Role of the superexchange interaction in magnetic transition and polaron crossover

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The Hubbard-Holstein model is studied including double-exchange interaction and superexchange interaction using a variational phonon basis obtained through the modified Lang-Firsov (MLF) transformation followed by the squeezing transformation. The kinetic energy, polaron crossover and magnetic transition are investigated as a function of electron-phonon (e-ph) coupling and electron concentration for different values of antiferromagnetic superexchange interaction (J) between the core spins. The polaron crossover, magnetic transition and the suppression of ferromagnetic transition with J are discussed for the model.

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Recently the interest in the double exchange model [1] has grown considerably with the discovery of very large negative colossal magnetoresistance (CMR) [2] and anomalous magnetotransport properties in doped manganites [3], namely in \(R_{1-x}A_x\text{MnO}_3\) (where \(R=\text{La, Pr and A}=\text{Ca, Sr, Ba}\)). Ferromagnetism in these compounds (for \(x\sim 0.2-0.4\)) is believed to be due to the ‘double-exchange’ (DE) mechanism which operates when local Mn-ion spins are strongly coupled by Hund’s rule with the spins of the itinerant electrons occupying a narrow band. However, the experimental results [3] in manganites, namely the sharp change in resistivity near \(T_c\) and the physics of CMR, cannot be explained by the DE alone [4]. Millis suggested the lattice polaron effects due to strong electron-phonon (e-ph) interaction as a necessary extension [5]. Röder et al. [6] also examined the combined effect of e-ph interaction and DE on \(T_c\) using the variational wave function techniques. In fact, the contribution of the lattice polaron to carrier mobility was pointed out earlier by Goodenough [7]. Several theoretical models have been proposed based on lattice-carrier coupling [6,8–11]. Many experiments [12] indicate evidence of strong lattice-electron coupling in Manganese Oxides [12] which shapes the properties of manganites crucially. Moreover, small to large polaron crossover is reported by many experimental groups [13,14]. There are models [8,9,11] which incorporate DE interaction in a polaronic model. Min and co-workers [8] studied the combined model of spin double exchange and lattice polaron to investigate the effect of small to large polaron crossover on the magnetic and transport properties under the mean-field approximation scheme. However, the superexchange interaction also plays an important role in manganites and a study considering e-ph and superexchange interactions in a double exchange model is important.

In manganites, a competing tendency towards the localization comes through the e-ph interaction which stabilizes a local distortion of the Oxygen octahedron surrounding each Manganese ion. DE favours the ferromagnetism whereas superexchange interaction (SE) antiferromagnetism; hence the DE and SE interactions compete with each other. The interplay between lattice-carrier coupling, DE and the SE interactions is the reason for the rich phase diagram of the manganites. So it would be of great interest to study the role of SE interaction (J) in the combined model of DE and e-ph interaction. In this work we will follow a method based on variational phonon basis [15] which is promising for Holstein [16–18] and related models [19] to predict the correct results up to intermediate range of hopping \((t)\) \((t \leq \omega_0\) where \(\omega_0\) is the phonon frequency) [17]. The importance of a variational phonon basis in predicting accurate results has been proved for a two-site system over the entire range of e-ph couplings [17]. Our previous study [19] on the ‘two-site’ double exchange model with a single polaron as a function of e-ph couplings reveals that the ferromagnetic (FM) to antiferromagnetic (AFM) crossover does not coincide always with the polaron crossover. If it occurs for some suitable value of \(J/t\), large changes in the effective hopping and lattice distortion occur in the crossover region on application of the magnetic field. In ref. [19] a possibility of an FM insulating state in between the FM large polaron and AFM small polaron state has also been observed for small values of \(J\). In this paper we consider a many site and many electron double exchange system and study the role of the superexchange and e-ph interaction on the magnetic crossover.

The Hubbard Holstein Hamiltonian in presence of double exchange and superexchange interaction is given by

\[
H = - \sum_{<i,j>,\sigma} t \cos(\theta) n_{i\sigma} c_{j\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow} + \omega_0 \sum_i b_i^\dagger b_i + J \sum_{<i,j>} S_i^x S_j^x + g\omega_0 \sum_{i,\sigma} (b_i + b_i^\dagger)
\]

(1)
where \( c_{i\sigma} (c^\dagger_{i\sigma}) \) is the annihilation (creation) operator for the electron with spin \( \sigma \) at site \( i \) and \( n_{i\sigma} \) is the corresponding number operator, \( U \) is on-site Coulomb repulsion, \( b_i \) and \( b_i^\dagger \) are the annihilation and creation operators, respectively, for the phonons corresponding to intramolecular vibrations at site \( i \); \( g \) denotes the on-site \( e\text{-}ph \) coupling strength. \( \vec{S}_i \) and \( \vec{S}_j \) are the core-spins at the site \( i \) and \( j \) respectively, \( \theta \) is the angle between the core-spins \( \vec{S}_i \) and \( \vec{S}_j \) and \( J \) is the AFM-SE interaction between the neighbouring core-spins. The transfer hopping integral \( (t) \) is modified to \( t \cos(\frac{\theta}{2}) \) by the strong Hund’s coupling between the spins of the core electron and itinerant electron [1]. The localized spins are treated classically here. It may be mentioned that many workers [6,8] have followed the single orbital approximation on the ground state as the Jahn-Teller (JT) effect (static and dynamic) will split the \( e_g \) double degeneracy [20] and the mobile \( e_g \) electron would occupy the lower energy orbital at low temperature. The present assumption of single orbital is expected to be reasonable for doping regime \( (x < 0.4-0.5) \) where CMR occurs.

For a general value of \( e\text{-}ph \) coupling, the spread and depth of lattice deformations can be studied using Modified Lang-Firsov (MLF) transformation. To treat the lattice deformations that produced at different sites around the electron variationally we use the MLF transformation [15],

\[
\tilde{H} = e^R H e^{-R}
\]

(2)

\[
R = \sum_i \left[ \lambda_0 n_i (b_i^\dagger - b_i) + \sum_{\delta} \lambda_1 n_i (b_{i+\delta}^\dagger - b_{i+\delta}) \right]
\]

(3)

with \( \lambda_0 \) and \( \lambda_1 \) represent the lattice deformations at the electron site and next-nearest neighbour sites, respectively. When \( \lambda_0 = g \) and \( \lambda_1 = 0 \), MLF transformation reduces to Lang-Firsov (LF) transformation [21]. At zero temperature the simplest procedure is to make zero phonon averaging to obtain an effective polaronic Hamiltonian. But for a many electron system it is better to use a two-phonon coherent state [22] for phonon averaging

\[
|\psi\rangle_{ph} = \exp\left[\alpha \sum_i (b_i b_i^\dagger - b_i^\dagger b_i)\right] |0\rangle_{ph}
\]

(4)

\( \alpha \) is the squeezing parameter and treated variationally. \( \alpha \) is nonzero and its effect becomes significant only for intermediate \( e\text{-}ph \) coupling and finite carrier concentration [15]. Increasing \( \alpha \) enhances the overlapping of the phonon wavefunctions at the nearest-neighbor sites, hence, increases the polaronic hopping. For a many electron system, consideration of \( \alpha \) lowers the ground state energy (for intermediate coupling) and smoothens the polaron crossover compared to those obtained by MLF and zero phonon averaging.

The MLF-transformed Hamiltonian, averaged over the squeezed phonon state, yields the effective polaronic Hamiltonian as

\[
\tilde{H}_{eff} = \sum_{i,\sigma} \epsilon_p n_{i,\sigma} - t_p \cos(\frac{\theta}{2}) \sum_{<i,j>,\sigma} c^\dagger_{i\sigma} c_{j\sigma} + U_{eff} \sum_i n_{i\uparrow} n_{i\downarrow} + J S^2 \cos \theta + V_1 \sum_{i,j} n_i n_j + V_2 \sum_{i,\delta \neq 0} n_{i+\delta} n_{i+\delta} + N \omega_0 \sin^2(2\alpha)
\]

(5)

where \( \epsilon_p \) is the polaronic self-energy, \( t_p \) is the polaronic hopping, \( U_{eff} \) is the effective on-site interaction, \( V_1 \) and \( V_2 \) are interactions between polarons at nearest-neighbour and next-nearest-neighbour sites, respectively. These quantities are obtained as

\[
\epsilon_p = -\omega_0 (2g - \lambda_0) \lambda_0 + z \omega_0 \lambda_1^2
\]

\[
t_p = t \exp\left[\exp(-4\alpha)\{-(-\lambda_0 - \lambda_1)^2 - (z - 1)\lambda_1^2\}\right]
\]

\[
U_{eff} = U - 2 \omega_0 (2g - \lambda_0) \lambda_0 - z \omega_0 \lambda_1^2
\]

\[
V_1 = -2(g - \lambda_0) \omega_0 \lambda_3
\]

\[
V_2 = \omega_0 \lambda_1^2
\]

(6)

\( N \) is the total number of sites in the system.

The ground state energy \( (E_G) \) of the system per site is obtained in the framework of Hartree-Fock approximation

\[
\frac{E_G}{N} = \epsilon_p x_e - \frac{z p t_p \cos(\frac{\theta}{2})}{2} + \frac{U_{eff}}{4} x_e^2 + \frac{J}{2} S^2 \cos \theta + V_1 z x_e^2 + V_2 z^2 x_e^2 + \omega_0 \sin^2(2\alpha)
\]

(7)

where \( z \) is the number of nearest neighbours, \( x_e \) is the number of electrons per site,

\[
x_e = \frac{1}{N} \sum_i \langle n_i \rangle, \quad z' = \sum_{\delta \neq 0} 1
\]

\( p = \langle c^\dagger_{i,\sigma} c_{j,\sigma} \rangle \) = \( \frac{S_d}{z N} \sum_q \gamma_q n_q \gamma_q \)

\( \gamma_q = \sum' e^{i\vec{q}(\vec{R}_i - \vec{R}_j)} \) and \( S_d = 2 \) is the spin degeneracy.

For simplicity we choose a square density of states, then one obtains at zero temperature \( p = \frac{z}{4} (2 - x_e) \) [15]. The polaronic variational parameters \( \lambda_0 \), \( \lambda_1 \) and \( \alpha \) as well as the magnetic variational parameter \( \theta \) are determined from the minimization of the ground state energy. For \( \theta \) a simple analytical expression is obtained as,

\[
\cos(\frac{\theta}{2}) = \frac{p t_p}{2 J S^2} \quad (\text{for nonzero solution of } \theta)
\]

(8)

For \( p t_p \geq 2 J S^2 \), \( \theta \approx 0 \) which corresponds to FM state. In this work we will limit to small values of \( t \) \((t < \omega_0)\) so that the error encountered in phonon averaging is small and does not change our results significantly. We have considered lattice deformations only up to the nearest-neighbour sites (around the electron) to avoid too many variational parameters and because of the fact that for \( t < \omega_0 \) the inclusion of variational parameters describing lattice distortions at distant sites do not change the
qualitative behaviour of the results. For numerical calculation in this paper we consider $z$ and $z'$ are 4 and 12, respectively and energy parameters $t$, $U$ and $J$ are expressed in unit of $\omega_0=1.0$.

In Fig. 1 we plot the angle ($\theta$) between the core spins on nearest-neighbor sites, the effective hopping ($t_{\text{DE}} = t_p \cos(\theta/2)$) of the itinerant electron and the on-site lattice deformation ($\lambda_0/g$) as a function of $e$-ph coupling ($g$) for different values of $J$ and $t$. Figs. 1(a) and 1(b) (for $t=0.7$) show that for small $g$ the ground state is the FM with large polaron as carriers. The signature of large polaron is evident from weak polaronic reduction in hopping and the reduced value of $\lambda_0/g$. For large $g$ the ground state is the AFM state ($\theta=\pi$) with small polarons as carriers. The above result may be understood considering the fact that increasing $e$-ph coupling leads to a polaronic reduction of the kinetic energy which in turn destroys the FM state since the stability of the FM state requires $p t_p \geq 2 J S^2$. Similar behavior has also been obtained by recent numerical studies [23]. Fig. 1 shows that the magnetic transition occurs simultaneously with the large to small polaron crossover within the present model. With increasing $J$ the magnetic transition as well as the polaron crossover shifts towards lower values of $e$-ph coupling and becomes smoother. Similar effect is also obtained by decreasing the value of $t$ (Figs. 1(c) and 1(d)). For $t=0.5$ and higher values of $J$ ($J S^2=0.1$) the canted magnetic state is stable for weak $e$-ph coupling and the transition from the canted state to the AFM state with increasing $g$ is very smooth. Fig. 1 also shows that the nature of the magnetic transition depends on both $t$ and $J$.

![Graph](image1)

FIG. 1. Plot of $\lambda_0/g$, $t_{\text{DE}}/t$ and $\theta$ (in radian) for $x_e=0.3$, $U=1.0$ as a function of $g$. (a) $t=0.7$ and $J S^2=0.035$; (b) $t=0.7$ and $J S^2=0.07$; (c) $t=0.5$ and $J S^2=0.05$ and (d) $t=0.5$ and $J S^2=0.1$.

![Graph](image2)

FIG. 2. (a) Plot of $\theta$, $t_{\text{DE}}/t$, $\lambda_0/g$ and $\lambda_1/\lambda_0$ as a function of electron concentration ($x_e$) for $t=0.5$, $U=1.0$, $J S^2=0.016$ and $g=1.8$. Inset figure for higher values of $J S^2$ and $g$. (b) Plot of $\theta$, $t_{\text{DE}}/t$ vs. $x_e$ with $t=0.5$, $J S^2=0.01$ for different values of $e$-ph coupling.

In Fig. 2(a) the variations of $\lambda_0$, $\lambda_1$, $t_{\text{DE}}$ and $\theta$ with electron concentration ($x_e$) are shown for different values of $g$ and $J$. For low electron concentrations, the ground state is AFM and the carriers are small polarons. As the electron concentration increases $\lambda_0$ decreases while $\lambda_1$ increases depicting a small to large polaron crossover. For intermediate electron concentrations the ground state is FM with large polaronic carriers. The Hamiltonian (1), that we considered, has a particle-hole symmetry. This is reflected in Fig. 2(a) where all the physical quantities (presented in the figure) are symmetric with respect to half filling ($x_e=1$). In Fig. 2(b) we have plotted $\theta$ and $t_{\text{DE}}$ against $x_e$ for different values of $e$-ph coupling. In absence of $e$-ph coupling ($g=0$) spin canting ($0 < \theta < \pi$) starts at the smallest carrier concentration and the cant-
ing increases with $x_c$ until the material becomes ferromagnetic at a low value of critical concentration $x_{cr}$ [24]. With increasing $g$ the AFM small polaronic state remains the ground state for a range of low carrier concentration and the value of $x_{cr}$ increases. For $JS^2/t=0.02$, which is reasonable for manganites, the AFM-FM transition occurs around $x_c \sim 0.2$ for $g=1.8$. Fig. 2(b) shows that the region of AFM small polaron state extends at the expense of the FM large polaronic region with increasing $J$ or $g$ (also evident in the inset of Fig. 2(a)). This is simply due to the fact that the FM large polaron state is destroyed by increasing the AFM interaction as well as by the suppression of the kinetic energy with increase of $e$-$ph$ coupling. Hence the combined role of $e$-$ph$ coupling and SE interaction determines the physics of the system.

It may be mentioned that near half filling ($x_c \sim 1$) the system is susceptible to show charge ordering depending on the choice of the parameters. However, we have not addressed this issue here, because our main interest in this paper is in the region from low to intermediate filling where a transition from an AFM small polaronic state to FM large polaron state occurs as the density of the carriers increases and the $e$-$ph$ coupling plays a crucial role in this transition.

In manganites there are SE interactions between nearest neighbor $e_g$ electrons. This interaction originates from the virtual hopping of $e_g$ electrons and is proportional to the square of the hopping matrix element and inversely proportional to the increase in energy ($\sim$ on-site Coulomb repulsion $U_{eff}$) in the intermediate state when two electrons occupy the same site. The SE interaction between the $e_g$ electrons determines the orbital ordering temperature in undoped manganite [25]. A relevant question may be asked whether this SE interaction will be reduced by the small polaron formation as the polaronic hopping is suppressed. One of us [26] has shown earlier in the context of Hubbard model that the SE interaction is not reduced by the polaron formation because in virtual hopping the lattice deformations are not transferred from site to site. Rather a slight decrease in the value of the on-site repulsion due to polaron formation may slightly increase the SE interaction between $e_g$ electrons.

In Fig.3 we plot the electronic effective half-bandwidth ($W$) as a function of the AFM interaction for different (intermediate) values of $e$-$ph$ coupling. It is seen that the bandwidth has a unique dependence on $J$ also. In the metallic FM region the bandwidth is independent of $J$; whereas in the canted state the bandwidth is suppressed drastically with increasing $J$. Narrowing of the electronic bandwidth is considered to be one of the origins of the suppression effect of the transition temperature $(T_c)$ for doped manganites. Strong $e$-$ph$ interaction favours the band narrowing due to the small polaron formation. The AFM-SE interaction may be considered as another candidate for band narrowing mechanism. Our mean-field result is qualitatively consistent with the Monte Carlo study of FM Kondo lattice model [27]. Fig. 3 also shows that increasing $e$-$ph$ coupling extends the AFM small polaron phase with negligible bandwidth in the $JS^2$ space, similar to that observed as a function of electron concentration in Fig. 2(a).

In summary, we have studied the role of SE interaction ($J$) in a many-site DE-Holstein model within the mean-field approximations using the variational phonon basis. The polaron crossover and the magnetic transition are studied as a function of $e$-$ph$ coupling ($g$) and electron concentration for different values of $J$. The suppression of the FM phase and the narrowing of the bandwidth with both $J$ and $g$ are observed. The small to large polaron crossover as well as the AFM-FM transition is found to occur at a higher electronic concentration as $J$ or $g$ increases.

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