Novel electronic states close to Mott transition in low-dimensional and frustrated systems

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Abstract. Recent studies demonstrated that there may appear different novel states in correlated systems close to localized–itinerant crossover. Especially favourable conditions for that are met in low-dimensional and in frustrated systems. In this paper I discuss on concrete examples some of such novel states. In particular, for some spinels and triangular systems there appears a “partial Mott transition”, in which first some finite clusters (dimers, trimers, tetramers, heptamers) go over to the itinerant regime, and the real bulk Mott transition occurs only later. Also some other specific possibilities in this crossover regime are shortly discussed, such as spin-Peierls–Peierls transition in TiOCl, spontaneous charge disproportionation in some cases, etc.

1. Introduction

The subdivision of electronic states into delocalized, itinerant, and localized, strongly correlated states is one of the most fundamental ones in the description of solids. Crudely, delocalized states exist when the intersite electron hopping is larger than the typical electron–electron interaction energy, and localized states exist in the opposite limit. In quantum chemistry these two limits correspond e.g. to the description of electrons in terms of molecular orbitals (Mulliken description, known in chemistry as molecular orbital–linear combination of atomic orbitals (MO–LCAO) method), and strongly correlated electrons are described by the Heitler–London approximation. For concentrated solids these two regimes give either standard band systems (metals or semiconductors), or Mott insulators.

The electron–electron repulsion, e.g. the Hubbard’s $U$, is essentially an atomic property and does not depend on interatomic distance, whereas the electron hopping strongly depends on this distance. This leads to the concept, largely advocated e.g. by Goodenough [1], that there should exist a critical interatomic distance $R_c$ (different for different transition metal (TM) ions) dividing the regions of localized and itinerant behaviour of electrons. When this distance changes, e.g. under pressure, there should occur an insulator–metal (Mott) transition.

Usually Mott transition in TM compounds such as TM oxides is supposed to occur homogeneously in the whole sample. But, as became clear recently, this is not the only possibility. There may appear novel, inhomogeneous states close to a Mott transition, so that we have, in a sense, a “partial” Mott transition: in some parts of the system, in some particular clusters, the interatomic distances may already be smaller than $R_c$, so that these clusters may be better described using molecular orbitals, whereas the distance between such clusters will still remain
large, so that there will be no net metallic conductivity. The formation of such “metallic”
clusters has much in common with the valence bond solids.

This phenomenon, i.e. such “fractional” Mott transition, is most often observed in low-
dimensional and in frustrated systems. Indeed, in regular three-dimensional lattices such as
perovskites we usually have homogeneous ordered states, e.g. 3d antiferromagnetic ordering.
Molecular-type clusters such as valence bond states are much more plausible in low-dimensional
and frustrated systems. Below I will describe this situation using several specific examples of
systems with triangular and pyrochlore (spinel) lattices, and also on some quasi-one-dimensional
systems. I will also shortly mention some other possible novel phenomena, which may appear
in systems close to the localized–itinerant crossover.

2. Formation of dimers in spinels

Metal–insulator transitions with the formation of unusual structures are observed in many
spinel. The recent examples are MgTi$_2$O$_4$ [2], CuIr$_2$S$_4$ [3] or AlV$_2$O$_4$ [4]. Structural studies
have shown that in all these cases rather unusual structural modifications take place, which often
can be described as the formation of molecular clusters. In MgTi$_2$O$_4$ there appears a “chiral”
structure [2], in CuIr$_2$S$_4$ Ir octamers are formed [3], but both these phenomena can in fact be
explained by the formation of Ti or Ir singlet dimers, which in a frustrated lattice of B-sites of
a spinel finally give rise to these chiral or octamer structures [5]. And in AlV$_2$O$_4$ the molecular
clusters formed consist of 7 vanadiums — real large “heptamer molecules”.

Figure 1. Formation of one-dimensional electronic spectrum for $t_{2g}$ electrons in a lattice of
B-sites of a spinel. The $xy$ and $yz$ orbitals are shown.

In all these cases the formation of these clusters is largely caused by specific features of the
B-site spinel lattice, which may be represented as a collection of 1d chains running in $xy$ (or
$x\bar{y}$), $xz$ and $yz$ directions, see Fig. 1. The $t_{2g}$-orbitals of Ti or V ions on this lattice have a
strong direct $d$–$d$ overlap, such that e.g. the electrons from the $xy$-orbitals can hop to the same
orbitals in neighbouring ions in the $xy$-direction, see Fig. 1, or similarly $yz$-electrons can hop
in the $yz$-direction, etc. As a result the electronic structure in these, basically cubic crystals,
has essentially one-dimensional character. And in the insulating phase one forms a Peierls state with singlet dimers in these 1d chains [5], which for a spinel lattice give the chiral structure in MgTi$_2$O$_4$, the heptamers in AlV$_2$O$_4$ and octamers (consisting actually of dimers) in CuIr$_2$S$_4$. Note that the interatomic distances in these clusters are rather short: they are shorter than the critical distance $R_c$ for the localized–itinerant crossover [1], so that one can consider the electronic state in these clusters as forming molecular orbitals, i.e. in these clusters we are already on the “metallic” side of the Mott transition. But the distance between these clusters is larger than $R_c$ and as a result the total compound is insulating.

The “metallic” clusters in the examples discussed above are singlet. But this is not the only possibility. Magnetic (e.g. triplet) clusters can also be formed in some cases. This seems to happen in ZnV$_2$O$_4$ [6]. V spinels such as MgV$_2$O$_4$, ZnV$_2$O$_4$, CdV$_2$O$_4$ show cubic–tetragonal structural transitions [7] with the formation of a very specific magnetic structure at lower temperatures, with $\uparrow\uparrow\downarrow\downarrow$ pattern in $xz$- and $yz$-chains (and with $\uparrow\downarrow\uparrow\downarrow$ ordering in the $xy$-direction) [8], see Fig. 2. Usually the properties of these systems are explained by some type of orbital ordering: the $xy$-orbitals are always occupied due to tetragonal distortion with $c/a < 1$, and the remaining second $t_{2g}$ electron of the V$^{3+}$($d^2$) ions is supposed to form an additional orbital ordering of some type [9, 10, 5]. But our recent ab initio calculations [6] have shown that there should exist in ZnV$_2$O$_4$ a V dimerization in $xz$- and $yz$-chains, see Fig. 2, with, surprisingly, ferromagnetic bonds becoming shorter (thick bonds in Fig. 2)! One can explain this tendency by noticing that, in contrast to most examples of valence bond solids with singlet bonds, here we are dealing not with ions with one electron with $S = \frac{1}{2}$, but with $d^2$ ions with $S = 1$. One can argue that the extra delocalization of one of two electrons in a short bond enhances the ferromagnetic (actually double-exchange) interaction between these $d^2$, $S = 1$ ions. The ab initio calculations of another material of this family, CdV$_2$O$_4$, done by a different method, have confirmed the formation of these dimers, and demonstrated, in addition, that their formation can lead to the appearance of ferroelectricity, which was indeed observed in CdV$_2$O$_4$ [11].

![Figure 2. Formation of short (bold) and long (dashed) V–V bonds in ZnV$_2$O$_4$, following [6]; the same pattern also exists in CdV$_2$O$_4$ [11].](image)

Interestingly enough, short V–V distances obtained theoretically for ZnV$_2$O$_4$ are only 2.92 Å — again shorter than the critical V–V distance 2.94 Å [1]. Thus again these V dimers may
be considered as “metallic”, though the material itself remains insulating, albeit with a rather small energy gap \( \sim 0.2 \text{ eV} \) [6].

3. “Metallic” clusters in layered materials

Some more examples of “metallic” clusters in an overall insulating matrix are found in layered materials, notably with triangular lattices, such as LiVO\(_2\) [12], LiVS\(_2\) [13], TiI\(_2\) [14]. This lattice is usually considered as frustrated, meaning that it is not bipartite. But in LiVO\(_2\), LiVS\(_2\), TiI\(_2\) we are dealing with ions Ti\(^{2+}\), V\(^{3+}\) with two \( t_{2g} \) d-electrons, which, besides spin, have also triple orbital degeneracy. And, if one cannot subdivide a triangular lattice into two sublattices, one can naturally subdivide it into three! That is indeed what happens in these materials [12], see Fig. 3, in which the occupied orbitals are shown. After forming this orbital superstructure, we have strong antiferromagnetic exchange in the shaded triangles of Fig. 3, and in effect these bonds become shorter than the others, and there are singlet states formed on such trimers (three \( S = 1 \) ions with strong antiferromagnetic coupling have a singlet ground state with \( S_{\text{tot}} = 0 \)). Our recent detailed ab initio calculations [15] confirmed this picture and gave a strong antiferromagnetic exchange in a trimer, the exchange interaction between trimers being much weaker and ferromagnetic. Lattice optimization gave V–V distances in a trimer of 2.56 Å, in good agreement with the experimental value. Note that in this case the short distance in a cluster — here a trimer — is even shorter than the V–V distance in V metal, 2.62 Å, i.e. these clusters can indeed be considered as “metallic”.

![Figure 3. Orbital ordering in LiVO\(_2\) with three orbital sublattices, leading to the formation of spin singlet states on tightly bound V triangles (shaded), following [12].](image-url)
even shorter; this is what happens in LiVO$_2$ and LiVS$_2$. If, however, the system has localized $d$-electrons and is far from the Mott transition, the $d$–$d$ overlap is exponentially small, and the second effect, the bond–charge repulsion, may become stronger, as a result of which it is favourable to make such bonds longer, to reduce this repulsion further. This is apparently what happens in NaVO$_2$.

![Figure 4. Orbital and magnetic ordering in NaVO$_2$ [16].](image)

Until now we saw the formation of different types of TM clusters, mostly singlet ones: dimers (MgTi$_2$O$_4$, CuIr$_2$S$_4$), trimers (LiVO$_2$, LiVS$_2$, TiI$_2$), or larger clusters such as heptamers in AlV$_2$O$_4$. Also singlet tetramers can be formed, especially in layered materials. One such example is CaV$_4$O$_9$ [17], with the interesting “chiral” lattice, in which the singlets are formed by four V ions around an “empty” plaquette. In all these cases either low-dimensionality or the frustrated nature of the lattice apparently plays an important role. As mentioned above, valence bond solids are indeed especially easily formed in frustrated or quasi-one-dimensional systems — this is in fact the essence of the Peierls phenomena.

4. Spin-Peierls-to-Peierls transition in TiOCl

A very clear example of this phenomenon, in particular its features close to the localized–itinerant crossover, is observed in TiOCl. This quasi-one-dimensional material is insulating with localized $d$-electrons at ambient pressure, and it has a spin-Peierls transition at $\sim 60\,\text{K}$ (with an incommensurate phase at $60\,\text{K} < T \leq 90\,\text{K}$). Under pressure its energy gap strongly decreases, and it approaches an insulator–metal transition at $\sim 10\,\text{GPa}$ [18, 19].

However direct dc resistivity measurements have shown [20] that TiOCl actually remains insulating even for $P > 10\,\text{GPa}$, at least up to $30\,\text{GPa}$, albeit with a smaller gap. Surprisingly, ab initio calculations with lattice optimisation have shown [21] that in the high-pressure phase, in which indeed the energy gap strongly decreases, the Ti–Ti dimerization itself does not decrease but *increases* instead, see Fig. 5!

A qualitative explanation can be obtained, using again the idea of the proximity of this material to the localized–itinerant crossover. At $P = 0$ the $d$-electrons are localized, and we have a spin-Peierls transition, with $T_c$ and with the degree of dimerization $\delta d/d$ proportional to

$$T_c \sim \frac{\delta d}{d} \sim J e^{-1/\lambda}$$

where $J$ is the exchange interaction, $J \sim t^2/U$, and $\lambda$ is the spin–phonon coupling constant. Note that the energy gap in this regime is still of the Mott–Hubbard type, i.e. it is large, $E_g \sim U$. 
Figure 5. Change of dimerization in TiOCl with pressure [20].

Under pressure TiOCl approaches the insulator–metal transition, as observed in [18, 19]. But after crossing to the itinerant regime, the system still “knows” that it is one-dimensional, and as such it has a Peierls instability, with $T_c$ ($\sim$ degree of dimerization $\sim$ energy gap)

$$T_c \sim E_g \sim \frac{\delta d}{d} \sim t e^{-1/\lambda'},$$

with $\lambda'$ being the electron–electron coupling constant in this regime. That is, the very nature of insulating state in this regime is due to Peierls dimerization, and is not of Mott insulator type. But the dimerization is in this regime proportional to the bandwidth, or the hopping matrix element $t$, and not to $J \sim t^2/U$. Thus apparently we have here, simultaneously with the localized–itinerant crossover, also a spin-Peierls–Peierls transition.

5. Other possible specific phenomena close to a Mott transition

As we have discussed above, a possible situation, especially in low-dimensional and frustrated systems, is that the Mott transition occurs not in the whole system simultaneously, but “piecewise”, first in some finite clusters such as dimers, trimers, tetramers etc. But other nontrivial states may also occur in the vicinity of Mott transitions, different both from those typical for strong Mott insulators and for normal metals. These situations can occur also for simple lattices such as those of perovskites. In this chapter for completeness I will also shortly discuss some of these phenomena.

5.1. Spontaneous charge disproportionation vs orbital ordering

In some systems with strongly correlated electrons charge ordering occurs with decreasing temperature. Usually it appears in systems with noninteger electron concentration (fractional number of electrons per TM ion). The well-known examples are the Verwey transition in magnetite Fe$_3$O$_4$ or charge ordering in half-doped manganites such as La$_{0.5}$Ca$_{0.5}$MnO$_3$, see e.g. [22]. But there are also systems in which charge ordering, or rather spontaneous charge disproportionation, appears in case of, formally, integer electron occupation, or integer valence. Such is for example the situation in CaFeO$_3$, in which there occurs charge segregation

$$2\text{Fe}^{4+}(d^1) \Rightarrow \text{Fe}^{3+}(d^5) + \text{Fe}^{5+}(d^3).$$
A phase transition with the formation of a $\text{Fe}^{3+}$-$\text{Fe}^{5+}$ superstructure occurs in $\text{CaFeO}_3$ at $T_c = 290$ K and is simultaneously a metal–insulator transition [23]. Note that a similar compound $\text{SrFeO}_3$ with somewhat broader bands remains metallic down to lowest temperatures. Apparently the phenomenon of charge disproportionation in this case occurs in the system close to the localized–itinerant crossover.

Similar spontaneous charge disproportionation occurs also in $\text{La}_{2/3}\text{Sr}_{1/3}\text{FeO}_3$ [23] ($3\text{Fe}^{4+} \implies 2\text{Fe}^{3+} + \text{Fe}^{5+}$), but also e.g. in nickelates $R\text{NiO}_3$, especially those with small rare earths $R = \text{Lu}, \text{Y}$, etc. [24, 25, 26]. In nickelates charge disproportionation may be described by the “reaction”

$$2\text{Ni}^{3+}(t^6_{2g}e^1_{g}) \implies \text{Ni}^{2+}(t^6_{2g}e^2_{g}) + \text{Ni}^{4+}(t^6_{2g})$$  \hspace{1cm} (4)

($\text{Ni}^{3+}$ and $\text{Ni}^{4+}$ here are in the low-spin state). In these systems charge disproportionation is also a metal–insulator transition.

Yet other systems showing the same phenomenon are materials formally containing $\text{Au}^{2+}(d^9)$, which at normal conditions always disproportionate into $\text{Au}^{1+}(d^{10}) + \text{Au}^{3+}(d^8)$. This occurs e.g. in $\text{CsAuCl}_3$ which at ambient pressure contains two inequivalent Au sites (its formula is usually even written as $\text{Cs}_2\text{Au}_2\text{Cl}_6$). Under pressure this system also becomes metallic with equivalent Au ions [27].

One can notice three specific features, which apparently are important for the very phenomenon of spontaneous charge disproportionation. First, in TM compounds such charge disproportionation occurs in systems in which the TM ion in the “original” state would have been a strong Jahn–Teller ion, with double orbital degeneracy ($\text{Fe}^{4+}(t^6_{2g}e^1_{g})$; low-spin $\text{Ni}^{3+}(t^6_{2g}e^1_{g})$; $\text{Au}^{2+}(t^6_{2g}e^3_{g})$). Thus it seems that this spontaneous charge disproportionation appears in $\text{Fe}^{4+}$ and $\text{Ni}^{3+}$ compounds instead of the Jahn–Teller or orbital ordering, when the systems are close to localized–itinerant crossover [28, 26]. But in “$\text{Au}^{2+}$” compounds such charge disproportionation is stabilized by the enhanced JT distortion instead [29]. Second, the TM ionic states involved typically correspond to states with unusually high oxidation states, or unusually high valence ($\text{Fe}^{4+}$ and $\text{Fe}^{5+}$; $\text{Ni}^{3+}$ and $\text{Ni}^{4+}$; $\text{Au}^{3+}$). As follows from the standard classification [30, 31], these states correspond to the situation with small or negative charge-transfer gaps and with a large contribution of ligand (e.g. oxygen) $p$-holes. In effect e.g. the reaction (3) should be rather written as

$$2\text{Fe}^{3+} + L \implies \text{Fe}^{3+} + \text{Fe}^{3+} + L^2,$$  \hspace{1cm} (5)

where $L$ denotes the ligand hole (e.g. $\text{Fe}^{3+} + L$ instead of $\text{Fe}^{4+}$ denotes the state $\text{Fe}^{3+}(d^5)\text{O}^-(2p^5)$). Apparently the large contribution of ligand holes facilitates the process of charge disproportionation (the increase of Coulomb repulsion in the reaction (5) is definitely much smaller than if it would occur on the $d$-shells (3)).

These factors lead to the third conclusion: that the spontaneous charge disproportionation is typically observed in systems close to an insulator–metal transition. Experimentally this is indeed the case: in the examples mentioned above such disproportionation coincides with metal–insulator transition.

5.2. Phase separation
Without going into details, let us shortly mention yet another specific phenomenon, which is typically observed close to metal–insulator transitions. This is the phenomenon of phase separation, which often occurs especially in doped Mott insulators. It is found experimentally in many cases; in manganites [32, 33, 34]; in cobaltites [35]; and apparently also in cuprates [36]. The tendency towards phase separation is also seen theoretically in many models: in the Hubbard [37] and in the $t$–$J$ models [38]; in the double-exchange models [39], etc. The resulting state may be visualised as a random system with metallic regions in an insulating matrix. The properties
of such state can be described by percolation theory — a classical description of random systems, although quantum effects in this case can also be very important.

5.3. Large spontaneous currents in frustrated systems

Typical for many frustrated systems, which contain triangles or tetrahedra as building blocks, is an extra degeneracy, which can be characterized by spin chirality. Thus the ground state of an equilateral triangle of \( S = \frac{1}{2} \) spins with an antiferromagnetic interaction is a quartet, with the total spin \( S_{\text{tot}} = \frac{1}{2} \) and with extra double degeneracy, which can be characterized by the scalar spin chirality

\[
\chi_{123} \sim S_1 \cdot [S_2 \times S_3].
\]  

(6)

The physical meaning of the scalar chirality was clarified in [40] (see also [41]), where it was shown that the states of a triangle with nonzero chirality (6) carry a spontaneous circular electric current \( j \sim \chi_{123} \). Correspondingly, such triangle would have an orbital magnetic moment \( M \sim j \sim \chi_{123} \). In the nondegenerate Hubbard model with strong interaction \( U \gg t \) the expression for this current, obtained in perturbation theory in \( t/U \ll 1 \), has the form

\[
j = \frac{24et^3}{\hbar U^2} (S_1 \cdot [S_2 \times S_3]).
\]  

(7)

In this limit the current and the corresponding orbital moment are small. But one can show on general grounds, by using symmetry arguments, that such currents would be proportional to the chirality (6) in the general case, for \( t \gtrsim U \), and also close to Mott transition. In such situations the corresponding current and orbital moments can be quite large. Indeed, estimates done in [42], using the exact solution for a triangle, show that for reasonable values of parameters the orbital magnetic moments can be as large as \( \sim 0.7\mu_B \) — comparable with the spin moment. The authors of [42] suggested to use this degree of freedom for quantum computations. This is yet another nontrivial property of frustrated systems, which can lead to large and potentially useful effects close to Mott transitions.

6. Conclusion

In conclusion, I want to stress once again that the systems close to Mott transition, or to a localized—iterinant crossover, can show a variety of specific properties, different from those of states deep in the Mott insulator regime or those of conventional metals. Especially interesting is the situation of a “partial Mott transition”, in which first certain finite clusters go over to the regime with uncorrelated (“iterinant”) electrons, and only later there occurs a real Mott transition in the whole sample. As I tried to show on many examples, the most favourable conditions for this phenomenon are met in low-dimensional and in frustrated systems; they are less probable in simple lattices such as perovskites. But also other specific phenomena, less sensitive to the type of the lattice, such as spontaneous charge disproportionation, can occur close to insulator—metal transitions. Thus this crossover region between localized and itinerant electronic states presents a rich playground for interesting physics, with eventually some novel states appearing in this situation.

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