A surprising relation between double exchange and Heisenberg model spectra:
Application to half-doped manganites

Roland Bastardis, Nathalie Guihéry, Nicolas Suaud
Laboratoire de Physique Quantique, IRSAMC/UMR5626, Université Paul Sabatier,
118 route de Narbonne, F-31062 Toulouse Cedex 4, FRANCE
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The Zener polarons recently found in half-doped manganites are usually seen as mixed valence entities ruled by a double exchange Hamiltonian involving only correlated electrons of the metals. They can however be considered as ferrimagnetic local units if the holes are localized on the bridging oxygen atoms as implicitly suggested by recent mean-field \textit{ab initio} calculations. In the latter case, the physics is ruled by a Heisenberg Hamiltonian involving magnetic oxygen bridges. This paper shows that the spectra resulting from the resolution of both models are \textit{analytically identical}. This single resulting model spectrum accurately reproduces the spectrum of Zener polarons in Pr$_{0.6}$Ca$_{0.4}$MnO$_3$ manganite studied by means of explicitly correlated \textit{ab initio} calculations. Since the physics supported by each model are different, the analysis of the exact Hamiltonian ground state wave function should \textit{a priori} enables one to determine the most appropriate model. It will be shown that neither the spectrum nor the wavefunction analysis bring any decisive arguments to settle the question. Such undecidability would probably be encountered in experimental information.

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Strongly correlated materials have attracted the interest of chemists and physicists for their fascinating macroscopic properties. Adequate treatments of collective effects as well as the resolution of the microscopic origin of these properties are crucial to the understanding of these materials. Both alike require the determination of accurate effective Hamiltonians. In doped manganites as well as in many oxides, the various phase transitions occurring under doping are not fully understood. As well, relevant and quantitative effective Hamiltonians able to reproduce the microscopic order in the most complex phases are rarely available.

A recent crystal determination of Pr$_{0.6}$Ca$_{0.4}$MnO$_3$ manganite has revealed the presence of Zener polarons \textit{i.e.} trappings of holes (or electrons) within pairs of Manganese sites. The Zener polaron was initially assumed to be ruled by a double exchange model giving rise to an octet ground state of the dimer. In this description each hole is delocalized over two Mn sites resulting in a resonance between Mn$^{3+}$O$^2$−Mn$^{3+}$ and Mn$^{4+}$O$^2$−Mn$^{3+}$. However, recent \textit{ab initio} calculations on the closely related La$_{0.5}$Ca$_{0.5}$MnO$_2$ show an important O to Mn charge transfer, resulting in a localization of the holes on the bridging oxygens. This charge distribution suggests a dominant purely magnetic local order (Mn$^{3+}$O$^2$−Mn$^{3+}$) in which the Zener polarons would be ferrimagnetic entities involving an antiferromagnetic coupling between the magnetic oxygen and the high spin manganese centers. In the latter case the model Hamiltonian which provides a relevant description of the local electronic order is a Heisenberg Hamiltonian. The holes localization has been a matter of debate in the literature and concerns a large number of materials like doped cuprates (where there is at most one unpaired electron per metal resulting in a $t$-$J$ model), nickelates or manganites (in which there are several open-shells per center leading to a double exchange interaction). Besides, as far as the correlated electrons are only localized on the metallic centers, the comparison of the models has been the subject of intense discussion and controversy which ended up with the demonstration that the two models were strictly different and lead to different spectra. The aim of this paper is to show that when considering a magnetic oxygen in the Heisenberg model the analytical resolution of the two Hamiltonians leads to identical spectra. For this purpose we have derived an analytical solution of the Heisenberg Hamiltonian energies for three magnetic centers.

Since the discrimination between the two models is impossible from the spectrum determination, we will then address this question from wavefunction analysis. Indeed, the projection of the \textit{ab initio} ground state wavefunction onto both model spaces should \textit{a priori} determine the choice. However, it will be shown that when the charge of the oxygen is around -1.5, the wavefunction analysis does not infer any decidable argument. In order to illustrate this assertion, we have extracted the two corresponding models from the correlated \textit{ab initio} calculated spectrum of the Pr$_{0.6}$Ca$_{0.4}$MnO$_3$ manganite Zener polaron and analyzed both its spectrum and its ground state wave function.

The here-developed solutions are analytical and could be applied to any material having a bridging ligand and an odd number of correlated electrons per metallic dimer. Thus, the here-developed equations have been generalized to any number $n$ of open-shells per center. The first considered model, is the Zener double exchange model including the Heisenberg-type antiferromagnetic contribution proposed by Papaefthymiou and Girerd. It is likely to describe configurations compatible with a $M(d^{n-1/2})O^2−M(d^{n-1/2})$ mixed valence...
The electronic structure resulting from a resonance between $M(d^{n})O^{2-}M(d^{n-1})$ and $M(d^{n-1})O^{2-}M(d^{n})$ where $n$ and $n-1$ are the numbers of open shells on the two metallic centers. The model is based on the idea that the spectrum can be reproduced by considering the metallic ions in their atomic ground states and two effective interactions, namely the hopping integral $t$ of the extra electron between the two metal-centered orbitals and an overall Heisenberg exchange integral $J$ between the electrons of the other open shells. The delocalization of the extra electron favors the highest spin state (of total spin $S_{\text{max}}$) while the exchange integral stabilizes the low and intermediate spin states for an overall antiferromagnetic contribution ($J < 0$). In the particular case of a symmetric homonuclear bimetallic complex, the eigenenergies of the double exchange model are analytically known. This Hamiltonian generates two eigenstates for each value of the total spin $S$, the energies of which $E^{Z}(S, \pm)$ are given by the expression:

$$E^{Z}(S, \pm) = \pm \frac{t}{S_{\text{max}}^{2} + 1/2} \left( S + \frac{1}{2} \right)$$

where the zero of energy is taken as the mean value of the highest spin states energies.

If the electronic structure is dominated by $M(d^{n})O^{2-}M(d^{n})$ charge transfer configurations, a Heisenberg Hamiltonian is expected to rule the physics of the system. Its specific form is $H^{H} = -J_{1}S_{t}S_{O} - J_{2}S_{r}S_{O} - J_{2}S_{l}S_{r}$, where $J_{2}$ is the overall spin exchange interaction between the left ($S_{t}$) and right ($S_{r}$) metal spin, and $J_{1}$ the magnetic interaction between the metal and the oxygen ions. The Heisenberg model space is also built from products of atomic ground states. The $S^{2}$ operator can be written as

$$S^{2} = (S_{t} + S_{r} + S_{O})^{2} = S_{l}^{2} + S_{r}^{2} + O^{2} + 2(S_{l}S_{O} + S_{r}S_{O} + S_{l}S_{r})$$

Replacing $S_{t}, S_{r}$ by their expression as function of $S^{2}$ in the Hamiltonian, one gets

$$H^{H} = -(J_{1} - J_{2})S_{l}S_{O} - \frac{J_{2}}{2}(S_{t}^{2} + S_{r}^{2} - S_{O}^{2})$$

where $S_{O} = S_{l} + S_{r}$. As $S_{l}S_{O} = \frac{1}{2}(S^{2} - S_{l}^{2} - S_{r}^{2} - S_{O}^{2})$, the Hamiltonian can be rewritten as:

$$H^{H} = -(J_{1} - J_{2})E_{0} + \frac{J_{2}}{2}(S_{l}^{2} + S_{r}^{2} - S_{O}^{2})$$

Since the oxygen has only one unpaired electron, i.e. $S_{O} = 1/2$, the values of $S_{l}$ can only be $S_{l} = S_{l} \pm 1/2$ and an analytical expression of the eigenenergies can be found:

$$E^{H}(S, \pm) = \frac{J_{1} - J_{2}}{2} \left[ 1 \pm \left( S + \frac{1}{2} \right) \right]$$

$$- \frac{J_{2}}{2}(S^{2} + 1 - S_{l}^{2} - S_{r}^{2} - S_{O}^{2} - 1/4)$$

where $S_{l}^{2} = S_{l}^{2} + S_{r}^{2} + 1/4$. For the highest spin multiplicity state, only the $E^{H}(S, +)$ root has a physical meaning since $S_{l}^{2}$ has the single value $S_{l} = S_{l} + 1/2$.

In order to compare the two models, the same zero of energy must be used in equations (1) and (5). Let us use the double exchange model zero of energy. Its expression as a function of the Heisenberg model is:

$$E_{0} = \frac{E^{H}(S_{\text{max}}^{Z}, +)}{2} + \frac{E^{H}(S_{\text{max}}^{Z}, -)}{2}$$

$$= \frac{J_{1} - J_{2}}{2} \left[ S_{\text{max}}^{Z}(S_{\text{max}}^{Z} + 1) - \frac{1}{2}(S_{\text{max}}^{H} + 1/2)^{2} - 1/4 \right]$$

The relation between $S_{\text{max}}^{Z}$ and $S_{\text{max}}^{H}$ is fixed by the number $n_{u}$ of unpaired electrons in the two models ($n_{u}^{H}$ and $n_{u}^{Z}$ for the Heisenberg and double exchange models, respectively). If $n_{u}^{H} = n_{u}^{Z}$, then $S_{\text{max}}^{H} = S_{\text{max}}^{Z}$. On the contrary, if $n_{u}^{H} = n_{u}^{Z} + 2$ then $S_{\text{max}}^{H} = S_{\text{max}}^{Z} + 1$. These two situations are illustrated in figure 1. The first one (schemes a) corresponds, for instance, to doped nickleates. The delocalized electron of the double exchange model (left scheme) jumps from a doubly occupied orbital towards a singly occupied one. The second situation (schemes b) is representative of half-doped manganites. The hopping electron of the double exchange model jumps from a singly occupied orbital towards the empty orbital of the other manganese.

The Heisenberg energies shifted by the mean value $E_{0}$ of the $S_{\text{max}}^{Z}$ states become:

$$E^{H}(S, \pm) = \pm \frac{J_{1} - J_{2}}{2} \left( S + \frac{1}{2} \right)$$

$$- \frac{J_{2}}{2}(S^{2} + 1 - S_{\text{max}}^{Z}(S_{\text{max}}^{Z} + 1))$$
Thus, from comparisons between equations \([1] \text{ and } [7]\), an important conclusion is that the energies of the two models are exactly the same if one replaces \(t\) and \(J\) by

\[
t = \frac{1}{2} (J_1 - J_2) \left(S_m^Z + \frac{1}{2}\right) \quad \text{and} \quad J = J_2 \quad (8)
\]

Let us notice that when \(S_{\text{max}}^H = S_{\text{max}}^Z + 1\), the energy of the \(S_{\text{max}}^H\) state cannot be obtained in the double exchange model, since this state does not belong to the model space. Its energy is only given by the Heisenberg expression. That means, in dopped manganites case, that the double exchange model contains two doublet, two quartet, two sextet and two octet \((S = 7/2)\) states whereas the Heisenberg model also describes a decuplet state \((S = 9/2)\). On the contrary, when \(S_{\text{max}}^H = S_{\text{max}}^Z\), the \(E^H(S_{\text{max}}^H, +)\) solution is meaningless for the Heisenberg model (see eq. [5] and its explanation) whereas \(E^Z(S_{\text{max}}^Z, +)\) is a solution of the double exchange model. Nevertheless, we still have \(E^H(S_{\text{max}}^H,+) = E^Z(S_{\text{max}}^Z, +)\). So, the complete description of the spectrum is possible from the Heisenberg expression while the Heisenberg model space does not contain the \(E^H(S_{\text{max}}^H, +)\) state. One therefore has the unexpected situation in which two model Hamiltonians working on different model spaces generate spectra which coincide except for one state. If \(S_{\text{max}}^H = S_{\text{max}}^Z + 1\) the double exchange spectrum is included in the Heisenberg one while it is the Heisenberg spectrum which is fully described by the double exchange model when \(S_{\text{max}}^H = S_{\text{max}}^Z\).

In order to check the relevance of the two considered models on a real material, let us turn now to the explicitly correlated \(ab\) \textit{initio} study of the \(\text{Pr}_{0.6}\text{Ca}_{0.4}\text{MnO}_3\) manganite. Since the choice between the two models turns out to be impossible from the only determination of the spectrum, the analysis of the ground state wavefunction becomes compulsory in order to discriminate between them. The \(\text{Mn}_2\text{O}_{11}^+\) cluster (constituted of the dimer of Mn sites surrounded by the oxygen atoms of their coordination sphere) is analyzed using the embedded cluster method. In order to reproduce the crystal environment, the cluster is embedded in a bath that reproduces its main effects (Madlung and Pauli exclusion \([3, 12]\)). Then the cluster is studied using correlated \(ab\) \textit{initio} calculations and large basis sets \([13]\). MS-CASPT2 calculations \([14]\) (the many-body second order perturbation scheme of the MOLCAS code \([15]\)

\[J_1, J_2 \quad t \quad J \quad \text{error (\%)}
\]

\[
\begin{array}{cccc}
\text{Heisenberg} & 0.59 & 0.07 & - & - & 3.3 \\
\text{Double exchange} & - & - & 1.05 & 0.07 & 3.3 \\
\end{array}
\]

\(\text{TABLE I: Effective interactions (in eV) of the two models extracted from the } ab \text{ \textit{initio} spectrum and errors of the corresponding predicted spectrum compared to the } ab \text{ \textit{initio} one.}\)

\[\text{FIG. 2: Canonical delocalized orbitals (a); strongly localized orbitals (b) and left or right semi-localized orbitals (c).}\]

In order to discriminate between the two hamiltonians we have compared the weight of the ground state model wavefunctions in the exact Hamiltonian ground
state wavefunction. Model Hamiltonians assume localized orbitals sets which must be properly defined. The symmetry-adapted orbitals set is not appropriate to the analysis of the Heisenberg wave functions due to the large delocalization of orbitals (1) and (3) (see fig.2a). In order to calculate the weight of the Mn$^{3+}$O$^{-}$Mn$^{3+}$ electronic configuration, orbitals (1), (2) and (3) have been relocalized using Boys localizations.$^{17}$ The three strongly localized orbitals are represented in Figure 2b.

The Heisenberg Octet ground state wave function is:

$$\psi^H \left( \frac{7}{2}, - \right) = \frac{\sqrt{2}}{6} \left[ (Q_1)_r D_{+1/2}(Q_2)_r - 4(Q_2)_r D_{-1/2}(Q_2)_r ight],$$

where $(Q_2)_r D_{-1/2}(Q_2)_r$ is the product of the local left and right $S_z = 2$ quintet component $(Q_2)_r$ on the two Mn sites and a local $S_z = -1/2$ doublet component $D_{-1/2}$ on the oxygen. $(Q_1)_r D_{+1/2}(Q_2)_r$ (resp. $(Q_2)_r D_{+1/2}(Q_1)_r$) is the product of the right $(Q_1)_r$ (resp. left $(Q_1)_r$) quintet $S_z = 1$ component on Mn$_r$ (resp. Mn$_l$) and $D_{+1/2}$ is the $S_z = +1/2$ doublet component on O.

The projection of the calculated ground state wave function onto the Heisenberg ground state gives a weight of 0.74 showing the adequation of this model Hamiltonian to reproduce the polaron physics.

The same wave function analysis has been performed on the double exchange model space. The double exchange octet ground state wave function is:

$$\psi^Z \left( \frac{7}{2}, - \right) = \frac{1}{\sqrt{2}} \left[ (Q_2)_l Q_{3/2} (Q_1)_r + (Q_3/2)_l (Q_1)_r \right],$$

where $Q_{3/2}$ is the $S_z = 3/2$ component of a local quartet. This model assumes a two-electron occupied orbital centered on the oxygen which is actually well described within the symmetry-adapted delocalized picture. The double exchange eigenvectors are linear combinations of two resonant forms where the extra electron is either on a left or on a right localized orbital. The adequate metallic orbitals are semi localized on the left and on the right metals with correct delocalization tails of the bridging oxygen. The so-obtained three orbitals are represented in Figure 2c. The weight of the calculated wave function on the double exchange model space in this orbitals set is 0.72 (to be compared to 0.74 for the Heisenberg model), revealing that both models are equivalently suitable for describing the physics of the polaron.

As a conclusion, since the spectra of the double exchange and the Heisenberg models are identical, the only criterium to choose the most appropriate model for a specific system should be the wavefunction projection onto both model spaces. In limit cases where the oxygen charge is close to -1 (or -2), i.e. for dominant M(d$^9$)O$^{-}$M(d$^9$) (or M(d$^{10}$)O$^{2-}$M(d$^{10}$)) electronic structure, a wavefunction analysis would enable one to decide which model is the most appropriated. On the contrary, for intermediate occupation of the oxygen orbital (which is the case in many correlated materials), the exact Hamiltonian wave function projection amplitudes onto both model spaces are almost the same provided that one uses proper orbitals sets. Consequently, the discrimination between the double exchange and Heisenberg model Hamiltonians, which is a matter of numerous discussions, is simply not possible, neither from the spectrum nor from the wave function analysis. It is likely that this undecidability will be encountered in the interpretation of experimental informations.

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