

# Quantum Treatment of the Anderson-Hasegawa Model – Effects of Superexchange and Polarons

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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 quantum considerations further lead to new results when polaronic effects, believed to be ubiquitous in manganites due to electron-phonon coupling, are included. The consequence of these results for the magnetic phase diagrams and the thermal heat capacity is also carefully analysed.

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## I. 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 fifty years ago [2], is encapsulated within a simple two site model of Anderson and Hasegawa [3, 4, 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 3 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 kinetic energy 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  $\theta$ , 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  $\theta$  equals  $\pi$ , the core spins have antiferromagnetic (AFM) coupling and hopping of the itinerant electron is totally inhibited. On the other hand, if  $\theta$  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  $S \rightarrow \infty$ , 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.

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 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 in a nontrivial manner if the core spins are dealt with quantum mechanically, which leads to a correlated diagonal disorder in these systems, even in the cleanest samples. Our starting point therefore is the Hamiltonian for a two site one electron model, including the superexchange interaction, given by

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

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  $\tau$ ,  $J_H$  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.

With the preceding background, the motivation behind our work and the plan of this paper are as follows. 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 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, in our opinion, about the classical limit of infinitely large core spins. This has led to some confusion about the interpretation of parameters in the model which needs to be cleared. As the value of the core spins in most studied CMR systems is indeed finite — three-halves for manganese — it is important to delineate the quantum versus classical effects, especially while considering additional phenomena, e.g., polaron-induced hopping and thermodynamics. With this aim in mind, we organize the paper as follows. We present in Sec. II, the exact quantum mechanical solution to the

Anderson-Hasegawa model with an additional superexchange term, take the large Hund's rule coupling limit and discuss the outcome of a hitherto ignored 'site-disorder' term. In Sec. III we reexamine the issue of polaron-assisted hopping in the light of our fully quantum calculation. The results in this section are then employed in Sec. IV for the computation of heat capacity and phase diagram, wherein we also specify the difference between our results and those which treat the core spins classically. Finally, in Sec. V, we present some concluding remarks.

## II. EXACT SOLUTION FOR THE ANDERSON-HASEGAWA MODEL

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,

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

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,

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

where,

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

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  $\alpha$  and  $\theta$  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,

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

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,

$$2E = \frac{J_H}{2} + K_1(J) \pm \sqrt{4t^2 + K_T^2(J) + K_3^2(J) \pm 4t \cos(\theta/2) \sqrt{K_T^2(J) + K_3^2(J)}}, \quad (8)$$

where,

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

$$K_T(J) = \left[ \frac{J_H(2S+1)}{2} + K_2(J) \right] \quad (9)$$

$$K_2(J) = J \cos(\alpha) \left( S_0 + \frac{1}{2} \right) \quad (10)$$

$$K_3(J) = J \sin(\alpha) \left( S_0 + \frac{1}{2} \right). \quad (11)$$

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 (upto  $O(1/J_H)$ ). We find that the lowest energy eigenvalues are given by

$$E_m = -\frac{J_H S}{2} - t \cos(\theta/2) + \frac{J}{2} [\bar{S}'(\bar{S}' + 1) - 2S(S+1)] + J \sin^2(\alpha/2) \left( S_0 + \frac{1}{2} \right), \quad (12)$$

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 parameters  $\cos(\theta/2)$  and  $\cos(\alpha/2)$  take 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,

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

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

There are primarily three important points to be made about  $\Delta E_J$  :

(a) This term is an on-site term : It does not involve physical transfer of the itinerant electron from one site to the other.

(b) This term vanishes in the absence of the itinerant electron. Thus, it exists only on the site at which the electron resides and hence, at any site  $i$ , it will be proportional to  $n_i$ , where  $n_i$  is the number of itinerant electrons at the site  $i$  and is taken to be either 1 or 0 in the absence of double occupancy.

(c) At any site  $i$  this term depends on 3 spin values : the spin of the itinerant electron on the site  $i$  ( $\sigma_i$ ), 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  $i$ .

Thus, the extra energy term  $\Delta E_J$  corresponds to a site energy term which is correlated with the core spins of the nearest neighbors. We may therefore propose an effective double-exchange Hamiltonian in the full lattice as

$$H_{\text{eff}} = \sum_i \epsilon_i n_i - t \sum_{\langle ij \rangle} \cos(\theta_{ij}/2) (c_i^\dagger c_j + H.C.) + \sum_{\langle ij \rangle} J_{ij} \vec{S}_i \cdot \vec{S}_j, \quad (14)$$

where

$$\epsilon_i = \sum_j \frac{J_{ij}}{2} \frac{2S - S'_{ij}}{2S + 1} (S'_{ij} + 1), \quad (15)$$

and

$$S'_{ij} = | \vec{S}_i + \vec{S}_j |. \quad (16)$$

We have explicitly taken  $J_{ij}$  in order to accomodate effects of anisotropic superexchange also.

The classical limit of the extra term is given by

$$\Delta E_J^{Cl} = \frac{J}{2} (2S + 1) [1 - \cos(\theta/2)] \cos(\theta/2), \quad (17)$$

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 the on site disorder and the hopping, correlated



with the spins on the lattice. A variety of interesting physical phenomena could be studied by taking into consideration the quantum Hamiltonian. One of these concerns the polaron effects, which are discussed below in Section III.

### III. ANDERSON-HASEGAWA-HOLSTEIN MODEL

Experiments in manganites - both thermodynamic and transport - seem to suggest the importance of polaron formation and the consequent localization of charge carriers [9]. The minimal model which reflects such lattice carrier interaction on the double-exchange can be introduced by dovetailing the Holstein mechanism on the Anderson-Hasegawa Hamiltonian. Therefore, in view of the results presented in Sec. II, in the limit of large Hund's rule coupling, we may write a two site Anderson-Hasegawa-Holstein Hamiltonian as,

$$\begin{aligned}
H = & \epsilon \sum_{i=1}^2 \sum_{\sigma} n_{i\sigma} - \sum_{\sigma} t \frac{S_0 + \frac{1}{2}}{2S + 1} (c_{1\sigma}^{\dagger} c_{2\sigma} + c_{2\sigma}^{\dagger} c_{1\sigma}) + g_1 \omega_0 \sum_{i=1}^2 \sum_{\sigma} n_{i\sigma} (b_i + b_i^{\dagger}) \\
& + g_2 \omega_0 \sum_{\sigma} \left[ n_{1\sigma} (b_2 + b_2^{\dagger}) + n_{2\sigma} (b_1 + b_1^{\dagger}) \right] + \omega_0 \sum_{i=1}^2 b_i^{\dagger} b_i + J \vec{S}_1 \cdot \vec{S}_2 + \Delta E_J, \quad (18)
\end{aligned}$$

where,  $g_1(g_2)$  denotes the on-site (intersite) electron-phonon coupling strength and  $\epsilon$  is the bare site energy. This site energy is to be contrasted with the site energy which was derived in the previous section. Here, since we are interested in doing a two-site model, the extra term in the Hamiltonian due to the superexchange interaction, has been introduced simply as  $\Delta E_J$ . Note that we have considered a single phonon mode for interatomic vibrations of frequency  $\omega_0$  for which  $b_i$  and  $b_i^{\dagger}$  are the annihilation and creation operators.

We separate out the in-phase mode and the out-of-phase mode by introducing new phonon operators  $a = (b_1 + b_2)/\sqrt{2}$  and  $d = (b_1 - b_2)/\sqrt{2}$  in the Hamiltonian. The in-phase mode does not couple to the electronic degrees of freedom whereas the out-of-phase mode does, leading to a Hamiltonian  $H_d$ , given by,

$$H_d = \omega_0 d^{\dagger} d + \epsilon \sum_{i=1}^2 n_i - t \left( \frac{S_0 + \frac{1}{2}}{2S + 1} \right) (c_1^{\dagger} c_2 + h.c.) + g_- \omega_0 (n_1 - n_2) (d + d^{\dagger}) + J \vec{S}_1 \cdot \vec{S}_2 + \Delta E_J, \quad (19)$$

which represents an effective electron-phonon system. Following [10] we use a Modified Lang-Firsov (MLF) transformation with variable phonon basis and obtain,

$$\begin{aligned}
\tilde{H}_d &= e^R H_d e^{-R} \\
&= \omega_0 d^\dagger d + \sum_i \epsilon_p n_i - t \frac{S_0 + \frac{1}{2}}{2S + 1} [c_1^\dagger c_2 \exp(2\lambda(d^\dagger - d)) + c_2^\dagger c_1 \exp(-2\lambda(d^\dagger - d))] \\
&+ \omega_0 (g_- - \lambda)(n_1 - n_2)(d + d^\dagger) + J \sum_{\langle ij \rangle} \vec{S}_i \cdot \vec{S}_j + \Delta E_J,
\end{aligned} \tag{20}$$

where  $R = \lambda(n_1 - n_2)(d^\dagger - d)$ ,  $\lambda$  is a variational parameter related to the displacement of the  $d$  oscillator,  $g_- = (g_1 - g_2)/\sqrt{2}$  and  $\epsilon_p = \epsilon - \omega_0(2g_- - \lambda)\lambda$ . The basis set is given by  $|\pm, N\rangle = \frac{1}{\sqrt{2}}(c_1^\dagger \pm c_2^\dagger) |0\rangle_e |N\rangle$ , where  $|+\rangle$  and  $|-\rangle$  are the bonding and the antibonding electronic states and  $|N\rangle$  denotes the  $N$ th excited oscillator state within the MLF phonon basis. The diagonal part of the Hamiltonian  $\tilde{H}_d$  in the chosen basis is treated as the unperturbed Hamiltonian ( $H_0$ ) and the remaining part of the Hamiltonian  $H_1 = \tilde{H}_d - H_0$ , as the perturbation. The unperturbed energy of the state  $|\pm, N\rangle$  is given by

$$\begin{aligned}
E_{\pm, N}^{(0)} &= \langle N, \pm | H_0 | \pm, N \rangle \\
&= N\omega_0 + \epsilon_p \mp t_{eff} \left[ \sum_{i=0}^N \frac{(2\lambda)^{2i}}{i!} (-1)^i N_{C_i} \right] + J \vec{S}_1 \cdot \vec{S}_2 + \Delta E_J
\end{aligned} \tag{21}$$

where  $t_{eff} = t \frac{S_0 + \frac{1}{2}}{2S + 1} \exp(-2\lambda^2)$ ,  $N_{C_i} = \frac{N!}{(N-i)! i!}$ . The general off-diagonal matrix elements of  $H_1$  between the two states  $|\pm, N\rangle$  and  $|\pm, M\rangle$  may be calculated for  $(N - M) > 0$  as in Ref. [10].

The unperturbed ground state is the  $|+\rangle|0\rangle$  state and the unperturbed energy,  $E_0^{(0)} = \epsilon_p - t_{eff} + J \vec{S}_1 \cdot \vec{S}_2 + \Delta E_J$ . However, in this exact quantum limit of core spins, for given values of  $g_-$  and  $J$ ,  $E_0^{(0)}$  can have four values corresponding to ferromagnetic (FM), canted 1 (CA1), canted 2 (CA2) and antiferromagnetic (AFM) orientation of the two spins for  $|\vec{S}_{12}| = |\vec{S}_1 + \vec{S}_2| = 3, 2, 1, 0$  respectively. Minimizing the unperturbed ground state energy  $\lambda$  is calculated and is given by

$$\lambda = \frac{\omega_0 g_-}{\omega_0 + 2t_{eff}}. \quad (22)$$

We have evaluated the perturbation correction to the energy upto the sixth order and the wave function upto the fifth order. The convergence of the perturbation series is very good for  $t/\omega_0 \leq 1$ . To obtain the ground state spin order of the core spins we calculate the energy for each set of values of  $g_-$  and  $J$  with four possible  $\vec{S}_{12}$  and find out the combination for which the energy is the minimum. Further, to study the effect of an external magnetic field ( $\vec{h}$ ) we include a term  $-\tilde{g}\mu_B(\vec{S}_1 + \vec{S}_2) \cdot \vec{h}$  to the Hamiltonian in equation (18),  $\tilde{g}$  being the Lande g factor. We assume that the external magnetic field is along the direction of  $\vec{S}_{12}$  and is expressed in units of  $\mu_{eff}(=\tilde{g}\mu_B)=1$ .

It is expected that the charge transfer from site ‘1’ to ‘2’ depends on the spin order of the core spins as well as the electron-phonon interaction. In the double-exchange model, the effective hopping reaches its maximum value in the ferromagnetic state and decreases as it approaches the antiferromagnetic limit. Moreover, in a lattice, the electron produces lattice deformations and which in turn localize the electron for strong electron-phonon coupling. To study the polaronic character one calculates the static correlation functions  $\langle n_1 u_1 \rangle_0$  and  $\langle n_1 u_2 \rangle_0$ , where  $u_1$  and  $u_2$  are the lattice deformations at sites 1 and 2 respectively, produced by an electron at site 1 [10, 11]. In the present report with a two-site one electron model, following [11], we calculate  $-\langle n_1(u_1 - u_2) \rangle_0 / g_- = \frac{\lambda^{corr}}{g_-}$  and study the nature of the polaron crossover for different ranges of  $g_-$  and  $J$ . In the ‘large’ polaron limit this parameter takes a small value, while with increasing electron-phonon coupling it tends to unity, showing a distinct crossover from ‘large’ to ‘small’ polaron behavior. The measure of delocalization of the electron for various ranges of  $g_-$  as well as  $J$  will be evident from the kinetic energy. So we have also calculated the kinetic energy, given by,

$$t_{eff}^{KE} = -E_{Kin} = \langle \psi_G | t \frac{S_0 + \frac{1}{2}}{2S + 1} [c_1^\dagger c_2 \exp(2\lambda(d^\dagger - d)) + c_2^\dagger c_1 \exp(-2\lambda(d^\dagger - d))] | \psi_G \rangle, \quad (23)$$

where  $\psi_G$  is the ground state wave-function, is evaluated upto the fifth order in the perturbation. The numerical evaluation of  $E_{Kin}$  will be presented below in Sec. IV.

#### IV. PHASE DIAGRAMS AND SPECIFIC HEAT

Recently, there have been many experimental reports on manganites at low doping and low temperatures with and without an external magnetic field [12, 13, 14]. Okuda et al have estimated the electronic specific heat for  $La_{1-x}Sr_xMnO_3$  in the ferromagnetic regime and concluded that the carrier mass-renormalization near the metal-insulator transition at  $x = 0.16$  is minimal. They have also observed a decrease in the low temperature specific heat in the presence of a magnetic field. Motivated by these observations, we have carried out a calculation of the specific heat, based on the partition function of the system which, from a cumulant expansion upto the 2nd order, is given by [15],

$$Z(\beta) = Z_0(\beta) \exp\left(-\int_0^\beta d\beta' \int_0^{\beta'} d\beta'' \langle \tilde{H}_1(\beta') \tilde{H}_1(\beta'') \rangle\right), \quad (24)$$

where  $Z_0(\beta) = Tr(e^{-\beta H_0})$ ;  $\tilde{H}_1(\beta) = e^{\beta H_0} H_1 e^{-\beta H_0}$ , and  $\beta = \frac{1}{k_B T}$ . The expression  $\langle \rangle$  denotes the usual canonical averaging. The specific heat is then calculated (in arbitrary units) from the well known relation:

$$C_V = -\frac{d}{dT} \left( \frac{d}{d\beta} \ln Z(\beta) \right), \quad (25)$$

and in the low temperature regime, to which only the zero-and one-phonon states contribute.

If the localized core spin at each site is  $\frac{3}{2}$  then the possible values of  $|\vec{S}_1 + \vec{S}_2| = S_{12}$  are 3, 2, 1 and 0. The ferromagnetic (FM) and antiferromagnetic (AFM) orders are obviously related to  $S_{12} = 3$  and 0, whereas  $S_{12} = 2$  and 1 are referred as canted 1 (CA1) and canted 2 (CA2) states respectively. The Fig. 1 shows the phase diagram for the four possible spin orders for our system, in the  $g_-$  vs  $J$  plane. For small values of  $g_-$  and  $J$ , the FM state is the most stable one, and with increasing  $J$ , the ground state first becomes CA1 and then CA2.

For a very large value of the superexchange interaction  $J$ , the system is in an AFM order for any value of  $g_-$ . However, with increasing electron-phonon interaction  $g_-$ , the CA1 and CA2 phase become narrower. Indeed, for larger values of  $g_-$  the FM state appears for very low  $J$  but with a small increase of  $J$  the system transits to the AFM phase. The CA1 and CA2 phases in fact do not appear at all as the phase changes from the FM to AFM state with increasing superexchange interaction  $J$ , for large values of  $g_-$ . It can be further shown that for a very large value of  $g_-$  the ground state is AFM for any value of  $J$ .

It is evident from the phase diagram that for a particular value of  $J$  the ground state changes as the electron-phonon coupling ( $g_-$ ) increases (Fig. 1). But the change of phase from one to another is not continuous with  $g_-$ , for the quantum consideration of the core spins. This is shown in Fig. 2. For small values of  $J = 0.01$ , the FM state exists even for a large value of  $g_-$  and then it sharply changes to the AFM state. On the other hand, for larger values of  $J = 0.04, 0.09$ , the system passes sharply to the canted phases (CA1 and CA2) and then the AFM state, with increasing  $g_-$ . For  $J = 0.04$  the CA1 and CA2 regimes are very narrow and for  $J = 0.09$  the CA1 and CA2 orders persist for a wider range of  $g_-$ . This is to be contrasted with the classical core spin model in which a similar study shows that the transitions to different core spin orientations are continuous for the same range of values for  $g_-$  and  $J$  [11]. In the classical case only three phases (FM, AFM and Canted) are present. The relative angle  $\theta$  between classical core spins can take any value from 0 to  $\pi$ , so any spin orientation other than FM ( $\theta = 0$ ) and AFM ( $\theta = \pi$ ) yields a canted phase. Hence, in the classical limit of the core spins, for certain values of  $J$ , the FM-AFM transition is a smooth and continuous transition with  $g_-$ , whereas for spin  $\frac{3}{2}$ , the FM-AFM transition with  $g_-$  is never continuous for any  $J$ .

The probability of hopping of the itinerant electron from site to site is a maximum in the FM state as would be expected from the double-exchange mechanism. But, for a very strong electron-phonon coupling  $g_-$ , the electron may be localized forming a small polaron. For low values of  $J$  we find both small and large polaron ground states in the FM phase (Fig. 3). The large to small polaron crossover is indicated by the relative deformation of

the two lattice sites which is measured by the static correlation function  $\frac{\lambda_{corr}}{g_-}$ . In Fig. 3 the kinetic energy  $t_{eff}^{KE}$  is large for small values of  $g_-$ , where the polaron is large, and for large  $g_-$ , the kinetic energy reduces rapidly, while  $\frac{\lambda_{corr}}{g_-}$  rises, showing a smooth crossover to the small polaron regime. The classical and quantum formulations of the double-exchange model turn out to be the same in the FM limit of the core spins. So the nature of the kinetic energy and the polaron crossover in the FM state, as shown in Fig. 3, will be unaltered in the classical limit of core spins. However, in the AFM limit the two approaches (classical and quantum) are not equivalent, as has been argued earlier also. In the  $S \rightarrow \infty$  limit the hopping probability is zero for the AFM case, while for  $S = \frac{3}{2}$  the parameter modifying the hopping probability  $t$ , takes a finite value 0.25 resulting in a finite charge transfer, even in the AFM limit.

In Fig. 4 we show the nature of variation of the kinetic energy as well as the polaron crossover in different magnetic ground states. For  $J = 0.09$  the ground state is FM for low  $g_-$ , and with increasing  $g_-$ , the ground state changes sharply to CA1, CA2 and lastly to the AFM state. Since at each transition (from FM  $\rightarrow$  CA1  $\rightarrow$  CA2  $\rightarrow$  AFM) the effective hopping reduces due to the double-exchange interaction, it is obvious that the kinetic energy will show a sharp drop at each transition point. It is expected that the polaron crossover will also show concomitant sharp jumps at each magnetic transition and the crossover to small polaron behavior will occur at lower value of  $g_-$  than in the FM limit. This is shown clearly in Fig. 4. It is further evident that in a double-exchange system, both the magnetic transitions and the electron-phonon coupling localize the electron, when the polaron crossover and magnetic transitions are overlapping. The locations of the large polaron region (A) and the small polaron region (B) are indicated in the  $g_-$  vs  $J$  phase diagram (Fig. 1). In Fig. 1, for large values of  $g_-$ , the CA1 and CA2 phases are very narrow and appear as a single phase boundary of FM-AFM region. So the line of separation of polaronic regimes (A and B) appears as a point for CA1 and CA2 in Fig. 1. Thus the results presented in Fig. 3 and Fig. 4 have a bearing on the transport behavior of our model.

Having discussed transport we now redirect our attention to thermodynamic properties.

With this in mind we show in Fig. 5 the variation of the specific heat in the low temperature region in the FM state with zero and one phonon states. With application of an external magnetic field  $\vec{h}$ ,  $C_V$  takes lower values than for  $\vec{h} = 0$  which is expected, as the average energy decreases with application of  $\vec{h}$  in the FM state. For CA1 ( $|\vec{S}_{12}| = 2$ ), CA2 ( $|\vec{S}_{12}| = 1$ ) and AFM ( $|\vec{S}_{12}| = 0$ ) states the external magnetic field will tend to align the core spins to ferromagnetic order ( $|\vec{S}_{12}| = 3$ ). For CA1, CA2 and AFM states at low field and low temperatures it can be shown from the present calculation that  $C_V$  does not change much from the  $\vec{h} = 0$  limit as long as  $\vec{h}$  does not shift  $|\vec{S}_{12}|$  to higher values. For larger  $\vec{h}$ , as the ground state changes from lower  $|\vec{S}_{12}|$  to a higher one,  $C_V$  decreases in the low temperature region. For CMR materials, there are some reports on measurements of  $C_V$  but these are measured in the FM state [12, 13, 14]. In such cases, it was found that for low doping regions,  $C_V$  decreases with an increasing magnetic field. Our present calculation of  $C_V$  seemingly agrees with these experimental findings. The difference in the quantum and classical cases for specific heat, as far as the core spins are concerned, is exemplified in Fig. 6 and Fig. 7 for FM and AFM cases respectively. The quantum results evidently yields the correct low-temperature limit.

## V. CONCLUSIONS

The Anderson-Hasegawa model, though almost fifty years old, is able to capture all the crucial features of the double-exchange mechanism, 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. With this in mind, we have felt the need of carefully reexamining the exact quantum solution of the Anderson-Hasegawa model, for realistic values of the core spins. We have further used this model as the basic building block, in order to incorporate one or the other phenomena of relevance to manganites. These include superexchange and polarons, which have been the focus of our attention here. Indeed, we have found that Superexchange, when properly treated in conjunction with quantum spin dynamics of the core spins, leads to additional terms in the Anderson-Hasegawa Hamiltonian, which are absent in the classical approximation of the core spins. A similar effect can also be observed with the exact solution of the Anderson-Hasegawa model, with the addition of phonon coupling. This may lead to the enhancement of the site energy term, which will have important consequences in these systems, especially in the paramagnetic state of the manganite systems. Moreover, the discreteness associated with the effective hopping in this quantum case was shown to have further consequence for thermodynamic and transport properties. In conclusion, therefore, we find that the Anderson-Hasegawa model continues to remain relevant for the understanding of topically important issues in manganites.

## VI. ACKNOWLEDGEMENT

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### Figure Captions :

FIG. 1. The  $g_-$  vs  $J$  phase diagram ( $\vec{h} = 0$ ) for  $|\vec{S}_1| = |\vec{S}_2| = \frac{3}{2}$  and  $t = 1$ . (A) and (B) denote large polaron and small polaron region respectively.

FIG. 2. Variations of ground state spin configuration  $|\vec{S}_1 + \vec{S}_2|$  with  $g_-$  for  $t = 1$  and  $J = 0.01, 0.04$  and  $0.09$ ,  $h = 0$  (in units of  $\omega_0 = 1$ ).

FIG. 3. Variations of  $t_{eff}^{KE}$  and  $\lambda_{corr}/g_-$  with  $g_-$  for  $t = 1.0$ ,  $J = 0.01$  and  $h = 0$ .

FIG. 4. Variations of effective kinetic energy  $t_{eff}^{KE}$  (dashed line) and polaron crossover  $\lambda_{corr}/g_-$  (solid line) with  $g_-$ , for  $t = 1.0$ ,  $J = 0.09$  and  $h = 0$ . The sharp jumps in  $t_{eff}^{KE}$  and  $\lambda_{corr}/g_-$  occur at values of  $g_-$  where the magnetic transitions take place (see Fig. 2).

FIG. 5. Variations of  $C_V$  (in arbitrary units) for  $g_- = 0.6$ ,  $J = 0.01$  and  $t = 1$ , for different values of the magnetic field  $h = 0, 0.01, 0.05$ .

FIG. 6. Variations of  $C_V$  (in arbitrary units) for  $g_- = 0.2$ ,  $J = 0.02$ ,  $h = 0$  and  $t = 1$ , in classical (solid line) and quantum (dashed line) formulation of the core spins. The ground state is FM.

FIG. 7. Variations of  $C_V$  (in arbitrary units) for  $g_- = 0.9$ ,  $J = 0.2$ ,  $h = 0$  and  $t = 1$ , in classical (solid line) and quantum (dashed line) formulation of the core spins. The ground state is AFM.

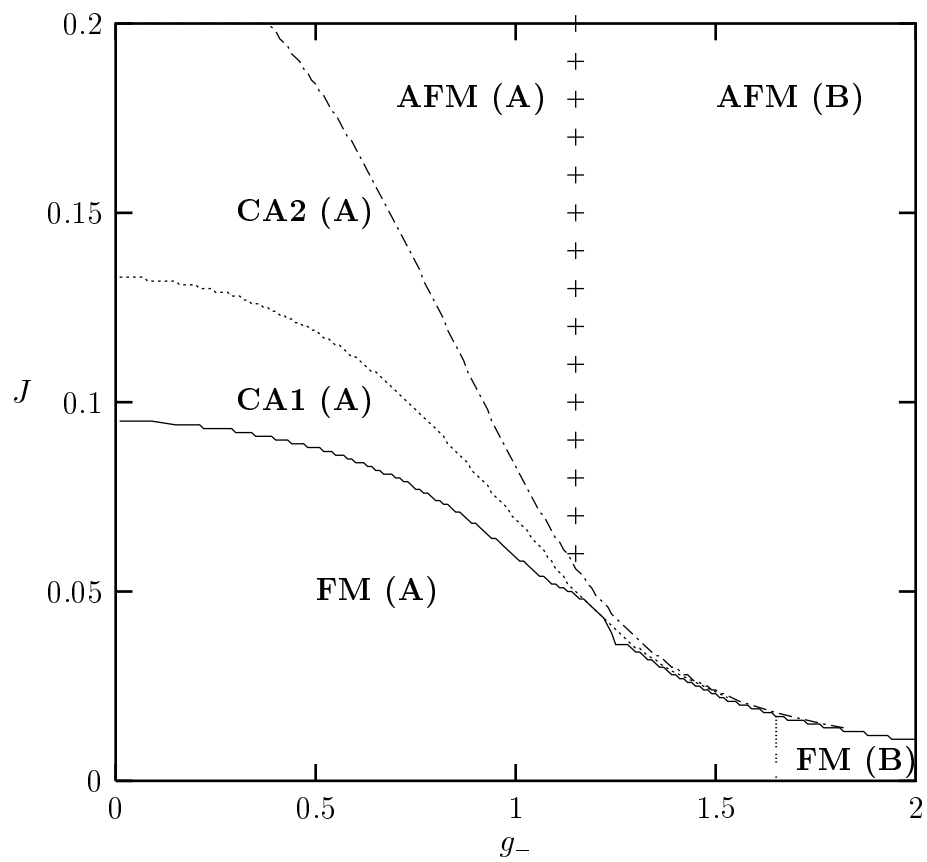


FIG. 1

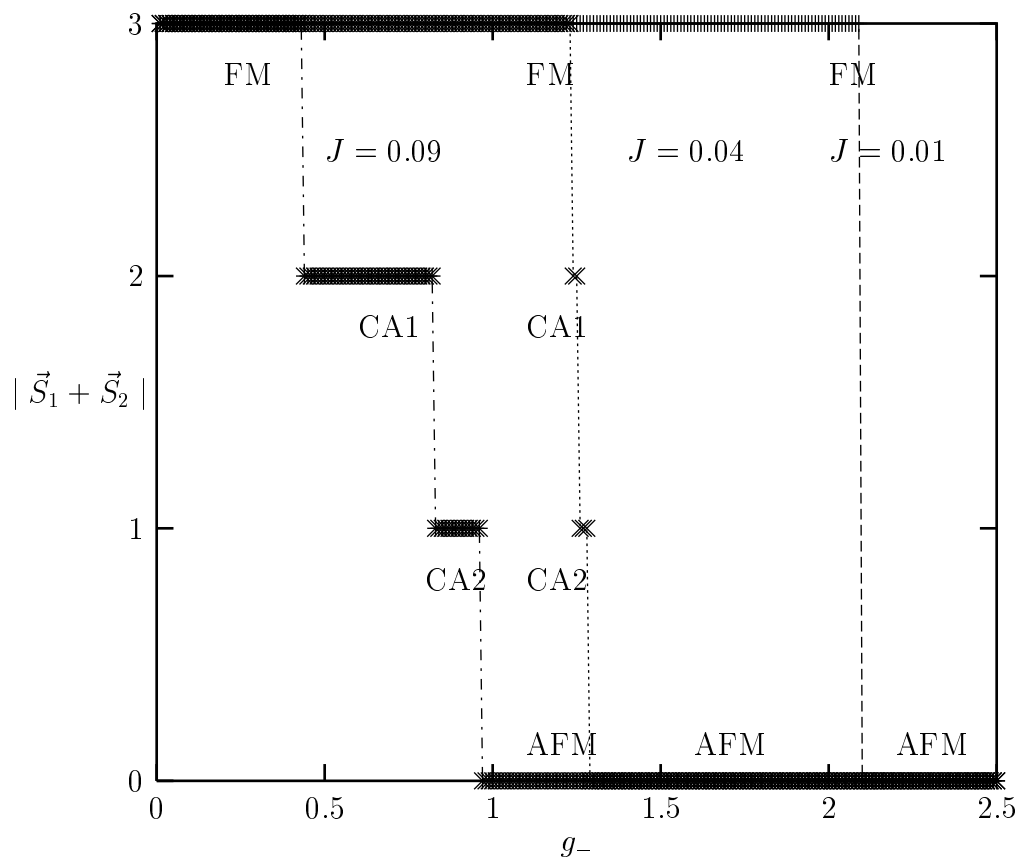


FIG. 2

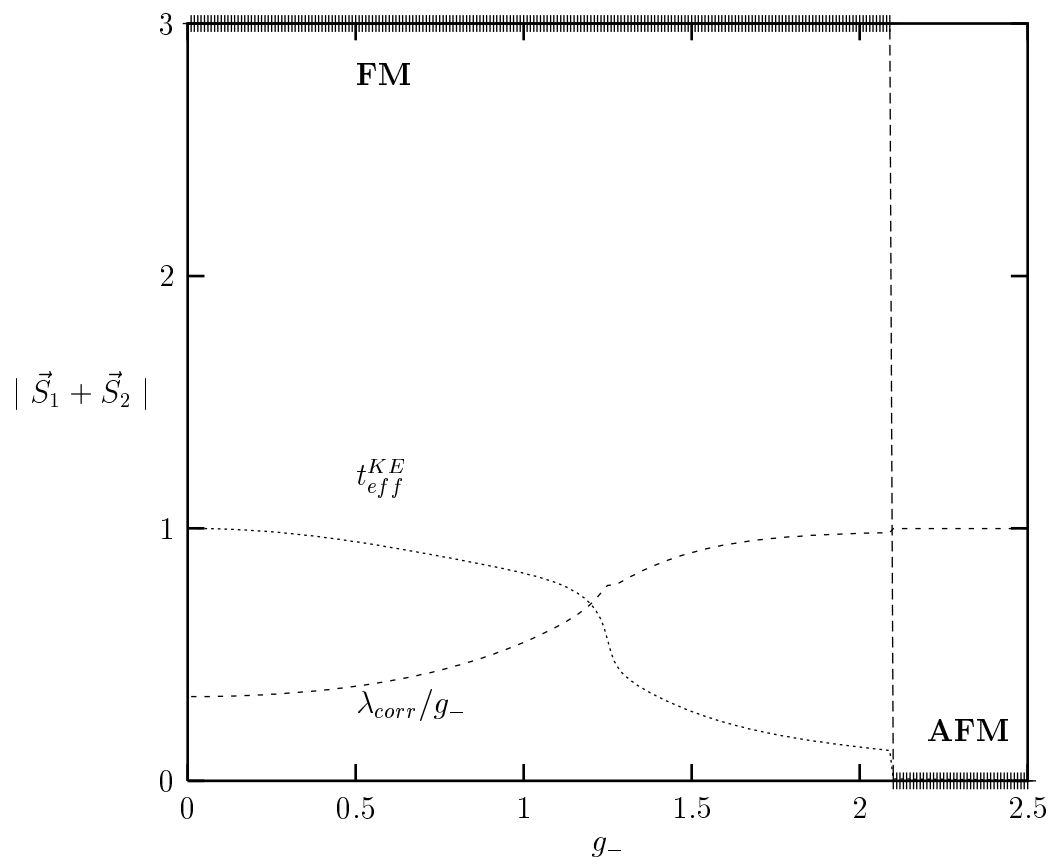


FIG. 3

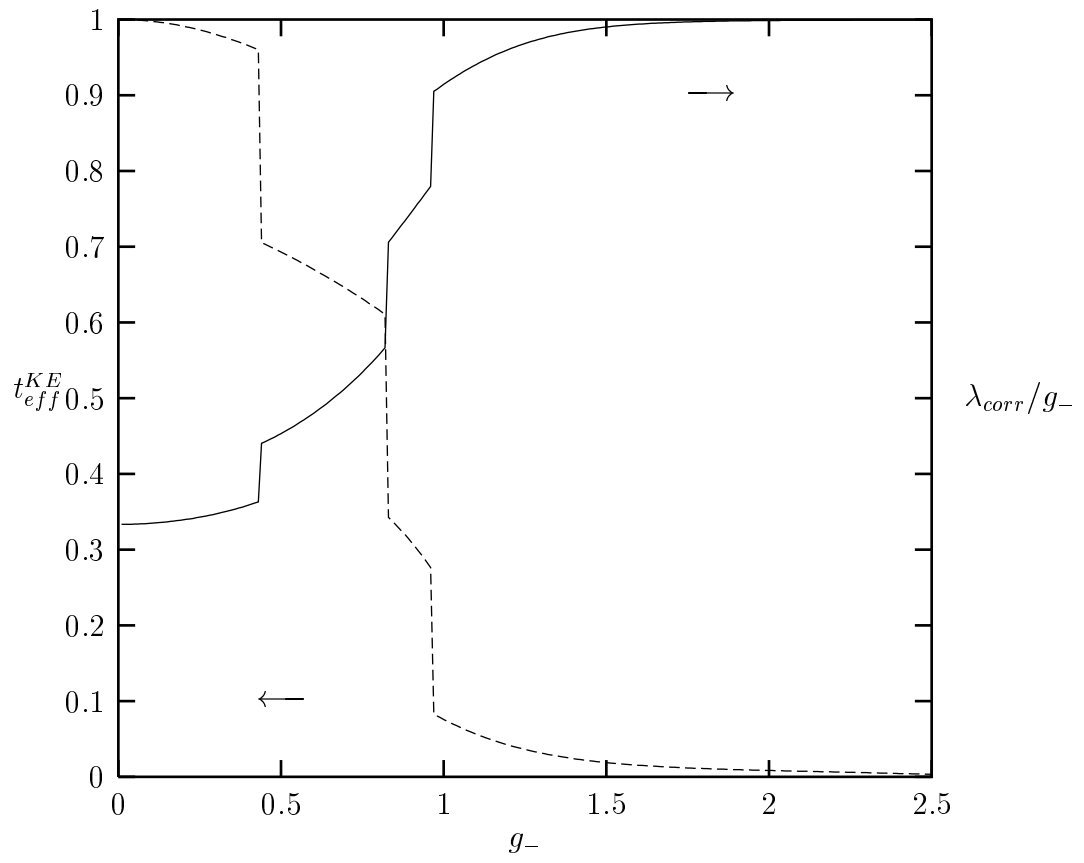


FIG. 4

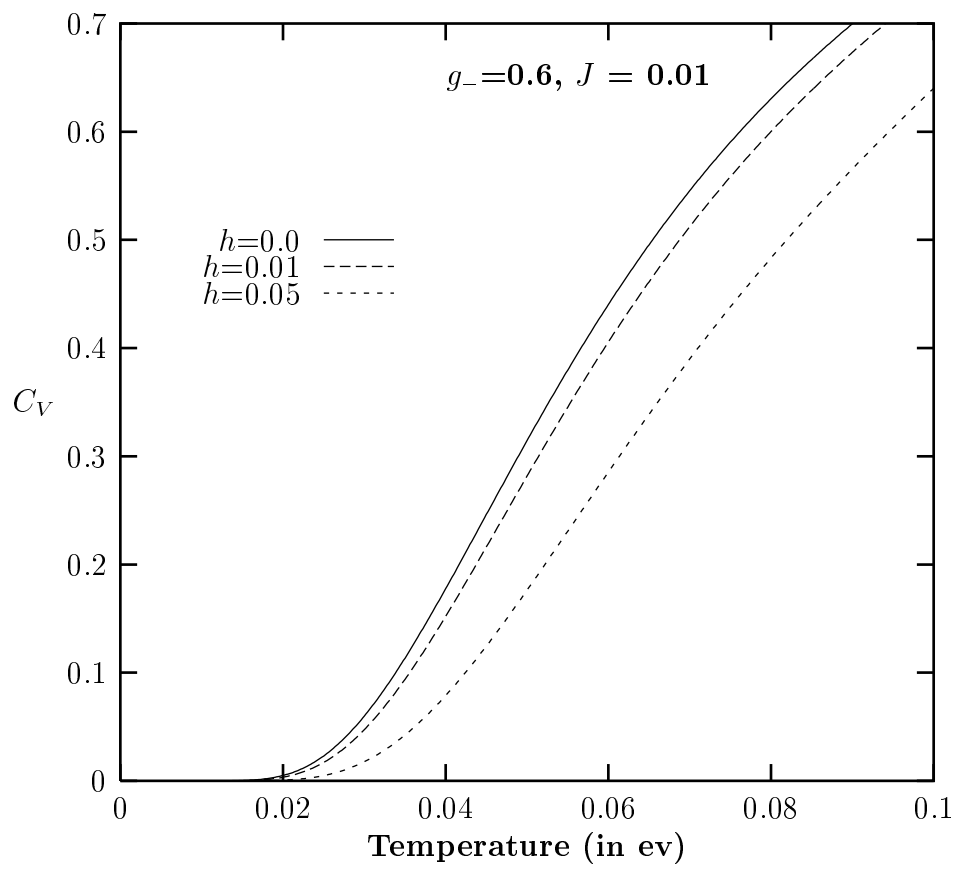
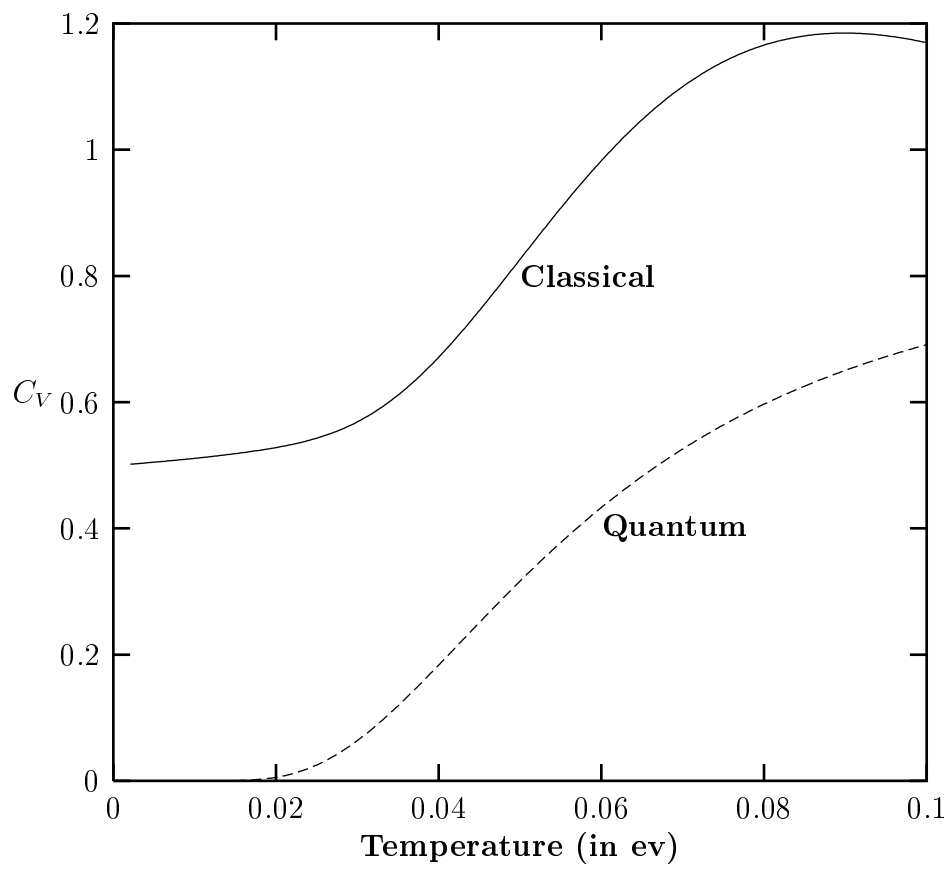


FIG. 5



**FIG. 6**



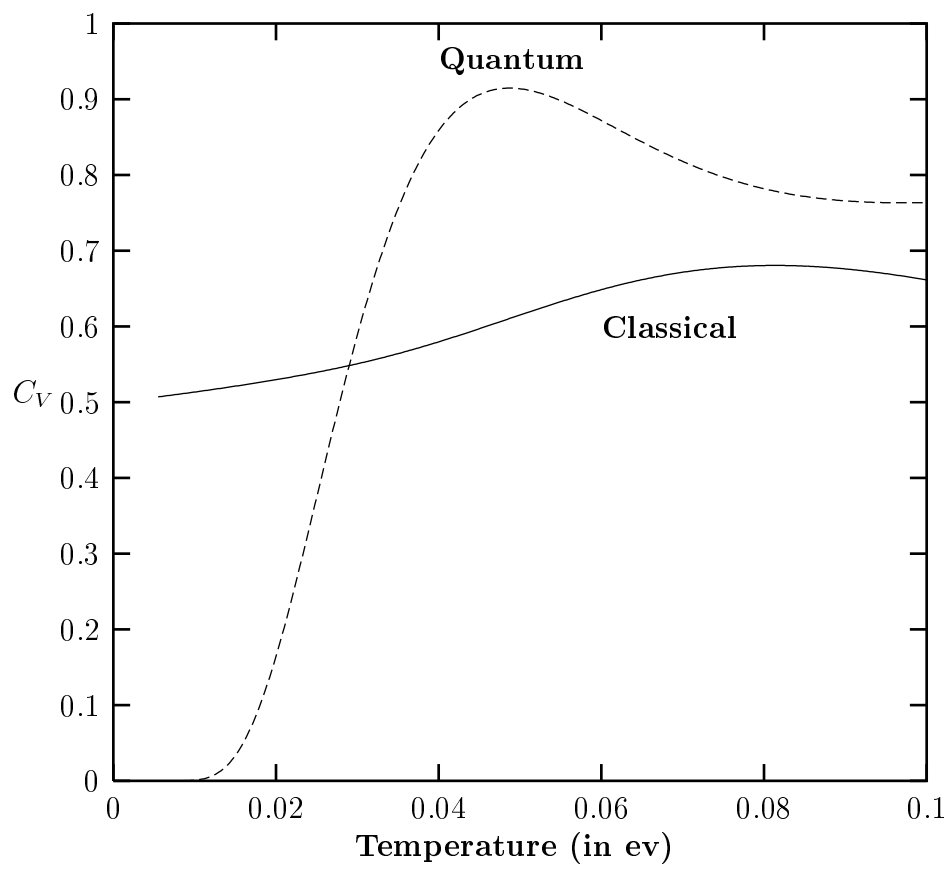


FIG. 7