Electron instabilities in nanoclusters, nanostructures and inhomogeneous nanomaterials: bottom up approach

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ABSTRACT

Spatial inhomogeneities in nanomaterials with strong local electronic correlations are creating a new world vision in condensed matter physics. These nanomaterials with intrinsic inhomogeneities have electronic and magnetic properties that are profoundly different from the conventional materials. Few prominent examples are the high temperature superconductors (HTSCs), colossal magnetoresistance (CMR) and multiferroic materials. The behavior of electrons in contrasting bipartite and nonbipartite topologies are quite different. The electron pairs in ensemble of clusters in a real space are complying to the Bose-Einstein and Fermi-Dirac statistics can be condensed or fully polarized in inhomogeneous media. Phase diagrams display a number of inhomogeneous, coherent and incoherent nanoscale phases seen recently in high T_c cuprates, manganites and CMR nanomaterials using scanning tunelling microscopy.

Keywords: high T_c superconductivity, incoherent pairing, spontaneous phase separation, crossover, charge and spin (pseudo)gaps, magnetism

1 INTRODUCTION

Despite tremendous experimental and theoretical efforts, there is still no microscopic theory that can yield comprehensive support for pairing correlations, phase separation and pseudogap phenomena in clusters, small nanoparticles, transition metal oxides and high-Tc superconductors (HTSCs). The concentrated materials with strong local electronic correlations, intrinsic inhomogeneities seen in scanning tunelling microscopy (STM) measurements [1]–[6] have properties that are quite different from the conventional solids. The HTSCs, multiferroics and colossal magnetoresistance (CMR) materials [7]–[9] have been under scrutiny for nearly three decades about a role of Coulomb interaction in mechanisms of electron instabilities and pairing. Strong intraatomic (local) interactions can contain the key to some of the perplexing physics observed in the these materials using STM. The test of these conjunctures proposed early on by Anderson [10] for large thermodynamic systems is currently unavailable for two and three dimensional Hubbard-like systems. Motivated by this challenging problem and discovery of novel materials, we have embarked on a study of finite size two and three dimensional Hubbard clusters using the exact diagonalization technique in quantum statistical mechanics. From this perspective, exact studies of electron charge and spin instabilities and quantum critical points (QCPs) at various inter-site couplings $U>0$ and cluster topologies in the ground state and finite temperatures can provide important answers for the understanding of charge/spin inhomogeneities and local deformations for the mechanism of pairings and magnetism in "large" concentrated systems in the absence of long range order. The exact calculations of thermodynamic properties go beyond the reach of approximate schemes. At sufficient low temperatures, the charge and spin redistribution in an ensemble of clusters can produce incipient inhomogeneities typical for nano and heterostructured materials. Pairing instabilities, phase separation and inhomogeneities in certain regions of phase space in simple Hubbard clusters have been observed in our previous studies (see Refs. listed in [11]–[15]). In our opinion, these regions of phase space have much more intriguing clues to offer, when other variables such as the temperature, chemical potential and magnetic field are included.

Magnetic inhomogeneities seen in various transition metal oxides at the nanoscale level, widely discussed in the literature, are crucial for the understanding of spin pairing instabilities, origin of ferromagnetism [16], superconductivity and ferroelectricity. Important aspects of spontaneous phase separation and electron instabilities that we found in a real space [13] strongly depend on both, the Coulomb repulsion U and cluster topology. For instance in bipartite geometries, the charge separation leads to coherent pairing also at small and moderate U values, while Nagaoka type ferromagnetic instabilities for spins occurs at large U [16]. In frustrated geometries, spontaneous transitions lead to coherent pairing and saturated ferromagnetism for all U depending on the sign of the hopping term t (energy spectrum). In what follows, we identify these phenomena as electron instabilities in a phase space defined by suitable variables. We observe such instabilities due to competition between high and low spin states. Such phenomena appear to be generic provide important clues to long standing mystery tied to spontaneous phase separation in the HTSCs and CMRs.

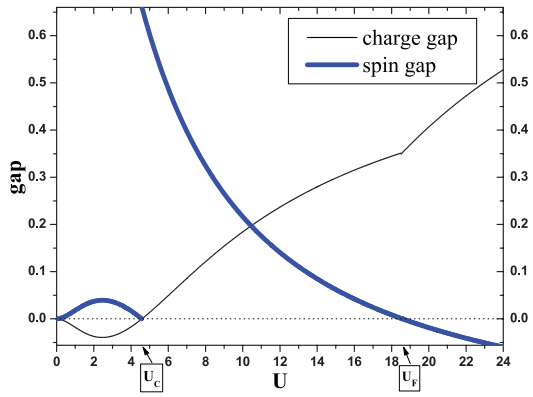

Figure 1: Charge Δ^c and spin Δ^s gaps versus U in an ensemble of squares at $\langle N \rangle \approx 3$ and $T = 0$. Phase A: Charge and spin pairing gaps of equal amplitude at $U \leq U_c$ describe bose condensation of electrons similar to BCS-like coherent pairing with a single energy gap. Phase B: Mott-Hubbard-like insulator at $U_c < U < U_F$ leads to $S = \frac{1}{2}$ spin liquid behavior. Phase C: Parallel (triplet) spin pairing ($\Delta^s < 0$) at $U > U_F$ displays $S = \frac{3}{2}$ saturated ferromagnetism.

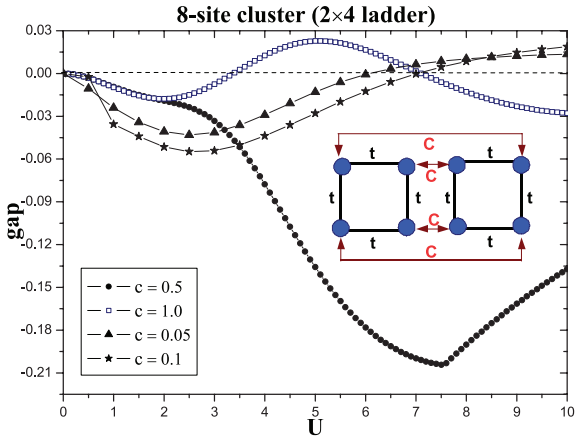

Figure 2: Charge gaps for the 2x4 cluster at $T = 0$ for various couplings c between the ensemble of coupled square clusters. The doping level is one electron off half-filling and the couplings t within the squares are set to 1, as indicated. There is an effective electron-electron attraction in the negative gap regions which corresponds to the coherent state with the charge and spin pairing gaps of equal amplitude, $\Delta^s = -\Delta^c$.

These exact results have direct practical applications in search of novel assembled nanoclusters, inhomogeneous nanomaterials.

2 BASIC METHODOLOGY

2.1 Model

A key aspect of our study is the Hubbard model

$$H = -t \sum_{\langle ij \rangle \sigma} c^{+}_{i\sigma} \; c_{j\sigma} + U \sum_{i} n_{i\uparrow} n_{i\downarrow} \qquad (1)$$

with nearest neighbor hopping t and on-site Coulomb interaction $U > 0$. Focusing on this simple model gives unprecedented advantages to analyze (with great accuracy) the many body correlation effects, which are nontrivial. In our previous publications, we have outlined most of the details pertaining to the method (see Refs. [11]–[15]).

2.2 Canonical gaps

Depending on the value of the Coulomb repulsion U, Hubbard model for small clusters exhibits different pairing behavior which is evident when suitable gaps are defined and their properties examined. In a particular doping region, with one hole off half filling, when the chemical potential μ lies in an interval $[\mu_+(T), \mu_-(T)]$ with $\mu_- > \mu_+$, charge pairing is found. The boundaries of the interval are defined as $\mu_+(T) = E(N+1) - E(N)$

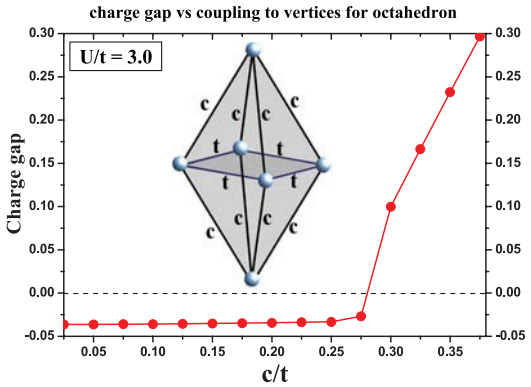

Figure 3: The zero temperature charge gap at one hole off half filling in an octahedron (at U/t =3) as a function of the coupling strength c/t to the vertices. The negative charge gap up to c/t =0.28 displays a necessary condition for charge pairing instability in deformed octahedron structures. This also underlines the role of vertex coupling and the quasi two-dimensional character of pairing which may be related to HTSC perovskites.

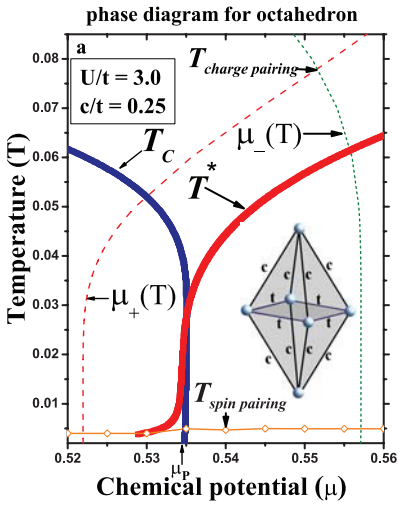

Figure 4: A part of the phase diagram for the octahedron (U/t =3) in Fig. 3 at c/t =0.25 showing the region of instability in the chemical potential with charge and spin susceptibility peak positions (T_c and T^*) as well as spin and charge pairing temperatures. The spin rigidity of the pairs in the plane is similar in both cases although the octahedron spin susceptibilities are, of course, affected by the spins attached to the vertices.

and $\mu_-(T) = E(N) - E(N-1)$ where $E(N)$ denotes the average canonical energy in an N electron state at temperature T, and the charge gap is defined as $\Delta^c(T) = \mu_+ - \mu_-$. The gap at $T \geq 0$, which depends on U, has to be negative for a spontaneous (charge) phase separation to occur. Analogously, we calculate a canonical spin gap as the difference in the average energies between the two cluster configurations with spin S and $S+1$ states, $\Delta^s(T) = E(S+1) - E(S)$, where $E(S)$ is the average canonical energy in the spin sector at fixed N.

2.3 Pairing instabilities

We define critical parameters for the level crossing degeneracies or corresponding QCPs from the condition $\Delta^{c,s}(U_c, \mu) = 0$. The sign of the gap manifests the regions for electron charge and spin instabilities, such as the electron-electron (Δ^c <0), electron-hole (Δ^c >0) pairings in the charge sector or the parallel (Δ^s <0) and opposite (Δ^s >0) spin pairings in the spin sector. The relationship between the charge gap Δ^c, and its corresponding spin counterpart Δ^s, is important in identifying the stability of phases in various cluster topologies [13]. A positive excitation gap indicates phase stability and (smooth) transition or crossover, while a negative excitation gap in the many body ground state shows an energy instability for spontaneous phase transition.

2.4 Grand canonical gaps

In the grand canonical approach, using exact analytical expressions for the grand canonical potential and partition functions, we can monitor the charge $\chi_c(\mu)$ and zero field spin $\chi_s(\mu)$ susceptibilities as a function of the chemical potential μ and temperature. The energy difference in terms of μ between the two consecutive susceptibility peaks can also serve as a natural order parameter. The distances between the peaks in double peak structures in the charge and spin density of states determine *pseudogap*. In equilibrium, the critical temperatures T_c and T^* are defined as the temperature at which the separation between the two consecutive charge or zero spin susceptibility peaks vanish. The energy (pseudo)gaps obtained from the maxima according are positive and, therefore, the transitions in the grand canonical method are always smooth.

3 DISCUSSION

3.1 Bipartite clusters

Here we carry out numerical calculations for bipartite linked 4-site clusters. Fig. 1 illustrates the charge and spin gaps at small and moderate U in ensemble of square clusters (see details Ref. [13]). The vanishing of gaps at QCPs, $U_c = 4.584$ and $U_F = 18.583$, indicates energy level crossings and electron instabilities for charge and spin, respectively. Similar QCPs and instabilities we find also in Fig. 2 for coupled 2x4 clusters, where the hopping term or coupling c between the two squares was allowed to be different from the coupling within a given square. The pairing fluctuations that are seen for the 4-site cluster exist even for these ladders at optimal doping, and most of the trends observed for the 4-site clusters remain valid here. Thermal and quantum fluctuations in the density make it energetically more favorable to form charge pairs.

3.2 Frustrated clusters

The tetrahedron cluster has a topology of square with the next nearest neighbor coupling may be regarded as a primitive unit of frustrated system [13]. Here we consider an ensemble of octahedron (or square pyramids) clusters, which are a building blocks of perovskite structure in HTSC cuprates [12]. The parental (undoped) material is an insulator. However, when excess apex oxygen is introduced, hole carriers are supplied into CuO_2 planes, and material shows superconductivity. Figure 3 shows the charge gap at fixed $U = 3$ and $\langle N \rangle \approx 4$ under the variation of the coupling term c between the plane and the apex atoms in $Bi_2Sr_2CaCu_2O_{8+\delta}$. This picture gives surprisingly plausible evidence for understanding the detrimental role of excess electron on

charge pairing for possible distortions of pyramidal crystalline structure in perovskites [6]. The negative charge gap, identical to the spin gap, exists only below this QCP, $c/t = 0.28$ for level crossing degeneracy. Calculated electron distribution, as a function of c, shows that electron charge residing on the apical site does not contribute to the pairing whenever c is less than c_0. In Fig. 3, the distortion of the octahedron reproduces a charge pairing gap modulation seen in STM imaging experiments [6]. Thus we find a direct correlation between the size of the energy gap characterizing the local superconducting state and a modulation of the atomic positions seen in HTSCs [6]. These results illustrate the relevance of two dimensionality as observed in the perovskite structures, and the coupling values in this region lead to charge pairing, for one hole off half filling, as seen in the bipartite clusters; spin pairing is seen to occur at a much lower temperature as evident from the phase diagram in Fig. 4.

3.3 Nagaoka Ferromagnetism

For large U in the (repulsive) Hubbard model at one hole off half filling, there is a well-known Nagaoka theorem known for bipartite and nonbipartite topologies at $T = 0$, which claims that in higher dimensions, such systems would exhibit fully saturated ferromagnetism. Our exact results, obtained for non zero temperatures, are supporting the above statement [16], [13]. Cluster frustration appears to play a significant role. For t =+1, there is no spin saturation (which has also been verified at large U). For t =-1, there is a saturated ferromagnetic state (S_z^{max} =5/2), which is insulating, at sufficiently large U (in units of $|t|$) as shown in the figure. Therefore, in these frustrated systems with spin degeneracies in the energy spectrum, (ferromagnetic) Nagaoka saturation is observed only for one type of hopping (t =-1).

4 KEY RESULTS

Pairing instabilities and inhomogeneities found from exact diagonalization in small bipartite and non-bipartite topologies provide novel insights into several mysterious many body problems in condensed matter physics and ultracold fermionic atoms. Rigorous Nagaoka type criteria are formulated for spontaneous phase separation, electron instabilities and magnetism driven by interaction strength, geometrical frustration, inter-site couplings (connectivity), transverse magnetic field, etc. The following is a list of properties, resulting from our exact Hubbard cluster studies:

(i) Vanishing charge and spin pairing gaps in the ground state can be directly linked to the QCPs [13].

(ii) Negative charge gap at a critical set of parameters is leading to electron charge pairing and spontaneous phase separation below T_c^P.

(iii) The pseudogap, inhomogeneities, incoherent pairing behavior below T^* but above spin pairing T_s^P similar to what is seen in the NMR and STM experiments [5].

(iv) Formation of coherent state of rigidly bound opposite spin and (doubled) paired charge below T_s^P.

(v) Phase diagrams describes pair modulation and multitude of fascinating phases, seen recently in high T_c cuprates, manganites and CMR nanomaterials using scanning tunelling microscopy [1]–[6].

(vi) The presence of a dormant magnetic state above the spin pairing temperature, observed recently [3].

(vii) Negative spin pairing gap is leading to electron spin pairing, spontaneous phase separation and Nagaoka ferromagnetism at zero and non zero temperatures [13].

Our exact calculations in finite size clusters have strong impact and immediate applications to nano systems (nanotechnology) can motivate further studies of electronic and magnetic instabilities with correlated electrons in contrasting cluster topologies. These ideas could be exploited in the nanoscience frontier by synthesizing clusters or nanomaterials with unique magnetic and electronic properties.

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