Jahn–Teller distortions and the magnetic order in the perovskite manganites

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Abstract
We introduce an effective model for eg electrons to describe three-dimensional perovskite (La1−xSrxCa1−ydMnO3) manganites and study the magnetic and orbital order on a 4 × 4 × 4 cluster using correlated wavefunctions. The model includes the kinetic energy, and on-site Coulomb interactions for eg electrons, antiferromagnetic superexchange interaction between \( S = \frac{3}{2} \) core spins, and the coupling between eg electrons and Jahn–Teller modes. The model reproduces the experimentally observed magnetic order: (i) an A-type antiferromagnetic phase in the undoped insulator LaMnO3, with alternating eg orbitals and with small Jahn–Teller distortions, changing to a conducting phase at 32 GPa pressure, and (ii) ferromagnetic order in one-eighth-doped La7/8Sr1/8MnO3 and in quarter-doped La3/4Sr1/4MnO3 compounds. For half-doped La1/2Ca1/2MnO3 one finds a competition between a ferromagnetic conductor and the CE insulating phase; the latter is stabilized by the Jahn–Teller coupling being two times larger than for the strontium-doped compound. Altogether, there is a subtle balance between all Hamiltonian parameters and the phase diagram is quite sensitive to the precise values they take.

1. Introduction

Much effort has been put into understanding what is going on in doped perovskite manganese oxides both on the theoretical [1–14] and the experimental [14–26] sides. Early expectations that simple physical mechanisms, such as involving for example only Jahn–Teller (JT) interactions and Hund’s exchange but without Coulomb interaction, or pure electronic Coulomb interactions while neglecting Hund’s exchange, could explain the phase diagram and the phase transitions observed in the manganites were not confirmed [1, 8]. Also relatively early it was realized that the core \( t_{2g} \) electrons, even if dynamically passive, play an essential role for the stability of magnetic and orbital order [4, 11]. Altogether, the evidence has accumulated that there is a delicate balance between several competing physical mechanisms which lead to a rather complex phase diagram of the perovskite manganites [1, 11, 13].

Investigation of doped manganites is challenging as the Jahn–Teller distortions may lead to charge order which will also favour particular orbital order [1, 27]. To make the complex situation in doped manganites tractable in the theory, several theoretical papers were focused in the past on single-layer and double-layer manganites as the description of quasi-two-dimensional (2D) systems was simpler than the one necessary for three-dimensional (3D) doped perovskite manganites (see for example [11] and the references therein). Realistic 3D systems were more difficult to tackle at least on a better basis than simple mean-field type approaches. Due to strong local correlations, however, such approaches were not quite appropriate to provide a better insight into the competition between different possible physical mechanisms present in these strongly correlated electron systems. The present paper is one attempt (among the others) to fill this gap.

Similar to model studies [5, 11], it has also been recognized in the electronic structure calculations performed within the local density approximation (LDA) that the local interactions are important and one has to use either LDA + U or LDA + DMFT [12, 28], i.e., take into account also the dynamical aspects in the dynamical mean-field theory. These calculations confirmed the earlier point of view [5, 29] that electron–electron interactions and the Jahn–Teller terms...
support each other and both are necessary to reproduce the observed orbital order in the undoped compound. In particular, by studying the effect of pressure it was concluded that LaMnO$_3$ is not a Mott–Hubbard insulator, but rather a Jahn–Teller insulator, however, it has been recognized that the correlations also play an important role [28].

The paper is organized as follows. First, we introduce (in section 2) a realistic model for eg electrons in the perovskite manganites which includes the electron Coulomb interactions, the coupling between eg electrons with s = 1/2 spins and t$_{2g}$ core S = 3/2 spins, superexchange interaction, and the interactions of eg electrons with local distortions due to the Jahn–Teller terms (section 2.1). In this section we also present the method to determine approximate ground states using a 4 × 4 × 4 cluster. We treat electron correlation effects in the ground state beyond the Hartree–Fock (HF) approximation using the so-called local approach (section 2.2). The numerical results are presented and analysed in section 3. Here we address the question of which values of the parameters of the effective Hamiltonian are appropriate to account for the experimentally observed situation and present results obtained for the undoped LaMnO$_3$, and for La$_{1-x}$Sr$_x$MnO$_3$ at doping levels x = 0.125, 0.25 and 0.50. Finally, section 4 contains a short summary of the paper and general conclusions.

2. The model and calculation method

2.1. The model for eg electrons

We study strongly correlated electrons in undoped and doped 3D perovskite manganites La$_{1-x}$Sr$_x$MnO$_3$ (or La$_{1-x}$Ca$_x$MnO$_3$) using an effective model describing only Mn sites renormalized by surrounding oxygens. At each site we consider Wannier orbitals of the eg character composed out of manganese and oxygen orbitals [12]. One of them is filled at Mn$^{3+}$ ions, and both are empty at Mn$^{4+}$ ions in a doped system. In both cases the t$_{2g}$ orbitals on Mn ions are occupied by three ‘core’ electrons with total spin S = 3/2 (treated as frozen and classical). Thus the active electrons here are only eg electrons. We investigate the system by using a model Hamiltonian

\begin{equation}
H = H_{\text{kin}} + H_{\text{int}} + H_{\text{spin}} + H_{JT}
\end{equation}

which consists of the kinetic energy, the on-site Coulomb interactions, spin interactions, and the Jahn–Teller term. This model and/or the essential parts of it, were studied earlier by several groups, see [1, 7, 8, 11–13, 19, 30–33].

The kinetic part $H_{\text{kin}}$ is expressed using a local eg orbital basis at each site, which reads in short notation,

\begin{equation}
|z\rangle \equiv (3z^2 - r^2)/\sqrt{6}, \quad |x\rangle \equiv (x^2 - y^2)/\sqrt{2}.
\end{equation}

Using this local eg orbital basis at each site one finds anisotropic phase-dependent hopping [8, 11, 12]

\begin{equation}
H_{\text{kin}} = -\frac{1}{\varepsilon_0} \sum_{i} \sum_{\langle ij \rangle \neq \langle ab \rangle, \sigma} \left\{ (3d_{i\sigma}^\dagger d_{j\sigma} + d_{i\sigma}^\dagger d_{j\sigma}) + \sqrt{3}(d_{i\sigma}^\dagger d_{j\sigma} + d_{i\sigma}^\dagger d_{j\sigma}) \right\} - t_0 \sum_{\langle ij \rangle \neq \langle ab \rangle, \sigma} d_{i\sigma}^\dagger d_{j\sigma}.
\end{equation}

Here $d_{i\sigma}^\dagger$ are creation operators for an electron in orbital $\mu = x, z$ with spin $\sigma = \uparrow, \downarrow$ at site $i$. The $\langle i, j \rangle$ runs over pairs of nearest neighbours and gives two contributions for each bond $\langle i, j \rangle$; $\pm$ is interpreted as plus sign for the bond $\langle i, j \rangle$ being parallel to the crystal axis $a$ and minus for the bond $\langle i, j \rangle$ parallel to the axis $b$. (The crystallographic axis $c$ is assumed to be aligned with the Cartesian z-axis.)

The $H_{\text{int}}$ and $H_{\text{spin}}$ terms follow from the Coulomb interactions within a degenerate d band [34]: these terms are

\begin{equation}
H_{\text{int}} = U_0 \sum_{i} n_{i\uparrow} n_{i\downarrow} + (U_0 - \frac{1}{2}J_{\text{HF}}) \sum_{i} n_{i\uparrow} n_{i\downarrow},
\end{equation}

\begin{equation}
H_{\text{spin}} = -\frac{1}{2}J_{\text{HF}} \sum_{i} (n_{i\uparrow} - n_{i\downarrow}^\dagger)(n_{i\downarrow} - n_{i\uparrow}^\dagger)
- \frac{1}{2}J_{\text{HF}} \sum_{\langle ij \rangle} S_i^\dagger S_j^\dagger + \frac{1}{2}J_{\text{HF}} \sum_{\langle ij \rangle} S_i^\dagger S_j^\dagger.
\end{equation}

Here $H_{\text{int}}$ describes the charge interactions within the eg subsystem and plays a role in doped manganites. The spin interactions $H_{\text{spin}}$ include the leading part of Hund’s exchange $J_{\text{HF}}$, both between two eg electrons at the same site, and between $s = 1/2$ spin of a single eg electron and the $S = 3/2$ core t$_{2g}$ spin at each site. On-site intraorbital Coulomb interaction is denoted as $U_0$, and the interorbital Coulomb interaction is a linear combination of this term and Hund’s exchange $J_{\text{HF}}$ [34]. Note that we include here only the leading Ising part of Hund’s interaction terms, which is an approximation. However, within the present method using the correlated wavefunctions which are obtained by correcting the wavefunctions found in the HF approximation, the remaining transverse terms do not contribute, compare [32, 33]. The term $\propto J'$ is the antiferromagnetic (AF) superexchange generated by charge excitations of t$_{2g}$ electrons, which lead to AF Heisenberg interaction between frozen core t$_{2g}$ electrons [8, 12, 29]. This frozen core approximation for $S = 3/2$ core spins works well for the description of the ground state properties as shown by earlier studies, see e.g. [11, 35].

Finally, the Jahn–Teller $H_{JT}$ part is [1, 7, 13, 36, 37]:

\begin{equation}
H_{JT} = \sum_{i} \left\{ g_{\text{JT}}(Q_{ii}(n_{i\uparrow} + n_{i\downarrow}) + Q_{2i}^\dagger \tau_{i\uparrow}^\dagger + Q_{3i}^\dagger \tau_{i\downarrow}^\dagger) + \frac{K}{2}(Q_{ii}^2 + Q_{2i}^2 + Q_{3i}^2) \right\},
\end{equation}

and includes three different Jahn–Teller modes $(Q_{ii}, Q_{2i}, Q_{3i})$ at each site. The operators $\tau_{i\sigma}^\dagger$ in $H_{JT}$ are constructed for $\tau = 1/2$ orbital pseudospin for eg electrons at site $i$ [1, 8, 11–13],

\begin{equation}
\tau_{i\uparrow}^\dagger \equiv \sum_{\alpha} (d_{i\alpha\sigma}^\dagger d_{i\alpha\sigma} + d_{i\alpha\sigma}^\dagger d_{i\alpha\sigma}),
\end{equation}

\begin{equation}
\tau_{i\downarrow}^\dagger \equiv \sum_{\alpha} (d_{i\alpha\sigma}^\dagger d_{i\alpha\sigma} - d_{i\alpha\sigma}^\dagger d_{i\alpha\sigma}),
\end{equation}

while $Q_{ii}$, $Q_{2i}$ and $Q_{3i}$ denote the active Jahn–Teller deformation modes of the $i$th octahedron. (For simplicity the harmonic constant of the isotropic Jahn–Teller (breathing) mode $Q_{ii}$ is assumed to be double with respect to those corresponding to $Q_{2i}$ and $Q_{3i}$ antisymmetric modes as discussed in [11]. The breathing mode is quite often neglected in the effective models for the perovskite manganites, and plays no
role in the undoped system. As we are dealing here with doped systems, we decided to keep it to investigate its consequences.

The crystal field splitting between $z$ and $x$ orbitals (2) was assumed to be zero (this approximation seems reasonable in quasi-cubic 3D manganites [13] though some authors [12] assume instead small finite values). Below we describe the numerical simulations performed on finite 3D clusters with the above model (1). The variants of the described model reproduced the observed sequence of magnetic phases for increasing hole doping in 2D monolayer and bilayer manganites [32, 33].

2.2. Cluster approach including electron correlations

We studied $4 \times 4 \times 4$ clusters with periodic boundary conditions (PBC) filled by different number of $e_g$ electrons, corresponding to the undoped LaMnO$_3$ system, and to systems with doping of one-eighth ($x = 0.125$), one-quarter ($x = 0.25$) and a half ($x = 0.5$). All calculations were performed at zero temperature ($T = 0$ K). First, the calculations within the single-determinant HF approximation were performed to determine the ground state wavefunction $|\Phi_0\rangle$. Also the energetic distance $\Delta$ between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) (HOMO–LUMO gap) was extracted at this step.

In the next step each HF wavefunction was independently modified to improve the energy and to include the electron correlations using the so-called local ansatz (for details see [30–33]). We used the ansatz for the correlated ground state,

$$|\Psi\rangle = \exp \left( \sum_i \eta_i O_i \right) |\Phi_0\rangle,$$

where $\{\eta_i\}$ are variational parameters, and $\{O_i\}$ is a set of local correlation operators. These operators include the leading local density–density correlations in the present model for the perovskite manganites, in analogy to the 2D layered manganites, see [32, 33]. These local operators used in the present model correspond to the subselction of the most important two electron excitations within the ab initio configuration–interaction method. The variational parameters $\{\eta_i\}$ were found by minimizing the total energy

$$E_{tot} = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle}.$$

In this way the correlation energy,

$$E_{corr} = E_{tot} - E_{HF},$$

was obtained.

Coming to technical details, in the first step HF computations were performed for each considered electron filling, starting from one of several different initial conditions (about a thousand for each set of Hamiltonian parameters), i.e., from predefined (some symmetric but mostly random) charge distribution, spin configuration, the latter selected from eight predefined patterns of core $t_{2g}$ spins (see figure 1 of [33]), and from several predefined sets of classical variables $\{Q_1, Q_{2l}, Q_3\}$. For each fixed set of the starting parameters and starting initial conditions on convergence we obtained a HF wavefunction which was a candidate for the ground state wavefunction. This self-consistent procedure was performed to provide energy minimum also with respect to the $\{Q_1, Q_{2l}, Q_3\}$ classical variables [32, 33].

After completing the HF computations we performed correlation computations (as a second step for each investigated wavefunction) obtaining the total energy (9) and the correlation energy (10) (for more details see [30–32]). After obtaining the total energy for one configuration, we repeated the entire procedure from the beginning, i.e., we took another (second) set of HF initial conditions and repeated all computations to obtain the second candidate for the ground state. Similarly for the third, fourth, . . . , etc, set of initial conditions. Finally, the resulting set of total energies was inspected and the lowest one was identified as a good candidate for the true ground state.

3. Numerical results

As the parameters of the model (1) are known only with certain accuracy, the computations were repeated for many sets of the Hamiltonian parameters. The values of the parameters which one should consider as realistic for La$_{1-x}$(Sr,Ca)$_x$O$_3$ were extensively discussed in the literature (for a review in the context of the present paper see [1, 11, 32, 33]). Following the standard parameter sets [32, 33], we assumed that $t_0 = 0.4$ eV and the intraorbital Coulomb element is limited in the range $5 < U/t_0 < 12$. The values of Hund’s exchange are larger than $t_0$ [9, 29, 38], and we considered $t_0 < J_H < 2t_0$. The Jahn–Teller constant $K$ was fixed as $K = 13$ eV Å$^{-2}$ [1, 2, 30, 32, 39]. Not much is known about the value of the coupling constant $g_{JT}$, therefore following discussion in [1] we assumed that $2$ eV Å$^{-1} < g_{JT} < 3.7$ eV Å$^{-1}$. And, finally, following the recommendation of [13, 29] we use the experimental value of the Néel temperature in CaMnO$_3$ [40], where $e_g$ electrons are absent and the isotropic superexchange between core $t_{2g}$ spins follows solely from the excitations of $t_{2g}$ electrons, to fix $J' = 3$ meV. Thus we have three fixed and three free parameters.

The aim was to identify the set (or sets) of these three free parameters which lead to good agreement of the model predictions with experimental data. This task turned out to be rather difficult especially with respect to the Jahn–Teller parameter $g_{JT}$. Actually almost all values of $g_{JT}$ either yield conducting state for both $x = 0.125$ and 0.25 doping levels, or they yield an insulator, also for both above doping levels. This contradicts the experimental situation as La$_{1-x}$Sr$_x$MnO$_3$ manganite is weakly insulating for $x = 0.125$ and conducting for $x = 0.250$ [41]. This insulator-to-metal transition turned out to be very useful as it allowed us to fix all three free parameters. The values of the parameters which can bring out the agreement with the experimental data form a small isolated region within the parameter space, and finding them required making hundreds of scans through the parameter space. We have found that only for $U/t_0 = 8$, $J_H = 0.7$ eV and $g_{JT} = 2.2$ eV Å$^{-1}$ are we able to reproduce the experimental results.
Table 1. Hartree–Fock energies $E_{\text{HF}}$ and total ground state energies $E_{\text{tot}} (9)$, both in eV, as obtained for a $4 \times 4 \times 4$ cluster versus the doping $x$. Parameters of the Hamiltonian: $t_0 = 0.4$ eV, $U = 8t_0$, $J_H = 0.7$ eV, $K = 13$ eV $\AA^{-1}$, $g = 2.2$ eV $\AA^{-1}$, $J' = 3$ meV.

| $x$  | $E_{\text{HF}}$ | $E_{\text{tot}}$ |
|------|-----------------|-----------------|
| 0.000| -96.016         | -96.114         |
| 0.125| -88.217         | -88.315         |
| 0.250| -79.374         | -79.521         |
| 0.500| -58.666         | -58.896         |

3.1. Undoped LaMnO$_3$

The insulating phase in LaMnO$_3$ was reproduced by the present calculations. For the magnetic order we obtained robust A-AF structure, which has ferromagnetic (FM) order in $ab$ planes, coupled by AF interaction in the $c$ direction. This phase is almost generic and can be reproduced on the phase diagram for many sets of Hamiltonian parameters. Moreover, the correlation energy is small (see table 1) and does not change the magnetic and orbital order obtained from the HF wavefunctions. To give an example, let us show one 2D section of our simplified phase diagram. Note that as long as we ignore the global structural distortion of the lattice below that structural phase transition, all cubic directions are equivalent and A-AF order shown in figure 1 applies also e.g. to FM order in $ac$ planes accompanied by the AF coupling along the $b$ direction.

As already mentioned, the experimental data on conductivity fix the electron interaction parameters $U/t_0 = 8$ and $J_H = 0.7$ eV, as well as $g_{RT} = 2.2$ eV $\AA^{-1}$. For these parameters the ground state ordering for LaMnO$_3$ is shown in figure 2. The Jahn–Teller $Q_2$, and $Q_3$ distortions measured in [23] (at $T = 200$ K) are only roughly in agreement with our results. (Note that for simplicity the cubic Jahn–Teller terms [7, 13] in $H_{\text{JT}}$ were omitted. Therefore, the Jahn–Teller distortions obtained are only estimations rather than precise values.)

We have found a large HOMO–LUMO gap $\Delta$ for LaMnO$_3$ which is an indicator that the obtained A-AF phase is insulating, see figure 3. It is known that at a pressure of 32 GPa LaMnO$_3$ becomes conducting [42]. In order to investigate the effect of pressure we followed the heuristic arguments presented in [43]—it has been argued there (see figure 2 in [43]) that the effect of 32 GPa pressure can be reproduced in a model similar to our effective model (1) when $t_0$ and $K$ Hamiltonian parameters are renormalized in the following way: $t_0 \rightarrow 1.4t_0$ and $K \rightarrow 3.3K$. Following [43], the other parameters (of the model) were left unchanged. We note that this assumption is somewhat unrealistic as at least the superexchange $J'$ would also increase under pressure, but this effect is not important as long as we investigate the ground state and the magnetic structure does not change. $U_0$ and other effective parameters of the Hamiltonian should also show some limited variation under increasing pressure.
Inserting the new renormalized values of hopping and Jahn–Teller constant into our computations we found that the high pressure phase is indeed a conductor and we could identify the conducting phase as a perfect charge homogeneous, FM phase with zero Jahn–Teller distortions and with perfect half-to-half \((x^2 - y^2)\) and \((3z^2 - r^2)\) orbital electron density on each individual site. This orbital liquid state occurs in the doped FM manganites under normal pressure \([44]\).

To provide better evidence for such a prediction we plotted the HOMO–LUMO gap \(\Delta\) for increasing pressure. For simplicity it was assumed that \(t_0(p)\) and \(K(p)\), where \(p\) denotes pressure, vary linearly from \(t_0\) and \(K\) at \(p = 0\) to 1.4\(t_0\) and 3.3\(K\) at \(p = 32\) GPa. Anyway, the transition from insulating to conducting phase can be deduced from figure 3 and it occurs around \(p \approx \) 30 GPa where the gap becomes small enough, \(\Delta \approx 0.1\) eV. Note that in the present finite cluster one finds always a gap between HOMO and LUMO, but we have estimated that \(\Delta \approx 0.1\) eV would correspond to a metallic ground state in the bulk. To close the discussion on LaMnO\(_3\) under pressure let us mention \([45]\) where magnetic and orbital order under uniaxial strain (only JT modes were pressure-renormalized) was studied by using a similar (to our) Hamiltonian.

### 3.2. One-eighth-doped \(\text{La}_{0.875}\text{Sr}_{0.125}\text{MnO}_3\)

In one-eighth-doped manganite one finds an insulating phase with FM order, both in the HF and for the correlated wavefunctions. The correlation energy is small, see table 1, and does not change the magnetic and charge order in the system. The breathing mode Jahn–Teller distortions are small and uniform, \(Q_{ji} \approx -0.08\) Å. This phase is characterized by a rather interesting charge and orbital distribution, with a distinct alternation in charge density between even and odd planes. Consequently, this phase is an insulator, in agreement with the experiment \([41]\), though a weak one as indicated by rather small HOMO–LUMO gap shown in figure 4 (curve in the middle, squares). Note that the gap is reduced by a factor close to 3 from the value obtained for LaMnO\(_3\).

The alternation of \(e_g\) electron density occurs between even and odd planes. First, in even numbered planes there are somewhat fewer electrons and the orbitals are of \((x^2 - y^2)\) character, \(Q_{2j} \approx 0\) and \(Q_{3j}\) take the value of \(-0.1\) Å. These distortions favour the \(x\) orbitals. However, there are also some exceptions, i.e., occasionally on a site we find the \((3z^2 - r^2)\) orbital occupied and \(Q_{3j} \approx +0.1\) Å. The charges are distributed in a slightly non-homogeneous way, with the site to site variations of charge being at most \(0.2e\). Second, in the odd numbered planes one finds a little larger average charge density per site than in the even planes and almost homogeneous charge distribution. In contrast to the even planes, one finds predominantly \((3z^2 - r^2)\) orbitals occupied. The Jahn–Teller distortions are \(Q_{2j} \approx \pm0.1\) Å and \(Q_{3j} \approx \pm0.1\) Å. Again, we have seen also some exceptions, with \(x\) orbitals occupied at a few sites and the corresponding modified Jahn–Teller distortions, similar to those in the even planes. In fact, this result shows that sites with differently occupied orbitals can proliferate between the even and odd planes and form charge and orbital defects in each plane. This shows that the inhomogeneous charge distribution is a generic feature in this range of doping.

### 3.3. Quarter-doped \(\text{La}_{0.75}\text{Sr}_{0.25}\text{MnO}_3\)

Also for quarter-doped manganites, such as \(\text{La}_{0.75}\text{Sr}_{0.25}\text{MnO}_3\), one finds FM order and weakly non-homogeneous charge distribution with the present parameters (see figure 5). These results are similar to the ground state found for \(x = 0.125\)—we have found again nonequivalent alternating planes, as described below. The correlations do not change this result, and are again weak (table 1) as the local moments have formed and the main effects are already captured in the HF approach.

On the one hand, within even numbered planes in the ground state one has weak charge order in the form of a stripe phase, with vertical or horizontal charge-minority lines alternating with charge-majority lines (charge difference of about \(0.2e\)). Charge-minority sites have mixed half-to-half \(x\) and \(z\) orbital occupancy and negligible Jahn–Teller distortions, which is characteristic for the orbital liquid in the metallic
Figure 5. Magnetic A-AF, charge and orbital order for eg electrons as obtained in quarter-doped manganates, $x = 0.25$. Four single ab planes (perpendicular to the c axis) extracted from the $4 \times 4 \times 4$ cluster are shown. Core $t_{2g}$ spins are not shown; their directions agree with higher electron density (i.e., those with $z$ orbitals and with negligible $Q_{1i}$, $Q_{2i}$) distortions, whereas $Q_{2i} \approx -0.13 \text{ Å}$. The other half of these sites carries the mixture of $z$ and $x$ roughly in proportion $2:1$ and negligible $Q_{2i}$ distortions, whereas $Q_{2i} \approx -0.13 \text{ Å}$. These sites with higher electron density (i.e., those with $x$ orbitals and those with $2:1$ orbitals $z$ and $x$) alternate along the charge-majority lines.

On the other hand, on odd numbered planes the orbitals and Jahn–Teller distortions are much the same as the ones on even numbered planes (as described above). However there is a difference—along charge-minority lines (each second line in the cluster) we did not find homogeneous charge density but, instead alternating charge-minority and charge-majority sites.

The FM phase at $x = 0.25$ doping should be a metal which follows from quite small HOMO–LUMO gap ($\Delta \approx 0.1 \text{ eV}$), see figure 4. This result agrees with the phase diagram for the perovskite manganites [1, 46].

### 3.4. Half-doped La$_{0.5}$Sr$_{0.5}$MnO$_3$—stability of the CE phase

Surprisingly, for half-doped La$_{0.5}$Sr$_{0.5}$MnO$_3$ one finds again almost the same ground state as for $x = 0.25$, namely FM spin order, accompanied by weakly non-homogeneous charge distribution and a conducting phase (HOMO–LUMO gap is about 0.12 eV). The ratio of $x$ to $z$ orbitals on each site is half-to-half, while the Jahn–Teller interactions are very small. These findings reproduce the experimental situation in La$_{0.5}$Sr$_{0.5}$MnO$_3$, where no CE phase was observed.

On the contrary, the CE phase was found in half-doped La$_{0.5}$Ca$_{0.5}$MnO$_3$ [47, 48]. A somewhat imprecise but still common point of view is that a manganite doped with strontium is more metallic than the manganite doped with calcium (more insulating) which in turn might be attributed to weaker coupling to the lattice by the Jahn–Teller interactions in strontium compounds and a larger role of these interactions in calcium compounds. Indeed, the FM phase was found insulating in a broader range of doping in La$_{1-x}$Ca$_x$MnO$_3$ than in La$_{1-x}$Sr$_x$MnO$_3$ [49]. If this is the case then our effective model should provide a different prediction for the ground state when $g_{JT}$ is larger.

When we discussed the precise values of Hamiltonian parameters following the discussion presented in [1] we assumed $2 \text{ eV Å}^{-1} < g_{JT} < 3.7 \text{ eV Å}^{-1}$. Then for strontium manganite La$_{1-x}$Sr$_x$MnO$_3$ we found that $g_{JT} = 2.2 \text{ eV Å}^{-1}$. Now for the sake of the ongoing discussion for calcium doped manganite we will accept $g_{JT} = 3.7 \text{ eV Å}^{-1}$, the largest value which is allowed. This change of the unique parameter immediately provides us with the expected result. Now the spin order in the ground state is indeed in the form of FM zig-zags with AF order between them, characteristic for the CE phase, and the charge order is of checkerboard type (figure 6). The CE phase is quite robust, it is identified at the HF level and the correlations when added do not change this result. This is in contrast to what happens in bilayer half-doped manganites where the correlations stabilize the CE phase [33]. We note, however, that the magnetic moments are larger in the 3D system, and therefore the role of electron correlations in the magnetic states such as the CE phase is reduced.

### 3.5. Switching off Jahn–Teller distortions

The results presented up to now indicate the importance of Jahn–Teller interactions. Due to them local distortions are created at each doping level, and they influence both the electronic structure and the magnetic properties. It seems that the value of $g_{JT}$ coupling is the primary factor which determines whether the 3D perovskite system is a conductor...
that all these interactions enter on equal footing and seem to be essential for a correct interpretation of the experimental data. Indeed, we have performed also calculations with several sets ignoring one or other interaction term, and the results were very unsatisfactory in all cases, i.e., such simplified models were not able to reproduce the experimental observations.

We would like to emphasize that the realistic Jahn–Teller coupling plays a rather special and a very important role in the manganites as it controls the conductivity of the perovskite 3D systems. We have presented evidence that this interaction generates local distortions in the entire investigated range of hole doping $0.125 \lesssim x \lesssim 0.50$ which leads to charge inhomogeneities, defects in the orbital occupancy, and influences the magnetic order. Such states have been seen before in the experimental data on doped manganites [50] and were also suggested to follow from the theoretical models [51]. Unfortunately, reliable studies of systems with charge disorder and local distortions are very difficult to perform, but the present results demonstrate that these states might decide about the colossal magnetoresistance and select one or the other type of magnetic order. Particularly at half-doping ($x = 0.5$) we have found a subtle balance between the FM phase and the CE phase, the latter stabilized by large Jahn–Teller interactions. This is not surprising as the nearest neighbor JT coupling might not be sufficient to stabilize the observed zigzag FM chains in the CE phase for the realistic parameters. The mechanism invoked in [52] to stabilize the CE phase is subtle and employs the cooperative JT interaction between next-nearest $\text{Mn}^{3+}$ neighbors mediated by the breathing mode distortion of $\text{Mn}^{4+}$ octahedra and displacements of $\text{Mn}^{2+}$ ions.

As found before for monolayer and bilayer doped manganites, see [30, 32], we have obtained many metastable ground states in the 3D system which are possible in principle. Such states are not discussed in detail in the present paper, but we just point out that they represent local energy minima and could be also realized at finite temperature. Therefore, the search for the best candidate for the true ground state requires examination of numerous phases with different kinds of non-homogeneous charge distribution. Therefore, we suggest as a general conclusion that non-homogeneous charge distribution is a generic feature of the doped perovskite manganites. It follows that the theoretical predictions which are based on models assuming just a few $a$ priori selected candidates for the ground state (especially the ones with high symmetry of charge or orbital order) cannot be fully conclusive unless they are based on reliable experimental data.

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