Exact Bond Ordered Ground State for the Transition Between the Band and the Mott Insulator

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We derive an effective Hamiltonian $H_{\text{eff}}$ for anionic Hubbard chain, valid for $t \ll U, \Delta$, where $t$ is the hopping, $U$ the Coulomb repulsion, and $\Delta$ the charge transfer energy. $H_{\text{eff}}$ is the minimal model for describing the transition from the band insulator (BI) ($\Delta - U \gg t$) and the Mott insulator (MI) ($U - \Delta \gg t$). Using spin-particle transformations (Phys. Rev. Lett. 86, 1082 (2001)), we map $H_{\text{eff}}(U = \Delta)$ in a SU(3) antiferromagnetic Heisenberg model whose exact ground state is known. In this way, we show rigorously that a spontaneously dimerized insulating ferroelectric phase appears in the transition region between the BI and MI.

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It is well known that the insulating state can have different origins. The simplest case is the BI since it is one of the possible solutions for non-interacting electrons moving in a periodic potential. In particular, the BI occurs when the number of particles per unit cell is even, so the bands are either full or empty. The other traditional example of insulating MI’s, in general, are antiferromagnets while the BI’s are paramagnets. This observation rises from the local Coulomb interaction and goes asymptotically to $U \gg \Delta$.

In the MI, this gap is a function of the Coulomb repulsion and goes asymptotically to $U$ in the strong coupling limit. These two insulating states have completely different properties. For instance, the BI’s are paramagnets while the MI’s, in general, are antiferromagnets. This observation raises the following question: what happens when a system evolves continuously from the BI to the MI state?

To find an answer to this question has been the main motivation for studying the Ionic Hubbard model (IHM) during the last ten years. The IHM was originally proposed in the 80’s to describe the neutral-ionic transition in mixed stack charge-transfer organic crystals. This model is a Hubbard Hamiltonian on a bipartite lattice with different diagonal energies for the two sublattices. The difference between both energies is $\Delta$. During the 90’s, there was a renewed interest in the IHM due to the potential applications to the description of the ferroelectric (FE) perovskites. At half filling, the ground state of the IHM is an ionic or BI for $\Delta \gg U$ and a MI for $U \gg \Delta$. Field theory arguments in dimension one pointed out the existence of an intermediate bond ordered insulating (BOI) phase for $\Delta \ll U \ll t$. For $t \ll U, \Delta$, perturbation theory clearly describes the BI ($t \ll \Delta - U$) and the MI ($t \ll U - \Delta$). The numerical solutions of finite chains and have difficulties and contradictory conclusions were reported. The reason will become clear after deriving the main result of the present paper.

Contrary to the cases of the BI and the MI states, no exact solution having long range bond ordering is known for the transition regime. Finding an exact ground state is not only crucial to prove the existence of the BOI phase rigorously, but also to understand its microscopic origin and fundamental properties. This result becomes even more important if we consider that the BOI phase is an electronically induced spin-Peierls instability that generates a FE state out of the spin-singlet dimer pairs. In particular, a bond ordered FE state was observed in the pressure-temperature phase diagram of the prototype compound, tetrathiafulvalene-p-chloranil. In addition, as it was pointed out by Egami et al., the microscopic origin of the FE transition in covalent perovskite oxides like BaTiO$_3$ is still unclear. It is known that a picture based on static Coulomb interactions and the simple shell model is inadequate to describe some FE properties. The exact result presented here demonstrates that when an ionic insulator gets close to a charge transfer instability (strong covalency), an electronic mechanism for ferroelectricity takes place.

In this paper, we first derive an effective Hamiltonian, $H_{\text{eff}}$, for the limit $U \gg t$ and $\Delta \gg t$ of an extended IHM that includes a nearest neighbor Coulomb repulsion $V$. By means of the generalized spin-particle transformations introduced in Refs [14, 15, 16], we map $H_{\text{eff}}$ into an anisotropic SU(3) antiferromagnetic Heisenberg model that becomes isotropic for $U = \Delta$ and particular values of the other parameters. The isotropic model is exactly solvable and is also equivalent to the biquadratic $S = 1$ Heisenberg model. The exact ground state is a dimerized spin system that becomes a BOI when translated back to the original fermionic variables.

We will start considering an IHM with an additional Coulomb interaction $V$ between nearest neighbors:

\begin{equation}
H = -t \sum_{i,\sigma} (f^\dagger_{i+1\sigma} f_{i\sigma} + \text{H.c.}) + \frac{\Delta}{2} \sum_i (n_i - 1)^2 - \frac{1}{2} \sum_i (n_i - \frac{1}{2})^2 + U \sum_i (n_{i\uparrow} - \frac{1}{2}) (n_{i\downarrow} - \frac{1}{2}) + V \sum_i (n_i - 1) (n_{i+1} - 1),
\end{equation}

where $n_{i\sigma} = f^\dagger_{i\sigma} f_{i\sigma}$, $n_i = \sum_\sigma n_{i\sigma}$, and $t > 0$. Note that $\Delta > 0$ is the diagonal energy difference between sites in different sublattices.

We will only consider the half-filled case $\rho = 1$, i.e., one
particle per site. If \( t = 0 \), the ground state of \( H \) is a non-degenerate BI for \( U < \Delta + 2V \). There is only one low-energy state per site: the odd sites are doubly occupied and the even sites are empty (see Fig. 1). For \( U > \Delta + 2V \) the ground state is a degenerate MI (one particle per site) and the low-energy subspace has two states per site due to the spin degeneracy. When \( t \) is finite and small, far from the transition region the low-energy Hamiltonian of the MI is a Heisenberg model and the degeneracy is lifted in favor of a spin-density wave \([2, 3]\) (see Fig. 1). However, to describe the transition region, we need to include three states per site in the low-energy subspace \( \mathcal{H}_0 \). In order to construct an effective Hamiltonian in \( \mathcal{H}_0 \), it is convenient to perform an electron-hole transformation for the odd sites:

\[
\begin{align*}
    c_{i\uparrow}^\dagger & = -f_{i\downarrow}, \quad c_{i\downarrow}^\dagger = f_{i\uparrow}, \quad \text{for odd } i \\
    c_{i\sigma}^\dagger & = f_{i\sigma}, \quad \text{for even } i
\end{align*}
\]  

(2)

After this transformation, \( H \) becomes invariant under a translation of one lattice site (\( i \to i + 1 \)). The low energy subspace \( \mathcal{H}_0 \) is now defined as the set of states with no double occupied site. The only term of \( H \) is a degenerate MI (one particle per site) and the low-energy Hamiltonian of the MI is a Heisenberg model and the ground state has one particle per site. 

\[
\begin{align*}
    \mathcal{H}_0 = & t \sum_{i \in \sigma} (\bar{c}_{i\sigma} \bar{c}_{i+1\sigma} + H.c.) + \frac{\Delta - U}{2} \sum_i \bar{n}_i \\
    & + J \sum_i (s^x_i \bar{s}^x_{i+1} - s^y_i \bar{s}^y_{i+1} - s^z_i \bar{s}^z_{i+1} - \frac{1}{4} \bar{n}_i (1 - \bar{n}_{i+1}) \\
    & - V \sum_i (1 - \bar{n}_i)(1 - \bar{n}_{i+1})
\end{align*}
\]  

(4)

where \( \bar{n}_i = \sum_{\sigma} \bar{c}_{i\sigma} \bar{c}_{i\sigma} \) and \( s^\alpha = 1/2 \sum_{\tau, \tau'} c_{i\tau} \sigma^{\alpha}_{\tau \tau'} c_{i\tau'} \) with \( \alpha = \{ x, y, z \} \) (\( \sigma^\nu \) are the Pauli matrices). The exchange interaction \( J = 2t^2/(U + \Delta - V) \) comes from a second order process in the hopping \( t \). In this derivation we have neglected the second order three-site hopping term. The negative sign for the \( xx \) and \( yy \) interactions is just a consequence of the gauge transformation of Eq. 4.

If \( t \sim V \sim U \gg 1 \), the ground state of \( H_{\text{eff}} \) is the empty state that corresponds to the BI in the original language. For \( U \gg \Delta \), the ground state has one particle per site. By eliminating states with empty sites with another canonical transformation, \( H_{\text{eff}} \) reduces to the Heisenberg model that describes the strong coupling limit of the MI. We are interested in the case, where \( U < \Delta + 2V \), the ground state of \( H_{\text{eff}} \) is an ionic insulator and the low-energy Hamiltonian is proportional to \( t^2 \).

\[
\mathcal{S}(j) = \begin{pmatrix} 0 & K_j^\dagger \bar{c}_{j\uparrow} & K_j \bar{c}_{j\downarrow} \\
\bar{c}_{j\downarrow}^\dagger K_j^\dagger & \bar{n}_j - \frac{1}{4} & \bar{c}_{j\downarrow}^\dagger \bar{c}_{j\uparrow} \\
-\bar{c}_{j\downarrow}^\dagger K_j & \bar{c}_{j\downarrow}^\dagger \bar{c}_{j\uparrow} & \bar{n}_j - \frac{1}{4}
\end{pmatrix}
\]  

(5)

where \( K_j \) is the kink operator \([14]\):

\[
K_j = \text{exp}[i\pi \sum_{k < j} \bar{n}_k].
\]  

(6)

that transmutes the statistics. The components \( S^{\mu\nu} \) are generators of the \( su(3) \) algebra with commutation relations \( [S^{\mu\nu}(j), S^{\rho\sigma}(j')] = \delta^{\mu\rho} S^{\nu\sigma}(j) - \delta_{\nu\rho} S^{\mu\sigma}(j) \). We also make use of the conjugated or “anti-quark” representation:

\[
\tilde{S}(j) = \begin{pmatrix} 0 & -K_j^\dagger \bar{c}_{j\uparrow} & -K_j \bar{c}_{j\downarrow} \\
-K_j^\dagger \bar{c}_{j\downarrow} & \bar{n}_j - \frac{1}{4} & -\bar{c}_{j\downarrow}^\dagger \bar{c}_{j\uparrow} \\
-K_j \bar{c}_{j\uparrow} & -\bar{c}_{j\downarrow}^\dagger \bar{c}_{j\uparrow} & \bar{n}_j - \frac{1}{4}
\end{pmatrix}
\]  

(7)

to describe the degrees of freedom of the \( B \) sublattice. Eqs. 5 and 7 are generalizations of the Jordan-Wigner transformations to \( su(3) \) spins \([13, 14]\). The resulting \( H_{\text{eff}} \) is as an anisotropic \( su(3) \) Heisenberg model with an applied “magnetic field”:

\[
H_{\text{eff}} = \sum_{i \in A, \mu, \nu} J_{\mu\nu} S^{\mu\nu}(i) \tilde{S}^{\mu\nu}(i + 1) - B \sum_i S^{00}(i),
\]  

(8)
with $J_{01} = -V$, $J_{02} = J_{12} = -t$, $J_{11} = J_{22} = -J/2$, $J_{1\mu} = J_{2\mu}$, and $B = 2V/3 - J/3 + U/2 - \Delta/2$. Note that this model connects SU(3) spins in the $A$ sublattice with the conjugate SU(3) spins (anti-quark representation) in the $B$ sublattice. Let us now consider $V = J/2 = t$ and $U = \Delta$. For this line in the space of parameters $H_{eff}$ is an isotropic SU(3) antiferromagnetic Heisenberg model that is invariant under staggered conjugate SU(3) rotations, $R$ and $R^\dagger$, on sublattices $A$ and $B$ respectively. This model is integrable [17, 18, 19] and the exact solution is a spin-dimerized ground state. In the original language this is equivalent to saying that the charge and the spin are both dimerized (bond ordering). The exact ground state energy per site is $\epsilon_0/t = -1.796864...$. The value of the gap is $\Delta/t = 0.173178$, a rather small value, and the correlation length $\xi = 21.0728505...$ is very large [19]. This explains the numerical difficulties for identifying this phase.

To make clear the relation between the dimerization in SU(3) and the bond ordering of the fermionic variables, we just need to translate the corresponding order parameter from the SU(3) language back to our original fermionic language. The spin-dimer SU(3) order parameter is [21, 22]:

$$D = |h_{i-1,i} - h_{i,i+1}|$$  (9)

where $h_{i-1,i} = |i - 1,i\rangle\langle i - 1,i|$ is a projector on the SU(3) singlet spin state, $|i - 1,i\rangle$, at the bond $(i - 1,i)$. Note, in addition, that $h_{i-1,i}$ is the isotropic SU(3) Heisenberg Hamiltonian for the same bond. In the fermionic language, $|i - 1,i\rangle$ has the following expression:

$$|i - 1,i\rangle = \frac{1}{\sqrt{3}} (1 - \hat{c}_{i-1}^\dagger \hat{c}_{i}^\dagger - \hat{c}_{i+1}^\dagger \hat{c}_{i}^\dagger) |0\rangle$$  (10)

In terms of the original $f$-fermions [see Eqs.(2) and (3)], this is a linear combination of an on-site singlet and a nearest-neighbor singlet state that is illustrated at the bottom of Fig. 1: Xian showed that $D = 0.4216D_0$ where $D_0$ is the value of $D$ for a perfect dimerized state [21]. Replacing (10) in (9), it becomes clear that $D$ is a BOI order parameter. From a calculation of the charge Berry phase [7] we obtain that the shift in polarization of the two perfect dimerized states (see the bottom of Fig.1) relative to the MI is $\pm e/6$. Eq. (10) shows that the dimer formation is just a consequence of the charge transfer instability between the two sublattices. In this sense, this exact ground state unveils the fundamental role of covalency for the stabilization of a bond ordered FE state [3, 11, 12, 13]. This is not only relevant to describe one dimensional systems like tetraethylfulvalene-p-chloranil [11, 12, 13] but also helpful to gain a deeper understanding of the FE transition of covalent perovskites [3].

Using some sets of transformations that connect the constrained fermions with SU(2) $S = 1$ spins [12]:

$$S^+ = \sqrt{2} (\hat{c}_{i}^\dagger K_j + \hat{K}_j^\dagger \hat{c}_{j})$$
$$S^- = \sqrt{2} (\hat{K}_j^\dagger \hat{c}_{j}^\dagger + \hat{c}_{j}^\dagger K_j)$$
$$S^z = \tilde{n}_{j}^\dagger - \tilde{n}_{j}$$  (11)

we can also write $H_{eff} (V = J/2 = t)$ as an $S = 1$ biquadratic Heisenberg model [15] with a single-ion anisotropy:

$$H_{eff}(V = J/2 = t) = -t \sum_i (\hat{S}_i \cdot \hat{S}_{i+1})^2 + E \sum_i (S^z_i)^2,$$  (12)

where $E = (\Delta - U)/2$. The strength of the anisotropy term is determined by the difference $\Delta - U$. If $E$ is large and positive $(\Delta \gg U)$, the spin system has an easy plane anisotropy. Each site is most of the time in the $S^z = 0$ state, which means that the magnetization is perpendicular to the $z$-axis. The ground state is non-degenerate (there is no broken symmetry) and corresponds, in the original language, to the band insulator. If $E$ is large and negative $(U \gg \Delta)$, the system has a strong easy axis anisotropy and each site is in the $S^z = \pm 1$ state, i.e., the local magnetization is parallel to the $z$-axis. The ground state is critical due to the antiferromagnetic correlations which characterize the MI. In between, for $U = \Delta$, we have demonstrated that there is a dimerized state which corresponds to the BOI. In terms of the original variables, the strong quantum fluctuations that appear in the proximity of the charge transfer instability break the $Z_2$ inversion symmetry by increasing the strength of one bond relative to the next one.

The $S = 1$ version of $H_{eff}$ also provides a simple way of studying the low energy excitations of our exact bond ordered state. The excitations of a dimerized spin 1/2 chain are spinons that carry a spin $S = 1/2$. In the same way, the excitations of our $S = 1$ dimer state are $S = 1$ spinons. Each spinon is a soliton or anti-phase boundary for the $Z_2$ spin-dimer order parameter. The two regions with opposite dimerization are separated by a local $S = 1$ defect which is attached to the anti-phase boundary. In terms of the original language, the $S_1 = 0$ spinons correspond to $s = 0$ solitons (charge excitations), while the $S_2 = \pm 1$ spinons are $s = 1/2$ solitons (spin and charge excitations). From Eqs. (9) and (12), the total charge operator relative to half-filling is $Q = \sum_{\alpha} (S_\alpha^z)^2 - \sum_{\alpha} (S_\alpha^z)^2$. For a general dimerized solution with arbitrary $E$ we have on each site: $\langle (S_\alpha^z)^2 \rangle = 1 - \alpha$ with $\alpha = 1/3$ for the exact solution at $E = 0$. When the defect is localized on site $j$ (the extension of the defect does not affect the charge or spin of the excitations because they are topological invariants) we have $\langle (S_\alpha^z)^2 \rangle = 1$. Since the defect separates two regions with opposite dimerization, it is easy to check that the $s = 0$ solitons (anti-solitons) have charge $Q = \pm (1 - \alpha)$ while the charge of the $s = 1/2$ solitons (anti-solitons) is $Q = \pm \alpha$. For $E = 0$, both excitations are degenerate as a consequence of the SU(3) invariance. These excitations coincide with those obtained by Fabrizio et al [5], who treat the bosonized IHM as a phenomenological Ginzburg-Landau energy functional. The magnitude $\alpha$ is proportional to their jump in the charge field. In particular, the $s = 1/2$ excitations interpolate between an ordinary electron near the BI-BOI boundary ($\alpha = 1, E > 0$) and a spinon near the BOI-MI boundary ($\alpha = 0, E < 0$).

In order to obtain an exact ground state of $H_{eff}$ we used a value of $J = 2t$ which is beyond the region allowed by perturbation theory. Therefore, to connect our exact solution with the IHM, it is important to discuss the effect of reducing the value of $J$. In addition, since most of the previous papers do not include the $V$ term, it is also important to an-
alyze its effect. A simple first order estimation of the energy change for the three competing phases, \( \delta E_{BI} = \delta U/2 + t \), \( \delta E_{MI} = 2t \ln 2 \), \( \delta E_{BOI} = \delta U/6 - 5e_0t/9 \), when \( J \) and \( V \) are reduced to zero, indicates that the BOI survives if the difference \( U - \Delta \) is simultaneously increased to a value of order \( t \). This conclusion is supported by different numerical results [7, 8, 9] that report a bond ordered ground state of \( H(V = 0) \) for the same region of parameters \( (U - \Delta \sim t \text{ and } U, \Delta \gg t) \). These observations suggest that our exact solution is continuously connected with the BOI phase which was numerically found in the IHM.

In summary, we have derived an effective low energy Hamiltonian, \( H_{eff} \), for the \( U, \Delta \gg t \) limit of the IHM. \( H_{eff} \) is a minimal model to describe the BI to MI transition. Its simple form and the fact that it operates in a reduced Hilbert space of local dimension \( D = 3 \) provide a new framework to understand this transition. Using the spin-particle transformations introduced in Refs. [14, 15, 16], we mapped \( H_{eff} \) into an anisotropic SU(3) antiferromagnetic Heisenberg model. By increasing the value of \( J \) beyond the region allowed by perturbation theory, we have shown that there is an exactly solvable SU(3) invariant point for \( U = \Delta \) and \( V = J/2 = t \). In this way, we demonstrated the existence of a bond ordered phase for the transition regime between the BI and the MI. The large value of the correlation length \( \xi = 21.0728505 \ldots \) explains the numerical difficulties for detecting this phase in finite size systems. This exact solution provides an answer to the question that was formulated in the introduction: in the transition regime the system resolves the competition between the BI and the MI by creating a rather local resonance which can be visualized on each dimer as a linear combination of a unit cell of the BI and a nearest-neighbor singlet that is related with the MI (see Fig.). One of the most important physical consequences of this non-trivial phenomenon is the generation of a new mechanism for ferroelectricity [3] that should be relevant for ionic insulators which are close to a charge-transfer instability. This result should motivate a careful reexamination of the ferroelectricity in covariant materials.

In addition to the SU(3) mapping, we used a second spin-particle transformation \([14]\) that maps the constrained fermions into \( S = 1 \) SU(2) spins. In this new language \( H_{eff}(V = J/2 = t) \) is a biquadratic Heisenberg model with a single-ion anisotropy along the \( z \)-axis which is proportional to \( \Delta - U \). The transitions between the BI, BOI, and MI phases have been re-interpreted in the \( S = 1 \) language. We have also shown that the \( S = 1 \) version of \( H_{eff} \) provides the most natural frame to understand the low energy excitations of the BOI. These excitations are solitons that carry a fractional charge and spin \( s = 0 \text{ or } s = 1/2 \). The relevance of these results illustrates the elegance and the potential of the generalized spin-particle transformations introduced in Refs. [14, 15, 16].

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