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Spin chirality and nontrivial charge dynamics in frustrated Mott insulators: spontaneous currents and charge redistribution*

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Abstract

The standard point of view is that at low energies Mott insulators exhibit only magnetic properties, while charge degrees of freedom are frozen out because electrons are localized. We demonstrate (Bulaevskii *et al* 2008 *Phys. Rev.* B **78** 024402) that in general this is not true: for certain spin textures there exist quite nontrivial charge effects in the ground and lowest excited states. We show that in frustrated systems *spontaneous orbital currents* may exist in the ground state, proportional to the *scalar spin chirality*. For other spin structures *spontaneous charge redistribution* may exist, so that the average charge at a site is different from 1. This can lead to the appearance of dipole moments and possibly of the net *spontaneous polarization*. This is a novel, purely electronic mechanism of *multiferroic behaviour*. We also discuss some dynamic consequences, such as dipole-active 'ESR' transitions. Also, the possibility of using chirality instead of spin in memory applications is briefly discussed.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The standard way to consider Mott insulators with strong correlations (on-site Hubbard repulsion $U \gg$ hopping integral t) and with one electron per site is to say that due to electron repulsion electrons are localized, one at a site, and the system becomes insulating. In this case one always accepts that charge degrees of freedom are frozen out and only spin degrees of freedom remain, which determine the magnetic properties of such systems. Correspondingly, if one describes this situation by the simplest model—the nondegenerate Hubbard model

$$H = -\sum_{ij\sigma} t_{ij} c^{\dagger}_{i\sigma} c_{j\sigma} + U \sum_{i} n_{i\uparrow} n_{i\downarrow}, \qquad (1)$$

for one electron per site $\langle n_i \rangle = \langle c^{\dagger}_{i\uparrow} c_{i\uparrow} + c^{\dagger}_{i\downarrow} c_{i\downarrow} \rangle = 1$ and for $U/t \gg 1$ one can go over from the electron Hamiltonian (1) to the effective spin model

$$H_{\text{eff}} = \frac{4t^2}{U} \sum \boldsymbol{S}_i \cdot \boldsymbol{S}_j. \qquad (2)$$

Thus one always implicitly assumes that for strong Mott insulators charge degrees of freedom are of no interest, the ground state and the lowest excited state are purely magnetic, and charge excitations and charge response start from temperatures T or energies $E \gtrsim U$.

We recently considered [1] this situation for frustrated lattices (with triangular, tetrahedral or pentagonal building blocks), and demonstrated that this general point of view is not correct for these systems: there may exist quite interesting *charge effects* even in the ground state and lowest excited states of such systems. In particular, it was shown in [1] that for certain spin textures *spontaneous orbital currents* may appear in such systems, reminiscent of the persistence currents in superconductors with trapped magnetic flux. For other spin textures *spontaneous charge redistribution* or spin-driven charge density waves (S-CDWs) should occur, so that the number of electrons at a particular site is not 1, but more than 1 at certain sites and less than 1 at others. As a result *electric dipole moments* will appear in the system, which in some cases can give rise to net polarization, i.e. to ferroelectricity. This could be a novel, purely electronic mechanism of multiferroic behaviour (magnetically driven, or type-II multiferroic [2]),

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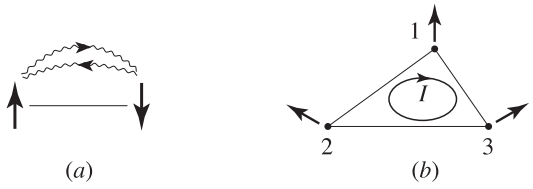

Figure 1. (a) Virtual hoppings of electrons on a pair of sites, giving superexchange (2) $\sim t^2$. (b) Possibility of current state in a triangle, requiring three electron hops (the effect $\sim t^3$).

which in principle would require neither spiral magnetic structures nor electron–lattice (magnetostriction) interaction. As a result of strong mixing of charge and spin degrees of freedom, low-energy magnetic excitations, such as the usual spin waves, acquire electric activity and contribute not only to the magnetic response $\chi(\boldsymbol{q}, \omega)$ but also to the electric response function—the dielectric function $\epsilon(\boldsymbol{q}, \omega)$ (see also [3]). Thus there should be different manifestations of spins in optical properties: dipole-active 'ESR'-like transitions, etc, will appear.

We stress right away that all these effects appear without the involvement of relativistic spin–orbit interaction, which can also lead to similar effects and which is now actively studied in the field of spintronics, especially in semiconductors [4]. On the other hand, the effects we discuss require the presence of geometric frustration in the form of odd-segment loops on which electrons can hop.

In this paper I will discuss the main ideas underlying this development; I will briefly summarize the results obtained in [1] (one can find the details in the original publication), and will discuss possible implications and some recent developments.

As I have said above, the standard paradigm in Mott insulators is to consider electrons as localized exactly one per site, and go over from the electronic Hamiltonian (1) to the effective Heisenberg Hamiltonian (2) describing only spin degrees of freedom. This is done by using perturbation theory in $t/U \ll 1$ up to the second order. But more attentive reasoning immediately shows that already at this level the electrons do not stay forever at their sites. To get the (super)exchange interaction (2) they have to virtually move from site to site, hopping to nearest neighbours and back (figure 1(*a*)). In second order in t/U (two hops) this gives a preference to antiparallel orientation of neighbouring spins (the Pauli principle does not forbid such hops, in contrast to their parallel arrangement) and provides a mechanism of antiferromagnetic superexchange (2). Thus without such hopping of electrons from site to site there would be no magnetic exchange at all!

Similar reasoning applied, for example, to the triangle {123} in figure 1(*b*) immediately gives a hint that similar hoppings in this case can lead to circular currents running clockwise or anticlockwise along this triangular loop. Similar to the case of figure 1(*a*), one can expect that the very presence and magnitude of these currents would depend on the magnetic structure on this triangle, i.e. on some correlation functions involving spins $\boldsymbol{S}_1$, $\boldsymbol{S}_2$, $\boldsymbol{S}_3$. But, in contrast to the usual superexchange, here the electrons should hop (at least) *three times*, i.e. one can find these effects in the third order, $\sim t^3$, in contrast to the second order $\sim t^2$ in figure 1(*a*) and in (2).

This is essentially what was done in the original paper [1]. There we calculated different effects up to the order $(t/U)^3$, and found corresponding expressions for spontaneous current, charge density etc. Technically this can be done in two ways: we can calculate particular quantities, such as the current

$$\boldsymbol{I}_{ij} = \frac{\mathrm{i}et_{ij}\boldsymbol{r}_{ij}}{\hbar r_{ij}} \sum_{\sigma} (c^{\dagger}_{j\sigma} c_{i\sigma} - c^{\dagger}_{i\sigma} c_{j\sigma}), \tag{3}$$

or the electron density

$$n_i = c^{\dagger}_{i\uparrow} c_{i\uparrow} + c^{\dagger}_{i\downarrow} c_{i\downarrow} \tag{4}$$

for sites i, j belonging to the triangle $\{ijk\}$ up to the 3d order in t, and express the results via spin operators[1]. Alternatively, we can calculate the effective Hamiltonian H_{eff} up to order t^3, adding to the original Hamiltonian (1) the coupling to a scalar potential $\phi(\boldsymbol{r}) = -e\sum_i \phi_i n_i$ and to a vector potential $\boldsymbol{A}(\boldsymbol{r})$, introduced via the Peierls substitution $t_{ij} \longrightarrow t_{ij} \mathrm{e}^{-\frac{2\pi \mathrm{i}}{\Phi_0}\int_{x_i}^{x_j} \mathrm{d}\boldsymbol{x}\cdot\boldsymbol{A}}$. From the resulting expression for $H_{\mathrm{eff}}\{\boldsymbol{A}, \phi\}$ we can then obtain the electron density $n_i = -\partial H_{\mathrm{eff}}/\partial(e\phi_i)$ and the current in the triangle $I_{ijk} = -c\partial H_{\mathrm{eff}}/\partial\Phi_{ijk}$, where $\Phi_{ijk} = \oint_{ijk} \mathrm{d}\boldsymbol{x}\cdot\boldsymbol{A}$ is the magnetic flux through the triangle. Both methods give identical results [1], presented below.

2. Spontaneous currents and orbital moments

The expression for the current running on a bond {12} belonging to a triangle {123} (by continuity, this will be net current running along the whole triangle {123}) is

$$\boldsymbol{I}_{12,3} = \frac{\boldsymbol{r}_{12}}{r_{12}} \frac{24et^3}{\hbar U^2} \boldsymbol{S}_1 \cdot [\boldsymbol{S}_2 \times \boldsymbol{S}_3] = \frac{\boldsymbol{r}_{12}}{r_{12}} \frac{24et^3}{\hbar U^2} \chi_{123} \tag{5}$$

where χ_{123} is the *scalar spin chirality*, $\chi_{123} = \boldsymbol{S}_1 \cdot [\boldsymbol{S}_2 \times \boldsymbol{S}_3] = \boldsymbol{S}_2 \cdot [\boldsymbol{S}_3 \times \boldsymbol{S}_1] = \boldsymbol{S}_3 \cdot [\boldsymbol{S}_1 \times \boldsymbol{S}_2]$. Thus we see that as soon as the scalar spin chirality χ_{123} has nonzero average, there should be a *real circular electric current* running along this triangle. This current will cause a corresponding *orbital moment*, always directed perpendicular to the plane of the triangle, $L^z \sim I \sim \chi$. Thus this orbital moment is an Ising variable, in contrast to the usual spins which are $SU(2)$-invariant. Consequently, for example, whereas in 1d and 2d systems at $T \neq 0$, according to the Mermin–Wagner theorem, there should be no long-range

[1] We recall that in the case of strong Mott insulators $n = 1$, $t/U \ll 1$, all the lowest excited states belong to the Hilbert space of 2^N nonpolar states. In this subspace one can always go over from the electron operators $c^{\dagger}$, c to spin operators S, using the well known rules $c^{\dagger}_{i\uparrow} c_{i\uparrow} \longrightarrow \frac{1}{2} + S^z_i$, $c^{\dagger}_{i\downarrow} c_{i\downarrow} \longrightarrow \frac{1}{2} - S^z_i$, $c^{\dagger}_{i\uparrow} c_{i\downarrow} \longrightarrow S^+_i$, $c^{\dagger}_{i\downarrow} c_{i\uparrow} \longrightarrow S^-_i$. Accordingly the second order in t/U terms, like those necessary to go from the Hamiltonian (1) to (2), would contain products of *four* electronic operators, which combine into the Heisenberg exchange $\boldsymbol{S}_i \cdot \boldsymbol{S}_j$ (2). Similarly, third-order terms would contain products of *six* electronic operators, which would give some combinations of *three* spin operators $\boldsymbol{S}_i$, $\boldsymbol{S}_j$ and $\boldsymbol{S}_k$. Note that in principle *all operators*, including spin operators themselves, would also be renormalized by terms of higher order in (t/U) [5]. It would not, however, modify our main results such as the expressions for electric current (5) or charge redistribution (6), because the extra terms in spin operators would give terms in (5) and (6) of higher order in (t/U).

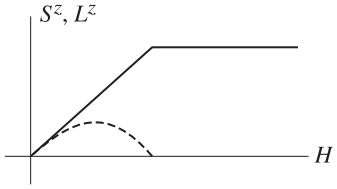

Figure 2. Schematic change with magnetic field of the total spin of a triangle (solid line) and of the orbital moment following from equation (5) (dashed line); for the opposite sign of the hopping t the dashed curve would be inverted.

spin ordering, $\langle \boldsymbol{S}_i \rangle = 0$, this does not apply to the orbital moment, i.e. to scalar spin chirality: there may be in principle situations in which $\langle \boldsymbol{S} \rangle = 0$, but in which the scalar spin chirality (a third-order spin correlation function) and orbital moments proportional to it are nonzero, $\langle \chi \rangle \sim \langle L^z \rangle \neq 0$, even at finite temperatures. One such example was considered in [6], where this was shown to be the case for a certain range of parameters in a kagome lattice with nearest and next nearest neighbour interactions. Note that this state with $\langle \chi \rangle = \langle \boldsymbol{S}_1 \cdot [\boldsymbol{S}_2 \times \boldsymbol{S}_3] \rangle \neq 0$ is a *magnetic state*, and breaks time reversal invariance. Nevertheless it does not have the usual long-range magnetic order, i.e. it is an example of a time-reversal-broken spin liquid.

The result (5) discloses the physical meaning of the scalar spin chirality, which has been invoked in many situations. Our results show that physically nonzero scalar chirality means the presence of real electric orbital currents and corresponding orbital moments. Thus this chirality will have a linear coupling to the magnetic field $\sim -L^z H_z \sim \chi_{123} H_z$, and in some cases it can be the primary order parameter (coupling of scalar spin chirality to the magnetic field was also noticed in [7]).

A few more remarks are in place here. First, we see that the current (5) and the orbital moment L^z are odd functions of t. Thus they may have a different sign, depending on the sign of t. Scalar spin chirality χ_{123} is in fact a measure of the solid angle created by three spins $\boldsymbol{S}_1$, $\boldsymbol{S}_2$, $\boldsymbol{S}_3$ (for small solid angle), and quasiclassically $\langle \chi \rangle \neq 0$ when spins are noncoplanar. In this case there will be a net total spin of the triangle $\langle \boldsymbol{S}_{\rm tot} \rangle = \langle \boldsymbol{S}_1 + \boldsymbol{S}_2 + \boldsymbol{S}_3 \rangle \neq 0$, and the orbital moment L^z will change with $\boldsymbol{S}_{\rm tot}$. But this change can be nontrivial. Thus, for example, if there exists an easy-plane anisotropy, e.g. coinciding with the plane of the triangle, a perpendicular magnetic field will 'bend' spins, originally forming a 120° structure in the plane. The total spin of the triangle will then behave as shown in figure 2 by the solid line. But the currents and orbital moments, according to equation (5), will first increase but then, when the spins finally become collinear, they will decrease (figure 2 (dashed line)). Moreover, for the opposite sign of hopping t in (5) the orbital moment L^z will be *negative*, i.e. opposite to the spin moment $\langle \boldsymbol{S}_{\rm tot} \rangle$ (but still nonmonotonous).

However, in general, spin orientation should not be tied to the orientation of the triangle. Thus, for example, if the spin easy plane is perpendicular to the plane of the triangle, with 120° spin orientations in this easy plane, then it will be the field $H_\parallel$, lying in the plane of the triangle, which will 'bend' spins and create nonzero chirality $\langle \chi \rangle$. But the orbital moment, created by this, will still be in the z-direction, i.e. the field $H_\parallel$ will create an orbital moment perpendicular to it.

Another important remark is that *a posteriori*, after equation (5) has been derived, we can understand that this expression is the only possible expression for the current through spin operators. Its form is actually determined by symmetry requirements. Thus, current is odd with respect to time reversal, i.e. it has to contain an odd number of spins—in 3d order in t/U three spins[2]. Similarly, the requirement of the proper symmetry with respect to spatial inversion, mirror plane reflections etc uniquely determines the spin combination $\boldsymbol{S}_1 \cdot [\boldsymbol{S}_2 \times \boldsymbol{S}_3]$ entering (5). Of course to get numerical coefficients in the expression (5), one has to carry out real calculations [1].

From these arguments it is also clear why for all phenomena such as spontaneous currents we need frustrations. For $n = 1$ the system is invariant with respect to electron–hole transformation. But in such transformation, on the one hand, $t \longrightarrow -t$, and, on the other hand, electron–hole substitution changes the sign of the current, $j \longrightarrow -j$. Thus the expression for current should contain only *odd* powers of t. But this requires having odd closed loops such as triangles, pentagons etc (or a square lattice with diagonal hoppings added, which also allows for three-segment loops). For bipartite lattices, however, with only even loops, there should be no spontaneous currents.

The calculations presented above were carried out in perturbation theory in $t/U \ll 1$. Consequently one might think that all effects discussed above, though in principle present, will be numerically very small. This is indeed the case if $t/U \ll 1$. But, as argued above, the effects such as spontaneous currents should be present even when t becomes large. Thus there will be the same currents when the system approaches Mott transition from the insulating side. Corresponding currents will still be proportional to the same scalar spin chirality χ, but numerically the effects would be stronger—generally speaking of order one. Actually the solution of the Hubbard model on a triangle can be obtained exactly for all values of t/U [8], and estimates made in [8] show that for small U the values of the orbital moment due to currents of the type of (5) can for reasonable values of parameters be $\sim 0.7\ \mu_{\rm B}$—not a small value at all.

Until now we have considered only isolated triangles, often using the quasiclassical approximation (though in general the result (5) has an operator form, i.e. it has a general applicability; see below). There indeed exist real systems which to a good approximation can be considered as consisting of isolated triangles. Examples are many magnetic molecules or trinuclear clusters, or even some solids. But more often in concentrated systems we meet the situation where constituting triangles have common edges (e.g. 'triangular ladders', figure 3(*a*), or triangular lattices, figure 3(*b*)), or common vertices (e.g. kagome lattices, figures 3(*c*) and (*d*)). If for such systems we were to have *the same* chirality χ at each triangle, as in figure 3(*a*), we see that the currents on common inner edges would cancel. But then there will exist a net

[2] Note also that for systems containing spin triangles there will appear three-spin terms (ring exchange) $\sim t^3/U^2$ in the effective Hamiltonian (2).

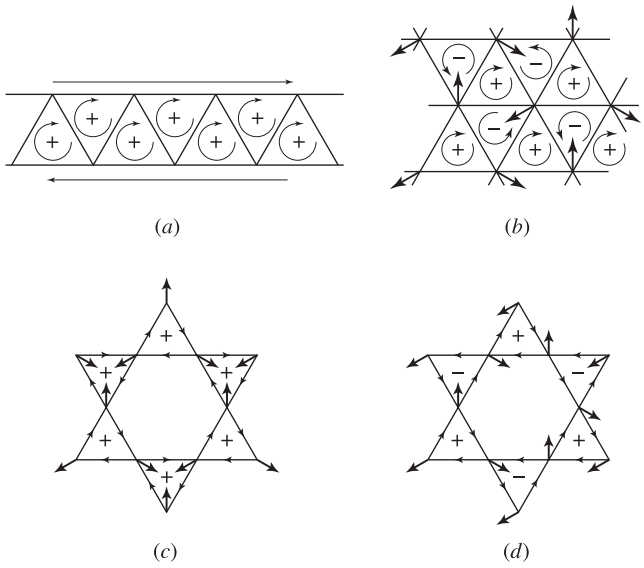

Figure 3. Possible currents on different frustrated lattices for different spin configurations. Large arrows denote spins, small arrows on the edges show the direction of electric currents. (a) Current running on the perimeter of the sample (here—'triangular ladder') with the same chirality at each edge-sharing triangle. (b) Staggered chiralities in a triangular lattice with 120° magnetic structure (scalar spin chirality will appear in a weak perpendicular field). (c) Homogeneous ($q = 0$) and staggered (d) chiralities for two typical states in a kagome lattice.

current running *on the perimeter* of the whole sample—much like persistence currents on the surface of superconductors. In this case there will be a nonzero total orbital moment of the whole sample.

If, however, we have the usual 120° coplanar spin structure (figure 3(*b*)) this would give for a triangular lattice a staggered vector chirality $\boldsymbol{S}_1 \times \boldsymbol{S}_2 + \boldsymbol{S}_2 \times \boldsymbol{S}_3 + \boldsymbol{S}_3 \times \boldsymbol{S}_1$. Spin 'bending' in a perpendicular magnetic field will then create a similar pattern of scalar spin chirality and corresponding alternating clockwise and anticlockwise currents, which, as one sees in figure 3(*b*), will exist on both the inner and outer bonds, creating regular pattern but not adding to a net orbital moment. However, we notice an interesting feature here: in this case the *constant* magnetic field will create *staggered* field for orbital moments [9]. Similarly, for the kagome lattice the patterns of figures 3(*c*) and (*d*), both being 120°-structures, would give different results for chiralities and orbital moments: homogeneous ($q = 0$) or staggered ($\sqrt{3} \times \sqrt{3}$) structures. Both situations have been seen in experiments in different situations. Note that if the structures of figures 3(*c*) and (*d*) were exactly equivalent (degenerate), then the application of a magnetic field perpendicular to the easy plane would lift this degeneracy—not because of spins (spin canting would be the same), but because of orbital moments: the total orbital moment L^z would be nonzero for the $q = 0$ structure of figure 3(*c*), but moments would cancel in the staggered case of figure 3(*d*). Which phase will then be stabilized by the external field depends on the value and *the sign* of the orbital moment. (Note that we have to take into account not only the moments of each small triangle, but also the opposite moments of currents running in opposite directions around the hexagons in figure 3(*c*).)

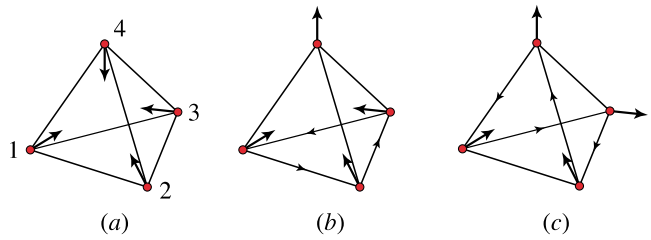

Figure 4. Typical classical magnetic states on a tetrahedron with the Ising-like magnetic anisotropy (spins pointing toward the center of tetraherdon or out of it), with the resulting currents. (a) 4-in (or 4-out) state; currents at each edge cancel. (b) 3-in, 1-out state (e.g. in a strong enough magnetic field pointing out). (c) 2-in, 2-out state (the state typical for the 'spin ice'). Cases (b) and (c) have nonzero currents and orbital moments. Notation for arrows is the same as in figure 3.

One meets an interesting situation in systems containing metal tetrahedra (isolated ones or forming pyrochlore lattices, for example) as building blocks. Often in this case we have strong uniaxial anisotropy such that the spins point towards the centre of the tetrahedron or away from it. The resulting structure can, for example, be 'four in' (or 'four out') (figure 4(*a*)). In a strong enough magnetic field, pointing up it will transform to the 'three in—one out' structure of figure 4(*b*). More familiar is the case of 'two in—two out' (figure 4(*c*))—the famous spin ice. Applying the expression (5) to these situations, we see that at each separate triangle we have noncoplanar spins with $\langle\chi\rangle \neq 0$, and consequently nonzero currents. However, in the case figure 4(*a*) the currents at each edge, belonging to two triangles, cancel. But similar treatment of the cases 4(*b*) and (*c*) shows that there will be nonzero currents running as shown there, with corresponding orbital moments parallel (or antiparallel) to the net spin moment of the tetrahedron.

The actual situation, however, is more complicated. The antiferromagnetic Heisenberg model for spins $\frac{1}{2}$ on a tetrahedron can be solved exactly, and the ground state of course is a singlet, $\boldsymbol{S}_{\text{tot}} = 0$, but it is doubly degenerate (see e.g. [10]). This degeneracy is nothing other than the chirality $\chi_{123} = \chi_{134} = \chi_{142} = \chi_{432}$ (see vertex numbering in figure 4(*a*)), or at least we can choose the basis states in a doubly degenerate ground state manifold so that they are eigenstates of this chirality. Corresponding states in which $\langle\chi\rangle \neq 0$ break time reversal invariance and are magnetic. Nevertheless the average spin $\langle\boldsymbol{S}\rangle = 0$, and there is also no net orbital moment here (similar to the case of figure 4(*a*), the currents at each edge cancel). One can also argue that due to symmetry the orbital moment (a vector) should indeed vanish—it 'would not know' in which direction in a tetrahedron to point. But, on the other hand, such states, with e.g. $\langle \boldsymbol{S}_1 \cdot [\boldsymbol{S}_2 \times \boldsymbol{S}_3] \rangle \neq 0$, are T-odd and are magnetic!

One can give arguments that what will be nonzero here is not the orbital moment (magnetic dipole) but the *magnetic octupole* (or it may be even the magnetic monopole [11]). Indeed the symmetry analysis shows that the situation

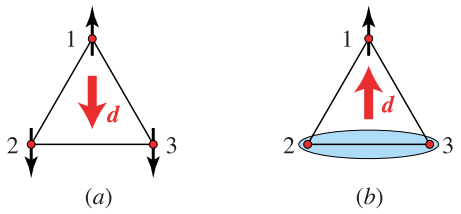

Figure 5. Schematic explanation of charge redistribution and formation of dipole moments in a triangle. (a) Typical classical situation. (b) Possible quantum state of a triangle. The blue oval is a singlet state of spins S_2 and S_3, spin S_1 pointing up or down. Here the black thin arrows are spins and thick red arrows are dipole moments.

here, with doubly degenerate states, corresponds to the E_g-representation of the rotation group, i.e. it is in fact equivalent to the E_g degeneracy in the Jahn–Teller problem (i.e. doubly degenerate e_g orbitals $|3z^2{-}r^2\rangle$, $|x^2{-}y^2\rangle$ in transition metal compounds; see e.g. [12]). As in that problem, one can describe this degeneracy by effective pseudospin (or isospin) $\tau = \frac{1}{2}$. One can then choose the states to be real (eigenstates of τ^z, τ^x) or one can choose complex combinations (eigenstates of τ^y). The first two are even with respect to time reversal, whereas the last ones, eigenstates of τ^y, are odd. And, similar to the case of e_g-orbitals, complex combinations, which are actually characterized by certain scalar chirality, $\tau^y \sim \chi$, correspond to states with *magnetic octupoles* [13].

3. Charge redistribution and polarization

Similar to the treatment of currents on a triangle, we can also calculate the effective electron density (an operator!). The resulting expression for the charge on site 1 belonging to triangle {123} is [1]

$$n_1 = 1 + 8\frac{t^3}{U^3}[\boldsymbol{S}_1 \cdot (\boldsymbol{S}_2 + \boldsymbol{S}_3) - 2\boldsymbol{S}_2 \cdot \boldsymbol{S}_3]. \qquad (6)$$

Thus we see that if the average correlation function $\langle \boldsymbol{S}_1 \cdot (\boldsymbol{S}_2 + \boldsymbol{S}_3) - 2\boldsymbol{S}_2 \cdot \boldsymbol{S}_3\rangle \neq 0$, the electron density at site 1 will be different from 1: it will be either more or less than 1 depending on the spin configuration (and the sign of t). Thus a certain charge redistribution will occur, with corresponding appearance of a S-CDW, and of corresponding dipole moment.

One can qualitatively explain this result in the simple picture of figure 5. In figure 5(*a*) a possible spin structure is shown. It is clear that in this case even in the lowest order in t the electrons can hop between sites (1, 2) and (1, 3), but because of the Pauli principle not between 2 and 3. Thus *the bonds* here are definitely inequivalent 'from the charge point of view'. And this is translated to the fact that also *site* charge densities become different, as described by equation (6).

In figure 5(*b*) we present a more realistic picture for a triangle of spins $\frac{1}{2}$ with the Heisenberg antiferromagnetic interaction. The ground state of this system may be written as a superposition of states of the type shown in figure 5(*b*): a singlet on one bond, with spin up (or down) on the remaining site. The ground states (doubly degenerate, see below) are usually taken as a symmetric superposition of such states with singlets on all three bonds. But we can also choose a different basis, e.g. with one state shown in figure 5(*b*), and another orthogonal state.

In this state, according to equation (6), we also have charge redistribution ($\boldsymbol{S}_1 + \boldsymbol{S}_2 = 0$, $\boldsymbol{S}_1 \cdot \boldsymbol{S}_2 = -\frac{3}{4}$). This charge redistribution will lead to the formation on the triangle of the corresponding electric dipole moment, e.g. pointing up (red arrow in figure 5). The orthogonal state will have dipole moment down. Thus by applying a small electric field in the appropriate direction, we will split the originally degenerate ground state in such a way that one state, e.g. that of figure 5(*b*), would go down in energy, and the orthogonal state up. This is completely analogous to the Zeeman splitting of spin up and down states in a magnetic field, and it justifies the possibility of choosing the state of figure 5(*b*) as one of the basis states. Without an electric field of course all such states are degenerate, and there will be no electric dipole, again exactly analogous to the case of a spin in a paramagnet.

If in a bulk system the dipole moments of all triangles were to have some nonzero value, this would correspond to total electric polarization, i.e. to the appearance of magnetically driven ferroelectricity. This would then be a purely electronic mechanism of multiferroic behaviour—type-II multiferroic, in the terminology of [2]. In many cases, however, such dipole moments on different triangles cancel. This is the typical situation in many *magnetization plateaux*, typical of frustrated systems. Thus the $\frac{1}{3}$ magnetization plateau in a kagome lattice has the structure shown in figure 6(*a*) [14], i.e. it consists of singlet hexagons, with up-spins in between. One sees that each elementary triangle in this case has a structure like in figure 5(*b*), i.e. it has a singlet base and spin up vertex. Correspondingly there will be charge redistribution, with charges of magnetic sites different from those on singlet hexagons. But the dipole moments thus created would cancel and would not add up to a net polarization. Nevertheless there will be this charge redistribution (formation of S-CDWs) on the magnetization plateau. This seem to be a typical situation at such plateaux: besides unusual magnetic behaviour, we would have here nontrivial charge effects.

In the same way the typical state of a diamond chain of figure 6(*b*) (found in the mineral azurite) would have charge redistribution, but dipole moments which cancel. However, for example, the similar state on a saw-tooth (or delta-) chain of figure 6(*c*) would give a nonzero net polarization. I know of only one material with this structure—(La/Y)$CuO_{2.5+x}$ [15]. Also the properties of domain walls (solitons) in these chains, shown in figure 6(*d*), might be very interesting: besides having nonzero spin (e.g. $S = \frac{1}{2}$) they should also be charged.

We stress again that this mechanism of magnetoelectric coupling, and of eventual multiferroicity, is purely electronic and does not require a spiral magnetic structure or relativistic spin–orbit interaction, as usual [2]: it can also work for a collinear magnetic structure. On the other hand it also does not require lattice distortion (magnetostriction), though the inclusion of this possibility leads to effects similar to those described above [1].

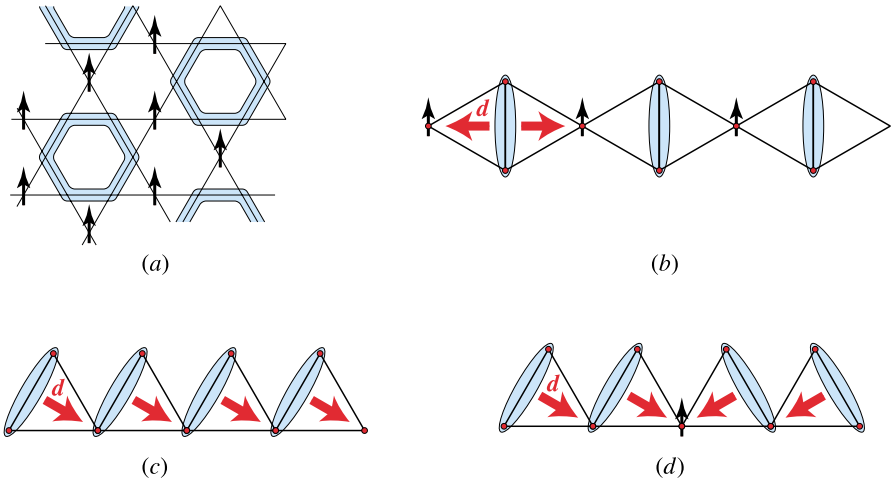

Figure 6. Charge redistribution and appearance of dipole moments in different situations. (a) Typical state of a kagome lattice at the 1/3 magnetization plateau which would be accompanied by spin-driven CDW. (b), (c) Dipole moments respectively in a diamond chain and in a saw-tooth (or delta-) chain. Figure (d) illustrates the appearence of a charged soliton on a domain wall in a saw-tooth chain. Notations are the same as in figure 5.

4. Currents or dipoles? Dynamic effects

We discussed above two possible nontrivial states of frustrated systems: the state with spontaneous orbital currents in the ground state and the state with charge redistribution and with dipole moments. According to equations (5) and (6) the choice of one or the other state is determined by the spin texture, characterized by corresponding spin correlation functions. If we have an ordered state, equations (5) and (6) tell us what would be the charge properties of corresponding states. However, in a quantum-mechanical treatment of an isolated triangle, for example, there should be no spontaneous breaking of any symmetry, but the ground state can be (and is) degenerate. Then we can choose a particular combination of the degenerate ground states such that the resulting state chosen would have one or the other nonzero average (we stress that it is true for one particular state). We already briefly discussed this above, and now we do so in more detail.

The solution for a triangle of spins $\frac{1}{2}$ with Heisenberg antiferromagnetic interaction is well known. The $2^3 = 8$ possible states are split into an upper quartet $S_{\rm tot} = \frac{3}{2}$, and the remaining four states belong to the ground state quartet with $S_{\rm tot} = \frac{1}{2}$ and with an extra double degeneracy, which is nothing other than the degenerate chirality $\chi = \pm 1$. At least one can choose the corresponding basis states so that they would be eigenstates of chirality:

$$|\chi = \pm 1, \uparrow\rangle = +\tfrac{1}{\sqrt{3}}(\downarrow\uparrow\uparrow + e^{2\pi\chi i/3}\uparrow\downarrow\uparrow + e^{4\pi\chi i/3}\uparrow\uparrow\downarrow)$$
$$|\chi = \pm 1, \downarrow\rangle = -\tfrac{1}{\sqrt{3}}(\uparrow\downarrow\downarrow + e^{2\pi\chi i/3}\downarrow\uparrow\downarrow + e^{4\pi\chi i/3}\downarrow\downarrow\uparrow). \quad (7)$$

But equally well we can choose as basis states of a triangle linear combinations of these states, such that these linear combinations would be real and T-even. And these states can be characterized by nonzero values of dipole moments.

There is an interesting and useful relation between these states and the operators describing them. We have the expression (5) for the current through the three-spin correlation function. Similarly, equation (6) gives the expression for the dipole moment from the middle of one edge to the opposite vertex (d_x in figure 7). But there is yet one more possibility: the state with a dipole moment in the y-direction (figure 7). The expressions for d_x and d_y are

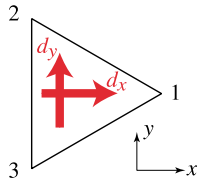

Figure 7. Possible directions of dipole moments, or electric polarization, for a triangle, see equation (8).

$$d_x = 4\sqrt{3}ea\left(\frac{t}{U}\right)^3 [\boldsymbol{S}_1 \cdot (\boldsymbol{S}_2 + \boldsymbol{S}_3) - 2\boldsymbol{S}_2 \cdot \boldsymbol{S}_3],$$
$$d_y = 12ea\left(\frac{t}{U}\right)^3 \boldsymbol{S}_1 \cdot (\boldsymbol{S}_2 - \boldsymbol{S}_3). \quad (8)$$

The first one is in fact equation (6), and the second can be obtained analogously. From equations (5) and (8) one can check that three operators, d_x, d_y and I, can be combined into one pseudospin $T = \frac{1}{2}$:

$$d_x = -CT^x, \qquad d_y = CT^y, \qquad \frac{\hbar a}{U} I = CT^z \quad (9)$$

where $C = 12\sqrt{3}ea(t/U)^3$. This also follows from the fact that doubly degenerate chirality states again, as was discussed above in treating the case of tetrahedra, belong to the E_g representation. One can choose the states to be eigenstates of current and chirality: in our notation the states with $T^z = \pm\frac{1}{2}$ are complex and magnetic. Or we can choose real states—eigenstates of $d_x \sim T^x$ or $d_y \sim T^y$, which would be the

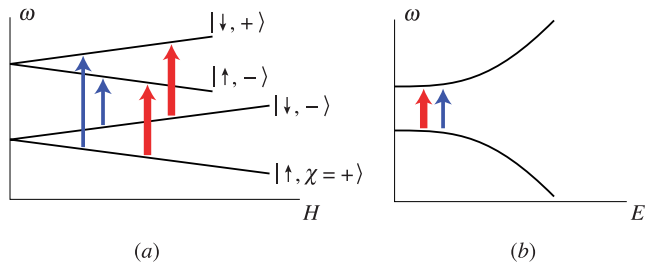

Figure 8. Schematic explanation of an ordinary ESR (thin blue arrows) and of a novel electric-induced dipole-allowed transitions (thick red arrows) in an external magnetic field (case (a), the usual ESR) and in an external electric field, case (b).

states with charge redistribution and with corresponding dipole moments. Thus for a triangle the complex states with currents correspond to magnetic dipoles (nonzero orbital moments), and real combinations—to electric dipoles. As we have argued above, for tetrahedra the corresponding complex states would give magnetic octupoles, and by analogy with Jahn–Teller systems (e_g electrons [12]) the real states (eigenstates of T^x and T^y) would give *electric quadrupoles* (one can easily check this directly from the exact solution for tetrahedra [10]).

One very important consequence is immediately seen from this. If we take states with definite chirality, i.e. eigenstates of T^z with $|T^z = \pm\frac{1}{2}\rangle$, operators T^x and T^y will have nondiagonal matrix elements in this basis. But T^x and T^y are dipole moments! This means that $\langle T^z = \frac{1}{2}\,|\boldsymbol{d}|\,T^z = -\frac{1}{2}\rangle \neq 0$, or that there will be dipole-allowed transitions between states with opposite chirality, $\langle \chi = +\,|\boldsymbol{d}\cdot\boldsymbol{E}|\,\chi = -\rangle \neq 0$. This was also noticed recently in [16].

This result immediately leads to many consequences. Thus because of that the low-lying magnetic states in this case would contribute not only to the magnetic susceptibility $\chi(\boldsymbol{q}, \omega)$, but also to the electric response function $\epsilon(\boldsymbol{q}, \omega)$. The fact that the same excitations contribute to both χ and ϵ leads to the existence of common poles in them, and close to these poles we would have a situation with both of them negative. This is the condition for having negative refraction, i.e. these system can be good candidates for metamaterials (of course the question of dissipation, or imaginary parts of χ and ϵ, remains).

One very spectacular and easy to understand consequence of the discussed results is the possibility of having dipole-allowed 'ESR' transitions. This is illustrated in figure 8, in which we show the ground state quartet levels of a triangle, where we have also included the often present antisymmetric (Dzyaloshinskii–Moriya) exchange $\boldsymbol{D}[\boldsymbol{S}_i \times \boldsymbol{S}_j]$, with the Dzyaloshinskii vector $\boldsymbol{D}$ perpendicular to the plane of the triangle (see e.g. the case of the V_{15} molecule [17]). This interaction splits the ground state quartet into two doublets, with $|S^z = \uparrow, \chi = +\rangle$, $|S^z = \downarrow, \chi = -\rangle$ and $|S^z = \uparrow, \chi = -\rangle$, $|S^z = \downarrow, \chi = +\rangle$. In ordinary ESR a magnetic component of ac field causes transitions with $\Delta S^z = \pm 1$ (thin blue arrows in figure 8(*a*)). However, if we put such a triangle into the point of a resonator where the ac magnetic field is zero but the electric field is maximum, there will be dipole-allowed transitions between the states with the same S^z, but with opposite chiralities (thick red arrows in figure 8(*a*)). Interestingly, in an external electric field these transitions coincide (figure 8(*b*)).

The estimates show [1] that the intensities of these 'electric' transitions should be in general comparable to those of the usual ESR. Such experiments would probably be the most direct test of the obtained results. The best objects could probably be some magnetic molecules with triangles of transition metal ions, such as V_{15} (for which all the parameters are known [17], and which even exist as single crystals).

5. Other possible effects

In conclusion I will briefly discuss some other possible consequences of the results presented above. The first is the possible anomalies in some other properties, e.g. the transport properties of such systems. One related effect is now well known and widely studied experimentally, namely the intrinsic (or Berry-phase) mechanism of the anomalous Hall effect in magnetic systems [18]. It is known to exist in systems with noncoplanar magnetic structures and with nonzero scalar spin chirality. However, corresponding studies were done on metallic systems, whereas we dealt above with strong Mott insulators. What the corresponding effects will be in this case is as yet unclear.

A related problem is the possibility of having time-reversal-broken states in high-T_c cuprates due to the formation of spontaneous orbital currents [19]. Again, one sees definite parallels with the physics discussed above (spontaneous currents on triangles, current as a primary order parameter), and again the treatment of [19] concerns metallic systems. Thus the question arises: what is the relation of our current states in insulators [1] and corresponding states in metals? The theoretical problem is how the results presented above would change if we slowly dope our frustrated Mott insulators. This question is now under investigation.

Yet another interesting possibility, a spin-off of the discussed physics, was suggested in recent works [16, 8]. The authors considered the possibility of using double degenerate chirality, described by pseudospin $T = \frac{1}{2}$, as a qubit instead of an ordinary spin $\frac{1}{2}$. From the results presented above we now know what corresponding states mean physically and how to control them: the states with $|\chi = \pm\rangle$ are magnetic, with nonzero orbital moment L^z, which can be addressed by a magnetic field, and an electric field can cause transitions between them. Moreover, we can think here not only of a binary but of a 'quaternary' logic, four relevant states being $|S = \pm\frac{1}{2}, \chi = \pm\rangle$. This is as yet only a theoretical suggestion, but it seems that it can be implemented in practice.

6. Conclusions

Summarizing, I want to repeat that, as we have seen, there may exist unexpected and quite nontrivial charge effects in strong Mott insulators—systems which were always thought to be electrically 'dead' (at least when undoped). We have shown that in case of geometric frustrations there may appear states with spontaneous electric currents, or, for other spin textures, there may occur a spontaneous charge redistribution, with

the formation of electric dipole moments and eventually even ferroelectricity. This is a novel, purely electronic mechanism of multiferroic behaviour. There are also many dynamic consequences of the proposed physics, such as the contribution of magnetic excitations not only to the magnetic but also to the electric response of the system, or a possibility of dipole-allowed ESR transitions ('electric ESR').

In many of these effects, an important role is played by the scalar spin chirality—the notion often invoked previously in different contexts, but the physical meaning of which remained somewhat obscure. We now know that nonzero chirality on a triangle means that there is a real electric orbital current, and corresponding orbital moment, on such a triangle. This shows that one can address and control such states by external magnetic and electric fields. This in principle can open the possibility of using chirality as a qubit instead of spin, or even create four-state logic. But probably most important is a conceptual realization that there may be very interesting and quite nontrivial charge effects in good strong Mott insulators.

Acknowledgments

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