The Curie Temperature of the Double-Exchange Interaction Systems

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We performed a fully quantum-mechanical calculation on the double exchange interaction and found the eigenvalues and eigenstates for two sites and a hole. A mean-field calculations showed that the double exchange interaction can give correct range of T_C .

KEYWORDS: double exchange interaction, colossal magnetoresistance

Recently the $\text{La}_{1-x}\text{A}_x\text{MnO}_3$ (A represents a divalent element) system has attracted much attention because of the rich physics it contains. It has many phases, varying from antiferromagnetic to ferromagnetic, and again to antiferromagnetic or charge ordering, as the doping concentration x increases. Its transport properties also varies from phase to phase. Most noticeably is the colossal magnetoresistance (CMR) where the resistivity drops sharply around the paramagnetic-ferromagnetic transition. A review on experimental works can be found in ref. 1. Zener²⁾ proposed the double-exchange (DE) interaction as the underlying mechanism. Intuitively, it is easy to understand that the ferromagnetic order favors the motions of holes created by doping. However, according to Millis *et al.*'s^{3,4)} calculation, DE is inadequate to explain the behavior of resistivity near T_C . They proposed that the Jahn-Teller effect should be considered. There are also experimental evidences for that, for example, the isotope effect on the thermoelectric power.⁵⁾ A possibly related issue is the evidence of polaron formation.⁶⁾ On the other hand, Sheng⁷⁾ *et al.* proposed a explanation of CMR based on the localization theory. We acknowledge the importance of the Jahn-Teller effect though its importance decreases with increasing doping.⁸⁾ However, we believe that DE is the fundamental interaction in this kind of systems. Therefore, it is worthwhile to perform an in-depth study.

Based on the work of Anderson and Hasegawa,⁹⁾ De Gennes¹⁰⁾ constructed a classical-spin model and gave an extensive analysis of the properties of this system. His method was widely used till now. An important progress was made by Kubo and Ohata who developed a fully quantum-mechanical method for DE.¹¹⁾ More recently, Furukawa¹²⁾ and Millis *et al.*'s⁴⁾ infinite-dimension Kondo lattice model, Okabe's¹³⁾ trial wavefunction method and Sheng and Ting's¹⁴⁾ path-integral analysis are notable progresses. Our work was motivated by the puzzle that from a rough estimate, T_C given by DE is at least an order of magnitude greater than the experimental data,¹¹⁾ thus raising the issue that DE is inadequate or even not essential in the manganites. In fact, this issue had been addressed by several authors.¹⁵⁻¹⁷⁾ Here, we studied this problem from a different point of view. We agreed with Müller-Hartmann and Dagotto¹⁸⁾

that it is crucial to have a proper quantum mechanical treatment of the spin system. As it will be shown, our method is quite simple and transparent. It is hoped that our work will give a more direct physical understanding of the double-exchange interaction.

We used the Hamiltonian of ref. 11. In this system, Mn^{+3} ions have spin $S = 2$. Doping creates holes so that Mn^{+4} ions have spin $3/2$. We assume the intraatomic Coulomb interaction is strong enough so that the Hund's rules are strictly obeyed. Hence, we use the Hamiltonian developed by Kubo and Ohata.¹¹⁾ It describes the hopping of holes,

$$H = -t \sum_{i,j,\sigma,\sigma'} c_{i\sigma}^\dagger (P_i P_j)_{\sigma\sigma'} c_{j\sigma'}. \quad (1)$$

Considering the effect of the on-site Coulomb repulsion, the projection operator P is used to projects out the states in which the spins of holes are antiparallel to the local spins:

$$P_i = \frac{S - \mathbf{S}_i \cdot \boldsymbol{\sigma}}{2S + 1}. \quad (2)$$

Since each term of the Hamiltonian involves two sites, we study the system from the point of view of bonds instead of spins. Each bond consists of two local spins and a hole which can be at either site. If we at this moment neglect the interaction with surrounding spins then the eigenstate of the bond has the form

$$\frac{1}{\sqrt{2}} \left(\left| S_L = S, S_R = S - \frac{1}{2}, J, J_z \right\rangle \pm \left| S_L = S - \frac{1}{2}, S_R = S, J, J_z \right\rangle \right), \quad (3)$$

where the local spin has $S = 2$ and in the presence of a hole $3/2$, subscript $L(R)$ denotes the left (right) site and J and J_z are the total spin and its z -component. The $\pm$ sign is for either bonding or antibonding state. The eigenvalues have the form

$$E_j^\pm = \pm (-1)^{J-2S+1/2} \frac{2J+1}{4(2S+1)} t. \quad (4)$$

Above results were obtained with a lengthy procedure of manipulating Clebsch-Gordan coefficients. The easiest way to check may be writing

$$H = \sum_{i,j,\sigma,\sigma'} H_{i,j,\sigma,\sigma'} \quad (5)$$

where

$$\begin{aligned} H_{i,j,\sigma,\sigma'} = & -\frac{t}{2} c_{i\sigma}^\dagger c_{j\sigma'} \left[S^2 + \mathbf{S}_i \cdot \mathbf{S}_j \right. \\ & - \left(SS_{iz} + SS_{jz} + \frac{1}{2} S_i^- S_j^+ - \frac{1}{2} S_i^+ S_j^- \right) \sigma_z \\ & - (SS_i^- + SS_j^- - S_{iz} S_j^- + S_i^- S_{jz}) \frac{\sigma^+}{2} \\ & \left. - (SS_i^+ + SS_j^+ + S_{iz} S_j^+ - S_i^+ S_{jz}) \frac{\sigma^-}{2} \right] \\ & + H.c., \end{aligned} \quad (6)$$

then applying $H_{RL\sigma\sigma'}$ to the state of $J_z = J$ in eq. (3).

Having known this, we now are able to calculate the magnetization and susceptibility with Weiss's mean-field approximation. The goal is to find the Curie temperature. Though the mean-field approximation cannot yield accurate results, it can give, based on above fully quantum-mechanical calculation, the correct range of T_C . Note that the states in (3) are the linear combinations of $|S, M, S - 1/2, M'\rangle$ which, in turn, can be decomposed into

$$\begin{aligned} & \left| S, M, S - \frac{1}{2}, M' \right\rangle \\ & = \sqrt{\frac{S + M' + 1/2}{2S + 1}} |S, M, S, M' + 1/2\rangle |\beta\rangle \\ & - \sqrt{\frac{S - M' + 1/2}{2S + 1}} |S, M, S, M' - 1/2\rangle |\alpha\rangle, \end{aligned} \quad (7)$$

where $|\alpha\rangle$ and $|\beta\rangle$ are the spin-up and -down states of the hole. We shall use them as basis because it is easier to calculate the mean-field energy. The total energy of a bond is

$$E^*(J, J_z) = E_j^0 + E_{MF}(J, J_z). \quad (8)$$

E_j^0 is the lower energy in eq. (4). We are going to neglect the higher-energy states because they are not important in the temperature range we are interested in. The mean-field energy $E_{MF}(J, J_z)$ is calculated in the following way. Site L with spin-polarization M_L has $z-1$

nearest neighbors besides site R where z is the coordination number. For a neighboring bond between site L and site i at state $|J', J'_z\rangle$, its contribution to the mean-field energy is

$$\begin{aligned} E(J', J'_z, M_L) = & \sum_{M_i, \sigma'} [(\langle J', J'_z | S, M_L, S, M_i \rangle | \sigma'_L \rangle)^2 \\ & + (\langle J', J'_z | S, M_L, S, M_i \rangle | \sigma'_i \rangle)^2] E_{J'}^0, \end{aligned} \quad (9)$$

where σ_L is the hole-spin state at site L .

$$\begin{aligned} E_{MF}(J, J_z) = & \frac{(z-1)x}{3} \sum_{M_L, M_R} \sum_{J', J'_z} p(J', J'_z) \\ & \times [E(J', J'_z, M_L) + E(J', J'_z, M_R)] \\ & \times [(\langle J, J_z | S, M_L, S, M_R \rangle | \sigma_L \rangle)^2 \\ & + (\langle J, J_z | S, M_L, S, M_R \rangle | \sigma_R \rangle)^2], \end{aligned} \quad (10)$$

where the probability of finding a bond at state $|J, J_z\rangle$ is

$$p(J, J_z) = \frac{e^{-\beta[E^*(J, J_z) - g\mu_B \mathcal{H} J_z]}}{Z}, \quad (11)$$

with Z being the partition function and $\mathcal{H}$ is the external field.

The magnetization has the form:

$$M = -\frac{Ng\mu}{Z} \sum_{J, J_z} J_z \exp\{-\beta[E^*(J, J_z) - g\mu_B \mathcal{H} J_z]\}, \quad (12)$$

where N is the total number of local spins. The susceptibility

$$\begin{aligned} \chi = & \frac{\partial M}{\partial \mathcal{H}} \\ = & -Ng\mu_B \sum_{J, J_z} J_z \frac{\partial p(J, J_z)}{\partial \mathcal{H}} \Big|_{\mathcal{H}=0} \\ = & -N(g\mu_B)^2 \beta \sum_{J, J_z} J_z^2 p(J, J_z) \Big|_{\mathcal{H}=0} \\ & + Ng\mu_B \sum_{J, J_z, J', J'_z} J_z R_{J, J_z, J', J'_z} \frac{\partial p(J', J'_z)}{\partial \mathcal{H}}, \end{aligned} \quad (13)$$

where

$$\begin{aligned} R_{J, J_z, J', J'_z} = & \frac{\beta(z-1)x}{3} \sum_{M_L, M_R, \sigma} [(\langle J, J_z | S, M_L, S, M_R \rangle | \sigma_L \rangle)^2 + (\langle J, J_z | S, M_L, S, M_R \rangle | \sigma_R \rangle)^2] \\ & \times \{ \sum_{M_i, \sigma'} [(\langle J', J'_z | S, M_L, S, M_i \rangle | \sigma'_L \rangle)^2 + (\langle J', J'_z | S, M_L, S, M_i \rangle | \sigma'_i \rangle)^2] \\ & + \sum_{M_i, \sigma'} [(\langle J', J'_z | S, M_R, S, M_i \rangle | \sigma'_R \rangle)^2 + (\langle J', J'_z | S, M_R, S, M_i \rangle | \sigma'_i \rangle)^2] \} E_{J'}^0, \end{aligned} \quad (14)$$

is one of the element of matrix $\mathbf{R}$. T_C is the temperature at which χ diverges or that makes the least eigenvalue of $\mathbf{R}$ equal to minus unity.

The resulting T_C is almost linearly proportional to x ,

$$T_C \simeq 0.027xB \quad (15)$$

where $B = 2zt$ is the band width. If $x > 0.5$, then electrons become charge carriers, and hence, x in (15) should be replaced $1 - x$. According to band structure calculation⁸⁾ $B \simeq 2.5$ eV, thus at $x = 0.3$, $T_C \simeq 240^\circ\text{K}$. This is within the range of experimental results. In previous calculations,^{10, 11)}

$$T_C \simeq \frac{(2S-1)(4S+1)}{15S(2S+1)}xB \simeq \frac{4}{15}xB, \quad (16)$$

which is nearly an order of magnitude greater. There are several reasons why our calculation gives a better T_C . Most importantly, the coupling is reduced by a factor of $2S+1$, shown clearly by the form of eigenvalues in eq. (4). Another indication is that the spin wave energy is also reduced by this factor.¹¹⁾ The reason why this happens is that the larger the S , the more states there will be and hence, the more channels the holes can hop. Therefore, the difference in hopping energy due to the different relative local spin orientation is reduced. But previous calculations did not account for this. Secondly, the coupling between two adjacent local spins by spin-up holes and spin-down holes cannot be added. For example, a spin-up hole cannot couple two local up-spins. In fact, holes with different spin orientations tend to give different couplings to different local spins configurations. The resulting couplings are similar for different orientations, thus further reduces the eigenvalue difference. Therefore, even if adjacent local spins are not parallel to each other, the holes still have many channels for hopping. Their kinetic energies are not so seriously affected by the relative spin orientation. In fact, numerical calculation¹⁹⁾ also give evidence that DE is able to give T_C within the range of experimental results. Thus, we provided a direct and intuitively clear explanation to this issue.

Now we discuss the difference between our work and others. Furukawa¹⁵⁾ studied the double-exchange interaction with the Kondo lattice model with $S \rightarrow \infty$ and $d \rightarrow \infty$ where d is the dimension of the system. Our work is useful in that we had shown that the double-exchange interaction gives the correct T_C at S and d being finite. Varma¹⁶⁾ treated the spin-interaction classically (even though he introduced quantum spins in the calculation of entropy). This is quite different from our method. Furthermore, in his approach the conduction electrons move in a fixed local spin configuration. In our case, a conduction electron can alter the orientation of the lo-

cal spin by flipping its own spin. Our starting point is completely different. Röder¹⁷⁾ used a high temperature series expansion to calculate T_C . Their method is very complicated and time-consuming. Our method has the advantage of being simple and transparent. Although the works mentioned above all give correct range of T_C , our method provides an alternative point of view which is helpful to understand the double-exchange interaction.

In summary, we have solved DE for two sites and a hole and obtained the eigenvalues and eigenstates. A simple mean-field calculation shows that DE can give correct range of T_C . DE is the fundamental interaction in the manganite perovskite systems and it needs to be studied more.

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