Ordered states of Manganite and Dynamical mean-field theory

Young Il Joe

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Abstract

Pure $LaMnO_3$ is an insulator. But, when doped with appropriate amount of doubly valenced impurities, it becomes a conductor retaining the ferromagnetism. Notion of double exchange has been devised to explain this phenomena. Along with this ferromagnetic conductivity, manganites show a variety of physical properties. Some of spin, charge, and orbital orderings are illustrated. Neutron scattering and electron diffraction is useful tool investigate the spin and charge ordered state of manganites. Also, resonance X-ray scattering can give a direct evidence of orbital orderings. Some aspect of Dynamical mean field theory is presented. In some sense, it has a analogue to classical mean-field theory. But it retinas the local fluctuation. This formalism is applied to the colossal magneto-resistance of manganite.

Manganite Manganese compounds of $AMnO_3$ $(A = \mathrm{La, Ca, Ba, Sr, Pb, Nd, Pr})$ have a perovskite structure. Depending of composition of A ions, manganites show a variety of electrical and magnetic properties, including magnetic, charge, orbital orderings, and metal-insulator transition. If A is all trivalent ions such as La, all of manganese ions are Mn^{3+}. If A is all divalent ions such Sr, all of manganese ions are Mn^{4+}. If A is the composition of trivalent and divalent ions, both of Mn^{3+} and Mn^{4+} are present. Recently, it's been shown that its electrical conductivity has a large dependence on the external magnetic fields. These are also know as colossal magneto-resistance(CMR).

Double Exchange One of remarkable attempt to understand doped manganites is the Double exchange mechanism. Zener propose this exchange mechanism in 1951. This still remain the core understanding of manganese these days. We know that the electronic structures are mostly determined by the d-orbital of Mn. In the presence of the cubic crystal field, the degenerate d-orbitals split into t_2 and e_{2g} orbitals. And it is believed that the Hund's exchange energy is large enough that all electrons in the e_{2g} orbital are aligned and form a $S = 3/2$ states. e_2g orbital is hybridized with oxygen 2p orbital. In doped manganites, Mn^{3+} and Mn^{4+} ions coexist and following two configurations are degenerate

$$\psi_1 : \mathrm{Mn^{3+}O^{2-}M^{4+}} \text{ and } \psi_2 : \mathrm{Mn^{3+}O^{2-}M^{4+}}$$

The transfer matrix between these two states is due to the simultaneous electrons transition from Mn^{3+} to O^{2-} and from O^{2-} to MN^{4+}. Because the strong Hund's exchange interaction, ferromagnetic configuration can lower the hopping energies. In this core electrons' ferromagnetic configuration, ψ_1 and ψ_2 are mixed and give a mechanism for the ferromagnetic conductivity.

Kubo and Otaha(1972) gave a complete double exchange treatment, Starting with following Hamiltonian

$$H = -J \sum_{i,\sigma,\sigma'} \left(\mathbf{S}_i \cdot \sigma_{\sigma,\sigma'}\right) c^{\dagger}_{i\sigma} c_{i\sigma'} + \sum_{i,j,\sigma} t_{ij} c^{\dagger}_{i\sigma} c_{j\sigma}$$

, where $c^{\dagger}_{i\sigma}$, and $c_{i\sigma}$ are creation and annihilation operators for e_g electrons, t_{ij} is a transfer matrix, J is a intra-atomic exchange interaction, S_i is the spin due to the t_{2g} core electrons. They treat t_{ij} transfer elements, which is considered very small compared to J, as perturbation, and restrict the Hilbert space to the subspace with each electron spin has spin parallel to the localized spin. Effective Hamiltonian is the following

$$\sum_{i,j,\sigma,\sigma'} t_{ij} \left(1 -_{i-\sigma}\right) c^{\dagger}_{i\sigma} \left(P^{\dagger}_i P^{\dagger}_j\right)_{\sigma\sigma'} \left(1 - n_{j-\sigma}\right) c_{j\sigma'}$$

and

$$\left(P^{\dagger}_i\right)_{\sigma\sigma'} = \frac{\mathbf{S_i} \cdot \sigma_{\sigma\sigma'} + (S+1)\,\delta_{\sigma\sigma'}}{2S+1}$$

They applied the spin wave approximation to this model, and calculated the temperature dependence of resistivity and found that it is proportional to $T^{9/2}$.

$LaMnO_3$ and $CaMnO_3$ structures These are two end compounds. Manganese ions have 3+ valencies in $LaMnO_3$ and 4+ in $CaMnO_3$. $LaMnO_3$ is orthorhombic, and its space group is *Pnma*. Magnetic ground state is anti-ferromagnetic, and is often called A-type. All the moments in the same $a-c$ planes are aligned but the moments of adjacent $a-c$ planes anti-aligned. CaMnO3 is cubic and its space is *Pm3m*. At ground state, it is also anti-ferromagnetic. This states are composed of two interpenetrating face-centered cubic lattices with opposite spins.

Its strong on-site Coulomb repulsion, charge ordering has been expected. Fig 3 shows some of super-lattice peaks of $La_{0.5}Ca_{0.5}MnO_3$ along with fundamental Bragg peaks. This system has same number of Mn^{3+} and Mn^{4+} ions. The fundamental Bragg peaks are labeled by (a), (b), and (c). These are (2,0,0), (0,2,0), (1,1,0), respectively. It clearly shows (1/2, 0, 0), (0, 1/2, 0) super-lattice peaks. In the schematics, open circles represent Mn^{4+} and close circles represent Mn^{3+} ions.

Figure 2. shows that the integrated intensity of $LaMnO_3$ of (3,0,0) reflection and the fluorescence data. From the flourescence data, we can locate the K-absorption edge of Manganese ion. It is about 6.552 KeV. (3,0,0) reflection is forbidden, but this shows a sharp peak about 3eV above the K-absorption edge.

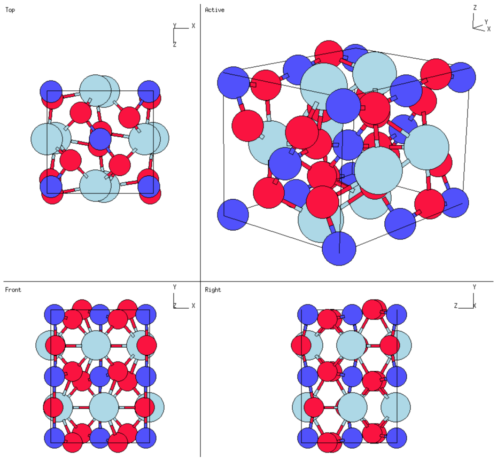

Figure 1: LaMnO^3
unit cell

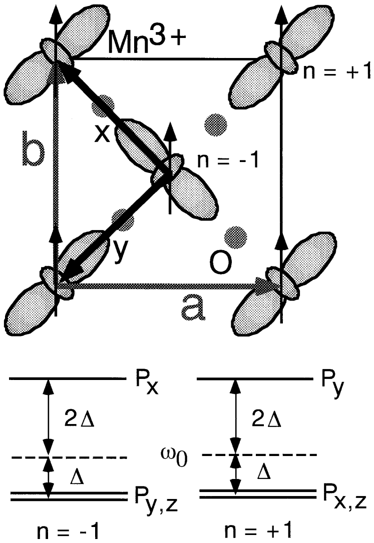

Figure 2: Orbital and Spin ordering of LaMnO$_3$ and energy level of Mn 4p orbital in ordered states.

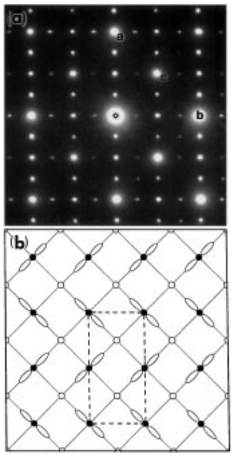

Figure 3: Electron diffraction image of $La_{0.5}Ca_{0.5}MnO_3$ and schematic of charge orderings

This can be explained by the resonance between 1s and 4p orbital through the dipole transition. Dipole transition to 3d orbital is allowed, but it is far below the K-absorption edge.

Colossal magnetoresistance Colossal magnetoresistance is the phenomenon of unusually large effect of external field on the electric resistivity. Initially discovered in 1993 by von Helmolt et al., these material has been intensely researched because of its potential use in the information technology. Magnetoresistance of conventional material is limited up to 5%. But the Colossal magnetoresistance material(usually magnates) have a order of magnitude change of resistivity. Depending on the magnitude, it is called either Giant magnetoresistance(GMR) or Colossal magnetoresistance(CMR). Because of its strong correlation of constituent particles, there is no unifying theory describing the physics of perovskite-like CMR materials.

Strongly Correlated System Materials with open d or f orbitals show some of properties that can not be explained by the band theory or self-consistent one-particle theory(e.g. Hartree Fock approximation). This is because the d and f orbitals are spatially confined, electrons in these orbitals experience strong Coulomb interaction with each other. This means that these strongly interacting electrons can not be described by the mean field theory, where each constituent particle experience the mean field generated by the all the particles in the system. In the mean field theory, all the correlation are averaged out, each particle moves independently in the mean field. At high temperature, with rapidly varying thermal fluctuation, this approximation usually gives a better results. But its applicability to the strongly correlated system is limited.

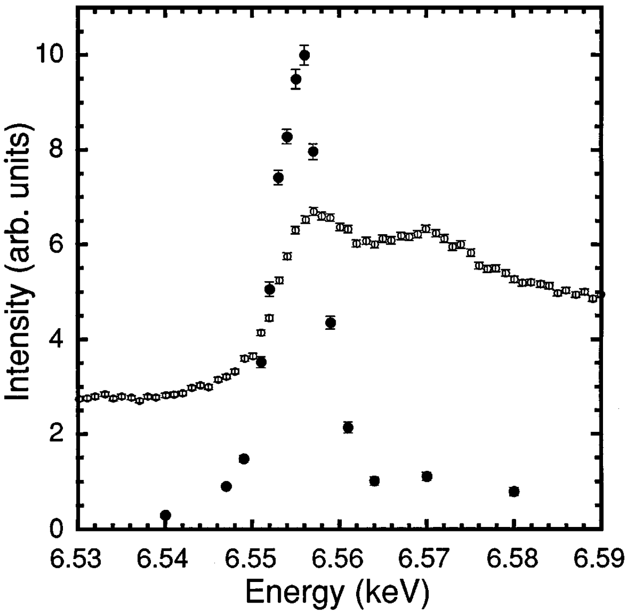

Figure 4: Closed circle indicates integrated intensity of (3,0,0) around K-absorption edge and open circles are flourescence

Dynamical Mean Field theory In Hartree-Fock approximation, Both of temporal and spatial fluctuation are "frozen out". But in some systems, without considering local fluctuation, we can't see the essential aspect of the system. In this sense, dynamical mean field theory is distinguished from the Hartree-Fock approximation. In DMF, the local fluctuations are taken into account to begin with. In this scheme, the single site is chosen, and we integrate out the all other parameter except those of that single site.

$$S_{\text{eff}} = -\int_0^\beta d\tau \int_0^\beta d\tau' \sum_\sigma c^\dagger_{o\sigma} \tau \mathcal{G}_0^{-1}\left(\tau - \tau'\right) c_{o\sigma}\left(\tau'\right) + U \int_0^\beta d\tau \ n_{0\uparrow}\left(\tau\right) n_{o\downarrow}\left(\tau\right)$$

$$G\left(\tau - \tau'\right) \equiv -\langle Tc\left(\tau\right) c^{\tau}\left(\tau'\right)\rangle_{S_{\mathbf{eff}}}$$

In contrary to the Weiss mean field theory, $\mathcal{G}_0^{-1}$ is a function of time instead of a single number. In the Weiss mean field theory, it is a just a effective magnetic field. this quantity is the equilibrium value of the microscopic magnetic field. This is the consequence of the fact that in the DMF, the local fluctuations are taken into account even though spatial fluctuation is integrated out. In close analogue to the Weiss mean field theory, the self consistency condition can be written as

$$\mathcal{G}\left(i\omega_n\right)^{-1} = i\omega_n + \mu + G\left(i\omega_n\right)^{-1} - R\left[G\left(i\omega_n\right)\right]$$

,where G is the local Green's function calculated from the effective action S_{eff}.

$$G\left(\tau - \tau'\right) \equiv -\langle Tc\left(\tau\right) c^\dagger\left(\tau'\right)\rangle_{S_{\text{eff}}}$$

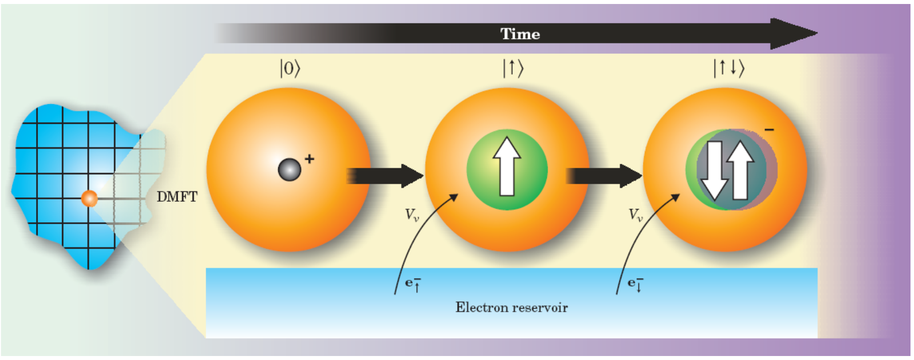

Figure 5: A single site is considered to be embedded in the electron reservoir, where the electron reservoir is described by a ”Weiss function” G^{-1}. Through the interaction with the reservoir, the state of singe site can change in time. All of its possible states are empty, spin-up, spin-down, doubly occupied states ($|0\rangle, |\uparrow\rangle, |\downarrow\rangle, |\uparrow\downarrow\rangle$)

and

$$G\left(i\omega_n\right) = \int_0^\beta G\left(\tau\right) e^{i\omega_n \tau}, \ \omega_n \equiv \frac{\left(2n+1\right)\pi}{\beta}$$

$R\left(G\right)$ is the reciprocal function of the Hilbert transform of the density of state of the lattice excluding the single site. if non-interacting density of state $D\left(\epsilon\right)$ is given,

$$D\left(\epsilon\right) = \sum_{\mathbf{k}} \delta\left(\epsilon - \epsilon_{\mathbf{k}}\right), \ \epsilon_{\mathbf{k}} \equiv \sum_{ij} t_{ij} e^{i\mathbf{k}\cdot\left(R_i - R_j\right)}$$

the Hilbert transforms and its reciprocal can be written as

$$\tilde{D}\left(\zeta\right) \equiv \int_{-\infty}^{\infty} \frac{D\left(\epsilon\right)}{\zeta - \epsilon}, \ R\left[\tilde{D}\left(\zeta\right)\right] = \zeta$$

Self-consistency condition The Hubbard model will be considered as an example here. It can be written as following

$$H = -\sum_{<ij>,\sigma} t_{ij}\left(c_{i\sigma}^\dagger c_{j\sigma} + c_{j\sigma}^\dagger c_{i\sigma}\right) + U\sum_i n_{i\uparrow} n_{i\downarrow}$$

The partition function of this model can be written as the functional integral over Grassman variables $c_i^\dagger$ and c_i.

$$Z = \int \prod_i D c_{i\sigma}^\dagger D c_{i\sigma} e^{-S}$$

$$S = \int_0^\beta d\tau \Big(\sum_{i\sigma} c_{i\sigma}^\dagger \partial_\tau c_{i\sigma} - \sum_{ij,\sigma} t_{ij} c_{i\sigma}^\dagger c_{j\sigma} - \mu \sum_{i\sigma} c_{i\sigma}^\dagger c_{i\sigma}$$

$$+U\sum_i n_{i\uparrow}n_{i\downarrow})$$

Integrating out over all the variables except $c^\dagger_{o\sigma}$ and $c_{o\sigma}$, effective action can be defined as

$$\frac{1}{Z_{\text{eff}}}e^{-S_{\text{eff}}}[c^\dagger_{o\sigma},c_{o\sigma}]\equiv=\frac{1}{Z}\int_{i\neq o}[dc^\dagger_{i\sigma}][dc_{i\sigma}]e^{-S}$$

Once we get the effective action S_{eff}, we can calculate the local correlation function of the original Hubbard model. Splitting the original action, $S = S^{(0)} + S_0 + \Delta S$, where S^0 is the action of the lattice excluding the single site, and

$$S_0=\int_0^\beta\sum_\sigma c^\dagger_{o\sigma}\left(\partial_\tau-\mu\right)c_{o\sigma}+Un_{o\uparrow}n_{o\downarrow}$$

$$\Delta S=-\int_0^\beta d\tau\sum_{i\sigma}t_{io}\left(c^\dagger_{i\sigma}c_{o\sigma}+c^\dagger c_{i\sigma}\right)$$

Thus, S_0 represents a free part of action of the single site, and ΔS represents the coupling between the single site and the rest of the system. In the limit of infinite dimensionality, this form can be simplified, because the coupling with the nearest neighbors are dominant.

$$\mathcal{G}_0^{-1}\left(i\omega_n\right)=i\omega_n+\mu-\sum_{ij}t_{oi}t_{oj}G^{(0)}_{ij}\left(i\omega_n\right)$$

, where $G^{(0)}_{ij}$ is a Green's function of Hubbard model with a single site removed. It has a following relation withe the original Hubbard model.

$$G^{(0)}_{ij}=G_{ij}-\frac{G_{io}G_{oj}}{G_{oo}}$$

Using the last two equations, we can compute the following

$$\sum_{ij}t_{io}t_{jo}G_{ij}-\left(\sum_i t_{io}G_{io}\right)^2/G_{oo}$$

Colossal magneto-resistance in manganite Millis and Shraiman(1996) showed that the colossal magneto-resistance of $\mathrm{La_{1-x}Sr_xMnO_3}$ is the consequence of the strong electron-phono coupling and double exchange effect. The phenomena of very large resistivity for $T > T_c$ and the sharp drop of resistivity below T_c cannot be explained by double exchange mechanism. Their argument is "For $T > T_c$, strong electron-coupling coupling localizes the conduction band electron as polarons, but the polaron effect is turned off as T is reduced below T_c, resulting in the metallic state"

$$H=H_{el}+H_{JT}$$

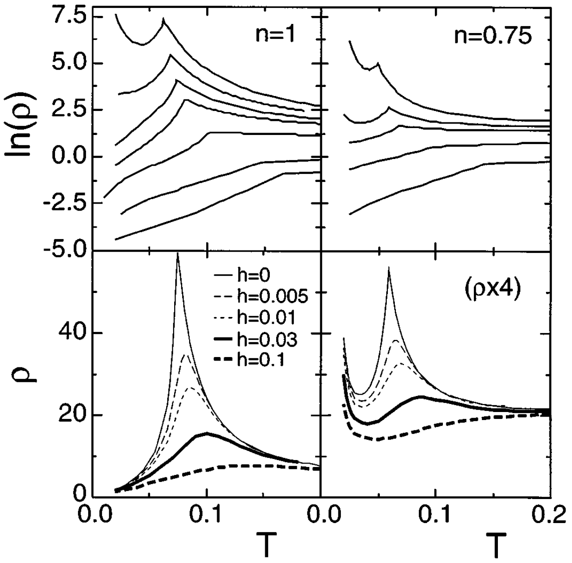

Figure 6: (Upper left) Resistivity calculated with different couplings $\lambda =$ 1.2(top), 1.12, 1.05, 0.95, 0.85, 0.71(bottom) (Lower left) Magnetic field dependence of resistivity. (Upper right) Resistivity calculated with different couplings $\lambda = 0.71$(bottom), 1.12, 1.41, 1.49, 1.58(top), (Lower right) Magnetic field dependence of resistivity.

$$H_{el} = -\sum_{ij\alpha} t_{ij}^{ab} d_{ia\alpha}^{\dagger} d_{jb\alpha} - J_H \sum_{i,a,\alpha} \mathbf{S}_c^i \cdot d_{ia\alpha}^{\dagger} \sigma d_{ia\alpha} + \sum_i \mathbf{h} \cdot \mathbf{S}_i$$

$$H_{JT} = g \sum_{ja\sigma} d_{ja\sigma}^{\dagger} Q^{ab}(j)\, d_{jb\sigma} + k \sum_j \left[Q^2(j) + \Pi^2(j)/2kM\right]$$

, where $d_{ia\sigma}$ is a creation operator for an outer-shell d electron of spin σ at i. "The local lattice distortions which cause the Jahn-Teller splitting transforms as a two fold degenerate representation of cubic group which we parameterize by a magnitude and an angle ϕ. They couple to the electron as a traceless symmetric matrix $Q = r\left[cos(\phi)\,\tau_z + sin(\phi)\,\tau_x\right]$." Taking $J_H \rightarrow \infty$ (because we are interest in high temperature phenomena) and treating the phonon and the core spin classically. Partition function can be written as

$$Z = \int r dr d\phi d\Omega exp[-tr^2/2T + \mathrm{Tr} ln\left(tG_{eff}^{-1} + \lambda \mathbf{r} \cdot \tau + J_H \mathbf{S_c} \cdot \sigma\right) + \mathbf{h} \cdot \mathbf{\Omega}].$$

, where $\mathbf{\Omega}$ is the unit vector along $\mathbf{S_c}$ and $t = D/4$ (D is a the bandwidth), and λ is a dimensionless electron-phonon coupling constant $\lambda = g/\sqrt{kt}$.

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