is shown in Fig. 2. The transition lines are extracted from the limits (i)-(v) discussed above and exact diagonalization calculations for intermediate parameter regimes. Apart from the Mott insulator (MI) and charge transfer insulator (CTI), our numerical analysis suggests the presence of a colossal insulator (CI) in the range \( \Delta \sim O(|t|) \) and \( U >> |t| \). Depending on the sign of \( t \), different spin arrangements occur as shown in Fig. 1. The condition \( J = 0 \) separates AF from the FM region which occurs in the parameter range: \( 5t < \Delta < \sqrt{2U} \) and is plotted in Fig. 2.

D. The model on two and four-site clusters

In this section we explore the nature of the ground state of the model (\( \Omega \)) on two and four-site clusters. The
two-site cluster incorporates charge ordering phenomena in the presence of on-site Coulomb interaction. The four-site toy model also contains geometrical frustration effects present in the full model [1]. Ground state properties of the clusters are discussed in terms of valence-bond (VB) theory when appropriate. For $t < 0$ and $U >> |t|$ the ground state wavefunction is accurately described by the resonance between possible valence bonds. Our analysis indicates that the charge gap of the clusters is enhanced with $\Delta$ due to the differences between the two-electron and three-electron bonds between the different $A$ and $B$ sites.

1. Two-site cluster

We first consider three electrons in two inequivalent sites (one $A$, the other $B$) separated by an energy $\Delta$. The energy levels for this cluster are sketched in Fig. 4. The energy levels for this cluster are plotted in the figure. For $U = 0$, the charge gap of the cluster is $\Delta_c = 0$ for any $\Delta$ due to the degeneracy of the ground state. In order to evaluate the dependence of the gap on $\Delta$ we first obtain the ground state energies with $N = 2$, 3 and 4 electrons:

$$H = -t(c_A^\dagger c_B + c_B^\dagger c_A) + U(n_{A^1}n_{A^1} + n_{B^1}n_{B^1}) + \Delta/2(n_A - n_B).$$  \tag{10}

For $U = 0$, the charge gap of the cluster is $\Delta_c = 0$ for any $\Delta$ due to the degeneracy of the ground state. In order to evaluate the dependence of the gap on $\Delta$ we first obtain the ground state energies with $N = 2$, 3 and 4 electrons:

$$E_0(2) = -2t^2 \left[ \frac{1}{U + \Delta} + \frac{1}{U - \Delta} \right], \quad U >> |t|$$

$$E_0(3) = U - \frac{\sqrt{\Delta^2 + 4t^2}}{2}$$

$$E_0(4) = 2U.$$  \tag{11}

In the limit $\Delta \to 0$ and $U >> |t|$, the charge gap of the cluster is

$$\Delta_c \approx 2|t| + \Delta^2 \left( \frac{1}{4t^2} - \frac{4t^2}{U^3} \right) - \frac{4t^2}{U}. \tag{12}$$

The first contribution to $\Delta_c$ is present even for $\Delta = 0$ as expected from the bonding-antibonding splitting of the cluster and will go to zero in the infinite system. The term proportional to $\Delta^2$ comes from the different dependences of $E(3)$ and $E(2)$ on $\Delta$: $E(2)$ has a weaker dependence than $E(3)$. This is due to the different nature of the two-electron and the three-electron bond. The former is accurately described by a correlated VB between an electron on an $A$ site and an electron on a $B$ site whereas the latter is described by a single hole in an antibonding “molecular” orbital. The two-electron and three-electron bond energies (the energy needed to break a bond between inequivalent sites) are $\Delta/2 - \sqrt{\Delta^2 + 4t^2}/2$ and $E_0(2)$, respectively. Hence, the two-electron bond becomes weaker with $\Delta$ while the three-electron bond is strengthened with $\Delta$. This is known from quantum chemistry and can be understood as being a consequence of the presence or absence of Coulomb repulsion between electrons.

2. Four-site cluster

We consider the four-site cluster (Fig. 4) with two $A$-sites shifted by $+\Delta/2$ and two $B$-sites shifted by $-\Delta/2$. The cluster shown contains $N = 6$ electrons (corresponding to $3/4$-filling). The model Hamiltonian in this case is

$$H = -t \sum_{i \in A,j \in B} \left( c_i^\dagger c_j + c_j^\dagger c_i \right) - t' \sum_{i,j \in A} \left( c_i^\dagger c_j + c_j^\dagger c_i \right) - U \sum_i n_{i\uparrow}n_{i\downarrow} + \Delta/2 \sum_{i \in A,j \in B} (n_i - n_j). \tag{13}$$

We first discuss the $\Delta \to 0$ limit. The exact ground state energies of the fully frustrated $t' = t$ cluster for $N = 5$, 6 and 7 electrons are plotted in Fig. 6 for $U = 100|t|$. Consistent with the results for the two-site cluster we find that, $E_0(5)$, has the weakest dependence on $\Delta$ of all the ground state energies. The ground state wavefunction for $N = 6$ can be well described in terms of resonating valence bonds as shown in the Appendix. In contrast, the wavefunction for $N = 7$ consists of a single hole hopping around the cluster and so contains no Coulomb interaction effects. In this case a “molecular” orbital with a single hole describes the cluster and its energy, $E_0(7)$, has the strongest dependence with $\Delta$. The different behavior of $E_0(5)$, $E_0(6)$ and $E_0(7)$ is responsible for the increase of the charge gap with $\Delta$ as shown in Fig. 6. This behavior is in contrast to the $U = 0$ case plotted in the figure.

Effects of frustration. We now discuss the four-site cluster with $t' = 0$. In this case analytical formulas may be obtained for $U = \infty$. The sign of the hopping is irrelevant here in contrast to the $t' \neq t$ case. The ground state energies are:

$$E_0(6) = -\sqrt{8t^2 + \Delta^2}$$

FIG. 4: (Color online) Ionic Hubbard model on two- and four-site clusters. The energy level diagram for 3 electrons on two sites (left) and the four-site cluster with six electrons (right).
FIG. 5: (Color online) Dependence of ground state energies with ∆ for the four-site cluster with $t' = t$ and $U = 100|t|$. The Coulomb interaction $U$, $2U$ and $3U$ have been subtracted from the total energies $E_0(5)$, $E_0(6)$ and $E_0(7)$, respectively, for convenience.

$$E_0(7) = -t - \frac{\sqrt{4t'^2 + \Delta^2}}{2}. \quad (14)$$

In the limit $\Delta \to 0$, we find $E_0(7) \approx -2t - \frac{\Delta^2}{4|t|}$ and $E_0(6) \approx -2\sqrt{2t - \frac{\sqrt{2}\Delta^2}{8|t|}}$. Thus, $E_0(6)$ has a weaker dependence on $\Delta$ than $E_0(7)$, similarly to the fully frustrated $t' = t$ cluster.

Our small cluster analysis indicates that the charge gap, $\Delta_c$, increases with $\Delta$ due to the different natures of the two-electron and three-electron bonds formed between inequivalent sites. This result is not affected by the presence of frustration in the cluster at the qualitative level. However, geometrical frustration ($t \sim t'$) leads to qualitatively different magnetic properties for different signs of $t$ in contrast to the unfrustrated ($t' = 0$) case.

FIG. 6: (Color online) Dependence of the charge gap on $\Delta$ for the four-site cluster. Note the increase of $\Delta_c$ for any $\Delta$ for $U \gg |t|$ of Fig. 5 and also how the dependence for $\Delta > |t|$ is quite different with $\Delta < |t|$.

III. GROUND STATE PROPERTIES OF THE IONIC HUBBARD MODEL ON A TRIANGULAR LATTICE

Intermediate parameter regimes are explored based on Lanczos diagonalization on finite clusters with $N_s = 12, 16$ and 18 sites and periodic boundary conditions. Different cluster shapes have been benchmarked against the exact solution of the non-interacting model and are shown in Fig. 8. The vectors defining the clusters are: $T_1 = n_{11}a_1 + n_{12}a_2$ and $T_2 = n_{21}a_1 + n_{22}a_2$, where $n_{ij}$ and $n_{2i}$ are integers. A straightforward finite size scaling analysis is not possible because of the complicated changes in the cluster shape as the lattice size increases.

We present results of the dependence of the charge order parameter, the charge gap and the spin correlations on $\Delta$. Numerical results are compared to the weak and strong coupling limits as appropriate.
A. Charge order

The charge order parameter is first computed for $U = 0$ and compared to exact tight-binding results on the infinite lattice. This serves to calibrate the importance of finite-size effects on a cluster. Second, the effect of $U$ on charge ordering is analyzed in detail.

The charge order parameter is

$$n_B - n_A = \sum_{k,\sigma} \langle \Psi_0 | (c_{Bk\sigma}^+ c_{Bk\sigma} - c_{Ak\sigma}^+ c_{Ak\sigma}) | \Psi_0 \rangle, \quad (15)$$

where $|\Psi_0\rangle$ is the ground state of the Hamiltonian $[1]$. In Fig. 6 the charge order parameter is plotted for both signs of $t$ on the $N_z=18$ site cluster of Fig. 5 and compared to the tight-binding result ($U = 0$) of the extended system. Since this cluster gives the best agreement with the infinite limit of the non-interacting model, among all of the clusters that we studied, we mostly show results for this cluster in the rest of this paper.

The effect of Coulomb repulsion on charge transfer is also shown in Fig. 6. The qualitative dependence of charge transfer remains unchanged with $U$. However, increasing $U$ does suppress $n_B - n_A$ a little for small and moderate $\Delta$.

$$H = \sum_{k,\alpha,\sigma} \epsilon_{\alpha}(k) c_{\alpha k,\sigma}^+ c_{\alpha k,\sigma} + \frac{1}{N_s} \sum_{k,k',\alpha_1,\alpha_2,\alpha_3,\alpha_4} V(k-q\alpha_1, k\alpha_2, k' + q\alpha_3, k'\alpha_4) c_{\alpha k,\sigma_1}^+ c_{\alpha k',\sigma_2}^+ c_{\alpha k',\sigma_3} c_{\alpha k,\sigma_4}, \quad (16)$$

where the $\alpha$'s refer to the two values + and − and $V$ is the Coulomb matrix describing the 16 different scattering processes between the bands: $\epsilon_{\alpha}(k)$ of Eq. [5]. The Coulomb matrix is

$$V(k_1, k_2, k_3, k_4) = \begin{cases} U \beta(k_1, k_2, k_3, k_4) = & \beta(k_1, k_2, k_3, k_4) = \beta(k_1, k_2) \beta(k_3, k_4), \\ & \beta(k_1, k_2) = \frac{1}{\alpha_k} \frac{A_{k+} - A_{k-}}{A_{k+} - A_{k-}}, \quad (18) \end{cases}$$

where $A_{k\pm}$ is given by [1] and $\alpha_k$, the normalization constant of Eq. [5].

The occupation of the non-interacting bands is obtained through the expression: $n_{\pm} = \sum_{\alpha \mp} \langle \Psi_0 | c_{\alpha k,\sigma}^+ c_{\alpha k,\sigma} | \Psi_0 \rangle$. In order to investigate the populations of the non-interacting bands at large $U$ we plot Lanczos results for $n_+ - n_-$ for $N_z = 18$ in Fig. 8. For $U = 2|t|$, we find that $n_+ - n_- = 1$. However, $n_+ - n_- < 1$ for large $U$. The interpretation of this result is complicated as $n_- - n_+$ conflates two effects: (i) charge transfer between the bands, effectively doping the $+\text{-}\text{band}$ with electrons from the lower band; and (ii) for $U \neq 0$ the bands are no longer eigenstates, thus the physical interpretation of $n_- - n_+$ is unclear for large $U$. In spite of this interpretative difficulties it is interesting to note that the behavior seen in Fig. 5 differs from a recent mean-field approach which includes local electron correlations only. However, at present, it is not possible to conclusively determine whether this is because non-local electron correlations may play an important role or because of the strong interband scattering induced by the large $U$ which will eventually destroy the reciprocal space description. This question is particularly important given the proposed role of tiny hole densities in the $+\text{-}\text{band}$ in explaining the apparent discrepancy between the insulating behaviour suggested by resistivity, ARPES and optical conductivity, and the observation of metallic quasiparticles via Shubnikov-de Haas experiments on Na$_{0.5}$CoO$_2$. This question requires future investigation.
C. Charge gap

In order to understand the electronic properties of model 1 we now discuss the charge gap and its dependence with charge order driven by $\Delta$ and the Coulomb repulsion. The charge gap is defined by equation (2).

When $t$ is small, the lowest order correction to excitation energies come from the kinetic energy gain due to the propagation along the B(A)-chains of a hole (doublon) when extracting (adding) an electron to the zeroth order ground state configuration. Using degenerate perturbation theory on Hamiltonian (8) the gap to $O(t^2/\Delta)$ is

$$\Delta_c = \Delta - 2|t| + 8t^2/\Delta - 2t^2_{c_{eff}} - 8t^3/\Delta^2$$

$$+ \delta E_{1D}^{t-J},$$

where $\delta E_{1D}^{t-J}$ is the energy change when adding a hole to a single half-filled A-chain modelled by the $t-J$ model with $J$ given by Eq. (7). The second order hopping term $t_{c_{eff}}^{(2)} = 2t^2/\Delta$, contributes to the propagation of an antiholon in the A-chain. In the antiferromagnetic case, $J > 0$, the energy, $\delta E_{1D}^{t-J}$ in (19) per A-chain site is given by the Bethe ansatz expression

$$\delta E_{1D}^{t-J} = -\frac{2|t|}{\pi} \sin(n_A \pi)$$

$$- 8J(\ln 2)n_A^2 \left[ 1 - \sin(2n_A \pi) \right] + J \ln 2,$$

where $n_A = 1 - 1/N_A^A$ is the number of electrons in a single A-chain of $N_A^A$ sites when a single hole has been added to the otherwise half-filled chain. In the ferromagnetic case ($J < 0$)

$$E_{1D}^{t-J} = -2|t| - J/2.$$  

Hence, the charge gap is found to be larger for $t < 0$ than $t > 0$, as shown in Fig. 9 due to the geometrical frustration. In contrast, on the square lattice, $\Delta_c$, does not depend on the sign of $t$. The dependence on the sign of $t$ becomes even more apparent for $\Delta^2/|t|$, where it is clear that for $t < 0$ the gap is significantly larger than for $t > 0$. Indeed, it may be that for small $\Delta^2/|t|$ and $t < 0$ the system is an insulator and for $t > 0$ it is metallic. However, finite size effects prevent us from making a definitive statement about the existence of a metallic state for small $\Delta^2/|t|$. We note that dependence on the sign of $t$ is the opposite from what one would expect from weak-coupling arguments. For $t > 0$ and $U = \Delta = 0$ and at $3/4$ filling the Fermi surface has perfect nesting and there is a van Hove singularity in the density of states at the Fermi energy. Hence, weak-coupling arguments would suggest that for this sign of $t$ the system would have a greater tendency to density wave instabilities and
insulating states. Further, our mean-field slave boson calculations also predict that the insulating state is more stable for $t > 0$ than $t < 0$, in contrast to the results reported in Fig. 9.

D. Magnetic order

Spin correlations in the model are analyzed through the static spin structure factor:

$$S(q) = \frac{1}{N_s} \sum_{ij} \exp(\imath q \cdot (R_i - R_j)) < S_i^z S_j^z > \quad (22)$$

where $S_i^z = (n_{i\uparrow} - n_{i\downarrow})/2$ is the $z$-component of the spin at the lattice site $R_i$.

The dependence on $\Delta$ of the spin structure factor, $S(q)$, is shown in Fig. 10 for two different wavevectors with $U = 100|t|$. For $t < 0$ the results indicate a transition to the magnetically ordered state with wavevector $Q_1 = (\pi, \pi/\sqrt{3})$ (which implies that the spins within the A-chains are antiferromagnetically ordered and antiferromagnetically coupled with neighbouring A-chains) at about $\Delta = 2|t|$. This is the spin pattern shown in Fig. 1. For $t > 0$ there is a range of $\Delta$ for which the A spins are ferromagnetically coupled. The FM region obtained from Lanczos diagonalization is in agreement with the condition $J < 0$ extracted from a strong coupling expansion. This condition gives a FM region for $5t < \Delta < \sqrt{2U}$.

The wavevector of the magnetic order and the associated magnetic moment of the ground state of the model with $t < 0$ and $U \gg \Delta \gg |t|$ (see Fig. 1) are consistent with the antiferromagnetic ordering wavevector observed in Na$_{0.5}$CoO$_2$.[36,37] However, the observed charge transfer between A and B chains in Na$_{0.5}$CoO$_2$.[36,37,39,40] is much smaller than the complete charge transfer sketched in Fig. 1. Such a large magnetic moment in the presence of a weak charge transfer between A and B sites is not expected from either classical or weak coupling arguments. Nevertheless, our previous exact diagonalization calculations for $U > W$ (see Fig. 4 of Ref. [7]) found a substantial magnetic moment and small charge transfer, even for small $\Delta$, consistent with the experimental results.

FIG. 9: (Color online) Dependence of the charge gap on the on-site potential $\Delta$. The charge gap for $U = 100|t|$ on a $N_s = 18$ tilted cluster (top) and a $N_s = 16$ ladder-type cluster (bottom) (see Fig. 3) is shown. Dashed lines denote the results of the strong coupling expansion (19) for comparison.

FIG. 10: (Color online) Development of magnetic order. The static spin structure factor $S(q)$ at the wavevectors (a) $Q_1 = (0, \pi/\sqrt{3})$, associated with C-type antiferromagnetism[35] (see Fig. 1, left panel), and (b) $Q_2 = (\pi, \pi/\sqrt{3})$, associated with G-type antiferromagnetism[35] (see Fig. 1, right panel), are shown for $U = 100|t|$ as a function of $\Delta$, the difference between the local energies on the A and B sublattices. Calculations are performed on the $N_s = 18$ cluster.
IV. DYNAMICAL PROPERTIES

In this section we discuss dynamical properties of the model (1). We use Lanczos diagonalization on $N_s = 18$ clusters to compute the one-electron spectral density and the frequency dependent conductivity.

A. One-electron spectral density

The spectral density per spin is

$$ A(\omega) = \sum_m |\langle \Psi_m(N-1)|c_\sigma|\Psi_0\rangle|^2 \delta(\omega + (E_m(N-1) - E_0(N))) $$

$$ + |\langle \Psi_m(N+1)|c_\sigma^+|\Psi_0\rangle|^2 \delta(\omega - (E_m(N+1) - E_0(N))), $$

where $E_m(N \pm 1)$ is the spectra of excitations of the full quantum many-body problem with $N \pm 1$ electrons and $|\Psi_m(N \pm 1)\rangle$ its associated wavefunctions. $E_0(N)$ is the ground state of the $N$ electron system with wavefunction $|\Psi_0\rangle$.

In Fig. 11 we show the spectral density for $U = 100|t|$ and $\Delta = 10|t|$. As the system is well into the strong coupling regime, $U >> \Delta >> |t|$, we can understand the main excitations observed on the basis of the atomic limit ($t = 0$).

For $t = 0$ extracting an electron from the lattice can lead to three possible excitation energies: $-3\Delta/2$, $\Delta/2$ and $-\Delta/2 + U$. While adding an electron we only have one excitation energy at $\Delta/2 + U$. Therefore, four peaks at these excitation energies are expected in $A(\omega)$. A gap of $\Delta_c = \Delta$ is therefore obtained when $t = 0$ typical of a charge transfer insulator. When the hopping is turned on, the lowest order correction to excitation energies comes from the propagation of a hole (doublon) along the B(A)-chains when extracting (adding) an electron to the zeroth order ground state configuration. As the hole (electron) added can be on any site of the chains...
the ground state is \( N_A \langle N_B \rangle \)-fold degenerate. This degeneracy is lifted at the first order in \( t \), where the excitation energies for removing an electron are \( \Delta/2 - 2|t| \langle \sin(k) - 1 \rangle \) and \( \Delta/2 - 2|t| \cos(k) \), from the A and B-sites respectively. Adding an electron to the A-chain leads to a doublon with excitation energy \( \Delta/2 + U + 2|t| \langle \sin(k) - 1 \rangle \) Thus, a characteristic one-dimensional broadening of \( 4|t| \) to the four peaks should be expected and the gap is reduced from the atomic limit result to \( \Delta_c = \Delta - 4|t| \). The hybridization between the chains lowers the ground state energy for the \( N \) electron configuration, due to virtual excursions from a B-site to a nearest-neighbour A-site, by \(-4|t|^2/\Delta \) with no cost in Coulomb repulsion energy. Therefore, the lowest \( N + 1 \) electron excitation energy is pushed upwards by \(+4|t|^2/\Delta \) and the \( N - 1 \) downward by \(-4|t|^2/\Delta \). This leads to an increase of the gap: \( \Delta_c = \Delta - 4|t| + 8t^2/\Delta \). The final charge gap, \( \Delta_c \), including the higher order corrections of Eq. (19) coincides with the numerical calculation shown in the inset of Fig. 11.

In Fig. 12 we show the evolution of \( A(\omega) \) with \( \Delta \) for \( U = 15|t| \). The four peak structure discussed above for the CTI remains for this smaller value of \( U \) and \( \Delta = 10|t| \). As \( \Delta \) decreases the peaks broaden due to hybridization between the A and B chains and shift in energy. For \( \Delta = |t| \), \( A(\omega) \) contains a lower Hubbard band (LHB), an upper Hubbard band (UHB) and most of the spectral weight is around the chemical potential \( \omega = \mu \). We find that the energy difference between the LHB and UHB is much larger than \( U \), which we attribute to hybridization between the chains. Thus we identify this regime as a covalent insulator (CI) [7,41].

B. Frequency dependent conductivity

The incoherent part of the optical conductivity is calculated through the current correlation function:

\[
\sigma(\omega) = \frac{\pi c^2}{N_s} \sum_{m \neq 0} \frac{|\langle \Psi_m(N) | j_x | \Psi_0 \rangle|^2}{E_m - E_0} \delta(\omega - (E_m - E_0)),
\]

(24)

where, \( j_x \) is the \( x \)-component of the current operator, \( j = \sum_{<ij>,\gamma} (R_i - R_j) c_{i\sigma}^\dagger c_{j\gamma} \), and \( R_i \) is the position of the \( i \)-th lattice site. All nearest-neighbor sites entering the sum in the current are denoted by \( \gamma \).

The evolution of the optical conductivity, \( \sigma(\omega) \), with \( \Delta \) is shown in Fig. 13. There are two main absorption bands in the optical spectra. One is fixed at large energies of about \( U \) and is associated with excitations between the Hubbard bands and a lower band which shifts with \( \Delta \). The lower absorption band is due to excitations associated with transferring an electron from the + band to the + band. These produce a continuum of particle-hole excitations of width of order \( W \approx 9|t| \).

We have also calculated the Drude weight for a range of parameters in the model Hamiltonian. We do not show the results here because due to finite size effects the detailed interpretation is not clear. However, the trend is clear: as \( U/|t| \) and \( \Delta/|t| \) increase, the Drude weight decreases significantly.

V. CONCLUSIONS

We have considered the electronic properties of an ionic Hubbard model at 3/4-filling with stripes of alternating
on-site potential. This model has a rich phase diagram, in which various types of insulating and metallic states compete. A charge transfer-type insulator, a Mott insulator and a covalent insulator occur in different $U$-$\Delta$-$t$ parameter regimes. The geometrical frustration of the triangular lattice leads to different magnetic properties depending on the sign of $t$. For $t < 0$ an antiferromagnetic interaction occurs whereas for $t > 0$ a ferromagnetic coupling occurs in a broad range of parameters.

At $U >> \Delta >> |t|$, a charge transfer insulator of doubly occupied chains of $B$-sites alternating with singly occupied $A$-chains occurs, i.e., $n_B - n_A = 1$. As $\Delta$ is decreased the system remains insulating although the charge disproportionation between sites is incomplete: $n_B - n_A < 1$.

The insulating state of $\text{Na}_0.5\text{CoO}_2$ is characterized by a small charge modulation, a small charge gap, and strong Coulomb interaction. Electronic structure calculations suggest that $\text{Na}_0.5\text{CoO}_2$ is in the parameter regime, $U >> |t|$ and $\Delta \sim |t|$ which is different to the strong coupling parameter regime. This regime is difficult to analyze within weak coupling perturbation theory and numerical approaches are helpful. The model with no charge modulation, $\Delta = 0$, reduces to a highly-doped Hubbard (or $t-J$) model on a triangular lattice which is believed to be metallic. However, under a weak external periodic potential, $\Delta \sim O(|t|)$, our exact diagonalization analysis suggests a non-zero charge gap.

Unlike the charge transfer insulators proposed previously for $\text{Na}_0.5\text{CoO}_2$ this insulator is characterized by small real space charge transfer: $n_B - n_A << 1$. An insulating state induced by strong hybridization of the non-interacting bands is realised and is reminiscent of the covalent insulator (CI) description of some transition metal oxides.

The behavior of the charge gap for $U >> |t|$ has been further explored by an exact analysis of two and four-site clusters which indicates that the charge gap is always enhanced with $\Delta$ even at small values. A different dependence on $\Delta$ of the ground state many-body energies $E_0(N)$, $E_0(N-1)$ and $E_0(N+1)$ is found which reflects the different nature of the bonds formed between inequivalent $A$ and $B$ sites. Two-electron bonds are well described as valence bonds which contain the effects of strong electronic correlations whereas three-electron bonds are accurately described by “molecular” orbitals which are uncorrelated. While the former type of bond depends weakly on $\Delta$ the latter does not.

Optical conductivity experiments suggest a gap of the order of $0.020 \text{ eV} (\sim |t|/5)$, a sharp peak at about $0.026 \text{ eV} (\sim |t|/4)$ which is at the lower edge of a continuum of excitations which reaches energies up to about $0.9 \text{ eV} (\sim 9|t|/4)$. This behavior is consistent with the low energy adsorption band found in the calculated $\sigma(\omega)$ (see Fig. 13) which is located at about $\Delta \sim O(|t|)$ with the continuum being the whole set of particle-hole excitations between the two hybridized bands which spread over the whole bandwidth $\sim W$.

Recent experiments on $\text{Na}_x\text{CoO}_2$ for $x = 2/3$ the Na ions induce a charge ordering pattern with filled non-magnetic Co$^{3+}$ ions arranged in a triangular lattice and Co$^{4+}$ magnetic sites forming a kagomé lattice structure with the transferred holes moving on it. These experiments are important as they relate the charge order with the different magnetic and electronic properties of the material. The present ionic Hubbard model modified to include such ordering patterns could be used to explore the unconventional metallic properties of $\text{Na}_x\text{CoO}_2$ at $x = 2/3$.

We now briefly discuss the relationship between the results we obtained here and those we recently obtained for the same model with a slave boson mean-field theory.\footnote{Slave bosons give an insulator only for $\Delta > 8|t|$ ($\Delta > 5|t|$ for $t < 0$) whereas exact diagonalisation suggests that the ground state is insulating even for $\Delta \sim |t|$.

An important open question that this study raises is, what is the ground state for small $\Delta/|t|$? The temperature dependence of the magnetic susceptibility of the $t-J$ model on the triangular lattice has been calculated using exact diagonalisation on small clusters.\footnote{The bottom left panel of Figure 6 in Ref. 15 shows that for $J = 0$ (i.e., $U \rightarrow \infty$ in the Hubbard model) that at $3/4$ filling that for all temperatures above about $0.4|t|$ that the susceptibility is the same as that for localised non-interacting spin-1/2 particles. The susceptibility has a maximum at about $0.3|t|$ and then decreases with decreasing temperature to a value about 2-3 times the value for $U = 0$.}

These results raise the question as to the nature of the ground state and the tendency of the electrons to become localised and the spins to antiferromagnetically order, even in the absence of an exchange interaction, due to kinetic antiferromagnetism.\footnote{APPENDIX A: HEISENBERG EXCHANGE COUPLINGS

In this section we discuss the various contributions to the nearest neighbour exchange coupling, $J$, between the $A$-sites. Taking $|\Psi_0 >$ as the ground state configuration in the strong coupling limit $U >> \Delta >> t$, there is no correction to the lowest order in the kinetic energy. To $O(t^2)$ we have the usual superexchange antiferromagnetic contribution: $J = 4t^2/U$. To $O(t^3)$ "ring" exchange processes around the 3-site plaquette of the type shown in Fig. 14 remove the spin degeneracy and were already discussed by Penc and collaborators in a Hubbard model on a zig-zag ladder. The energy of the singlet state in Fig. 14 is shifted by $4t^3/\Delta^2$ while the triplet state by $-4t^3/\Delta^2$. These shifts are opposite to the two site case. As there are two possible ways of going around the triangle in Fig 14 and there are two neighbouring $B$-sites (one below the two $A$-sites as shown in Fig. 13 and another above) the final contribution to the effective $J$ at $O(t^3)$ is $J = E_t - E_s = -8t^3/\Delta^2$ enhancing the ferromagnetic tendencies as compared to the ladder case by a factor.}
FIG. 14: (Color online) Three site "ring" exchange processes contributing to the exchange interaction, \( J \), between neighbour spins in an A chain of the \( t - J - J_\perp \) model (compare Equation (5)).

FIG. 15: (Color online) Four site "ring" exchange processes of \( O((t/\Delta)^3) \) contributing to the exchange interaction between two neighbouring sites in the A-chains in model (6). of two. In contrast "ring" exchange processes around a 4-site plaquette \( O(t^4) \) of the type shown in Fig. 15 lead to an AF contribution to \( J = 40t^4/\Delta^3 \). Including all possible exchange processes, a total contribution to \( J \) valid to \( O((t/\Delta)^4) \) is

\[
J = \frac{4t^2}{U} - \frac{8t^3}{\Delta^2} \frac{\Delta}{\Delta U} + \frac{16t^4}{\Delta^3} \frac{\Delta^2}{(2\Delta + U)} + \frac{16t^4}{\Delta^2 U} \tag{A1}
\]

APPENDIX B: GROUND STATE WAVEFUNCTIONS FOR THE FOUR-SITE CLUSTER AND VALENCE BOND THEORY

In this appendix, we discuss exact ground state wavefunctions on the \( N_s = 4 \) cluster of Fig. 4 with \( t' = t \) and \( N = 5, 6 \) and 7 electrons. Valence bond (VB) states, which are neutral configurations formed by two neighbour electrons in a single cluster are found to describe the exact wavefunction accurately for \( U >> |t| \) and \( t < 0 \) for \( N = 6 \). This is because ionic configurations have a negligible weight in the full wavefunction at large-\( U \) values.

1. Ground state for \( N = 6 \) electrons

The exact ground state wavefunction, \(|\Psi_0(6)\rangle\), is well described by the resonance between different possible VB states between electrons inside the cluster:

\[
|\Psi_0(6)\rangle \approx a \left| \uparrow \downarrow \downarrow \downarrow \right\rangle + b \left| \uparrow \downarrow \uparrow \downarrow \right\rangle + c \left| \uparrow \downarrow \uparrow \downarrow \right\rangle
\]

Here, and below, VB states are colored red. Note that the horizontal sites are A sites while the vertical sites are B sites as sketched in Fig. 4. For \( U = \infty \) and \( \Delta = 0 \), the energy of the RVB state is \( E_0^{RVB}(6) = -3.3723|t| \) and the weights of the wavefunction are \( a = b = 0.4544 \) and \( c = 0.3831 \). This RVB wavefunction gives an accurate description of the exact ground state energy which for \( U = 100|t| \) is: \( E_0(6) = -3.453|t| \) and a wavefunction described by \( |B1\rangle \) with \( a = 0.459 \), \( b = 0.445 \), \( c = 0.382 \), plus small ionic terms. Note that, on the four site cluster, the A and B sites are not equivalent even for \( \Delta = 0 \) due to geometry of the cluster (cf. Fig. 4).

The RVB wavefunction also accurately describes the ground state energy in the limit: \( U >> \Delta >> |t| \). The energy of the RVB state for \( \Delta = 10|t| \) is \( E_0^{RVB} = -10.433|t| \) and the wavefunction has weights \( a = 0.977 \), \( b = 0.021 \), and \( c = 0.1058 \). This is in good agreement with the exact ground state, which has \( E_0(6) = -10.453|t| \) and \( a = 0.976 \), \( b = 0.024 \) and \( c = 0.108 \) (plus small ionic terms). Thus the VB formed between the two A sites dominates the wavefunction.

2. Ground state for \( N = 7 \) electrons

The 7-electron system contains one hole which can hop around the cluster so the Coulomb interaction has no effect. The ground state is simply a linear combination of the states with one hole in the cluster:

\[
|\Psi_0(7)\rangle \approx d \left| \uparrow \downarrow \downarrow \uparrow \downarrow \right\rangle + e \left| \uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \right\rangle
\]

Note that the \( e \) and \( d \) coefficients are different even for \( \Delta = 0 \) due to the geometry of the cluster, cf. Fig. 4.
3. Ground state for $N = 5$ electrons

The 5-electron ground state wave function is well described by the resonance between the following states:

$$|\Psi_0(5)\rangle \simeq f \left( \left| \begin{array}{c} \uparrow \\
\downarrow \\
\uparrow \\
\downarrow \end{array} \right\rangle + \left| \begin{array}{c} \uparrow \\
\downarrow \\
\uparrow \\
\downarrow \end{array} \right\rangle \right) + g \left( \left| \begin{array}{c} \uparrow \\
\uparrow \\
\downarrow \\
\downarrow \end{array} \right\rangle + \left| \begin{array}{c} \downarrow \\
\uparrow \\
\downarrow \\
\downarrow \end{array} \right\rangle \right) + h \left( \left| \begin{array}{c} \uparrow \\
\downarrow \\
\uparrow \\
\downarrow \end{array} \right\rangle + \left| \begin{array}{c} \downarrow \\
\uparrow \\
\downarrow \\
\downarrow \end{array} \right\rangle \right) \right)$$

All many-body configurations contain VB singlets except for the last term (proportional to $h$). The electrons in the A and B sites prefer to align with antiferromagnetic order in contrast to predictions of RVB. This is due to the different number of spin up, 2, and down electrons, 3, for $N = 5$. When a spin up is located at an A site, the remaining two spin down electrons at the B sites gain energy by aligning AF with the A electron. This is more favorable energetically than having a VB between two electrons at A and B sites and a down spin at the left B-site. For $U = 100|t|$ and $\Delta = 0$, $f = 0.423$, $g = 0.326$ and $h = 0.462$ with ground state energy, $E_0(5) = 97.590|t|$. For $\Delta = 10|t|$ the wavefunction is approximately given by $f = 0.691, g = 0.076$ and $h = 0.107$ with ground state energy, $E_0(5) = 94.615|t|$.

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