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LETTER TO THE EDITOR

On the relation of the 'double-exchange' model to low-temperature magnetic properties of doped manganites

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Abstract. Exact calculations of energy eigenstates of the double-exchange (DE) model are carried out for rings with N sites and N_e electrons for a variety of even N and odd N_e values, the ground states being ferromagnetic. The shapes of the spin-wave spectra (energy versus wave vector) differ markedly from that of the Heisenberg model for general concentration $x = 1 - N_e/N$ and localized spin S, as expected from earlier work, in contrast to a recent theory. But there is a range of x, including 0.3, for which the dispersion shapes are close to Heisenberg for realistic S. This suggests that the Heisenberg spectrum observed recently in $La_{0.7}Pb_{0.3}MnO_3$ might still be explained by the DE model. Also, interesting asymptotic behaviour of the dispersion width for large S, large N, is clarified.

The remarkable metal $\rightarrow$ insulator and ferromagnetic $\rightarrow$ paramagnetic transitions found to occur [1] at the same temperature T_c in the doped rare-earth perovskite manganites, $La_{1-x}M_xMnO_3$, and studied theoretically [2–8] long ago, have been shown great interest in recent years [9–22]. Until very recently, the theoretical basis [3–6] for understanding the observations has been through approximate treatments of the so-called [2] double-exchange (DE) model, which is the Kondo lattice model with ferromagnetic intra-atomic exchange J in the limit of infinite J. Although this model was recently called into question [15, 16] for temperatures near and above T_c, its validity for these materials at low T has not yet been questioned in the literature.

Very recently, a surprising low-T result appeared, namely the observation, via inelastic neutron scattering, that the spin-wave dispersion throughout the Brillouin zone is described by the Heisenberg model with nearest-neighbour exchange (for $La_{0.7}Pb_{0.3}MnO_3$) [17]. This is surprising because in the DE model the dependence of the energy on the relative orientation of the localized spins differs markedly from that for Heisenberg spins: in a mean-field sense, the DE model gives energy $\sim |\cos(\theta/2)|$, as compared to $\cos\theta$ for the Heisenberg model, where θ is the angle between two spins [3, 4].

Nevertheless, an approximate spin-wave theory recently appeared which found the dispersion to be precisely nearest-neighbour Heisenberg in the infinite-J limit, independent of the concentration x and the localized-spin quantum number S [21]. Thus this theory seemed to explain the surprising experimental result [17]. Unfortunately, this theoretical picture is a poor approximation to the spectrum of the actual double-exchange model, as shown by our exact calculations, described below. Also, there is work of another group [19] which also involves exact calculations, where the spin-wave dispersion was found to be decidedly non-Heisenberg, a result emphasized by these authors [19].

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The question therefore remains, can one reconcile this non-Heisenberg aspect of the DE model with the neutron scattering experiments? We suggest the answer is yes. We have carried out exact calculations on N-site, N_e-electron rings. Although general values of concentration $x = 1 - N_e/N$ and S yield very *non*-Heisenberg spin-wave dispersion shapes, there is, for realistic S (=3/2), a range of x, including $0.1 < x < 0.5$ (poor in holes in the half-filled band, which is the experimental region), where the DE model predicts dispersion-curve shapes close to Heisenberg [23]. We also find that for large J the spin-wave dispersion approaches Furukawa's result [21] (Heisenberg shape) in the limit $S \to \infty$.

We study the following model, with Hamiltonian H. The conduction electrons move in a tight-binding band with one orbital per site (this standardly models the Mn e_g states), the hopping integral being t. These interact with localized spins, one at each site, of spin S, via Hund's rule or intratomic exchange of strength J; the localized spin comes from the three electrons in the Mn t_{2g} states. There is also on-site Coulomb interaction between the conduction electrons, of strength U.

The standard model of double exchange is this model in the limit $J \to \infty$. In this case, double occupancy of an e_g state is excluded by the exchange, so that all results are independent of U. The usual model for considering finite J is H with $U = 0$, see e.g. [19] and [21]. However, because for the physical systems of interest one expects $U \gg J$ [14], and because of relative simplicity in exact calculations, we consider only $U \to \infty$.

The Hamiltonian is

$$H = -t \sum_{i,\sigma} \left(c^+_{i\sigma} c_{i+1,\sigma} + \text{HC} \right) - J \sum \boldsymbol{s}_i \cdot \boldsymbol{S}_i + U \sum n_{i\uparrow} n_{i\downarrow}. \tag{1}$$

Here $c^+_{i\sigma}$ (the adjacent of $c_{i\sigma}$ creates an e_g electron at site i with spin σ, $n_{i\sigma} = c^+_{i\sigma} c_{i\sigma}$, $s^+_i = c^+_{i\uparrow} c_{i\downarrow}$, and $s^z_i = (1/2)(n_{i\uparrow} - n_{i\downarrow})$; $\boldsymbol{S}_i$ is the operator for the localized spin at site i, which runs from 1 to N. The number of electrons $N_e = \sum n_{i\sigma}$. H commutes with the square $\boldsymbol{S}^2_T$ of the total spin and any Cartesian component of $\boldsymbol{S}_T$; also, its energy spectrum is invariant under $t \to -t$ for a bipartite lattice.

We have considered only the cases where $S^z_T =$ its maximum value S_M and $S_M - 1$. The cases $s^z_T = S_m$, with each conduction electron in a Bloch function (ferromagnetic states), are eigenstates of (1), the lowest of which we call $|F\rangle$, with energy E_F. We have studied the following: (i) $(N, N_e) = (N, 1)$ and $(N, N-1)$ for $N = 4$, 6, 8, 10, 12, 16, 20, 40, 60, 80; (ii) $(N, N_e) = (N, N-3)$ for $N = 4$, 6, 8, 10, 12. Odd N_e, for which $|F\rangle$ is the ground state, is chosen because for even N_e the ground state is not ferromagnetic, as found in [8]; non-ferromagnetic behaviour was also found [19] for 2D and 3D clusters with periodic boundary conditions and certain numbers of electrons ('open-shell cases'). Arguments in [19] suggest that this deviation from ferromagnetism is a '1 in N' effect, a suggestion supported by Kubo's finding [8] that the ferromagnetic state is the ground state for *open chains*. We note that the very-long-wavelength spiral found for the non-ferromagnetic state [8, 19] would probably be shifted to the ferromagnetic state by a small, realistic, anisotropy (via spin–orbit interactions). For further recent discussion of the ground state problem see [22].

We begin discussion of our results with some characteristic properties which we describe in terms of the simple case of six sites and one electron, with $S = 1/2$. Here we take the infinite-J and U limits and, of course, subtract those terms from H. The energy eigenvalues (minus the ground-state energy $E_F = -2t$), all in units of t, are shown in figure 1, listed according to wave vector k, the translational-symmetry quantum number of the eigenstates. We note the existence of a low-lying 'branch' whose highest energy is a small fraction (about 1/20) of the total width of the spectrum. We also note the bunching of the eigenvalues around

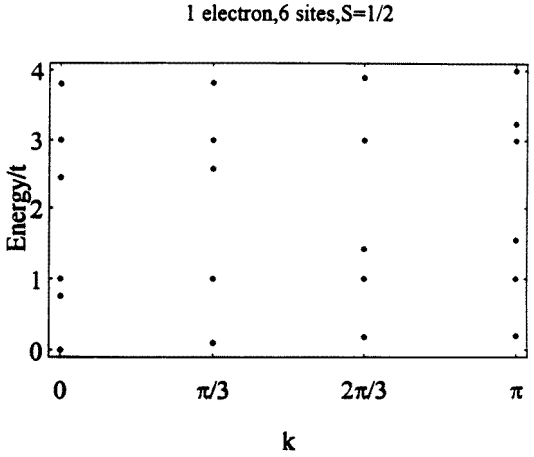

Figure 1. Energy eigenvalues measured from E_F in units of t, for one electron, six sites, $S = 1/2$, $J = \infty$.

the free-particle values (0, 1, 3, 4). This effect is more pronounced for $S = 3/2$; in particular the width of the lowest branch in this case is about 1/30 of the total width. A very similar effect is seen for other cases, e.g., for the cases $(N, N_e) = (6, 5)$, (10,7), (8,5) (6,1), all with $S = 3/2$, the ratios (spin-wave width/total free-electron width) = 0.036, 0.025, 0.030, 0.036, respectively (the corresponding hole concentrations are $x = 0.17$, 0.30, 0.375, 0.83). Thus there is a natural second 'energy scale' despite having only one parameter t in the Hamiltonian. This is probably the same second energy scale as found by Sarkar in a mean-field approximation [20]. However, the bunching at the higher energies tends to smear out for larger systems.

We studied the correlation functions, for $r \neq 0$, in the states of the lowest branch,

$$C_r^z = \left\langle S_i^z S_{i+r}^z \right\rangle$$
$$C_r^t = \left\langle S_i^+ S_{i+r}^- \right\rangle. \tag{2}$$

One can show that

$$C_r^z = S^2 - 2S/N \tag{3}$$

for any energy eigenstate (in this subspace) and arbitrary N. Further, this is identical to the result for any (ferromagnetic) Bloch spin wave. The transverse spin correlation function for a Bloch spin wave of wave vector k is given by $C_r^t(\text{Bloch}) = (2S/N)\cos kr$. Comparison of this with the corresponding results in table 1, where $S = 1/2$, shows that the correlation functions in these low-lying double-exchange states and in the single-magnon Heisenberg model states are very similar. Thus it is plausible to refer to these states in the DE model as spin-wave states.

We also mention that in these spin-wave states the probability of separation of the electron and the down spin shows an effective attraction for $k = 0$, this gradually changing as k increases to repulsion for $k = \pi$. This *spin-polaron* effect, which was also noted independently by Zang *et al* [19], will be discussed in detail elsewhere.

Figure 2 shows the spin-wave energies for $S = 3/2$, $J = 40t$, and for the Heisenberg model (solid curve), normalized to unity at the maximum (at $k = \pi$) so as to compare the *shapes* of the energy against k relations. (The results are quite insensitive to changes in

Table 1. Transverse correlation function C_r^t for the spin-wave states characterized by k. Because of the ring geometry, $C_4^v = C_2^v$ and $C_5^v = C_1^v$. Results for six sites, one electron, $S = 1/2$ and infinite J.

k	$r = 1$	$r = 2$	$r = 3$
0	0.142 86	0.142 86	0.142 86
$\pi/3$	0.076 22	−0.074 39	−0.147 21
$2\pi/3$	−0.076 72	−0.069 90	0.133 81
π	−0.152 52	0.135 64	−0.128 19

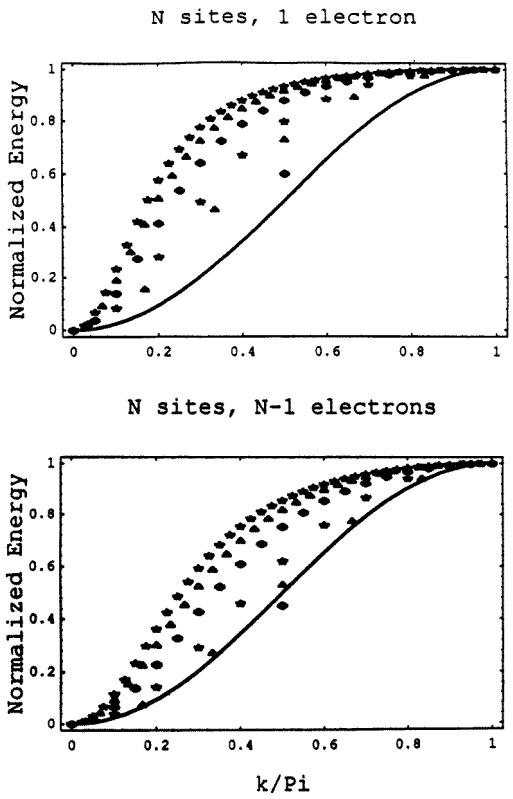

Figure 2. Spin-wave energies for $S = 3/2$, $J/t = 40$, and for the Heisenberg model (solid curve), normalized to unity at $k = \pi$, for $N = 4$, 12, 20, 40, 60, 80. At $k = \pi/2$, all these N-values appear; in both cases, $(N,\ 1)$, $(N,\ N-1)$, the lowest energy corresponds to the smallest N, the energy increasing with N.

J near such a large value—we have essentially the infinite-J limit.) In figure 2 the cases $(N,\ 1)$ and $(N,\ N-1)$ are shown for a subset of the N-values calculated, selected for clarity of presentation. We notice the large deviation from Heisenberg shape (HS) for small electron and small hole concentration ('hole' in our usage means hole in the half-filled band, so x is the hole concentration). We also see asymmetry between electrons and holes (as is consistent with the analysis of [6]): the large-N limits are similar, but not identical, and both differ radically from HS. Most importantly, while even the largest-electron-concentration cases shown in the $(N,\ 1)$ case $(N = 4,\ 12)$ deviate appreciably from HS, the largest *hole*

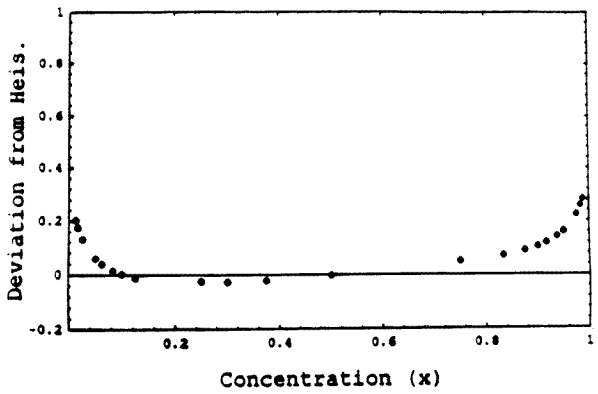

Figure 3. Deviation of the spin-wave spectrum from that of the Heisenberg model against hole concentration x.

concentrations in the $(N,\ N-1)$ set (again, $N = 4,\ 12$) actually *straddle* the Heisenberg shape, and are quite close to it. To study this behaviour in more detail, we calculated the deviation of each (normalized) spin-wave spectrum, $\epsilon(k)$, from the HS, as

$$Dev = (2/N)\sum_{k>0}\big[\epsilon(k) - \epsilon_{Heis}(k)\big]. \tag{4}$$

This is useful because in every case (each $(N,\ N_e)$), the bracketed quantity is of one sign; also it approaches the difference in areas as $N \to \infty$. This deviation is plotted in figure 3 as a function of x, and includes all the cases we studied as described above. The result is remarkably smooth, suggesting that the deviation is a strong function only of x (being only weakly dependent on N and N_e separately). This suggestion is supported by the fact that the deviations in the two cases $(12, 9)$ and $(4, 3)$ with the same x $(= 1/4)$ differ by only about 0.001, with about the same difference for $(12, 3)$ and $(4, 1)$ at $x = 3/4$. The deviation shows a rather broad range of x, including the experimental range, for which the DE and Heisenberg spectra have approximately the same shape, although for other x the deviation from HS is large. (The deviation at $x = 1/2$ (quarter-filled band) is not exactly zero, although it appears to be.)

So there is the distinct possibility that the shape of the spin-wave dispersion in the DE model is close to that in the Heisenberg model for the experimental situations so far encountered. The results suggest that in other situations a non-Heisenberg shape might be found.

We now consider the absolute values of the spin-wave excitation energies. In any sequence $(N,\ n)$ or $(N,\ N-n)$, with fixed n, the width of the spectrum vanishes as $N \to \infty$ ($x \to 1$ or 0). To address values of x like the experimental values, we consider $(N,\ N_e) = (8,\ 5)$ and $(10, 7)$ ($x = 0.375$ and 0.3). The widths of the spin-wave spectra in these cases are $0.294t$ and $0.246t$, respectively. The estimate $t \approx 0.2$ eV (Millis *et al* [15]) then gives about 0.06 and 0.05 eV for these cases—these are of the right order of magnitude, the measured width [17] being about 0.1 eV. Given that the present calculations are for 1D, the experimental material being 3D (cubic), this order-of-magnitude agreement is quite satisfactory.

The results described here, although limited to finite-size 1D systems, suggest that the DE model is appropriate to the systems that have been studied experimentally. The reason is not that the DE model produces a spin-wave spectrum which is of the Heisenberg shape,

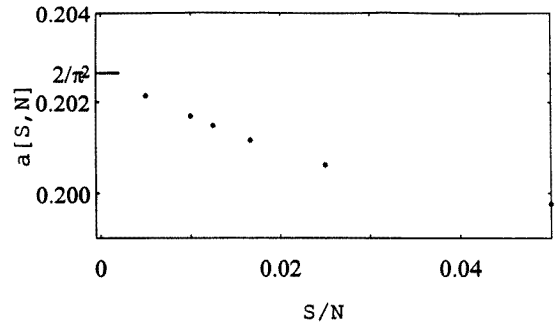

Figure 4. The parameter $a[S, N]$ against S/N. Shown are the values for $S = 1$, $N = 20$, 40, 60, 80, 100, 200. A similar plot for $S = 1/2$ shows values much closer to $2/\pi^2$ (=0.202 642). Straight-line extrapolation from the two last points (smallest S/N) gives 0.202 59 and 0.202 62 for the $S = 1$ and $S = 1/2$ cases, respectively.

independent of x and S, as claimed recently [21]. Rather, the spectrum in DE is in general very non-Heisenberg, but approximates Heisenberg behaviour for some concentrations at realistic S-values.

We looked numerically at large S to compare with Furukawa's results [21]. Indeed, we found in several cases that as S increases the spin-wave spectrum approaches the Heisenberg shape, in agreement with his result (which is to leading order in $1/S$). It is interesting to check the actual spin wave bandwidth. In 1D, his [21] formula, which takes $J \to \infty$, (8) gives

$$\omega_k = A\frac{1-\cos k}{2} \tag{5}$$

with

$$A = \frac{2t}{NS}\sum_{q}^{occ}\cos q.$$

For $(N, N_e) = (6, 1)$ and $(8, 5)$, this gives $A/t = 0.222$ and 0.402, respectively, to be compared with our exact results, 0.127 and 0.301, all for $S = 3/2$. Thus the result to leading order in $1/S$ is of the correct order of magnitude, although not very accurate.

Finally we discuss the following rather curious fact. For one electron, Furukawa's formula gives the width of the dispersion, $\omega_\pi \equiv w = 2/NS$, in units of t. We also numerically found that for large N, $w = \mathrm{O}(1/N^\alpha)$ with $\alpha \cong 2$, which seems to be at odds with the linear scaling in $1/N$ in Furukawa's result. We then realized that a rigorous upper bound on the excitation energy [19], namely $2[1-\cos(\pi/N)]$, confirms our finding [24]. Remembering that Furukawa's result is supposed to be the leading term in a $1/S$ expansion [21], it is clear that such an expansion cannot converge at large enough N, and maintain consistency between these two behaviours. We guessed the following reconciliation: $w = (2/NS)/(1 + aN/S)$, where a is slowly varying, and non-zero in the limits $S \to \infty$ and $N \to \infty$ (this gives the correct asymptotic behaviour in the two regions, $S \to \infty$, $N \to \infty$, and a $1/S$ expansion that does not converge for large N). From the calculated values of w as a function of S, N, we calculated $a(S, N)$. We found it to be slowly varying: $a(S, N) \approx 0.17$ for $S \to \infty$, and $a(S, N) \approx 0.20$ for $N \to \infty$ (for the latter we considered N up to 200). This justifies our guess. For small N ($\leqslant 40$) and S (1/2 to 3/2), the bound of Zang *et al* [19] is quite weak. However figure 4 gives strong numerical proof that the bound is in fact *exact*, asymptotically, for $N \to \infty$, for which the

bound is π^2/N^2, and our formula gives $2/aN^2$. We found quite similar behaviour for the case of one *hole*; we are in the process of comparing our numerical findings with the exact solution for this case by Ohata [7].

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[23] In the exact calculation of the spin-wave excitations in [19] only $x > 1/2$, and $S = 1/2$ were discussed. This probably explains why the near-Heisenberg behaviour for some x and $S = 3/2$ was missed by these authors.
[24] We thank Dr S A Trugman (private communication) for pointing this out.