Non-perturbative $V - J_{pd}$ model and ferromagnetism in dilute magnets

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Abstract – We calculate magnetic couplings in the $V - J_{pd}$ model for dilute magnets, in order both to identify the relevant parameters which control ferromagnetism and also to bridge the gap between first-principle calculations and model approaches. The magnetic exchange interactions are calculated non-perturbatively and disorder in the configuration of impurities is treated exactly, allowing us to test the validity of effective medium theories. Results differ qualitatively from those of weak coupling. In contrast to mean-field theory, increasing $J_{pd}$ may not favor high Curie temperatures: $T_C$ scales primarily with the bandwidth. High-temperature ferromagnetism at small dilutions is associated with resonant structure in the p-band. Comparison to diluted magnetic semiconductors indicate that Ga(Mn)As has such a resonant structure and thus this material is already close to optimality.

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The basis of our understanding of magnetism in metals is the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction [1]. The magnetic exchange results from interaction of inner $d$ or $f$ localized orbitals and the outer $s$ or $p$ that form the conduction bands. In the standard form it is calculated with perturbative treatment of the coupling between the moments and the carriers on a definite Fermi surface, which is itself weakly affected by the presence of the magnetic moments. This leads to successful interpretation of oscillating exchanges in, for example, transition or rare-earth metals. However, the same concepts are often applied in situations where this perturbative approach is not really applicable. There are many situations where the coupling between moments and itinerant carriers is not weak and it is important to determine changes in magnetic exchange in this regime, for example in the field of manganites [2], double perovskites [3] or in materials modelled by Kondo lattices [4]. In another field of great current interest, diluted magnetic semiconductors (DMS), a belief, incorrect in our view [5], in the applicability of weak coupling has resulted from an unhappy juxtaposition of two approximations: a simplified RKKY view of magnetic interactions and over-simplified molecular field theory for the thermodynamics. This leads to the estimate for the Curie temperature $T_{CF}^M = J_{pd} x n^{1/3} / t$, where $t \propto 1 / m^* = $ the inverse of the effective mass. $J_{pd}$ is the coupling between $d$-orbital moments and the primarily $p$-orbital conduction carriers, $x$ the concentration of magnetic impurities and $n$ the density of carriers. This estimate has even been influential in the search for new materials: attempts to increase $T_C$ at low doping have focussed on seeking large $J_{pd}$ and small bandwidth (large effective mass). We shall show that the widely used $T_{CF}^M$ is in fact very misleading in the non-perturbative limit. Part from potential applications [6], these materials are of fundamental interest for exploring ferromagnetism in a regime where geometric disorder is strong (because of the low concentrations of dopants) and the values of $J_{pd}$ are strong. Unfortunately these issues of principle have been obscured by insistence [7] on the weak-coupling picture, and has hidden richer underlying aspects. We argue that these systems are particularly interesting because the ferromagnetism, can only be understood if the crucial coupling $J_{pd}$ is treated non-perturbatively. An approach taking ab initio estimates of...
couplings and reliable treatment of the thermodynamics [5] can be successful, but the effective magnetic interactions found, which include a multitude of effects, have not been understood in simple terms. Calculations must be taken for each individual composition. A more systematic approach for finding promising new materials is possible if we have simple but accurate model systems. We can then identify which parameters are important: \( J_{pd} \), the carrier density or the bandwidth of the conducting band? We can also examine assumptions of the \textit{ab initio} approach: e.g. the Coherent Potential Approximation (CPA) for carrier disorder. The method we shall employ makes effective medium approximations neither in the deriving of the magnetic couplings nor in calculating magnetic properties. Thus an aim is to make a bridge between \textit{ab initio} and conceptually simpler model approach.

A practical question is whether \( T_C \) can be increased by choice of other chemical dopants. In lightly doped III-V semiconductors, it will appear that Ga(Mn)As is in fact close to optimal. Here we discuss the theory appropriate to dilute magnets where the dopants provide well-defined moments, but the concepts are relevant to a wider class of novel magnets (“\( d^m \) magnets”) in which there is no clear distinction between localized magnetic moments and the itinerant carriers of the (doped) host [8,9].

The \( V-J_{pd} \) model (or dilute Kondo lattice) is of a band of atomic \( d \)-orbitals coupled to an itinerant “\( p \)-band” of carriers via a Hund’s rule coupling. In the manganeseites, for example, the \( p \)-band is in fact constructed from \( c_{\sigma} \) orbitals:

\[
H = -\sum_{ij,\sigma} t_{ij} c_{i\sigma}^\dagger c_{j\sigma} + \sum_i J_i S_i \cdot \hat{S}_i + \sum_{i\sigma} V_i c_{i\sigma}^\dagger c_{i\sigma},
\]

\( t_{ij} = t \) for \( i \) and \( j \) nearest neighbors and zero otherwise. In the exchange between localized impurities spin and itinerant electron gas \( J_i \) is a random variable: \( J_i = J_{pd} \) and \( V_i = V \) if the site \( i \) is occupied by a magnetic impurity, and zero, otherwise. \( V_i \) is here to mimic the effect of chemical substitution that accompanies the presence of the magnetic moment. \( S_i \) is the magnetic impurity spin operator at site \( i \) and \( s_i = c_{i\alpha}^\dagger (1/2\sigma_{\alpha\beta}) c_{i\beta} \) the spin operator, at the same site, of the itinerant electron gas. The \( d \) spins are distributed randomly at low concentration \( x \) on a regular lattice, for simplicity taken to be simple cubic. We remark that this model can be extended trivially to include several bands, as would be appropriate for models of double perovskites or manganites, where both the hopping \( t_{ij} \) and on-site potentials \( V_i \) may be random [10,11]. The results that will follow are non-perturbative in the \( J_{pd} \) coupling and exact in the disorder. A crucial effect that will be seen, and is neglected to low order in perturbation theory, is that as \( J_{pd} \) increases, the conduction band is increasingly affected by the presence of the magnetic ions. The calculations are made in the ferromagnetic phase, whose stability is tested a \textit{posteriori}, and therefore start from the configuration of spins \( S \) that are fully aligned in some direction \( S_i^z = S \) for all occupied \( i \).

We diagonalize in the Hilbert space (spins plus electrons) defined by the fully polarized \( d \) spins provided that we ignore the transverse fluctuations of those spins, of order \( \frac{1}{2} \) [12]. Thus our theory is exact in the limit of large \( S \rightarrow \infty \). For the electronic degrees of freedom this leaves a Hamiltonian quadratic in fermion operators. The effect of the \( d \)-orbitals is to produce an effective spin-dependent term of \( V_{i,\gamma} = V_{i,\gamma} \pm \frac{2J_{pd}}{t} \) on each occupied state, \textit{i.e.} a random site potential for up (+) and down (−) carriers. For each configuration of disorder this Hamiltonian will be diagonalized exactly.

In fig. 1 we show the single-particle density of states for fixed \( J_{pd}S = 5t \) and concentration \( x = 5\% \) of magnetic impurities and different values of the \( d \)-orbital potential \( V/t = \{-1.2, -2.4, -3 \} \) and \(-5.4 \). The parameters were chosen to reproduce the general form seen in doped III-V semiconductors, as will be discussed in more detail below. For all calculations presented, the systems were sufficiently large (typically \( \sim 10^3 \) sites) that finite-size effects are negligible. As \( V \) increases from the smallest value, a well-defined impurity band for the minority band splits from the valence band. The Fermi energy is shown for different values of \( \gamma = n_h/x \), where \( n_h \) denotes the density of holes in a filled band. We will see below how the magnetic couplings are correlated with the form of the density of states and the position of the Fermi energy.

The magnetic exchange interactions are derived at all distances between the different moments from the carrier Green functions \( G_{\alpha\beta}^{\sigma} \) [13]. This defines an effective (dilute) Heisenberg model for the magnetic moments, still valid for spins in the classical limit, \( \mathcal{H}_{\text{Heis}} = - \sum_{i,j} J_{ij} S_i \cdot S_j \).

To perform the calculation of the Curie temperature we use the couplings computed at \( T = 0 \)K, as done in an \textit{ab initio} approach. Actually, this approximation is expected to be reasonable. Indeed, as often seen, the exchange couplings calculated assuming for the ground-state either
the fully polarized state or the DLM (disordered local moment) state lead to similar Curie temperatures. The DLM state mimics the paramagnetic ground state above the Curie temperature. For example, in ref. [14] the spin-spin correlation function above the Curie temperature depends weakly on the reference state used for the calculation of the couplings (see fig. 6 of [14]). Additionally, we have checked that using the couplings calculated \textit{ab initio} for the fully polarized state and for the DLM state leads to comparable values of the Curie temperature [15]. The exchanges are calculated by applying infinitesimal fields to the aligned ferromagnetic state [13]:

\[
J_{ij} = -\frac{1}{\pi} \int_{-\infty}^{E_F} \Sigma_i G_{ij}^{\uparrow}(\omega) \Sigma_j G_{ji}^{\downarrow}(\omega) d\omega. \tag{2}
\]

In the present case \(\Sigma_i = V_i^+ - V_i^-\).

We note that the calculations use no effective medium approximation. In fig. 2(a) we show the couplings averaged over different impurity configurations. We vary the hole doping per d-orbital \(\gamma\) for fixed \(x = 5\%\), \(V = -2.4t\) and \(J_{pd}S = 5t\) (corresponding to fig. 1(b)). These couplings clearly differ from RKKY for all fillings in that they do not oscillate around a mean value of zero and beyond 3 lattice spacings they essentially vanish. While varying sharply with distance they do not change in sign, at least for small \(\gamma\). The couplings at short distances increase monotonically with \(\gamma\) but for sufficiently large \(\gamma\) antiferromagnetic values appear at larger distances (see inset). In fig. 2(b) the \(J(r)\) with different potentials \(V\) are shown for fixed \(\gamma\). As |\(V|\) increases the interactions increase at short distances but become of very short range. For |\(V|\) small the longer-range oscillations appear clearly, as seen in the inset.

Thus from fig. 2 there is a range of \(V\) and \(\gamma\) where the couplings are all ferromagnetic (\(J(r) \geq 0\)). This is associated (see fig. 1(b)) with incipient development of a visible impurity band just at the band edge. This ferromagnetic “bias” results from the resonant form of the p-band as advanced in ref. [16]. In that paper we compared to exchange calculated in a toy model between two resonant states [17], arguing that particle-particle channels responsible for super-exchange should be suppressed. In contrast, in the present calculation there is no artificial separation between the resonant states and the rest of the conduction band nor between different contributions (particle-hole and particle-particle channels). The ideas are coherent in that the \(J_{pd}\) acting between the d spin and the resonant p-state suppress particle-particle virtual states. For the largest values of |\(V|\) the clear suppression of exchange for large distances (see inset to fig. 2(b)) is a precursor to the pure magnetic double exchange type [18].

For \(J_{pd}\) and \(V\) strictly infinite we expect the coupling to reduce to nearest neighbours: \(J_{ij} = t_{ij} (c_i\dagger c_j)\) [10]. For \(J_{pd}S\) finite, however, the exchange interactions extend further than nearest-neighbours [19].

We now calculate the Curie temperatures \(T_C\) by the self-consistent local random phase approximation (SC-LRPA) [5] which treats geometric disorder exactly, as is particularly important in the dilute limit. SC-LRPA has been successful in reproducing experimental \(T_C\) of DMS and agrees with Monte Carlo simulations [20,21].

Figures 3 and 4 show the Curie temperatures \(T_C\) as functions of \(\gamma\) and \(V\) at half-filling respectively, and for various values of \(J_{pd}\). Unlike the predictions of \(T_C^{MF}\), \(T_C\) increases monotonically \textit{neither} with \(J_{pd}\) nor with \(\gamma\). For \(\gamma = 0.1\), for instance, \(T_C\) decreases with \(J_{pd}\). Large values of \(J_{pd}\) are primarily useful in broadening the range of stability of ferromagnetism with \(\gamma\). For comparison we
show in the inset the results we have previously obtained in the RKKY regime [16] and recently confirmed by Monte Carlo simulations [22]. At the smallest values of $J_{pd}$ the region of stability (note the difference in scale $\gamma$) approaches the RKKY results, as expected. In fig. 4 we see that $T_C$ is less sensitive to $J_{pd}$ in the large $V$ limit. The ferromagnetic bias is then essentially the physics of double exchange [23], and the scale of $T_C$ is $\gamma$. Note that we make the assumption that the ferromagnetic $T_C$ calculated with couplings averaged over configurations is equal to that obtained, in the thermodynamic limit, with unaveraged couplings. We have checked this assumption and it is accurate.

In the following paragraph we discuss the case of doped Ga(Mn)As. From photoemission spectroscopy [24] it was shown that the antiferromagnetic coupling is $J_{pd} \approx 1.2$ eV. This is in agreement with the amplitude of $J_{pd} \approx 0.9$ eV found in the Infrared Spectroscopy theory of ref. [25] where the splitting extracted from EPR measurements [26] was used. From the band-structure of GaAs the effective mass can be estimated to be $m^* \approx 0.5 m_e$. With a lattice spacing $a_0 = 5.65 \, \text{Å}$, this leads to $t \approx 0.7$ eV and thus $J_{pd} S \approx 4 t$. The value of $V \approx -1.6$ eV ($V/t \approx -2.4$) was chosen to mimic the ab initio calculated density of states of Ga(Mn)As. This set of parameters gives rise to an impurity band in accordance with ab initio calculations [27,28] and with the experimental measurement of the optical conductivity [29]. Furthermore, for $x = 5\%$ the Zeeman splitting $\Delta$ obtained with these values of $V$ and $J_{pd}$ is $\Delta \approx 0.7$ eV in good agreement with that obtained from first-principle calculations [28] $\Delta \approx 0.6$ eV. From fig. 3, we obtain a maximum of $T_C^{band} \approx 65 \, \text{K}$ at $\gamma = 0.3$. Because there are two degenerate hole bands and we have neglected all correlations in the p-bands, we can simply extend to 2 independent bands: $T_C^{2band} = 2T_C^{band} \approx 130 \, \text{K}$, close to the measured value in annealed samples of Ga$_{0.95}$(Mn)$_{0.05}$As. This is a crude comparison as the lattice is face-centred cubic and not cubic and, at first sight, the natural concentration to choose for uncompensated samples might be two half-filled bands $\gamma = 0.5$ to give one carrier per dopant. We argue, however that $\gamma = 0.3$ is comparable to uncompensated Ga(Mn)As since it is at this doping that the density of states (calculated from the band structure [27]) most resembles that of fig. 1(b), with $E_F$ slightly above the maximum in the impurity peak. The apparently remarkable agreement for such a simple model is found for the range of concentrations relevant to experiments. We conclude that if $J_{pd}$ is treated non-perturbatively we do not need extensions such as the 6-band Luttinger model [7] to give accurate quantitative comparison. We can also understood from the position of the impurity band why Ga(Mn)As has a larger $T_C$ than Ga(Mn)N and In(Mn)As which resemble more cases (d) and (a) of fig. 1, respectively [5]. Since the estimated $J_{pd}$ and bandwidths for these materials are all very similar, the important difference is the potential $V$. From the calculated $T_C$’s shown in the figures and comparison with the density of states in fig. 1(b), we see that Ga(Mn)As is close to optimal parameters. This may explain failure to find higher values of $T_C$ in III-V semiconductors without invoking other effects: local clustering or increasing bandwidth.

To conclude, we have shown that in the non-perturbative regime the $V - J_{pd}$ model has effective magnetic couplings very different from those of RKKY and resemble those of ab initio calculations for the DMS. This similarity supports the accuracy of CPA as used in the first-principle calculations for calculating magnetic exchanges, an approximation that has often been questioned. While we have presented results in the dilute regime, we note that our approach, which gives the exchange interactions in real space, can be used in more general situations at higher concentrations or with inhomogeneities, as may be applicable in other materials described by the $V - J_{pd}$ model and its extensions. For dilute magnets a region of parameter space gives couplings that are all ferromagnetic. The reason [16] is made explicit: optimality is associated with a resonant structure seen in the p-band. The potential $V$ must be sufficiently strong for this to occur, but if it is too strong, couplings are too short-range to maintain long-range order. Unlike previous mean-field theories ($T_{MF}^C$), the temperature scale for ferromagnetism is controlled not by $J_{pd}$ but by the bandwidth $t$. The physics is essentially that of double exchange in this regime. The values of Fermi energy, $J_{pd}$ and the potential shift $V$ are important in obtaining optimal couplings.

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