

Ab initio study of the CE magnetic phase in half-doped manganites: Purely magnetic versus double exchange description

Roland Bastardis,^{1,2} Coen de Graaf,^{2,3} and Nathalie Guihéry¹

¹*Laboratoire de Physique Quantique, IRSAMC/UMR5626, Université Paul Sabatier, 118 route de Narbonne, F-31062 Toulouse Cedex 4, France*

²*Department of Physical and Inorganic Chemistry, Universitat Rovira i Virgili, Marcel·lí Domingo, s/n 43007 Tarragona, Spain*

³*Institució Catalana de Recerca i Estudis Avançats (ICREA), Passeig Lluís Companys 23, 08010 Barcelona, Spain*

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The leading electronic interactions governing the local physics of the CE phase of half-doped manganites are extracted from correlated *ab initio* calculations performed on an embedded cluster. The electronic structure of the low-energy states is dominated by double exchange configurations and O $2p_{\sigma}$ to Mn $3d$ charge transfer configurations. The model spectra of both a purely magnetic nonsymmetric Heisenberg Hamiltonian involving a magnetic oxygen and two nonsymmetric double exchange models are compared to the *ab initio* one. While a satisfactory agreement between the Heisenberg spectrum and the calculated one is obtained, the best description is provided by a double exchange model involving excited non-Hund atomic states. The energy eigenvalues of this refined double exchange model are derived as a function of the local lattice distortions, and it is shown that in the absence of non-Hund states, an incorrect ground state is obtained.

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I. INTRODUCTION

Although numerous theoretical and experimental studies have been devoted to the understanding of the various phase transitions occurring in doped manganites,¹ their electronic structure near half doping is still not fully understood.² $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ is antiferromagnetic below the Néel temperature T_N and paramagnetic for $T > T_{\text{CO}}$, where CO stands for charge ordered. For intermediate temperatures $T_N < T < T_{\text{CO}}$, two different electronic structures have been proposed. In the first one, a charge order prevails and the magnetic phase exhibits a CE-type ordering of the magnetic moments.^{3,4} In the second electronic structure,⁵ the holes are trapped in pairs of equivalent Mn ions of intermediate valence state $\text{Mn}^{3.5+}$ resulting from the double exchange (DE) interaction between the two limit $\text{Mn}^{3+}\text{O}^{2-}\text{Mn}^{4+}$ and $\text{Mn}^{4+}\text{O}^{2-}\text{Mn}^{3+}$ electronic configurations. The latter electronic structure is referred as a Zener polaron order in reference to Zener who first proposed the DE mechanism.⁶

Ab initio calculations confirm the existence⁷ of a charge-ordered phase (partial localization of the holes on one type of Mn ions) in the crystallographic structure of Radaelli *et al.*,⁴ while a polaronic order⁷⁻¹⁰ (delocalized holes between pairs of Mn ions) is obtained for the crystallographic structure of Daoud-Aladine *et al.*⁵ It is worth noting that in both cases, correlated *ab initio* calculations point out that there is a rather strong O to Mn charge transfer, resulting in a partial localization of the holes on the bridging oxygens. Unrestricted Hartree Fock (UHF) and density-functional theory periodic calculations¹¹⁻¹³ on $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ even lead to a dominantly $\text{Mn}^{3+}\text{O}^{2-}\text{Mn}^{3+}$ ground state charge distribution.

The impact of this partial localization of the holes on the oxygen sites has recently been studied in the peculiar case of a Zener polaron, i.e., using the crystal structure of Daoud-Aladine *et al.*⁵ The two Mn ions in the Zener polaron have an almost identical coordination, and hence, several symmetric models have been derived and their solutions contrasted with

ab initio results.^{8,9} It has been shown that (i) a truncated Hubbard in which all the dominant configurations are treated variationally can be mapped both on the Heisenberg and the usual DE model owing to the mixing of the bridging oxygen and Mn ions orbitals.⁹ (ii) The energies of the eight lowest states of the Heisenberg and the usual DE models are analytically identical and in qualitative agreement with those of the *ab initio* spectrum.^{9,10} (iii) a significant improvement is observed when the non-Hund excited atomic states are explicitly introduced in the modelization.⁸ The remarkable accuracy of the resulting model spectrum finally shows that the Zener polaron physics is actually ruled by a refined DE mechanism where non-Hund atomic states play a non-negligible role.

The present paper focuses on the local electronic structure of the charge-ordered crystallographic structure of $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$. For this purpose, we have studied an embedded cluster containing two corner-sharing MnO_6 octahedra using the crystal structure determined by Radaelli *et al.*⁴ The two Mn ions in the cluster have different coordination spheres. One site is Jahn-Teller distorted, while the other has six (almost) equivalent, rather short Mn-O distances. The two sites are commonly interpreted as occupied by $\text{Mn}^{3+}(3d^4)$ and $\text{Mn}^{4+}(3d^3)$, respectively. According to the position of the holes, different electronic orders are expected.

(1) If the holes are localized on the Mn sites, the resulting seven unpaired electron system is of mixed-valence nature. The DE mechanism induces a resonance between $\text{Mn}^{3+}\text{O}^{2-}\text{Mn}^{4+}$ and $\text{Mn}^{4+}\text{O}^{2-}\text{Mn}^{3+}$, which, in that peculiar case, will result in a charge ordering of the electronic structure, i.e., a partial localization of the e_g -like extra electron (or hole) on one Mn ion $\text{Mn}^{3.5+\delta}\text{O}^{2-}\text{Mn}^{3.5-\delta}$. The t_{2g} -like electrons are unpaired and strongly localized on each ion.

(2) If the holes are localized on the bridging oxygen, the corresponding charge distribution suggests a dominant purely magnetic local order ($\text{Mn}^{3+}\text{O}^{2-}\text{Mn}^{3+}$) in which the cluster would be a ferrimagnetic entity involving a magnetic

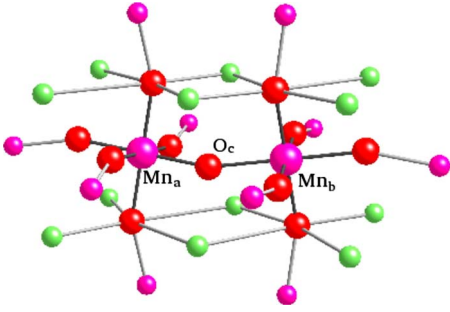


FIG. 1. (Color online) Mn_2O_{11} cluster embedded in Mn and (La,Ca) total ion potentials (TIPs).

oxygen and therefore nine unpaired electrons. The model Hamiltonian that provides a relevant description of such a local electronic order is a Heisenberg Hamiltonian involving nonsymmetric exchange integrals between each Mn ion and the magnetic oxygen.

In order to decide which Hamiltonian is most appropriate to describe the local electronic structure of this nonsymmetric two-center cluster, we compare the different model spectra with the *ab initio* one. The here-used procedure consists in extracting the local effective interactions of the model Hamiltonians from calculations performed with the exact electronic Hamiltonian. For this purpose, the low-energy spectrum of an embedded cluster of the material is studied by means of correlated *ab initio* calculations. The subsequent extraction of the model parameters makes use of the effective Hamiltonian theory of Bloch.^{14,15} The comparison of the resulting model spectra to the *ab initio* one provides rational arguments to determine the most appropriate model Hamiltonian.

Section II is devoted to the presentation of the embedded cluster computational procedure. Section III resumes the essential features of the Heisenberg and DE models. The partial localization of the e_g -like electron described in the DE models is accompanied by a lattice distortion: an expansion of the Mn coordination sphere on the site where the extra e_g -like electron is localized and a contraction on the Mn site with the hole. The effect of this lattice distortion on the eigenvalues is known for the usual DE model, but not for the refined DE model. Section III C gives the energy expressions of the DE states as function of the lattice distortion for the refined model. Finally, the comparison of the model spectra with the *ab initio* spectrum is discussed in Sec. IV.

II. DESCRIPTION OF THE CLUSTER AND COMPUTATIONAL PROCEDURE

The geometry of the Mn_2O_{11} cluster is derived from the 20 K modulated structure of $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ reported in Table I of Ref. 4. Two different types of Mn sites can be distinguished in the material, and the mean radius of their coordination spheres are, respectively, 1.971 and 1.916 Å. The distances between a bridging oxygen and the two distinct Mn sites are 1.915 Å for $\text{Mn}_a\text{-O}_c$ and 2.068 Å for $\text{Mn}_b\text{-O}_c$. The cluster is represented in Fig. 1 and is consti-

tuted of two different Mn ions in a distorted octahedral environment bridged by O_c and ten external oxygen atoms. Axis is chosen such that the origin of the coordinates is at half distance between the two Mn sites, z is the intermetallic axis, and the bridging O atom (O_c) lies on the xz plane.

To reproduce the crystal environment, the cluster is embedded in a set of optimized point charges which accurately reproduces the Madelung potential of the crystal. Total ion potentials (TIP) have been used to represent the Mn, La, and Ca cations coordinated to the oxygen atoms of the cluster (see Fig. 1). Additional information can be found in Ref. 7, where it is shown that this embedding provides reliable results on the ground state of the system. The reliability of the embedded cluster approach to extract effective model parameters has been established in many studies of different transition metal oxides. Parameters obtained within this local approach have been compared with results obtained in periodic calculation using the same approximation for the N -electron wave function,^{16–21} and the stability of the results has been tested against the size of the cluster.^{20–23} In both cases, the verifications show that a properly embedded cluster with two transition metals and its immediate neighbors gives a sufficiently reliable representation of the material for the extraction of local electronic structure parameters.

The electronic structure of the cluster has been studied using the complete active space second-order perturbation theory (CASPT2) method^{24–27} implemented in the MOLCAS package.²⁸ The orbitals are expanded with extended basis sets of ANO type:^{29,30} ($5s, 4p, 3d, 1f$) for Mn atoms, ($4s, 3p, 1d$) for the bridging O, and ($4s, 3p$) for external O. The CASPT2 method, which has successfully been applied to the study of many spectroscopic problems, introduces both non-dynamical and dynamical correlation effects. In a first step, a multireference wave function is optimized by the complete active space self-consistent field (CASSCF) procedure. This N -electron wave function includes the main nondynamical electron correlation. The here-considered active space contains all electronic configurations obtained by distributing nine electrons in the ten $3d$ orbitals of the two Mn ions and the $2p_\sigma$ orbital essentially localized on the bridging oxygen. Accurate relative energies of the ground state and lowest excited electronic states are computed by introducing the dynamical electron correlation in a subsequent second-order perturbation treatment applied to the zeroth-order CASSCF wave function.

Using the *ab initio* spectrum and the effective Hamiltonian theory of Bloch,^{14,15} it is possible to extract the main electronic interactions of the different models. Since the number of electronic interactions is smaller than the number of electronic states described by the model space, the value of the effective interactions is fitted to optimally reproduce the *ab initio* spectrum. The mean error per state can be evaluated with the following expression:

$$\epsilon = \frac{100 \sum_i |E_i^{AI} - E_i^M|}{N \Delta E^{AI}}, \quad (1)$$

where N is the number of states described by the model Hamiltonian, E^{AI} and E^M are, respectively, the *ab initio* and

model energies of state i , and ΔE^{AI} the *ab initio* spectrum width.

Both the comparison of the so-obtained model spectra to the *ab initio* one and the size of the error per state give rational arguments to discriminate between different modelizations.

III. DESCRIPTION OF THE DIFFERENT MODELS

A. Heisenberg model

If the holes are essentially localized on the oxygens O_c , then the wave functions of the lower-energy states are dominated by electronic configurations with nine unpaired electrons. This is compatible with a $Mn_a^{3+}-O_c^{-}-Mn_b^{3+}$ electronic structure and the appropriate model Hamiltonian is the Heisenberg Hamiltonian. In a nonsymmetric cluster, its specific form as a function of the exchange integrals between the three magnetic centers is

$$\mathbf{H}^{Heis} = -J_1 \mathbf{S}_{Mn_a} \cdot \mathbf{S}_{O_c} - J_3 \mathbf{S}_{Mn_b} \cdot \mathbf{S}_{O_c} - J_2 \mathbf{S}_{Mn_a} \cdot \mathbf{S}_{Mn_b}, \quad (2)$$

where J_1 is the magnetic interaction between Mn_a and O_c , J_3 the magnetic interaction between Mn_b and O_c , and J_2 the magnetic interaction between the two Mn centers. The difference between the J_1 and J_3 exchange integral values reflects not only the geometrical asymmetry (the Mn_a-O_c distance is shorter than the Mn_b-O_c distance) but also any possible asymmetry in the electronic structure.

The model space of this Hamiltonian is spanned by the products of the magnetic site ground states. In the considered case, each Mn atom has four unpaired electrons coupled to a quintet ground state. The bridging oxygen O_c has one unpaired electron in a local $2p_{\sigma}$ -like orbital leading to a doublet ground state. An analytical solution of the energies of the eigenstates of the Heisenberg model space has been derived for this simple case. Its expression is

$$E^H(S, \pm) = \pm \sqrt{[S_{max}^H(S_{max}^H + 1) - S(S + 1)]x^2 + \beta^2 \left(S + \frac{1}{2}\right)^2} + J_2[S(S + 1) - S_{max}^H(S_{max}^H - 1)],$$

where $x=J_1-J_3$ and $\beta=J_1+J_3-2J_2$. S_{max}^H is the maximal value that S can take in the Heisenberg model. $S_{max}^H=9/2$ in the here-considered cluster. The mean energy of the octet states is taken as the zero of energy.

B. Usual nonsymmetric double exchange model

With the holes localized on the Mn ions, the N -electron wave functions of the lower states are dominated by spin configurations presenting seven unpaired electrons, i.e., a $Mn_a^{3.5+\delta}-O_c^{2-}-Mn_b^{3.5-\delta}$ (closed shell oxygen) electronic structure. The cluster is of mixed-valence nature and the DE model should accurately reproduce its physics. In a charge-ordered phase, i.e., with $\delta \neq 0$, the electronic structure of the cluster is such that the extra electron (or hole) is partially localized on one of the two Mn ions. The nuclear relaxation resulting from this partial localization results in an enlargement of the coordination sphere (an increase of the average Mn-O distance) of the Mn ion bearing the extra electron and

a contraction of the coordination sphere of the Mn ion bearing the hole. Piepho *et al.*³¹ proposed a vibronic coupling model to describe this phenomenon in mixed-valence compounds. The relevant dimensionless coordinate in this so-called Piepho-Krausz-Schatz (PKS) model is q , which describes the nuclear relaxation during the electron transfer process.

In the PKS model, q corresponds to the antisymmetric combination of the local stretching mode of the coordination spheres. The here-considered coordinate q also includes the Jahn Teller distortion, since the cluster is studied at the experimental geometry which is Jahn-Teller distorted.

Let us call Φ_a and Φ_b the electron localized diabatic states corresponding to functions in which the extra electron is localized on Mn_a and Mn_b , respectively. In the usual DE models, these functions are products of the Mn ion ground state wave functions, i.e., in the $m_s=7/2$ subspace, $\Phi_a=Q_a^i \cdot Q_b$ and $\Phi_b=Q_a \cdot Q_b^i$, where Q^i is a quintet state and Q stands for a quartet state. Their energetic dependence to the coordinate q is usually assumed to be quadratic, so that the potential energy curves of Φ_a and Φ_b obey the equations $E_a=\Delta(q^2+2q)$ and $E_b=\Delta(q^2-2q)$, respectively, where Δ is the curvature of the diabatic spin state potential energy curves as functions of q . The PKS Hamiltonian expressed in the $m_s=7/2$ subspace is

$$\begin{pmatrix} \Delta(q^2+2q) & t \\ t & \Delta(q^2-2q) \end{pmatrix},$$

with t the hopping integral of the extra electron between the two metal centered orbitals (e_g -like in the present case). Its diagonalization generates the two adiabatic octet states $O_+=N(\Phi_a+\Phi_b)$ and $O_-=N(\Phi_a-\Phi_b)$ of energy

$$E^{PKS}(7/2, \pm) = \Delta q^2 \pm \sqrt{4(\Delta q)^2 + t^2}. \quad (3)$$

In a nonsymmetric and therefore charge-ordered system, the potential energy curve of the ground state O_+ as a function of the coordinate q presents a double well. The corresponding minima are associated with the two nonsymmetric geometries and the $Mn^{3.5-\delta}-O^{2-}-Mn^{3.5+\delta}$ or $Mn^{3.5+\delta}-O^{2-}-Mn^{3.5-\delta}$ charge-ordered electronic configurations.

The coupling between the lower m_s components of the local ground states Φ_a and Φ_b generates states of lower-spin multiplicity, namely, two sextet S_- and S_+ , two quartet Q_- and Q_+ , and two doublet D_- and D_+ states. In the general case of a nonsymmetric homonuclear bimetallic complex, the eigenenergies of the model are analytically known³²⁻³⁴ and are given by the expression

$$E^{DE}(S, \pm) = \pm \sqrt{4(\Delta q)^2 + B^2 \left(S + \frac{1}{2}\right)^2} + J[S(S + 1) - S_{max}^{DE}(S_{max}^{DE} + 1)], \quad (4)$$

where S_{max}^{DE} is the maximal value that S can take in the DE model, and $S_{max}^{DE}=7/2$ in the considered cluster. $B=\frac{t}{S_{max}^{DE}+\frac{1}{2}}$ is the leading interaction of the model. t favors a ferromagnetic order, in other words, it accounts for the appearance of a high-spin ground state. J is the overall exchange integral

which describes the electronic circulation in the other open shells, here the t_{2g} -like orbitals. This Heisenberg contribution is generally antiferromagnetic and has been introduced by Girerd *et al.*^{32,34} It causes a significant stabilization of the mean energies of the low and intermediate spin states with respect to the mean energy of the highest-spin states. The zero of energy is placed at the mean energy of the highest-spin states.

The values of t , J , and the product Δq are determined by minimizing ϵ , defined in Eq. (1).

The expression of the variable q_{min} at the minimum of the ground state energy can be obtained from the zero of the first derivative of the energy:

$$q_{min} = \frac{2\Delta q}{\sqrt{4(\Delta q)^2 + t^2}}. \quad (5)$$

Knowing the product Δq and the value of q at the minimum, it is possible to determine the value of the curvature Δ and to draw the full potential energy curves as a function of q .

The hopping parameter can also be extracted directly from the energies and wave functions of the two octet states without fitting the *ab initio* spectrum to a model Hamiltonian. To validate our numerical fitting procedure, we compare the t values obtained in both procedures. The symmetrically orthonormalized projections of the adiabatic octet state wave functions onto the model space are

$$\begin{aligned} |\Psi_1\rangle &= \cos \phi |\Phi_a\rangle + \sin \phi |\Phi_b\rangle, \\ |\Psi_2\rangle &= -\sin \phi |\Phi_a\rangle + \cos \phi |\Phi_b\rangle, \end{aligned} \quad (6)$$

where $\frac{\pi}{4} - \phi$ characterizes the charge localization. From these expressions, the des Cloizeaux¹⁵ formalism allows us to extract the hopping integral as follows:

$$t = \sin \phi \cos \phi [E(O, -) - E(O, +)]. \quad (7)$$

$$E_{NH}^{DE}(S, \pm) = \frac{1}{2} \left[\delta_H - \sqrt{\delta_H^2 + 16(\Delta q)^2 + 4t^2 \pm 4\delta_H \sqrt{4(\Delta q)^2 + B^2 \left(S + \frac{1}{2}\right)^2}} \right] + J[S(S+1) - S_m^{DE}(S_m^{DE} + 1)]. \quad (9)$$

Again, the electronic interactions t , δ_H , and J and the product Δq are numerically optimized such that the model spectrum optimally fits the *ab initio* one. Since the contribution of the non-Hund states is zero in the highest-spin states and therefore in the ground state, the extraction of q_{min} (and then Δ) is performed using Eq. (6).

IV. CONTRASTING THE MODELS TO *AB INITIO* RESULTS

A. Comparison of the spectra

Taking the CASSCF wave functions as references, we determined the second-order perturbation theory MS-CASPT2

C. Explicit treatment of the non-Hund excited atomic spin states

The explicit consideration of the excited atomic non-Hund states in the DE model was introduced by Anderson and Hasegawa³⁵ in the description of a symmetric (i.e., fully delocalized) cluster. In the symmetric case, the DE model can be written such as

$$\mathbf{H} = -t \sum_{(i,j)\sigma} (\mathbf{a}_{i\sigma}^\dagger \mathbf{a}_{j\sigma} + \text{H.c.}) - J_H \sum_i \mathbf{s}_i \mathbf{S}_j + J \sum_{(i,j)} \mathbf{S}_i \mathbf{S}_j, \quad (8)$$

where $\mathbf{a}_{i\sigma}$ is the annihilation operator for an electron with spin σ on site i . J_H is the Hund coupling between the localized t_{2g} spin and the e_g spin and $\mathbf{s}_i = \sum_{\gamma\alpha\beta} \mathbf{a}_{i\gamma\alpha}^\dagger \sigma_{\alpha\beta} \mathbf{a}_{i\gamma\beta}$ (γ is the orbital of site i , α, β the spin, and $\sigma_{\alpha\beta}$ the Pauli matrices). In comparison to the usual DE model, i.e., $J_H \rightarrow \infty$, the Anderson-Hasegawa model does not only consider the products of local ground states. Its model space is extended to products of an atomic ground state on one Mn ion and a single excited non-Hund atomic state on the other Mn ion. The so-obtained functions interact with the model space of the usual DE model through a term proportional to the hopping integral t . The main contribution of a variational treatment of these functions is antiferromagnetic. This means that the energies of the highest-spin states are not affected, while the intermediate and low spin states are stabilized by the non-Hund state contribution. As already shown in symmetric dimers,^{8–10,37–39} the best results are obtained using this refined DE model in combination with the antiferromagnetic contribution of Girerd-Papaefthymiou through a magnetic exchange integral J . Assuming that the potential energy curves of the electronic states formed by a product of a non-Hund state and an atomic ground state are parallel to those of the products of the atomic ground states, it is possible to generalize this refined model to the study of nonsymmetric clusters. Calling δ_H the relative energy of the non-Hund state, one obtains the following energy expression of the DE states:

spectrum for the low-lying states of the cluster. The ordering of the states is the following:

$$\begin{aligned} E(O_-) &< E(S_-) < E(Q_-) < E(D_-) < E(D_+) < E(Q_+) \\ &< E(S_+) < E(O_+), \end{aligned} \quad (10)$$

which is compatible with all the here-considered models. The electronic interactions of the different models optimized in order to reproduce at best the *ab initio* spectrum are given in Table I, and the corresponding model spectra are represented in Fig. 2 together with the MS-CASPT2 spectrum. Using Eq. (7), we validate the numerical fitting procedure. Unfortunately, the comparison cannot be done at the MS-

TABLE I. Effective parameters of the refined DE (non-Hund), usual DE [Zener-Girerd-Papaefthymiou (ZGP)], and Heisenberg model extracted from the MS-CASPT2 spectrum. The magnetic exchange (J) and hopping (t) integrals are in eV. q_{min} is the value of the effective parameter q at the minimum of the ground state potential energy curve, and Δ (in eV) is the curvature of the potential energy curves of the diabatic (i.e., before interaction) left and right states. ϵ is the mean error of the fit of the model Hamiltonian spectrum to the ab initio spectrum.

	Non-Hund	ZGP	Heisenberg
J_1			0.568
J_3			0.939
J_2			0.082
J	0.0405		0.0847
δ_H	4.993		
Δ	0.7177	0.6935	
q_{min}	± 0.38	± 0.32	
t	1.3292	1.3081	
ϵ	0.14	1.014	1.010

CASPT2 level since this method does not provide the necessary wave function coefficients.³⁶ Instead, we take the spectrum provided by the zeroth-order wave function and extract t both by fitting the usual DE Hamiltonian and by applying Eq. (7). The respective values of 0.9043 and 0.9108 eV compare very well.

From the comparison of the different spectra, it appears that the qualitative features of the *ab initio* spectrum are reproduced in all model spectra, legitimating the consideration of the three different models. Notice that this is not the case for all Hamiltonians: The mechanism proposed by Zener,⁶ which only considers the hopping integral and does not introduce any antiferromagnetic contribution, cannot reproduce the *ab initio* spectrum.⁸

Concerning the extracted electronic interactions and the mean error per state of the different models, several comments can be made.

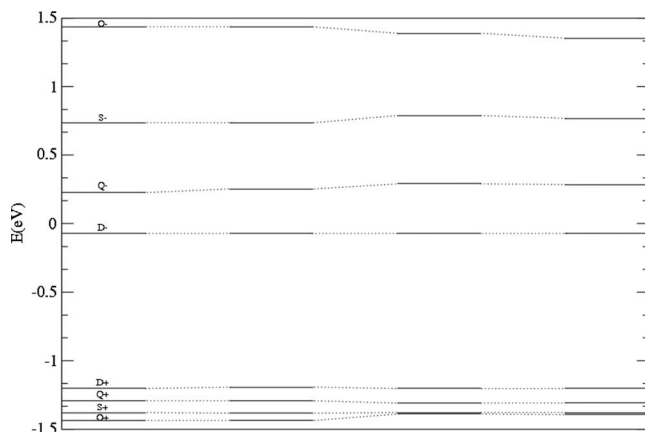


FIG. 2. Comparison of the MS-CASPT2 spectrum of the embedded cluster (column 1) with the outcomes of the refined DE model (column 2), the usual double exchange model (column 3), and the Heisenberg model (column 4).

(1) The mean errors per state of the usual DE and Heisenberg models are similar but not strictly identical as in the symmetric cluster.^{8,9}

(2) As already observed for symmetric DE compounds, the explicit consideration of the non-Hund atomic states improves quantitatively the reproduction of the *ab initio* spectrum and therefore the modelization. An error of only 0.14% is obtained for the refined DE model.

(3) The nonsymmetry of the cluster (which is responsible for the charge ordering) is reflected in the difference of the J_1 and J_3 exchange integral values of the Heisenberg model. The very large value of J_3 shows the covalent character of the interaction between Mn_b and the bridging O_c oxygen. Actually, the value is so large that it even questions the validity of a purely magnetic description of the cluster.

(4) The values of the electronic interactions t and J extracted from the two DE models are qualitatively different. In particular, the value of the exchange integral J of the usual DE model is twice as large as the one extracted from the refined DE model. A large difference between the two extracted values has already been observed in other studies.^{8,9,37,38} The participation of non-Hund states in the *ab initio* wave function enhances the covalent character of the interaction between the Mn sites. Their explicit inclusion in the model space results in an antiferromagnetic contribution, i.e., it stabilizes the low and intermediate spin states. In order to reproduce this antiferromagnetic contribution, the usual DE model overestimates the value of the antiferromagnetic exchange integral J and underestimates the value of t , i.e., of the ferromagnetic contribution.

B. Role of the non-Hund states on the spin multiplicity of the ground state

As already shown in the peculiar case of a symmetric cluster,^{8,9} both the exchange integral J which describes the electronic circulation in the t_{2g} -like orbitals and the non-Hund states stabilize the low and intermediate spin states with respect to the highest-spin one. If these antiferromagnetic contributions are large enough, they may even generate an intermediate spin ground state.^{38,39} We have seen in the previous section that the model spectra present the same qualitative features as the *ab initio* spectrum at the experimental geometry.

As shown in Sec. III B, the curvature Δ of the potential energy curves of the diabatic spin states can be extracted from the calculated spectrum. From the value of Δ and the optimized effective electronic interactions, it becomes possible to determine the full local potential energy curves of the adiabatic states as functions of the coordinate q for the two DE models. Figures 3 and 4 depict the curves of the eight spin states for the usual and the refined DE model, respectively. It is striking to see that while the octet state is the ground state at the experimental geometry in the usual DE model, the potential energy curves show more stable minima for low and intermediate spin states at larger values of q . On the contrary, the octet potential energy curve is the lowest state over the whole interval for the refined DE model.

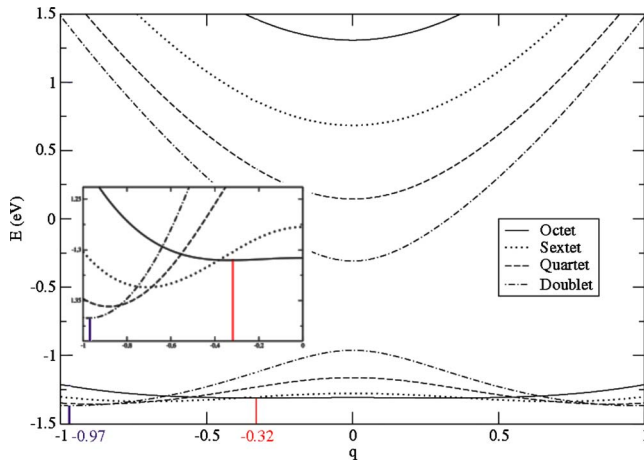


FIG. 3. (Color online) Potential energy curves of the eight states obtained from the optimized parameters of the usual DE model. The red line indicates the optimized value of q_{min} in the octet ground state, i.e., the geometry for which the *ab initio* spectrum has been calculated. The blue line indicates the position of the doublet state well.

This qualitative disagreement between the usual DE model and the *ab initio* calculation is due to the overestimation of the exchange integral J . In the absence of the hopping integral t (i.e., for the diabatic states), the potential wells associated with the left and right localized holes are such that the ordering of the eight lowest electronic states is governed by the Heisenberg contribution. This antiferromagnetic interaction induces an antiferromagnetic order and makes the doublet state the ground state. From Eqs. (4) and (7), it is easily seen that the coupling between the left and right diabatic states through the hopping integral is more effective in the highest-spin state. Hence, this interaction, which is the largest interaction of the DE mechanism, should induce a high-spin ground state. However, the artificially large J makes that the hopping interaction is not large enough to

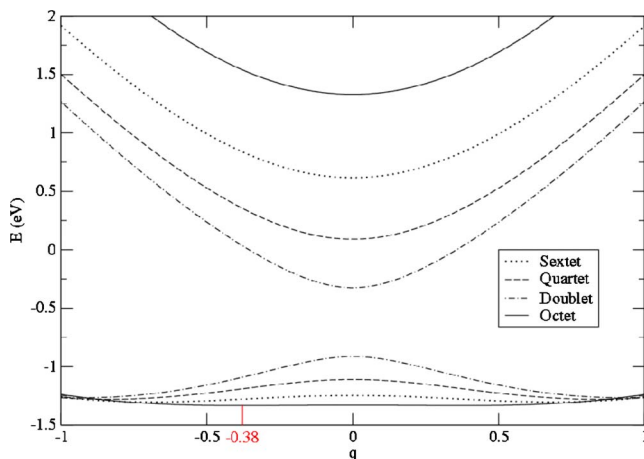


FIG. 4. (Color online) Potential energy curves of the eight states obtained from the optimized parameters of the refined DE model. The red line indicates the optimized value of q_{min} in the octet ground state.

restore a ferromagnetic order in the usual DE model. As a consequence, the lowest potential energy well is the doublet state one. The minimum of this potential energy curve lies at $q_{min} = \pm 0.97$, 0.06 eV below the minimum in the octet curve at ± 0.32 . Owing to the antiferromagnetic contribution of the non-Hund states in the refined DE model, the optimized exchange integral J is properly estimated and both the spectrum at the experimental geometry and the potential energy curves of the different states reproduce the correct physics of the system.

V. CONCLUSIONS

The extraction of local electronic structure parameters in the CE phase of the half-doped manganite $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ reveals that the local physics can accurately be described with a model Hamiltonian that includes the usual double exchange physics of mixed-valence compounds plus an additional term due to the non-Hund states. The large t value (1.3 eV) indicates a rather mobile electron and hence small charge disproportionation. In fact, Mulliken population analysis associates a slightly higher charge to the Mn ion in the Jahn-Teller distorted site. The difference between both sites is 0.07 electron. Although absolute Mulliken charges are not reliable, the relative values can be considered as indicative for tendencies. Moreover, the observed charge disproportionation of 0.07 is consistent with the maximum of 0.18 predicted in model Hamiltonian studies.⁴⁰

The PKS model provides a simple recipe to obtain the potential energy curves of the low-lying states as function of the distortion parameter q and hence obtain more detailed information about the local electronic physics. The curves for the low-lying states show a double well, where the minimum of the high-spin ground state curve lies at $q = \pm 0.38$. This corresponds to a situation in between the completely delocalized solution with $q_{min} = 0$ and the completely localized solution for $q_{min} = \pm 1$. The latter solution has a disproportionation of 1 electron, while for the $q_{min} = 0$ situation, there is no barrier and the charge disproportionation has completely disappeared.⁴¹

The height of the barrier between left and right localized solutions is 0.04 eV for the octet ground state of the embedded cluster. Our model study only considers local distortions around the two Mn sites considered in the cluster, and the collective nature of the distortions in the CE phase could lead to higher barriers. Obviously, these effects should be included in order to be conclusive about the nature of the local electronic structure of the half-doped manganite, charge ordered or delocalized (Zener polaron) as proposed in Ref. 5. Nevertheless, the smallness of the barrier is in line with the two different interpretations obtained by experimentalists and the controversy in the literature.

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