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# Quantum effects in double-exchange systems

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**Abstract.** The stability of ferromagnetism in the s–d model of double exchange is investigated variationally for quantum spins. It is shown rigorously that for $S = \frac{1}{2}$ and infinite Hund's rule coupling, the state of complete spin alignment is unstable for $0.12 < n < 0.45$, where $n$ is the number of electrons per atom in the conduction band. Band narrowing in the paramagnetic state is also investigated in the quantum spin model. The effect is found to be somewhat stronger than in the classical spin limit and depends on $n$.

## 1. Introduction

For nearly fifty years it has been known there is a correlation between magnetic order and conductivity in the manganites $La_{1-x}D_xMnO_3$, where D is a divalent ion such as Ca, Ba, Sr [1, 2]. Recently there has been renewed interest in these systems due to the discovery of colossal magnetoresistance (CMR), the name given to a huge reduction in resistivity in an applied magnetic field [3–6]. For $x = 0$, $LaMnO_3$ is an antiferromagnetic insulator, but on doping with $0.2 < x < 0.5$, the system becomes a ferromagnetic metal. In these doped systems the resistivity rises with increasing temperature to a peak near the Curie temperature $T_c$ and then falls continuously in the paramagnetic state. The CMR phenomenon is observed in the vicinity of $T_c$. The high resistivity, with a negative temperature gradient, in the paramagnetic state indicates insulating rather than metallic behaviour.

The essential ingredients for a model of these systems are local spins $S = 3/2$ on each Mn site, corresponding to three localized d electrons of $t_{2g}$ symmetry, and $n = 1 - x$ itinerant electrons per Mn atom occupying a band derived from Mn d states of $e_g$ symmetry. The itinerant electrons are coupled ferromagnetically by Hund's rule to the local spins. The simplest model is the s–d Hamiltonian [7–9]

$$H = -t \sum_{\substack{\langle ij \rangle \\ \sigma}} c_{i\sigma}^{\dagger} c_{j\sigma} - J \sum_i \boldsymbol{S}_i \cdot \boldsymbol{\sigma}_i = H_0 + H_1 \tag{1}$$

where the first term $H_0$ describes the hopping of itinerant electrons between nearest-neighbour sites $i, j$ ($t > 0$) and the second term $H_1$ is the ferromagnetic Hund's rule coupling ($J > 0$) between local spin $\boldsymbol{S}_i$ and itinerant spin $\boldsymbol{\sigma}_i$ on each site. Since we are interested in doped ferromagnetic systems, the antiferromagnetic interaction between neighbouring local spins plays no important role and is neglected here. Other simplifications are the use of a single s band, instead of two d bands based on orbitals of $e_g$ symmetry, and the neglect of coupling to phonons.

In much of the theoretical work [10–15] on this model, the local spins are treated as classical vectors (corresponding to $S \to \infty$). For $J \gg t$ the itinerant spin must always be

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parallel to the local spin on each site so that the effective hopping integral for hopping between sites $i$ and $j$ becomes $t\cos(\theta_{ij}/2)$, where $\theta_{ij}$ is the angle between the classical spins $\boldsymbol{S}_i, \boldsymbol{S}_j$. The resultant band narrowing in the paramagnetic state favours ferromagnetism, this being the so-called double-exchange mechanism, and there is a widespread belief that the Hamiltonian (1) with $J \to \infty$ has a ferromagnetic ground state, with complete spin alignment, for all band occupation $0 < n < 1$ even for quantum spins $S$. In section 2 we show rigorously that this is not the case for $S = \frac{1}{2}$ and investigate the condition for instability of the ferromagnetic state with $S = 3/2$ for finite $J$. Our method is equivalent to that of Okabe [16] but he did not point out the occurrence of ferromagnetic instability in the s–d model. Anderson and Hasegawa [9] and Kubo and Ohata [17] were the first to investigate the effect of quantum spins on the double-exchange mechanism.

The quantum nature of the local spins also plays a role in the band narrowing which occurs in the paramagnetic state. This is the subject of section 3 and we show that the band-narrowing effect is stronger than in the classical double-exchange model. This may be important in enhancing polaronic effects of coupling to the lattice in the paramagnetic state. Such effects have been proposed [13, 14] as the origin of the metal–insulator transition which occurs on passing through $T_c$.

## 2. Instability of the ferromagnetic state

The Hamiltonian may be written

$$H = \sum_{\boldsymbol{k}} \epsilon_{\boldsymbol{k}} c^{\dagger}_{\boldsymbol{k}\sigma} c_{\boldsymbol{k}\sigma} - J \sum_i \boldsymbol{S}_i \cdot \boldsymbol{\sigma}_i \tag{2}$$

where $c^{\dagger}_{\boldsymbol{k}\sigma}$ creates an electron in a tight-binding Bloch state of wave-vector $\boldsymbol{k}$ and spin $\sigma$, and

$$\epsilon_{\boldsymbol{k}} = -t \sum_{\boldsymbol{R}} \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}}. \tag{3}$$

The summation in equation (3) is over sites $\boldsymbol{R}$ which are nearest neighbours of the site at the origin. In the lowest-lying state $|F\rangle$ of complete spin alignment all local spins are aligned in the direction of spin quantization (the $z$-direction) and the $n$ itinerant electrons occupy Bloch states within the $\uparrow$-spin Fermi surface. This is an exact eigenstate of $H$ with total $z$-component of spin $N(S + \frac{1}{2}n)$, where $N$ is the number of atoms, and we wish to test the proposal that it is the ground state of the system for large $J$. The stability of this proposed ground state against reversing a spin may be tested rigorously by comparing its energy with that of a variational wave-function with total $z$-component of spin $N(S + \frac{1}{2}n) - 1$. If the variational energy is lower than the exactly known energy of $|F\rangle$ one can state rigorously that $|F\rangle$ is not the ground state of the system. As pointed out by Okabe [16] this approach closely parallels earlier work on the stability of the Nagaoka state in the Hubbard model [18–20]; as in the latter case, instability due to spin reversal occurs most readily through single-particle excitation rather than spin waves. Thus an $\uparrow$-spin electron is removed from the Fermi surface, with energy $E_f - \frac{1}{2}JS$, and a $\downarrow$-spin quasiparticle of wave-vector $\boldsymbol{k}$ is added with energy $E_1(\boldsymbol{k})$ determined variationally. Here $E_f$ is the Fermi energy in the band, so $\epsilon_{\boldsymbol{k}} = E_f$ represents the Fermi surface. Since the bottom of the $\downarrow$-spin quasiparticle band occurs at $\boldsymbol{k} = 0$, as for the bare band, the lowest excitation energy on spin reversal is given by

$$E = E_1(0) - E_f + \frac{1}{2}JS. \tag{4}$$

If $E < 0$, the state of complete spin alignment $|F\rangle$ is not the ground state. If $E > 0$, no definite conclusion can be drawn. If the local spins are treated classically they are rigid and $E_1(0) = \epsilon_0 + \frac{1}{2}JS$, so $E > 0$ for sufficiently large $J$. However, with quantum spins the $\downarrow$-spin particle of wave-vector $\boldsymbol{k}$ can scatter to a state $\boldsymbol{q}$ near the $\uparrow$-spin Fermi surface, exciting a magnon of wave-vector $\boldsymbol{k} - \boldsymbol{q}$. Multiple scattering of the $\uparrow$-spin particle and the magnon leads to a bound state below the scattering continuum, corresponding to a $\downarrow$-spin quasiparticle, which can result in $E$ being less than zero. This is familiar from the Hubbard model [18–20] and motivates the choice of variational *ansatz* in the present case.

In order to calculate $E_1(\boldsymbol{k})$ we wish to construct a wave-function for a state with a $\downarrow$-spin electron of wave-vector $\boldsymbol{k}$ added to the state $|F\rangle$. The simplest wave-function, the only possibility for classical spins, is

$$|\boldsymbol{k}\rangle = c^{\dagger}_{\boldsymbol{k}\downarrow}|F\rangle. \tag{5}$$

However, the crucial magnon–electron scattering states are given by

$$|\boldsymbol{k};\boldsymbol{q}\rangle = \frac{1}{\sqrt{N}}\sum_i \mathrm{e}^{\mathrm{i}(\boldsymbol{k}-\boldsymbol{q})\cdot(\boldsymbol{R}_i)}(\sigma_i^- + S_i^-)c^{\dagger}_{\boldsymbol{q}\uparrow}|F\rangle \tag{6}$$

where $S_i^-$ is the local spin-lowering operator and $\sigma_i = c^{\dagger}_{i\downarrow}c_{i\uparrow}$ is the corresponding itinerant-spin operator. The total spin-lowering operator $\sigma_i^- + S_i^-$ reduces the $z$-component of the total spin but preserves the parallelism of the local and itinerant spins on each site, which is essential for large $J$. The required variational *ansatz* is

$$|\Psi_{\boldsymbol{k}}\rangle = A|\boldsymbol{k}\rangle + \sum_{q>k_f} A_q|\boldsymbol{k};\boldsymbol{q}\rangle \tag{7}$$

where $q > k_f$ indicates summation over $\uparrow$-spin states unoccupied in $|F\rangle$. This is equivalent to Okabe's [16] equation (7.8). It is easily shown that minimizing $\langle\Psi_k|H|\Psi_k\rangle$ with respect to $A, A_{\boldsymbol{q}}$, enforcing the normalization condition $\langle\Psi_k|\Psi_k\rangle = 1$ by means of a Lagrange multiplier which is actually the energy $E_0 + E_1(\boldsymbol{k})$ where $E_0$ is the energy of $|F\rangle$, is equivalent to solving the Schrödinger equation within the subspace of states $|\boldsymbol{k}\rangle, |\boldsymbol{k};\boldsymbol{q}\rangle$. Thus

$$\langle\boldsymbol{k}|H - E_0|\Psi_k\rangle = E_1(\boldsymbol{k})\langle\boldsymbol{k}|\Psi_k\rangle \tag{8}$$

and

$$\langle\boldsymbol{k};\boldsymbol{q}|H - E_0|\Psi_k\rangle = E_1(\boldsymbol{k})\langle\boldsymbol{k};\boldsymbol{q}|\Psi_k\rangle \tag{9}$$

where $|\Psi_k\rangle$ is given by equation (7). The matrix elements are easily evaluated and equation (8) is found to involve the parameters only as $A^{-1}\sum_{q>k_f} A_{\boldsymbol{q}}$. Equation (9) may be solved for this quantity and the parameters $A, A_{\boldsymbol{q}}$ are thus eliminated. The resultant equation for $E_1(\boldsymbol{k})$ is

$$E_1(k) - \epsilon_{\boldsymbol{k}} + \frac{1}{2}JS = JS(1 + JSF_{\boldsymbol{k}})^{-1} \tag{10}$$

where

$$(n + 2S)F_{\boldsymbol{k}} = N^{-1}\sum_{q>k_f}\left[\epsilon_{\boldsymbol{q}} - \frac{1}{2}JS + \omega(\boldsymbol{k}-\boldsymbol{q}) - E_1(\boldsymbol{k})\right]^{-1} \tag{11}$$

and the approximate spin-wave energy $\omega(\boldsymbol{q})$ is given by

$$(n + 2S)\omega(\boldsymbol{q}) = N^{-1}\sum_{p<k_f}(\epsilon_{\boldsymbol{p}+\boldsymbol{q}} - \epsilon_{\boldsymbol{p}}). \tag{12}$$

For $\boldsymbol{k}$ near the origin, equation (10) has a solution $E_1(\boldsymbol{k})$ below the electron–magnon scattering continuum of energies $\epsilon_{\boldsymbol{q}} - \frac{1}{2}JS + \omega(\boldsymbol{k}-\boldsymbol{q})$, as discussed previously for the Hubbard model [18, 19], and the lowest of these solutions is $E_1(0)$. Thus the lowest spin-reversal excitation energy $E$, given by equation (4), satisfies the equation

$$E + E_f - \epsilon_0 = JS[1 + JSF_0(E)]^{-1} \tag{13}$$

where

$$(n+2S)F_0(E) = N^{-1}\sum_{q>k_f}[\epsilon_{\boldsymbol{q}} + \omega(\boldsymbol{q}) - E_f - E]^{-1} \tag{14}$$

since $\omega(-\boldsymbol{q}) = \omega(\boldsymbol{q})$. This corresponds to Okabe's equation (7.9); he points out that inclusion of an on-site Hubbard repulsive interaction $U\sum_i n_{i\uparrow}n_{i\downarrow}$ between the itinerant electrons merely replaces $JS$ by $JS+Un$ in equation (13). If all of the $z$ nearest-neighbour sites $\boldsymbol{R}$ are equivalent, and hence $\sum_{p<k_f}\exp(\mathrm{i}\boldsymbol{p}\cdot\boldsymbol{R})$ does not depend on the particular $\boldsymbol{R}$, it is straightforward to show from equation (12) that

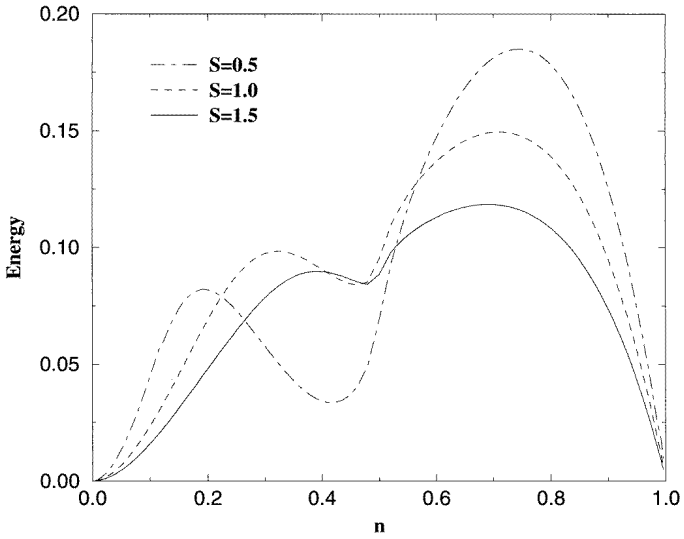
$$(n+2S)\omega(\boldsymbol{q}) = -(1+\epsilon_{\boldsymbol{q}}/zt)N^{-1}\sum_{p<k_f}\epsilon_{\boldsymbol{p}}. \tag{15}$$

We consider particularly the two-dimensional square lattice and the simple cubic lattice which is relevant to the Mn sublattice of the manganites. The summations in equations (14) and (15) may be carried out as energy integrals so that the nature of the lattice only enters as a density of states.

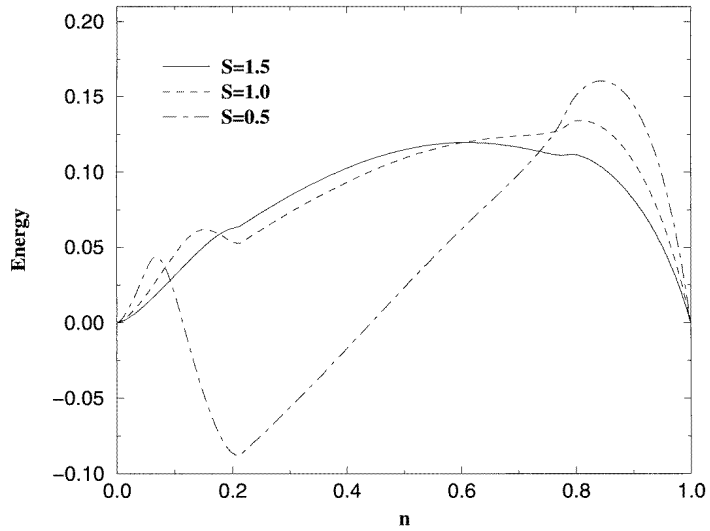
The limit of classical local spins corresponds to $S \to \infty$, $J \to 0$, such that $JS$ remains finite. Then $F_0(E) \to 0$ and the right-hand side of equation (13) becomes $JS$, so $E > 0$, indicating ferromagnetic stability, for sufficiently large $JS$ ($>E_f + zt$), as pointed out previously. The limit $J \to \infty$ with finite $S$ is quite different, with the right-hand side of (13) becoming $1/F_0(E)$. However, as $S \to \infty$ it is easy to show that $E > 0$ for all $n$. If we formally put $S = 0$ in this $J \to \infty$ limit, the results correspond to the Hubbard model with $U \to \infty$, as pointed out by Okabe [16].

In figure 1 we show results for the spin-reversal excitation energy $E$ as a function of band occupation $n$ in the limit $J \to \infty$, with $S = \frac{1}{2}, 1, \frac{3}{2}$ for (a) the square lattice and (b) the simple cubic lattice. Okabe [16] gives results only for $S = 0$ and $\frac{3}{2}$ in the square lattice and our results agree with his in these cases. (We do not show the $S = 0$ case corresponding to the Hubbard model, since this has been discussed exhaustively elsewhere [20].) The most interesting result is the instability ($E < 0$) of the completely aligned ferromagnetic state in the simple cubic lattice with $S = \frac{1}{2}$, where quantum effects are most important, for $0.12 < n < 0.45$. The increased stability of ferromagnetism in the two-dimensional case follows the same trend as in the Hubbard model [20]. The rather complicated variation of the curves in figure 1 as $S$ is changed is due to competing effects; the factor $n + 2S$ in $[F_0(E)]^{-1}$ tends to increase $E$ with increasing $S$, whereas the same factor in equation (15) leads to a decreasing spin-wave energy which tends to decrease $E$. The form of the curves depends sensitively on the form of the density of states. It is found that the dip in the $S = \frac{1}{2}$ curve in figure 1(b), which gives a region of ferromagnetic instability, disappears if the correct simple cubic density of states is replaced by a semi-elliptical one in the calculations.

As seen in figure 1(b), the present approximation indicates a stable ferromagnetic state for all $n$, with $J \to \infty$, in the physically interesting case of $S = \frac{3}{2}$, corresponding to $Mn^{4+}$ in the manganites. Figure 2 shows the development of an instability as $J$ is decreased although, as Okabe [16] points out, this will not occur in the presence of strong Coulomb repulsion $U$. The instability first occurs for $J$ of the order of the bandwidth with $n \simeq 0.7$. Even




(a)




(b)

**Figure 1.** The spin-reversal excitation energy $E$ (in units of $2t$) as a function of band occupation $n(J \to \infty)$ with $S = \frac{1}{2}, 1, \frac{3}{2}$ for (a) the square lattice and (b) the simple cubic lattice.

when the ferromagnetic ground state is stable there are clearly low-lying single-particle excitations of the type considered here when $n \sim 0.7$. These excitations correspond to removing an ↑-spin electron from the Fermi surface and putting it in a ↓-spin quasiparticle state, which is a bound state of an ↑-spin electron and a magnon, at the bottom of the band $\boldsymbol{k} = 0$. The energy of such excitations, with wave-vector $\boldsymbol{q}$ corresponding to the ↑-spin Fermi surface, will decrease with increasing temperature and they are presumably responsible for the observed damping of spin waves at large $q$ in $LaPb_{0.3}MnO_3$ at $0.8T_c$, where $T_c$ is the Curie temperature [21].

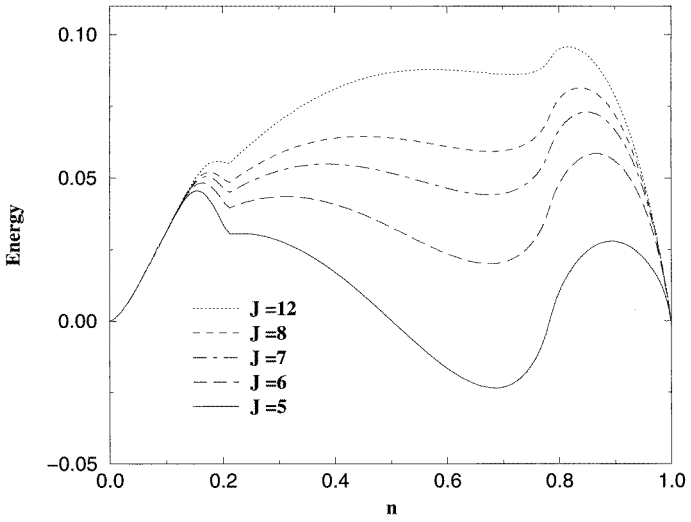



**Figure 2.** The excitation energy $E$ (in units of $2t$) as a function of $n$ for $S = \frac{3}{2}$ with various values of $J$ (in units of $2t$).

Finally we point out that the proven region of ferromagnetic instability could certainly be enlarged by use of improved variational wave-functions. Those used for the Hubbard model [20, 22] could be adapted for this purpose.

## 3. Band narrowing in the paramagnetic state

In the classical treatment of the model defined by equation (1), two sites are considered with one itinerant electron, and the limit $J/t \to \infty$ is taken. The energy of the system is $\pm t\cos(\theta/2)$, where $\theta$ is the angle between the classical vectors representing the two local spins. In an exact quantum-mechanical calculation, Anderson and Hasegawa [9] and Kubo and Ohata [17] classified the states of the two-site system with one electron according to the total spin $S_0$, which includes the electron spin as well as the two local spins. They found energies $\pm t_{eff}$ where

$$t_{eff} = t\left(S_0 + \frac{1}{2}\right)\Big/(2S+1) \tag{16}$$

with $S_0 = \frac{1}{2}, \frac{3}{2}, \ldots, 2S+\frac{1}{2}$. Kubo and Ohata also considered an equivalent picture in which the mobile carrier is a hole strongly coupled antiferromagnetically to local spins $\widetilde{S} = S + \frac{1}{2}$, so that the total spin on a site occupied by a hole is $S$ as it should be. Thus in equation (16), $S$ is replaced by $\widetilde{S}$ and, to preserve the same energies $\pm t_{eff}$ as in the electron picture, $t$ must be replaced by $t(2\widetilde{S}+1)/(2\widetilde{S})$.

To go beyond the two-site problem, Kubo and Ohata [17] introduced a virtual-crystal approximation in which the effective hopping integral $\bar{t}_{eff}$ is given by a weighted average of equation (16) over $S_0$. At high temperature, far above the Curie temperature, the weighting factor is just the degeneracy $2S_0 + 1$, and one finds

$$\frac{\bar{t}_{eff}}{t} = \frac{2}{3} + \frac{1}{3(2S+1)}. \tag{17}$$

As $S \to \infty, t_{eff}/t \to 2/3$, which is the classical result obtained by averaging $\cos(\theta/2)$ over the solid angle.

In the treatments discussed above, only one electron, or hole, is considered and the band-narrowing factor $\bar{t}_{eff}/t$ is due entirely to strong coupling to the local spins. Band narrowing due to correlation between electrons, as occurs in the Hubbard model, is not included. This effect certainly occurs, since the limit $J/t \to \infty$ excludes double occupation of a site just like the limit $U \to \infty$ in the Hubbard model. The aim of this section is to include this effect, using a Green's function equation-of-motion approach with Roth's decoupling approximation [23]. In the appendix, we show how this method, in its simplest form, relates to equation (16) for the two-site one-electron problem. For the ferromagnetic stability problem of section 2, it is equivalent to a variational treatment, considered by Okabe [16], which is somewhat cruder than that used in section 2. In the paramagnetic state at high temperature we find a stronger band-narrowing effect than that of equation (17) and it depends on $n$, the number of itinerant electrons per atom.

The Roth scheme [23] for calculating quasiparticle bands in a correlated system is to consider a retarded Green's function matrix $G$, with elements $G_{pq}(\omega) = \langle\langle A_q; A_q^\dagger\rangle\rangle$, where the operators $A_p$ are a set of fermionic operators suitable for describing one-particle excitations. A clever decoupling procedure for the equation of motion leads to the result

$$G(\omega) = N(\omega N - E)^{-1}N \tag{18}$$

where the energy and normalization matrices, $E$ and $N$, are given by the thermal averages

$$E_{pq} = \langle[[A_p, H], A_q^\dagger]_+\rangle \qquad N_{pq} = \langle[A_p, A_q^\dagger]_+\rangle. \tag{19}$$

The one-particle excitation energies $\omega$ are thus given by $\det(\omega N - E) = 0$. For the Hubbard model, Roth [23] used two operators for a given wave-vector $\boldsymbol{k}$ leading to an excitation spectrum consisting of two quasiparticle bands. Recent quantum Monte Carlo calculations [24] yield spectra which are dominated by two peaks for each $\boldsymbol{k}$, thus defining two quasiparticle bands. The Roth and Monte Carlo bands for $U = 8|t|$ are generally in remarkable agreement [25]. For $n = 0.75$, where $n$ is the number of electrons per atom, the two methods yield the same width of the narrowed lower band, but as $n$ increases towards 1 the bands obtained by the Roth method narrow more rapidly than in the Monte Carlo data. It should be mentioned that a different method of analysing Monte Carlo data leads to more spectral structure than the simple two-peak form [26]. For $U \to \infty$ the upper band is removed to infinity and the lower band is obtained in the Roth scheme with a single Bloch operator which ensures that no site is doubly occupied. We apply a similar procedure to the model defined by equation (1) with $J \to \infty$; in this case the operator must not only ensure that an electron does not hop onto a site which is already occupied, but that if it hops onto an unoccupied site it does so with spin parallel to the local moment, forming a state of total spin $S + \frac{1}{2}$. The required operator for the $\uparrow$-spin Green's function is

$$A_{\boldsymbol{k}} = N^{-1/2}\sum_i \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}_i}A_i \tag{20}$$

with

$$A_i = (S + 1 + S_i^z)(1 - n_{i\downarrow})c_{i\uparrow} + S_i^-(1 - n_{i\uparrow})c_{i\downarrow} \tag{21}$$

where $n_{i\sigma} = c_{i\sigma}^\dagger c_{i\sigma}$. For the single operator $A_{\boldsymbol{k}}$, the matrices $E$ and $N$, given by equation (19), are just numbers and the quasiparticle band is given by

$$\omega_{\boldsymbol{k}} = E_{\boldsymbol{k}}/N_{\boldsymbol{k}} \tag{22}$$

with

$$E_{\boldsymbol{k}} = \langle [[A_{\boldsymbol{k}}, H], A_{\boldsymbol{k}}^{\dagger}]_{+} \rangle \qquad N_{\boldsymbol{k}} = \langle [A_{\boldsymbol{k}}, A_{\boldsymbol{k}}^{\dagger}]_{+} \rangle. \tag{23}$$

Writing $H = H_0 + H_1$, as in equation (1), we have

$$E_k = \langle [[A_{\boldsymbol{k}}, H_0], A_k^{\dagger}]_{+} \rangle + \langle [[A_{\boldsymbol{k}}, H_1], A_k^{\dagger}]_{+} \rangle = E_0(\boldsymbol{k}) + E_1(\boldsymbol{k}). \tag{24}$$

It is easily shown that $[A_{\boldsymbol{k}}, H_1] = -\frac{1}{2} JSA_{\boldsymbol{k}}$, so $E_1 = -\frac{1}{2} JSN_{\boldsymbol{k}}$ and

$$\omega_{\boldsymbol{k}} = -\frac{1}{2} JS + E_0(\boldsymbol{k})/N_{\boldsymbol{k}}. \tag{25}$$

Clearly, from (23) and (20), $N_{\boldsymbol{k}} = \langle [A_i, A_i^{\dagger}]_{+} \rangle$, independently of $\boldsymbol{k}$, and

$$E_0(\boldsymbol{k}) = \langle [[A_i, H_0], A_i^{\dagger}]_{+} \rangle + N^{-1} \sum_{\langle i,j \rangle} \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{R}_i - \boldsymbol{R}_j)} \langle [[A_i, H_0], A_j^{\dagger}]_{+} \rangle. \tag{26}$$

Hence, from (25),

$$\omega_{\boldsymbol{k}} = \lambda \epsilon_{\boldsymbol{k}} + \boldsymbol{k} - \text{independent terms} \tag{27}$$

where the band-narrowing factor $\lambda$ is given by

$$\lambda = P/Q \tag{28}$$

with

$$P = -t^{-1} \langle [[A_i, H_0], A_j^{\dagger}]_{+} \rangle \tag{29}$$

$$Q = N_{\boldsymbol{k}} = \langle [A_i, A_i^{\dagger}]_{+} \rangle. \tag{30}$$

Here $i$ and $j$ are nearest-neighbour sites.

After a lengthy but straightforward calculation we find

$$\begin{aligned} P = \langle & (S + 1 + S_i^z)(S + 1 + S_j^z)[(1 - n_{i\downarrow})(1 - n_{j\downarrow}) + \sigma_i^- \sigma_j^+] \\ & + S_i^- S_j^+ [(1 - n_{i\uparrow})(1 - n_{j\uparrow}) + \sigma_i^+ \sigma_j^-] \\ & + (S + 1 + S_i^z) S_j^+ [(1 - n_{i\downarrow})\sigma_j^- + (1 - n_{j\uparrow})\sigma_i^-] \\ & + (S + 1 + S_j^z) S_i^- [(1 - n_{i\uparrow})\sigma_j^+ + (1 - n_{j\downarrow})\sigma_i^+] \rangle \end{aligned} \tag{31}$$

and

$$\begin{aligned} Q = \langle & (S + 1 + S_i^z)^2 (1 - n_{i\downarrow}) + (S + 1 + S_i^z) S_i^- \sigma_i^+ \\ & + S_i^+ (S + 1 + S_i^z) \sigma_i^- + (1 - n_{i\uparrow})(1 - n_{i\downarrow}) S_i^- S_i^+ + (1 - n_{i\uparrow}) n_{i\downarrow} S_i^+ S_i^- \rangle. \end{aligned} \tag{32}$$

In the appendix we show how the band-narrowing factor $P/Q$ calculated here relates to that of Kubo and Ohata (equation (16)), for the two-site one-electron case, and to a variational result of Okabe [16] for the ferromagnetic case. Here we concentrate on the band narrowing in the paramagnetic state. In this case it should be possible to write the thermal averages of $P$ and $Q$ in a rotationally invariant form, independent of the choice of spin-quantization axis. This may be achieved by symmetrizing $P$ and $Q$ under an interchange of $\uparrow$ and $\downarrow$ spins whereby $S_i^z \to -S_i^z$, $n_{i\uparrow} \to n_{i\downarrow}$, $S_i^- \to S_i^+$, $\sigma_i^- \to \sigma_i^+$ etc. Thus $P$ and $Q$ are each written as the means of two expressions, before and after the interchange. We also invoke

the symmetry of $P$ under interchange of $i$ and $j$. After some manipulation we find the rotationally invariant forms

$$P = \frac{1}{2}\left\langle [(S+1)^2 + \boldsymbol{S}_i \cdot \boldsymbol{S}_j]\left[2 - n_i - n_j + \frac{1}{2}n_i n_j + 2\boldsymbol{\sigma}_i \cdot \boldsymbol{\sigma}_j\right]\right\rangle + \frac{1}{2}(S+1)\langle(3 - n_i - n_j)(\boldsymbol{S}_i + \boldsymbol{S}_j)\cdot(\boldsymbol{\sigma}_i + \boldsymbol{\sigma}_j)\rangle + \langle(\boldsymbol{S}_j \cdot \boldsymbol{\sigma}_j)\boldsymbol{S}_i \cdot \boldsymbol{\sigma}_i\rangle - \langle(\boldsymbol{S}_j \cdot \boldsymbol{\sigma}_i)(\boldsymbol{S}_i \cdot \boldsymbol{\sigma}_j)\rangle \tag{33}$$

and

$$Q = (2S+1)\left(S + 1 - \frac{1}{2}n\right) \tag{34}$$

where $n_i = n_{i\uparrow} + n_{i\downarrow}$ and $n = \langle n_i \rangle$. In evaluating the thermal average for $Q$ we have used the result $\langle \boldsymbol{S}_i \cdot \boldsymbol{\sigma}_i \rangle = \frac{1}{2}nS$ which is appropriate for $J \to \infty$, the case considered in this section. We note that the normalization factor $Q$ $(=N_k)$ is independent of temperature in the paramagnetic state. Clearly the band-narrowing factor $P/Q$ depends on local and itinerant-spin correlations in a much more subtle way than the classical $\langle \cos\theta/2 \rangle$ result. To evaluate $P$ more explicitly, we consider the high-temperature limit where there is no correlation between neighbouring sites, so that the correlation functions can be factorized. Then

$$P = \left(S + 1 - \frac{1}{2}n\right)^2 + \langle(\boldsymbol{S}_i \cdot \boldsymbol{S}_j)(\boldsymbol{\sigma}_i \cdot \boldsymbol{\sigma}_j)\rangle - \langle(\boldsymbol{S}_j \cdot \boldsymbol{\sigma}_i)(\boldsymbol{S}_i \cdot \boldsymbol{\sigma}_j)\rangle = \left(S + 1 - \frac{1}{2}n\right)^2 \tag{35}$$

since the last two terms cancel on expanding the scalar products and factorizing. Hence, from (28), (34) and (35) the band-narrowing factor at high temperature is

$$\lambda = \frac{1}{2}\left(1 + \frac{1-n}{2S+1}\right). \tag{36}$$

Comparing this with Kubo and Ohata's factor, given by equation (17), we note a stronger band-narrowing effect, particularly as the occupation of the band approaches one electron/atom. In this limit, $\lambda$ is independent of $S$, and the same result $\lambda = \frac{1}{2}$ is obtained for all $n$ as $S \to \infty$. Kubo and Ohata's result is based on an average two-site problem, whereas we consider a correlated electron propagating through the crystal.

## 4. Conclusion

Much recent work on the double-exchange model uses the approximation of classical local spins, which ensures a stable ferromagnetic state. We have shown rigorously that for quantum spins $S = \frac{1}{2}$, and band occupation $n$ in the range $0.12 < n < 0.45$, the state of complete spin alignment is unstable against single-particle spin-flip excitation, even for infinite Hund's rule coupling.

The quasiparticle with reversed spin is a bound state of a majority-spin electron and a magnon. For the manganite case of $S = 3/2$, where the ferromagnetic state is stable in our approximation, similar low-lying excitations are expected to play an important role as the Curie temperature is approached, for example in the damping of spin waves and the transport properties. We have also investigated band narrowing in the paramagnetic state, particularly in the high-temperature limit. The band narrowing depends on occupation of the band and on spin $S$. Our calculation, in which we consider a correlated electron propagating

through the lattice, yields stronger band narrowing than that deduced from an averaged two-site problem. When combined with strong electron–phonon coupling, this effect may be important for understanding the insulating paramagnetic state of the manganites.

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**Appendix**

We first show how the method of section 3 relates to Anderson and Hasegawa's [9] and Kubo and Ohata's [17] two-site result quoted as equation (16). In the standard Roth procedure [23], the averages in the expressions for $E_k$ and $N_k$ (equation (23)) are independent thermal averages. For the simple system of two sites with one electron, we can adopt an alternative approach. Both expectation values can be calculated in an eigenstate of the system, classified according to the total spin $S_0$, and an averaging of the resulting band-narrowing factor $t_{eff}/t$, or $\lambda$ in equation (28), can be carried out subsequently, following Kubo and Ohata. A state of total spin $S_0$ is produced by adding an $\uparrow$-spin electron to an eigenstate $|S_0 - \frac{1}{2}, S_0 - \frac{1}{2}\rangle$ of the two-spin system with total spin $S_0 - \frac{1}{2}$ and $z$-component of the spin $S_0 - \frac{1}{2}$. Thus the expectation values $P$ and $Q$, given by equations (31) and (32), are evaluated in the state $|S_0 - \frac{1}{2}, S_0 - \frac{1}{2}\rangle$, with no electron present. Hence

$$P = \langle (S + 1 + S_i^z)(S + 1 + S_j^z) + S_i^- S_j^+ \rangle \tag{A1}$$

$$Q = \langle (S + 1 + S_i^z)^2 + S_i^- S_i^+ \rangle. \tag{A2}$$

Both are simply evaluated, using $\langle S_i^z \rangle = \frac{1}{2}(S_0 - \frac{1}{2})$ in the case of $Q$, and one obtains equation (16) for $t_{eff}/t = \lambda = P/Q$.

Finally we show how the Roth method of section 3 gives a result for the propagation of a single $\uparrow$-spin electron, with all local spins and other itinerant spins completely aligned down, which is equivalent to a variational result of Okabe [16]. In this case, with $\langle S_i^z \rangle = -S$,

$$P = \langle (1 - n_{i\downarrow})(1 - n_{j\downarrow}) \rangle \tag{A3}$$

$$Q = \langle (1 - n_{i\downarrow})(1 + S_i^- S_i^+) \rangle = (2S + 1)(1 - n) \tag{A4}$$

where $n$ is the number of $\downarrow$-spin electrons per atom. $P$ is readily evaluated in the Fermi sea of non-interacting $\downarrow$-spin electrons by transforming to Bloch operators. The final result for the $\uparrow$-spin band-narrowing factor $\lambda = P/Q$ is

$$\lambda = \frac{1}{2S + 1}\left[1 - n - \frac{E_g^2}{(zt)^2(1 - n)}\right] \tag{A5}$$

where

$$E_g = N^{-1} \sum_{\boldsymbol{k}} \langle n_{\boldsymbol{k}\downarrow} \rangle \epsilon_{\boldsymbol{k}}. \tag{A6}$$

This agrees with the factor in Okabe's [16] equation (5.2), apart from an obvious misprint. Hence, for the case of a single spin flip, our Roth method is equivalent to a variational *ansatz* which, although inferior to the *ansatz* of section 2, gives reasonable results for the corresponding $U = \infty$ Hubbard model. In fact, by putting $S = 0$ in (A5) we have the result of Shastry *et al* [27] for the Hubbard model.

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