Mean-Field Approach to Charge, Orbital, and Spin Ordering in Manganites

Sudhakar Yarlagadda and C. S. Ting
Texas Center for Superconductivity, University of Houston, TX 77204-5932
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We present a mean-field theory of charge, orbital, and spin ordering in manganites at 50% and 0% dopings by considering Jahn-Teller interaction, nearest-neighbor repulsion, and no single-site double occupancy. For spinless fermions, we show that Jahn-Teller distortion and charge-orbital ordering occur simultaneously. In our two-dimensional model at 50% doping, for small nearest-neighbor repulsion the system is orbitally polarized while for larger repulsion the system undergoes CE type ordering. As for the 0% doping case, the ground state is orbitally antiferromagnetic. Upon including spin degree of freedom, at both 50% and 0% dopings the ordering remains the same at small antiferromagnetic coupling between adjacent core spins.

Manganites of the form $A_{1-x}B_xMnO_3$ (with $A=$La, Pr, etc; $B=$Ca, Sr, etc) display a rich variety of phenomena and phases as the doping $x$ is varied [1]. In particular close to 0% doping the systems display orbital ordering at higher temperatures while at lower temperatures magnetic ordering results [2]. In narrow band materials like $Pr_{0.5}Ca_{0.5}MnO_3$ as the temperature is lowered to $T_{CO}$ the system undergoes CE type charge-orbital (CO) ordering and at a much lower temperature $T_N$ peculiar antiferromagnetic (AF) order sets in [3,4] (see Fig. 1). In wider band materials like $Nd_{0.5}Sr_{0.5}MnO_3$ ferromagnetic ordering occurs at higher temperatures and at lower temperatures simultaneous charge, orbital, and spin (AF) ordering results [5,6]. In layered-perovskites like $La_{0.5}Sr_{1.5}MnO_4$ it has been reported that $T_{CO}$ is higher than $T_N$ [5]. In systems where $T_{CO}$ and $T_N$ coincide, Solovyev and Terakura argue that the CO-ordering is a result of the peculiar AF ordering along with Hund’s rule physics [7]. van den Brink et al. too analyze systems like $Nd_{0.5}Sr_{0.5}MnO_4$ and find that because of a topological factor in the hopping, the one-dimensional ferromagnetic zigzag chains are orbitally ordered [8]. However Refs. [9,10] do not include electron-phonon interaction physics nor do they consider narrow band systems like $Pr_{0.5}Ca_{0.5}MnO_3$. Evidence of significant change in lattice parameters has been reported at $T_{CO}$ for $Pr_{1-x}Ca_xMnO_3$ (at $x=0.4, 0.5$) [9] and in $La_{0.5}Ca_{0.5}MnO_3$ [11].

In this paper we derive a general framework for analyzing the concomitant charge density wave (CDW) and orbital density wave (ODW) instability by considering Jahn-Teller interactions and showing that the two-dimensional (2D) ordering can be understood in terms of the one-dimensional (1D) Kohn anomaly at wavevector $q=2k_F$. The problem essentially reduces to comparing the energy resulting from the hopping term for various possible ordered states. We show that Jahn-Teller distortion is accompanied by CO-ordering for the carriers. We find that above a critical value of nearest-neighbor repulsion and for small antiferromagnetic coupling between adjacent core spins, CE type charge, orbital, and spin (COS) ordering is realized at 50% doping. At 0% doping orbital antiferromagnetic order results.

We first study the ordering phenomena without spin degree of freedom because $T_{CO}$ is higher than $T_N$. We begin by considering CDW instability for a 1D Holstein model given below:

$$H = -t \sum_{\langle ij \rangle} a_{i}^\dagger a_{j} + \sum_{\vec{q}} \omega_0 f_{\vec{q}}^\dagger f_{\vec{q}} + \frac{A}{\sqrt{N}} \sum_{\vec{q},\vec{k}} a_{\vec{k}+\vec{q}}^\dagger a_{\vec{k}} (f_{\vec{q}}^\dagger + f_{-\vec{q}}^\dagger),$$

(1)

where $a_j$ ($f_{\vec{q}}$) is the electron (phonon) destruction operator, $\langle \langle ij \rangle \rangle$ corresponds to nearest neighbors, $\omega_0$ is the optical phonon frequency ($\hbar=1$), $A(0<0)$ is the electron-phonon coupling, $t$ is the hopping integral, and $N$ is the number of sites. We know that in 1D the non-interacting polaronizability $\chi_0(\vec{q})$ (Lindhard polarizability) diverges at wavevector $q=2k_F$. Then even in the weak-coupling limit we will have a CDW instability because the expectation value $\langle \sum_\vec{q} a_{\vec{k}+\vec{q}}^\dagger a_{\vec{k}} \rangle$ diverges in the interaction part of the Hamiltonian. Furthermore, upon calculating the double derivative with respect to time of the ionic position coordinate $Q_{\vec{q}} = \sqrt{1/(2M\omega_0)}(f_{\vec{q}} + f_{-\vec{q}}^\dagger)$ by using the relation $\dot{Q}_{\vec{q}} = -[(Q_{\vec{q}}, H), H]$ we get $\dot{Q}_{\vec{q}} = -\omega_0^2 Q_{\vec{q}} - 2A^2 \omega_0 \chi_0(\vec{q}) Q_{\vec{q}}$. Thus we see that the renormalized phonon frequency becomes soft even for vanishingly small electron-phonon interaction leading to lattice distortion. The order parameter for the CDW state is $\langle f_{\vec{q}} \rangle = \Delta_{\vec{q}} e^{i\phi_{\vec{q}}}$, Then within mean-field we get from Eq. (1), after averaging over phonon coordinates, the following (see Ref. [11] for CDW in metals):

$$\tilde{H} = -t \sum_{\langle ij \rangle} a_{i}^\dagger a_{j} + \sum_{j} \omega_0 \Delta_j^2 + 2A \sum_{j} a_{j}^\dagger a_{j} \Delta_j \cos \phi_j.$$  (2)

The energy in the above equation is minimized for $\phi_j = 0$ and for $\omega_0 \Delta_j = -A(a_{j}^\dagger a_{j})$. 

71.45.Lr, 71.38.+i, 75.10.-b
We will now proceed for the CDW state at half-filling, using $\Delta_j = \Delta_0/2 + \Delta_1 \cos(\pi j)$. We first note that $\Delta_0 = -A/\omega_0$ and that $\Delta_1 \leq \Delta_0/2$. Next we add the nearest-neighbor interaction term $V_{NN} = V \sum_{j,j'} n_j n_{j'} \delta$ with $\delta$ being nearest-neighbors and make the mean-field approximation $n_j n_{j+1} = n_j (n_{j+1} - \langle n_{j+1} \rangle n_j)$. Then the Hamiltonian in momentum space, on folding the Brillouin zone, gets modified to be

$$H = \sum_j [H_k + H_{k+\pi} + 2AB_+ \Delta_1 (a_{k+\pi}^\dagger a_k + H.c.)] + \omega_0 N(B_- \Delta_0^2/4 + B_+ \Delta_1^2),$$

where $H_k \equiv (-2t \cos k + AB_+ \Delta_0) a_{k}^\dagger a_k$, $B_\pm = 1 \pm zV\omega_0/A^2$ with $z$ being the coordination number, and the reduced Brillouin zone is $-\pi/2 \leq k \leq \pi/2$. Then diagonalizing the above Hamiltonian yields the eigen energies $E_k^\pm = AB_+ \Delta_0 \pm \sqrt{4t^2 \cos^2 k + 4A^2 B_+^2 \Delta_1^2}$. Upon minimizing the total energy with respect to $\Delta_1$ we get the optimum $\Delta_1 \approx -A/(2\omega_0) \left[ 1 - (\lambda/B_\pm)^2 + 1/4(\lambda/B_\pm)^4 \right]$ for small values of $\lambda/B_\pm$. Then the minimized energy per particle is $-A^2/\omega_0 \left[ 1 + \lambda^2/B_\pm^2 - \lambda^4/(4B_\pm^4) \right]$ where the last two terms involving $\lambda$ represent the hopping term energy. We see that including nearest-neighbor interactions does not alter the results qualitatively although it enhances the charge modulation.

We will now proceed to consider manganite systems with two orbitals per site. The Hamiltonian consists of three parts $H = H_1 + H_2 + H_3$ where $H_1$ is the hopping term, $H_2$ the ionic term, and $H_3$ the electron interaction term. The hopping term is given by $-t \sum_{(ij)} e_i^j e_j^i$ where $(ij)$ corresponds to nearest-neighbors in the $\alpha(=x,y,or, z)$ direction and $e$ is the destruction operator of the orbital $\psi_{2s+1/2}$. Here it should be mentioned that for propagation in the $x$-direction the orbital basis is $\psi_{3x^2-r^2}$ and $\psi_{y^2-z^2}$ for $y$-direction it is $\psi_{3y^2-r^2}$ and $\psi_{x^2-y^2}$.

To analyze the ordering problem, we consider the orthonormal wavefunctions $\psi_{X,Y} = \frac{1}{\sqrt{6}}(\sqrt{3} + 1)\psi_{3x^2-r^2} + (\sqrt{3} - 1)\psi_{3y^2-z^2}$ for which will be given below. The interaction term in this basis is given by

$$H_3 = A \sqrt{2} M \omega_0 \sum_j [Q_{2j} (a_{Xj}^\dagger a_{Xj} - a_{Yj}^\dagger a_{Yj}) + Q_{3j} (a_{Xj}^\dagger a_{Yj} + a_{Yj}^\dagger a_{Xj})],$$

where $a_{Xj}$ and $a_{Yj}$ are the destruction operators of the electrons in $\psi_X$ and $\psi_Y$ orbitals at site $j$, with $Q_2$ and $Q_3$ corresponding to the two normal modes. The ionic part of the Hamiltonian is then given by

$$H_2 = \frac{K}{2} \sum_j (Q_{2j}^2 + Q_{3j}^2) + \frac{M}{2} \sum_j (Q_{2j}^2 + Q_{3j}^2).$$

We further enforce that at most only one orbital can be occupied at each site by setting $\langle a_{Xj}^\dagger a_{Xj} \rangle \langle a_{Yj}^\dagger a_{Yj} \rangle = 0$.

We study the problem in 2D (say the xy-plane) and observe that the overlap between $\psi_X$ and $\psi_{3x^2-r^2}$ is greater than 96.6% and $\langle \psi_X \psi_{3y^2-z^2} \rangle = \langle \psi_Y \psi_{3y^2-z^2} \rangle$. Hence based on the hopping term of the Hamiltonian, to bring out the essential physics, we approximate $H_1$ to be

$$H_1 \approx -2t \sum_k \left[ \cos k_x a_{Xk}^\dagger a_{Xk} + \cos k_y a_{Yk}^\dagger a_{Yk} \right].$$

The 50% doping case will be first considered. In $H_3$ we note that $\langle \sum_k a_{Xk}^\dagger a_{Xk} - a_{Yk}^\dagger a_{Yk} \rangle$ diverges at $q = \bar{Q} / 2 = [\pi/2, \pi/2]$ for the orbitally unpolarized case and at $q = [\pi, ...]$ or $q = [..., \pi]$ for the orbitally polarized case leading to a concomitant CDW and ODW instability with the phonon frequency corresponding to $Q_{2\bar{Q}}$ going soft. To see this transparently we first recognize that for the electrons in the $\psi_X (\psi_Y)$ orbitals the dispersion relation is like the 1D case due to which the Fermi sea is rectangular with $-\pi/4 \leq k_x (k_y) \leq \pi/4$ and $-\pi \leq k_y (k_x) \leq \pi$ for the orbitally unpolarized case. Hence, the Lindhard polarizability diverges at $[2k_x F, ...]$ and $[..., 2k_F]$ for $\psi_X$ and $\psi_Y$ electrons respectively. As for the orbitally polarized case, on choosing $\psi_Y$ orbitals with loss of generality, the Fermi sea is given by $-\pi/2 \leq k_y \leq \pi/2; -\pi \leq k_x \leq \pi$ and thus the non-interacting polarizability is singular at $[2k_F, ...]$. Furthermore $\langle \sum_k a_{Xk}^\dagger a_{Xk} - a_{Yk}^\dagger a_{Yk} \rangle$ is similar to the longitudinal (transverse) spin susceptibility in a Hubbard model with $\psi_X$ and $\psi_Y$ orbitals standing for up and down spins. Thus the system, to lower its energy, prefers $H_3$ to be diagonal in the $\psi_X$ and $\psi_Y$ orbital basis with only $Q_2$ mode getting excited at all sites. The Hamiltonian after averaging over the phonon coordinates yields the following two-orbital 2D version of Eq. (2) with optimum values of $\phi_j$ and $\Delta_j$:

$$H = -2t \sum_k \left[ \cos k_x a_{Xk}^\dagger a_{Xk} + \cos k_y a_{Yk}^\dagger a_{Yk} \right]$$

$$-\frac{A^2}{\omega_0} \sum_j (a_{Xj}^\dagger a_{Xj} - a_{Yj}^\dagger a_{Yj}) (a_{Xj}^\dagger a_{Xj} - a_{Yj}^\dagger a_{Yj})$$

$$+ \frac{A^2}{\omega_0} \sum_j (a_{Xj}^\dagger a_{Xj} - a_{Yj}^\dagger a_{Yj})^2.$$
\[ \langle a^\dagger_{xj} a_{xj} + a^\dagger_{yj} a_{yj} \rangle = \cos^2(\vec{Q}/2 \cdot \vec{R}_j). \]

We next introduce nearest-neighbor interaction \( V_{NN} \) and note that \( \langle n_j \rangle \langle n_{j+\delta} \rangle = 0 \) and thus the CDW is also compatible with nearest-neighbor repulsion. Then taking \( C = -1 \) without loss of generality, the total Hamiltonian is

\[
\hat{H} = \sum_{k,x,y} \sum_{n=0}^{3} H_n^{(x,y)} \hat{a}^\dagger_{x,y} \hat{a}_{x,y} + \frac{4}{\omega_0} \hat{a}^\dagger_{x,y} \hat{a}_{x,y} + \frac{1}{2} \left( \sin^2(k_x(x,y)) + \frac{B_-}{B_+} \right),
\]

where the momentum summation, for \( \psi_{X(Y)} \) electrons, is over the reduced Brillouin zone \(-\pi/4 \leq k_x(x,y) \leq \pi/4; -\pi \leq k_y(x,y) \leq \pi \) and

\[
H_n^{(x,y)} \equiv [-2t \cos(k_x + V_z)a^\dagger_{x,y} \hat{a}_{x,y} - (+) \Delta \alpha \left[ a^\dagger_{x,y} \hat{a}_{x,y} + (+) \eta \right] + \frac{1}{2} \sin^2(k_x(x,y)) \] \( \cos^2(k_y(x,y)) = 0 \).

We diagonalize the Hamiltonian in Eq. (3) to obtain

\[
\eta_{n}^{x,y} = \begin{cases} 
4V^{2}z^{2} - \Delta^{2} \delta_{0} - t^{2} & \text{if } n \text{ is even,} \\
4V^{2}z^{2} - \Delta^{2} \delta_{0} & \text{if } n \text{ is odd,}
\end{cases}
\]

where \( \eta_{n}^{x,y} \equiv E_{n}^{(x,y)} - 2Vz \) with \( E_{n}^{(x,y)} \) being the eigen energies for \( \psi_{X(Y)} \) electrons. Treating \( \lambda \) as a small parameter we obtain after some algebra the following expressions for the lowest energies

\[
E_{n}^{(x,y)} = -\frac{\lambda^{2}}{4B_{+}} \left( 2 + \frac{\sin^2(2k_x(x,y)) + B_-}{B_+} \right),
\]

where terms of order \( t \delta^5 \) or higher are neglected. On filling up the lowest band we obtain the energy per particle to be

\[
-\frac{\lambda^{2}}{\omega_0} \left[ 1 + \frac{\lambda^{2}/B_+ - \lambda^{2}/(4B_{+}^{2})}{1/2 + B_-/B_+} \right].
\]

As for the orbitally polarized case, the order parameter is given by \( \Delta_j = \Delta_0/2 + \Delta_1 \cos(\vec{Q} \cdot \vec{R}_j) \) and the problem is similar to the 1D one-orbital case. On choosing the \( \psi_{y} \) orbitals to be occupied, the reduced Brillouin zone is \(-\pi/2 \leq k_y \leq \pi/2; -\pi \leq k_x \leq \pi \). Then the minimized energy per particle is, as before,

\[
-\frac{\lambda^{2}}{\omega_0} \left[ 1 + \frac{\lambda^{2}/B_+ - \lambda^{2}/(4B_{+}^{2})}{1/2 + B_-/B_+} \right].
\]

It is of interest to note that for small nearest-neighbor repulsion \( V \), the energy of the orbitally polarized state is lower than that of the orbitally unpolarized state while for \( Vz > A^{2}/\omega_0 \) it is higher than that of the CE type state.

We will now consider the 0% doping case. Here we get an ODW instability at \( \vec{q} = \vec{Q} \) leading to an orbitally antiferromagnetic state. The reduced Brillouin zone for \( \psi_{X(Y)} \) orbital is \(-\pi/2 \leq k_y(k_x) \leq \pi/2; -\pi \leq k_y(k_x) \leq \pi \). The ground state energy per particle when \( \lambda \) is a small parameter is obtained to be

\[
Vz - A^{2}/\omega_0 \left[ 1 + \lambda^{2}/2 - 3\lambda^{4}/32 \right].
\]

As for the orbitally polarized case, the energy per particle is \(-A^{2}/\omega_0 + Vz \). Thus we see that the energy for the orbitally unpolarized case is lower than that for the orbitally polarized case at 0% doping.

We will now include spin degree of freedom and analyze the magnetic ordering that results from the CO-ordering derived above. We consider antiferromagnetic spin coupling between adjacent localized core spins of the form

\[
\frac{1}{2} \sum_{i \neq j} \bar{S}_i \cdot \bar{S}_j (J > 0 \text{ and } S = 3/2) \text{ and an infinitely strong Hund’s coupling between itinerant electrons and localized spins. Then in the Hamiltonian, the kinetic energy becomes } -\frac{1}{2} \sum_{[ij]} \cos(\theta_{ij}/2) \left[ \hat{a}^\dagger_{X,Y} \hat{a}_{X,Y} + \hat{a}^\dagger_{Y,X} \hat{a}_{Y,X} \right] \text{ where } [ij] \text{ are nearest-neighbors in the x(y)-direction for } \psi_{x(y)} \text{ orbital electrons, } \theta_{ij} \text{ is the angle between adjacent core spins } \bar{S}_i \text{ that are treated classically. As for the 2D two orbital case at 50% doping, for a CE type magnetic ordering we get the same expectation value for the kinetic energy because } \theta_{ij} = 0 \text{ when an electron in the } \psi_{x(y)} \text{ orbital tries to jump to the next unoccupied orbital in the x-(y-) direction (see Fig. 1).}

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[14] One can expect the observed stacking of like orbitals in the z-direction (see Ref. [3]) when antiferromagnetic coupling energy compensates for the nearest-neighbor repulsion in this direction.
[15] At 50% doping, in the absence of spin effects, for the exact kinetic energy term $-t \sum_{\langle ij \rangle} \epsilon_i^\uparrow \epsilon_j^\downarrow$, ordered state of $d_{x^2-y^2}$ orbitals has the lowest energy. However upon introducing spin effects, for sufficiently large $J$, the orbitally ordered state with $d_{x^2-y^2}$ orbitals (or $\psi_X$ orbitals in our approximation) is more favorable.

FIG. 1. CE ordering in x-y plane. Exaggerated $Q_2$ distortion is shown by the dash-dot line and the zig-zag ferromagnetic chains by dashed lines. The $Mn^{3+}$ sites are depicted by $\Psi_{X,Y}$ orbitals and core spins, the $Mn^{4+}$ sites by only core spins, and the oxygen sites by $\bigcirc$.

FIG. 2. Orbitally polarized state in x-y plane. Exaggerated $Q_2$ distortion is shown by the dash-dot line and the ferromagnetic chains by dashed lines. The $Mn^{3+}$ sites are depicted by $\Psi_Y$ orbitals and core spins, the $Mn^{4+}$ sites by only core spins, and the oxygen sites by $\bigcirc$.

FIG. 3. Phase diagram for the 50% doping case in 2D.
$\lambda = 0.25$

- AF ORDER
- ORB. POL.
- Ferro. Chains
- AF Coupled

$64JS^2 \omega_0 / A^2$

$Vz \omega_0 / A^2$