

Different Routes to Spin Gaps: Role of Orbital Ordering

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In many quantum spin systems, especially in low-dimensional ones, there exist states with spins forming singlets and with spin gaps. I consider several situations in which one gets such a state, paying main attention to the role of orbital occupation and orbital ordering. In particular, orbital ordering can reduce the effective dimensionality of the system and can lead to a Peierls-like state with the spin gap. It can also strongly influence the features of insulator-metal transitions in transition metal compounds, and can effectively remove frustrations in geometrically frustrated systems.

§1. Introduction

In many spin systems there appears states with spin gap. There exist different situations in which one gets such states: these may be spin dimers; Haldane spin-one chains (or more generally chains with even spin); even-leg spin ladders, etc. Often the appearance of a spin-gap state coincides with the phase transition to a new phase. Such is the situation in the well-known spin-Peierls transitions, e.g. in CuGeO_3 ¹ or in TiOCl .² The details of electronic structure of corresponding materials, in particular of their orbital occupation, play often crucial role in determining the features of corresponding transitions.

In this short article I will consider several situations in which one gets spin-gap states. Special attention will be paid to the role of orbital occupation and orbital ordering in these phenomena.

§2. Basic considerations

The most typical situation for the formation of spin-gap states is met in quasi-one-dimensional systems. The simplest phenomenon leading to a spin-gap state is a Peierls transition, e.g. dimerization in case of a half-filled band. It can occur even in systems with weakly interacting electrons, and the resulting dimerized state may be simply treated as a band insulator, with the gap simultaneously present in both the charge and spin channels. We usually do not use in this case the terminology “spin gap”.

Similar phenomenon can occur also in case of intermediate or strong electron correlations. In this opposite limit we are dealing with Mott insulators, electrons are localized and behave as localized spins, often with an antiferromagnetic exchange interaction. In this case also the resulting antiferromagnetic Heisenberg chain can be unstable with respect to dimerization. Especially strong is this tendency for $S = \frac{1}{2}$ ions: in this case indeed we gain large singlet energy when we make a dimerization. Very crudely one can understand this tendency by comparing energies of the simplest

competing states. For $S = \frac{1}{2}$ the first is a state with well-formed singlet pairs, with the wave function $\frac{1}{\sqrt{2}}(1 \uparrow 2 \downarrow - 1 \downarrow 2 \uparrow)$, which are decoupled from one another:

$$E_{singl}/N = -\frac{3}{8}J, \quad (2.1)$$

where N is the number of sites and J is the Heisenberg exchange constant (extra factor $\frac{1}{2}$ in the right-hand side in 2.1 comes from the fact that only half of the bonds have singlet pairs). The competing state is the state with eventual long-range magnetic order, which may appear in a quasi-1d system with the intrachain exchange interaction J and the weaker interchain exchange J' . In the simplest case the energy of such a state (we take a conventional Néel ordering) is

$$E_{Néel}/N = -\frac{1}{4}J - \frac{1}{4}J' \frac{(z-2)}{2}, \quad (2.2)$$

where z is the total number of nearest neighbours, and consequently $(z-2)$ is the number of neighbours in neighbouring chains (we assume here a nonfrustrated situation). Comparing 2.1 with 2.2, we see that the dimerized Peierls singlet state can be favourable for weak interchain coupling J' .

This trivial and well-known exercise is presented here to illustrate two points. When we generalize it for the case of arbitrary spin S (we mostly mean here half-integer spins; for integer spins we have a Haldane situation, and generally speaking the system does not have to have an instability towards dimerization), we get, instead of (2.1) and (2.2):

$$E_{singl}/N = -\frac{1}{2}JS(S+1), \quad (2.3)$$

$$E_{Néel}/N = -JS^2 - J'S^2 \frac{(z-2)}{2}. \quad (2.4)$$

By comparing Eqs. (2.3) and (2.4) we immediately see that the tendency for the formation of a spin-gap state is strongly suppressed for larger values of spin: this crude estimate would give that the dimerized state would become unfavourable already for $S \geq 1$ even for isolated chains. This is of course highly exaggerated, such a crude treatment ignores many important factors, but the tendency is caught correctly: indeed the systems with $S > \frac{1}{2}$ are more robust and have much weaker tendency to form spin singlets – they rather prefer to make long-range magnetic ordering, if it is not prevented by special factors such as frustrations. This can be seen for example by comparing VO_2 with V_2O_3 : both these systems have insulator-metal transitions, but VO_2 with V^{4+} ($d^1, S = \frac{1}{2}$) in the insulating phase has a diamagnetic (spin-singlet) ground state, whereas V_2O_3 with V^{3+} ($d^2, S = 1$) is antiferromagnetically-ordered, see e.g. Ref. 3). Thus, when we observe a spin-gap state in a system with $S > \frac{1}{2}$, one often has to think hard to understand what is the reason for that. A good example is provided by the system $\text{Tl}_2\text{Ru}_2\text{O}_7$ with the low-spin Ru^{4+} ($S = 1$), for which a spin-gap state appears below $T_c=120$ K.⁴⁾ Another such example is $\text{La}_4\text{Ru}_2\text{O}_{10}$, also with Ru^{4+} ($S = 1$), which has spin gap below $T_c=160$ K,⁵⁾ see also below.

Another lesson we can learn from this simple exercise is that in such low-dimensional systems it is favourable for the gap formation to have larger electron

wave function overlap and consequently larger exchange J along the chain, with as small interchain coupling J' as possible. This we can achieve in particular by using orbital degrees of freedom often present in real materials; this is the main topic of the present paper. Another message is that there are much higher chances to get a spin-singlet state in frustrated systems, where the competing state with long range ordering has smaller energy gain.

§3. Orbitaly-driven Peierls states

In systems with one-dimensional chains existing due to the very crystal structure of a material, one only has to worry that the coupling between chains is sufficiently weak. This is apparently the case in some organic materials, and in the first inorganic spin-Peierls system CuGeO_3 .¹⁾ This is also the case in another such system TiOCl ,²⁾ although in this case frustrations in the interchain interaction can also play some role. In the latter case an orbital occupation of one t_{2g} -electron of Ti^{3+} is such that the corresponding orbitals strongly overlap along the chains but much weaker between them.⁶⁾ Thus the orbital occupation apparently helps to make TiOCl essentially one-dimensional, despite the fact that the crystal structure rather consists of two-dimensional corrugated planes.

Much more interesting are situations in which we “create” 1d-chains in apparently 3d-material by using orbital degrees of freedom. One of the oldest materials of this type, many details of the physics of which however were revealed only recently, is the famous system VO_2 ,^{3),7)} in which there occurs a sharp insulator-metal transition at $\sim 70^\circ\text{C}$, below which there appears a spin-gap state. The apparent origin of this spin gap was known long ago: it originates from the formation of V-V pairs (V^{4+} ions have a configuration $d^1, S = \frac{1}{2}$) along the c -axis in the original rutile structure of VO_2 . But only recently was it established that there occurs a significant orbital repopulation in VO_2 below T_c , although the basic idea was already put forth by Goodenough long ago.⁸⁾ In the high-temperature metallic phase of VO_2 all three t_{2g} -orbitals are almost equally populated, and the properties of this system, e.g. electrical conductivity, are rather isotropic. However below T_c one d-electron of V occupies predominantly an orbital directed towards neighbouring V's along the c -chain. This was firmly established theoretically only recently by LDA+U⁹⁾ and LDA+DMFT¹⁰⁾ calculations and was proven experimentally in Ref. 11). Thus this orbital reorientation makes electronic structure of VO_2 below T_c quasi-one-dimensional and facilitates dimerization and formation of the spin-gap state. Apparently it also strongly influences the very insulator-metal transition in this system.

Such strong orbital reorientation is apparently instrumental also in the insulator-metal transitions with the spin-gap formation in two other systems: in spinels MgTi_2O_4 with Ti^{3+} ($d^1, S = \frac{1}{2}$)¹²⁾ and in CuIr_2S_4 (low-spin Ir^{3+} ($d^6, S = 0$) and Ir^{4+} $d^5, S = \frac{1}{2}$).¹³⁾ In both these systems metal-insulator transitions are accompanied by structural transitions from cubic to tetragonal phase and by the formation of very complicated and at first glance very puzzling superstructures: “chiral”

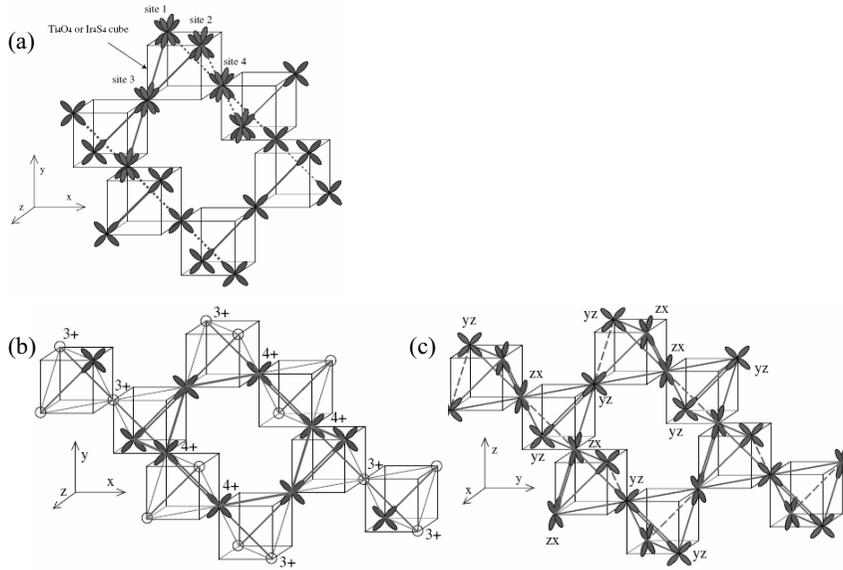


Fig. 1. (a) Overlap of different t_{2g} orbitals in the B-sublattice of spinels; (b) orbital ordering in MgTi_2O_4 ; (c) charge and orbital ordering in CuIr_2S_4 (by Ref. 16)). Singlets are shown by double lines.

structural distortions in MgTi_2O_4 ¹⁴⁾ and “octamer” ordering in CuIr_2S_4 .¹⁵⁾ These superstructures, however, with the corresponding spin-gap formation, become extremely simple and natural¹⁶⁾ if we look at the situation in straight Me-Me chains in B-sublattice of spinels (there are three sets of such chains, running in (xy) , (xz) and (yz) -directions). The type of relevant orbitals in these systems is such that one orbital, e.g. xy , has strong overlap only along xy -chains, xz -orbital — along xz -chain, and yz — along yz -chains, see Fig. 1(a). Consequently, each of these orbitals gives rise to a corresponding *one-dimensional* band, susceptible to a Peierls distortion. This is apparently what happens in MgTi_2O_4 and in CuIr_2S_4 :¹⁶⁾ there appears in them an orbital ordering with tetramerization along xz - and yz -chains (occurring in CuIr_2S_4 together with charge ordering), which leads to an insulating state, with the formation of Me-Me singlet dimers, see Figs. 1(b) and (c). Here an orbital ordering alone is in principle sufficient to open a spin gap, one even does not have to move atoms, although of course in reality lattice would respond, so that both these phenomena, orbital ordering and lattice distortion, occur simultaneously.

Actually the opening of a spin gap due to an orbital ordering does not necessarily require that it occurs at the metal-insulator transition. Probably the first clear example of such phenomenon was observed in an insulating pyroxene $\text{NaTiSi}_2\text{O}_6$.¹⁷⁾ In this system Ti^{3+} (d^1 , $S = \frac{1}{2}$) ions form zigzag chains. Below the phase transition at $T_c = 210$ K there apparently occurs in this system a ferro-orbital ordering such that the occupied orbitals are all directed along one type of segments of the zigzag, see Fig. 2. Consequently the overlap of the wave functions and the exchange interaction will be much stronger on these bonds, which will form spin singlets.

Apparently very similar situation do we meet also in $\text{La}_4\text{Ru}_2\text{O}_{10}$.⁵⁾ Low-spin Ru

ions ($d^4, S = 1$) also form zigzags, and strong structural distortion occurring in this system below 160 K is accompanied (and, may be, is driven by) an orbital ordering, after which the coupling within the pair of Ru ions becomes much stronger than with the other neighbours.

The original interpretation suggested in Ref. 5), that at this transition each Ru ion goes from the low-spin state $S = 1$ to the “ultra-low spin” nonmagnetic state $S = 0$, is most probably incorrect: for that the distortion should be so strong that the crystal field splitting of t_{2g} -levels of Ru should exceed the on-site Hund’s rule coupling, which for Ru is of order 0.6 eV. This seems to be rather unlikely, and the nature of the spin-gap state in $\text{La}_4\text{Ru}_2\text{O}_{10}$ is most probably connected with the formation of $S = 0$ dimers of *two* Ru ions. This picture is confirmed by the *ab-initio* LDA+U calculations.¹⁸⁾ The fact that Ru’s in this system remain $S = 1$ ions below T_c , is also confirmed directly by the X-Ray absorption measurements.¹⁹⁾

In principle the situation in $\text{La}_4\text{Ru}_2\text{O}_{10}$

could be somewhat more complicated than the simple scheme described above (which is similar to the one shown in Fig. 2): Ru ions in fact form here a corrugated *two-dimensional* RuO_2 sheets, and not simply 1d Ru zigzags. Thus one has to consider also the Ru-Ru coupling in the “third” direction, between zigzags in such a sheet. Calculations show that this coupling is still much weaker than the one within strong dimers. But even if it would not be so weak, we still could have a spin-gap state: topologically then we would have a situation of a two-leg spin ladder with strongly coupled dimers forming rungs of the ladder and intermediate “perpendicular” coupling – its legs. This leads us to our next topic: spin gaps in higher-dimensional systems and eventual role of orbitals in them.

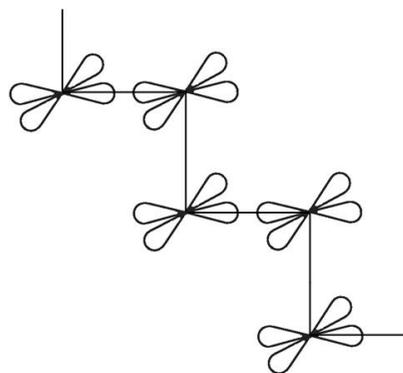


Fig. 2. Schematic structure of Ti zigzags and corresponding orbital ordering in pyroxene $\text{NaTiSi}_2\text{O}_6$, by Ref. 17). Similar situation apparently exists in $\text{La}_4\text{Ru}_2\text{O}_{10}$.

§4. Orbitals and spin gaps in higher-dimensional systems

When we want to consider spin-gap states in systems going beyond one-dimensional chains with singlets on dimers, the first generalization is the already mentioned spin ladders, see e.g. Ref. 20). The best-known examples are Cu^{2+} ladders, in which one hole on Cu^{2+} occupies $x^2 - y^2$ -orbital. There are also other examples of such two-leg ladders, for instance CaV_2O_5 .²¹⁾ Initially experimental data on this system were interpreted in the picture of doubly-degenerate orbitals zx , yz of V^{4+} ($d^1, S = \frac{1}{2}$) being lower. However later on it was established that one electron on each V occupies the nondegenerate xy -orbital. It is this orbital occupation which creates an effective two-leg ladder in CaV_2O_5 ,²²⁾ whose crystal structure actually consists of depleted 2d square lattice of VO_5 pyramids.

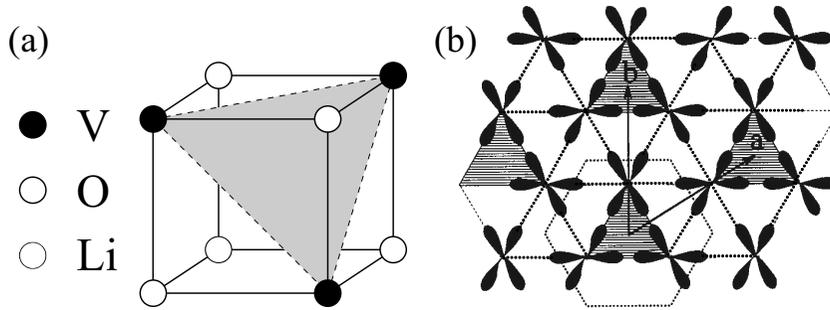


Fig. 3. Schematic crystal structure (a) and orbital ordering (b) in LiVO_2 , by Ref. 24).

The next level of complexity do we meet in the system LiVO_2 , containing quasi-2d triangular layers of V^{3+} ($d^2, S = 1$), see Fig. 3(a). In this system V ions actually form (111) layers in a rock-salt structure, next such layer being occupied by non-magnetic Li. There exists in this system a first order phase transition at 460 K, below which the susceptibility sharply drops, so that the contribution of localized spins practically disappears.²³⁾ The explanation of this phenomenon was suggested in Ref. 24). It was shown there that one can form in this system an orbital ordering of t_{2g} -orbitals with three sublattices, so that after such ordering there appears strong antiferromagnetic coupling of *three* V ions on a triangle, isolated from other similar triangles, see Fig. 3(b). As a result three spin-1 V ions on such a triangle form a spin-singlet state, which explains the drop of susceptibility and the change of crystal structure at the transition. Thus this system is an example of a “second level” of spin-singlet formation: whereas in most cases spin singlets are formed on *dimers*, here we have spin singlets on *trimers*, triangles of V^{3+} ($S = 1$). Recently similar state was observed also in TiI_2 with similar crystal and electronic structure.²⁵⁾

Note that here we also have an interesting situation: an orbital ordering apparently removes frustrations inherent in 2d triangular lattice. This is not the only such example. One may notice that this is also the case in MgTi_2O_4 and CuIr_2S_4 discussed above: the metal ions there form a pyrochlore-like lattice of corner-shared tetrahedra, which for the pure spin case would be heavily frustrated. Apparently an orbital ordering helps to lift or at least strongly reduce these frustrations.

There exist also systems with still “higher level” of singlet formation — spin singlets on a *plaquette*. Such situation is met in a material CaV_4O_9 ²⁶⁾ belonging to the same class of depleted VO_2 layers as CaV_2O_5 . The same xy -orbital occupation provides here strong antiferromagnetic interaction of four V’s surrounding an “empty” V site;²²⁾ these four V ions finally form a singlet state on such V_4 plaquette. Apparently for other orbital occupation the situation in both these materials would have been much different.²⁷⁾

Summarizing, I tried to illustrate in this paper that there exist different routes to spin gaps in solids. Singlet states can be formed on dimers, on trimers and on plaquettes. An alternative possibility is spin ladders and Haldane chains with even spin. (I discussed in this paper mostly the static, ordered structures, and did not

really touch upon possible spin-liquid states e.g. in frustrated systems, etc.). And in most of the real systems showing ordered states with spin gaps, an orbital occupation plays an important role. In many cases it is just due to orbital ordering that one creates either the conditions favorable for making singlet dimers (as in VO_2), or even the orbital ordering itself leads to the formation of such singlets on dimers (MgTi_2O_4 , CuIr_2O_4 , $\text{NaTiSi}_2\text{O}_6$, $\text{La}_4\text{Ru}_2\text{O}_{10}$) or on triangles (LiVO_2). Thus the orbital degrees of freedom can lead, in addition to the other well-known consequences,²⁸⁾ also to the formation of spin-singlet states.

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