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Quantum treatment of the Anderson–Hasegawa model in the presence of superexchange

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Abstract. We revisit the Anderson–Hasegawa double-exchange model and critically examine its exact solution when the core spins are treated quantum mechanically. We show that the quantum effects, in the presence of an additional superexchange interaction between the core spins, yield a term, the significance of which has been hitherto ignored. The importance of this term is further assessed by numerically exact computation for a four-spin system.

Keywords. Manganites; double-exchange; Hund's coupling; superexchange.

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1. Introduction

The emergence of manganites as a technologically important material due primarily to the occurrence of colossal magnetoresistance (CMR) in e.g. $La_{1-x}Ca_xMnO_3$ [1] has rekindled the interest of the condensed matter physics community in the double-exchange mechanism. The physics of double-exchange has successfully correlated ferromagnetism and metallicity in the doping range of $0.2 < x < 0.4$. The basic ingredient of double-exchange, proposed by Zener [2] fifty years ago, is encapsulated within a simple two-site model of Anderson and Hasegawa [3–5]. The latter has led to a plethora of theoretical and experimental investigations in recent years [6,7], which have gone on to add one or the other feature to the original model, often without abundant care, as we shall argue here.

The undoped manganite system is characterised by the presence of an incomplete d-shell of the manganese ions, which consists of three electrons in the t_{2g} state and one electron in the e_g state. The t_{2g} spins are deep inside the d-level and are assumed to be unimportant in the process of charge transfer. However, these spins do show a tendency to align antiferromagnetically both in the parent compound and in the completely doped system. The Coulomb energy cost for the e_g electrons to hop onto the adjacent manganese ion in the absence of a hole is very large. The undoped system is thus an insulator.

We will henceforth refer to the e_g electron as the itinerant electron, the t_{2g} electrons as the core electrons and the total spin in the t_{2g} level as the core spin. Doping the system with a divalent atom like Ca or Sr leads to creation of holes in the e_g level in a fraction of

the manganese ions. The itinerant electron from the occupied e_g level of one manganese site can then hop into its nearest neighbor oxygen site, which facilitates hopping to the nearest neighbor unoccupied e_g level of another manganese ion, thus leading to a finite conductivity. This process, called the 'double-exchange mechanism', plus the presence of strong Hund's rule coupling between the core spin and the itinerant electron, results in an indirect coupling between neighboring core spins. This in turn relates the magnetic order of the underlying lattice with the transport of the itinerant electron.

The conclusions derived by Anderson and Hasegawa [3] can be summarised as follows. In the limit when Hund's coupling is infinitely strong, the itinerant electron would like to have its spin aligned with the local core spin. Additionally, if the core spin is treated *classically*, the appropriate axis of quantization is the direction of the core spin vector, as far as the itinerant electron is concerned. Now, as the latter hops, it has to readjust its spin to be realigned with the new core spin partner, amounting to a rotation of the quantization axis by an angle θ, which is the polar angle between the core spins $\vec{S}_1$ and $\vec{S}_2$. From the property of the spin-1/2 rotation operator it follows that the hopping or the overlap matrix element t will be renormalized to $t\cos(\theta/2)$, assuming azimuthal symmetry. It then follows that if θ equals π, the core spins have antiferromagnetic (AFM) coupling and hopping of the itinerant electron is totally inhibited. On the other hand, if θ equals zero, the core spins have ferromagnetic (FM) coupling and hopping is accentuated, thus synergising transport with ferromagnetism. This is the first result of Anderson and Hasegawa. The latter then proceeded to a quantum treatment of the core spins, but still operating within the infinite Hund's coupling limit. Interestingly, it turns out that the energy eigenvalues are identical to the earlier classical case, provided $\cos(\theta/2)$ is identified as a *parameter* which equals $(S_0+1/2)/(2S+1)$, where $S=|\vec{S}_1|=|\vec{S}_2|$ and $S_0=|\vec{S}_1+\vec{S}_2+\vec{\sigma}|$, $\vec{\sigma}$ being the spin of the itinerant electron ($|\vec{\sigma}|=1/2$). Curiously, since $\vec{S}_1$, $\vec{S}_2$ and $\vec{\sigma}$ add up to $(2S+1/2)$ in the FM case for large Hund's coupling, the parameter $\cos(\theta/2)$ would indeed be equal to unity, as in the classical case. But in the AFM case, the parameter reduces to $1/(2S+1)$, which goes to the classical value of zero only when $S\to\infty$, thus necessitating an additional constraint on the core spin, if the 'classical' interpretation is to be taken seriously. Needless to say, in between FM and AFM cases, the parameter $\cos(\theta/2)$ would go through a set of discrete (and not continuous) values, thus pointing to the need of a more careful treatment of the core spins in the quantum case.

2. Quantum treatment of AH model

One of the directions in which the Anderson–Hasegawa treatment has been extended is to recognize the importance of an additional superexchange term between the core spins proportional to $\vec{S}_1\cdot\vec{S}_2$. It has been assumed in the literature till now that the superexchange term can be simply taken as an extra term, without modification, to be added to the Hamiltonian and that the large Hund's rule coupling affects only the process of charge transfer in these systems. In this paper we show inter alia that superexchange is itself modified if the core spins are dealt with quantum mechanically. Our starting point therefore is the Hamiltonian for a two-site one-electron model, including the superexchange interaction, given by

$$H = -t\sum_{\tau}(c_{1\tau}^{\dagger}c_{2\tau} + \text{h.c.}) - J_{\text{H}}\sum_{i=1}^{2}\vec{S}_i\cdot\vec{\sigma}_i + J\vec{S}_1\cdot\vec{S}_2. \tag{1}$$

Here t is the hopping matrix element for the itinerant electron between the two sites, $c_{i\tau}^{\dagger}(c_{i\tau})$ is the creation(annihilation) operator of the itinerant electron at site i having spin projection τ, J_{H} is the Hund's rule coupling strength, $\vec{S}_i$ is the core spin at site i and $\vec{\sigma}_i$ is the spin of the itinerant electron at the site i. The parameter J is the superexchange interaction strength between the core spins in the nearest neighbor sites. For our case we consider $|\vec{S}_i| = S$, i.e. the core spins on all the sites are taken to have the same value.

In order to find the ground state of the system we follow the quantum mechanical calculation carried out by Anderson and Hasegawa [3]. We first note that the Hund's rule coupling term, proportional to J_{H} is diagonal in the states given by $|\psi_1^{\pm}\rangle = |S_1, \frac{1}{2}, (S_1 \pm \frac{1}{2}), S_2; S_0, M\rangle$ and $|\psi_2^{\pm}\rangle = |S_1, \frac{1}{2}, S_2, (S_2 \pm \frac{1}{2}); S_0, M\rangle$, while the hopping part of the Hamiltonian connects these two sets of states, corresponding as it does to a recoupling of the itinerant electron's spin (1/2) from the site spin S_1 to S_2 and is thus given by the Wigner 6j (or Racah) coefficient (W) [8]. Here, $M = S_0^z$. The superexchange term proportional to J, is off-diagonal in the basis states chosen above. However, it is diagonal in the states given by $|\phi(S')\rangle = |\frac{1}{2}, S_1, S_2, (S'); S_0, M\rangle$, where $S' = |\vec{S}_1 + \vec{S}_2|$. We can then relate the states $|\psi_{1,2}^{\pm}\rangle$ to the states $|\phi(S')\rangle$ through appropriate Racah coefficients again and we find,

$$\begin{aligned}
|\psi_1^{\pm}\rangle &= \sum_{S'}\sqrt{\left[2\left(S_1 \pm \frac{1}{2}\right) + 1\right]}\sqrt{(2S'+1)}\, W\left(\frac{1}{2}S_1 S_0 S_2; \left(S_1 \pm \frac{1}{2}\right) S'\right)|\phi(S')\rangle, \\
|\psi_2^{\pm}\rangle &= \sum_{S'}\sqrt{\left[2\left(S_2 \pm \frac{1}{2}\right) + 1\right]}\sqrt{(2S'+1)}\, W\left(\frac{1}{2}S_1 S_0 S_2; \left(S_2 \pm \frac{1}{2}\right) S'\right)|\phi(S')\rangle.
\end{aligned} \tag{2}$$

Clearly, since S' (the total core spin) must couple to the itinerant electron spin to give the total angular momentum S_0, the only values of S' to be summed over are $S' = S_0 + \frac{1}{2}$ and $S_0 - \frac{1}{2}$. The particular Racah coefficients which occur (with $S_1 = S_2 = S$), have convenient closed expressions such as,

$$\begin{aligned}
|\psi_1^{+}\rangle &= \cos(\alpha/2)|\phi(S_0 - \tfrac{1}{2})\rangle + \sin(\alpha/2)|\phi(S_0 + \tfrac{1}{2})\rangle, \\
|\psi_1^{-}\rangle &= -\sin(\alpha/2)|\phi(S_0 - \tfrac{1}{2})\rangle + \cos(\alpha/2)|\phi(S_0 + \tfrac{1}{2})\rangle,
\end{aligned} \tag{3}$$

where

$$\cos(\alpha/2) = \left[\frac{\left(2S + S_0 + \frac{3}{2}\right)}{2(2S+1)}\right]^{1/2}. \tag{4}$$

The relations between $|\psi_2^{\pm}\rangle$ and $|\phi(S_0 \pm \frac{1}{2})\rangle$ states are the same as those between $|\psi_1^{\pm}\rangle$ and $|\phi(S_0 \pm \frac{1}{2})\rangle$. Note that the expression for $\cos(\alpha/2)$ can be written in terms of $\cos(\theta/2)$, which actually gives the relation between α and θ as $\alpha = \theta/2$. Thus the Hamiltonian matrix in the space of $|\psi_1^{\pm}\rangle$ and $|\psi_2^{\pm}\rangle$ can be written as follows:

$$\begin{pmatrix} P_1 & P_2 & -t\cos(\theta/2) & -t\sin(\theta/2) \\ P_2 & P_3 & t\sin(\theta/2) & -t\cos(\theta/2) \\ -t\cos(\theta/2) & t\sin(\theta/2) & P_1 & P_2 \\ -t\sin(\theta/2) & -t\cos(\theta/2) & P_2 & P_3 \end{pmatrix}, \tag{5}$$

where

$$\begin{aligned} P_1 &= \frac{J}{2}\left(R_1\sin^2(\alpha/2) + R_2\cos^2(\alpha/2)\right) - \frac{J_{\rm H}}{2}S, \\ P_2 &= \frac{J}{2}(R_1 - R_2)\cos(\alpha/2)\sin(\alpha/2), \\ P_3 &= \frac{J}{2}\left(R_1\cos^2(\alpha/2) + R_2\sin^2(\alpha/2)\right) + \frac{J_{\rm H}}{2}(S+1), \end{aligned} \tag{6}$$

and

$$\begin{aligned} R_1 &= \left(S_0 + \frac{1}{2}\right)\left(S_0 + \frac{3}{2}\right) - 2S(S+1), \\ R_2 &= \left(S_0 - \frac{1}{2}\right)\left(S_0 + \frac{1}{2}\right) - 2S(S+1). \end{aligned} \tag{7}$$

The eigenvalues (E) of the Hamiltonian matrix are obtained from

$$2E = \frac{J_{\rm H}}{2} + K_1(J) \pm \sqrt{4t^2 + K_T^2(J) + K_3^2(J) \pm 4t\cos(\alpha)\sqrt{K_T^2(J) + K_3^2(J)}}, \tag{8}$$

where

$$K_1(J) = J\left[\left(S_0 + \frac{1}{2}\right)^2 - 2S(S+1)\right],$$

$$K_T(J) = \left[\frac{J_{\rm H}(2S+1)}{2} + K_2(J)\right], \tag{9}$$

$$K_2(J) = J\cos(\alpha)(S_0 + \tfrac{1}{2}), \tag{10}$$

$$K_3(J) = J\sin(\alpha)(S_0 + \tfrac{1}{2}). \tag{11}$$

We reiterate that the expression in eq. (8) is valid for arbitrary strength of Hund's rule coupling and arbitrary value of the core spin.

While the exact result of eq. (8) may be of interest in its own right, we examine the limit of large Hund's rule coupling, by expanding the square root term (up to $O(1/J_{\rm H})$). We find that the lowest energy eigenvalue (which corresponds to the itinerant spin being parallel to the core spin) is given by

$$E_m = -\frac{J_{\rm H}S}{2} - t\cos(\alpha) + \frac{J}{2}\left[\bar{S'}(\bar{S'}+1) - 2S(S+1)\right] + J\sin^2(\alpha/2)(S_0 + \tfrac{1}{2}), \tag{12}$$

where $\bar{S'} = S_0 - 1/2$.

The first two terms in eq. (12) are the terms obtained by Anderson and Hasegawa. We emphasise once again that the parameter $\cos(\alpha/2)$ takes *discrete* values which depend on the quantum values of the core spins. The third term is the result of the superexchange interaction in the absence of the itinerant electron. The fourth term, a novel one, is purely due to the double-exchange mechanism in the presence of the itinerant electron. The explicit form of this term is given by

$$\Delta E_J = \frac{J}{2}\frac{2S-\bar{S'}}{2S+1}(\bar{S'}+1). \tag{13}$$

It is to be noted that in the ferromagnetic limit (i.e. $\bar{S'} = 2S$) ΔE_J vanishes exactly.

There are a few important points to be made about ΔE_J:

(a) This term arises from a proper quantum mechanical treatment of the Anderson–Hasegawa model in the additional presence of superexchange.

(b) This term vanishes in the absence of the itinerant electron and is proportional to n_i, where n_i is the number operator for itinerant electrons at the site i whose eigenvalue is taken to be either 1 or 0 in the absence of double occupancy.

(c) At any site i the strength of this term depends on 3 spin values: the spin of the itinerant electron on the site i (σ_i), the core spin at site i (S_i) and the core spin on the neighboring site (S_j), j being the neighbor of the site i.

(d) This term is proportional to J, the strength of superexchange.

The complete effective Hamitonian for the two-site one-electron model can then be written as

$$H_{12} = \Delta E_J(n_1+n_2) - t\cos(\theta_{12}/2)\,(c_1^\dagger c_2 + \text{H.C.}) + J\vec{S}_1\cdot\vec{S}_2, \tag{14}$$

where n_1 and n_2 are number operators at site '1' and '2' respectively. Since we restrict our calculation to the single-electron case and the large Hund's rule coupling limit in which the ground state configuration corresponds to the itinerant spin being parallel to the core spin, the spin index τ may be omitted without any loss of generality.

The classical limit of the extra term is given by

$$\Delta E_J^{\text{Cl}} = \frac{J}{2}(2S+1)\,[1-\cos(\theta/2)]\cos(\theta/2), \tag{15}$$

which goes to zero in both the ferromagnetic as well as the antiferromagnetic limits. Again, we see a clear distinction between the classical and the quantum results in the antiferromagnetic limit. We emphasise that in taking the purely classical expression, one actually loses the effect of the quantum fluctuations which are present in these systems not only because of the fluctuating spins but also due to hopping being correlated with the spins on the lattice.

3. Results and conclusion

In figure 1, we compare the variations of ground state energy with superexchange interaction J for a two-site one-electron system using eq. (1) (solid line) (after subtracting out a constant value $-J_{\text{H}}S/2$), eq. (14) (solid circle) and eq. (14) excluding the first term – i.e.,

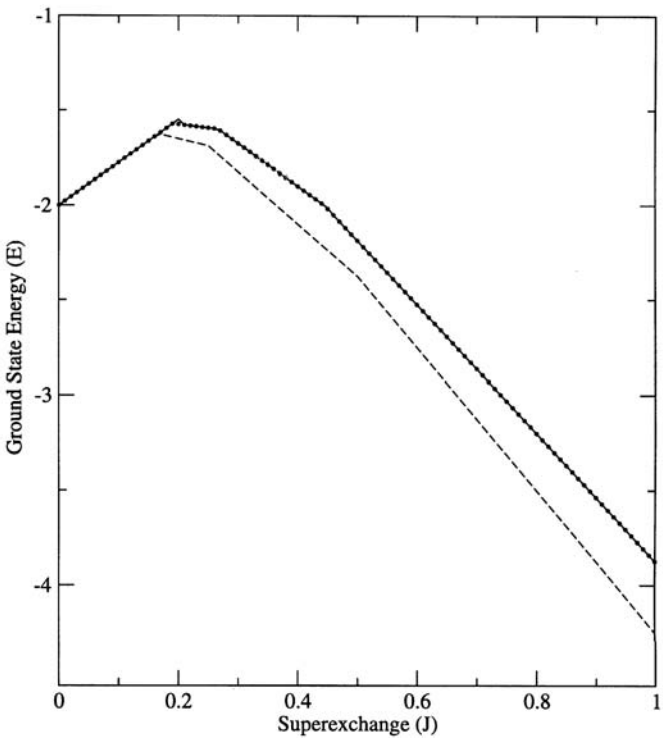

Figure 1. Ground state energy for the Anderson–Hasegawa model with superexchange in a two-site one-electron model, calculated by exact diagonalization. The parameter values chosen are as follows: $t = 1$, $J_{\mathrm{H}} = 10^5$, $S_1 = S_2 = 3/2$. The solid line represents the solution of eq. (1) after subtracting a constant given by $-((J_{\mathrm{H}}S)/2)$, while the solid circle represents the solution of eq. (14) and the dashed line represents the solution of eq. (14) without the quantum correction due to the superexchange interaction.

without the quantum correction due to superexchange interaction (dashed line), by exact diagonalization. Note that the first two curves overlap for the whole range of J. For low values of J, the ground state energy does not depend on the presence of the extra term. However, as J increases, the contribution of the extra term becomes more prominent. This is consistent with our earlier remark about the vanishing of the extra term in the ferromagnetic phase which occurs for low value of J. The same reason can be attributed for the decrease in the ground state energy as J increases when the system enters the antiferromagnetic phase.

The importance of the extra term is further assesssed by going beyond the two-site case and considering a four-spin cluster. In figure 2 we compare the results from exact diagonalization of the Hamiltonian given by eq. (1) (solid line) on a four-site lattice with one electron and that of the modified Hamiltonian with the extra term (circles) and without the extra term (dashed line). In figure 3 we show a similar plot for four sites and two electrons. Interestingly, in the larger system of four spins, the modified Hamiltonian with the extra term tends to deviate from the exact curve as the value of the superexchange J is increased. However, it is to be noted that even in this case, the modified Hamiltonian without the extra

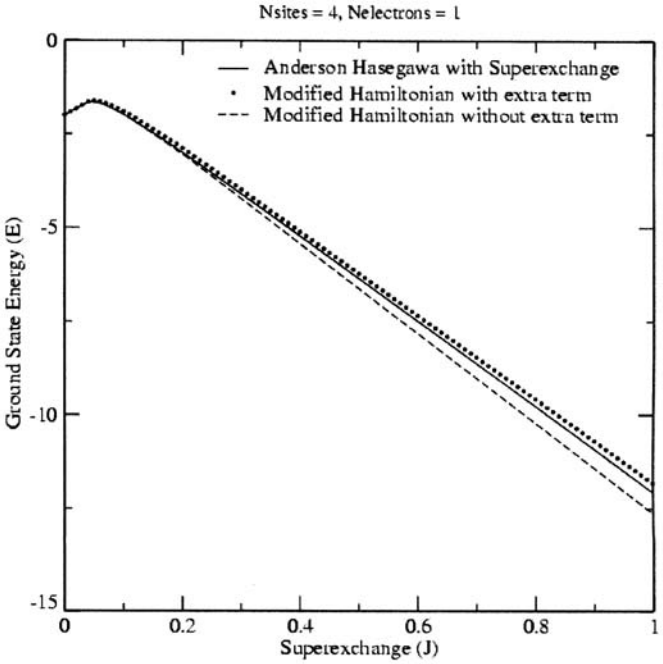

Figure 2. Ground state energy for the Anderson–Hasegawa model with superexchange in a four-site one-electron model, calculated by exact diagonalization. The parameter values chosen are as follows: $t = 1$, $J_{\mathrm{H}} = 10^5$, $S_1 = S_2 = 3/2$. The solid line represents the solution of eq. (1) after subtracting a constant given by $-((J_{\mathrm{H}}S)/2)$, while the solid circle represents the solution of eq. (14) and the dashed line represents the solution of eq. (14) without the quantum correction due to the superexchange interaction.

term gives a much poorer fit to the exact curve. We conjecture that unlike the two-site case, in a larger lattice the hopping of the electron from one site to another will be correlated not only to core spins of the sites between which it hops, but also to the neighbors. Hence the term in eq. (14) cannot be adapted directly from the two-site case into the four-site case. This is further indicated by the fact that a simple addition of the extra term leads to an overestimation of the ground state energy. Thus, what the quantum corrections are in the multisite, multielectron case require further analysis.

In conclusion, we reiterate that the two-site, single-electron, double exchange model is the simplest basic framework for interpreting a large number of fascinating properties of rare-earth manganites. While Anderson and Hasegawa did provide a quantum solution to the model, especially in the limit of large Hund's rule coupling, subsequent authors seem to have gone ahead in a somewhat cavalier fashion about the classical limit of the core spins. However, as the value of the core spins in most studied CMR systems is indeed finite – three-halves for manganese – we felt the need of delineating the quantum versus classical effects. The quantum effects are expected to be particularly important for properties associated with polaron induced hopping [9] and thermal heat capacity [10].

Finally, we would like to add that the Anderson–Hasegawa model, though almost fifty years old, is able to capture all the crucial features of the double-exchange mechanism,

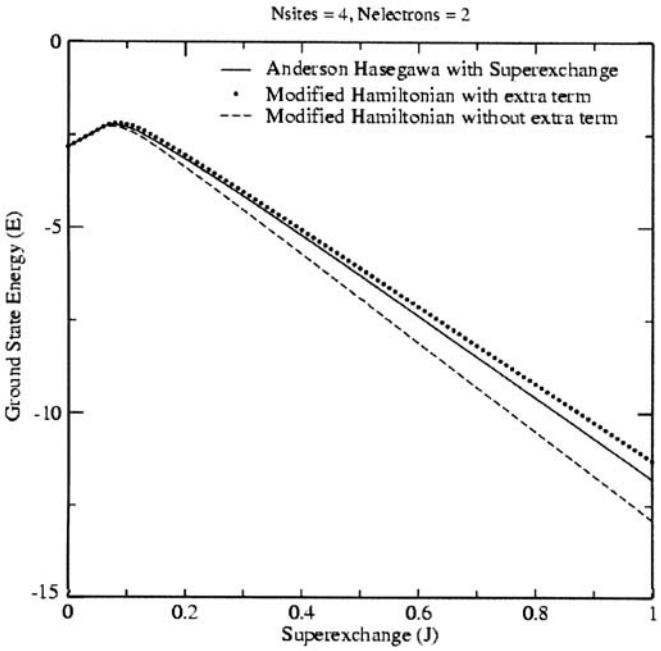

Figure 3. Ground state energy for the Anderson–Hasegawa model with superexchange in a four-site two-electron model, calculated by exact diagonalization. The parameter values chosen are as follows: $t = 1$, $J_{\mathrm{H}} = 10^5$, $S_1 = S_2 = 3/2$. The solid line represents the solution of eq. (1) after subtracting a constant given by $-((J_{\mathrm{H}}S)/2)$, while the solid circle represents the solution of eq. (14) and the dashed line represents the solution of eq. (14) without the quantum correction due to the superexchange interaction.

originally proposed by Zener. The model is restricted to just two sites but the limitation should not be too serious when the electron hopping, influenced by thermal fluctuations, lattice distortions, phonon effects and other interactions, is expected to be incoherent. Incoherent hopping, albeit quantum in nature, is quite distinct from coherent band-like propagation, and approximately follows a Markovian process as far as the quantum diffusion of the electron is concerned. For a Markovian process only the pre-hopping and post-hopping sites matter. Therefore, the two-site abstraction of the underlying three-dimensional lattice provides the simplest paradigm which can be exploited for analyzing a variety of phenomena which are of current interest in manganites. Indeed this is what has motivated us to carefully reexamine the exact quantum solution of the Anderson–Hasegawa model, for realistic values of the core spins.

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