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REGULAR ARTICLE

Possible use of DFT approaches for the determination of double exchange interactions

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Abstract DFT calculations are performed on a model mixed-valence system presenting a double exchange phenomenon. Due to the intrinsic multireference character of the lowest Ms components of the spin states, it is shown that the interactions involved in the double-exchange model cannot be simply extracted from the DFT energies as it is sometimes done. It is, however, possible to extract from different DFT single determinant energies the interactions of a generalized Hubbard Hamiltonian, from which, in a second step, the double-exchange spectrum may be evaluated. The problems generated by the charge and spin polarization are discussed in both symmetric and non symmetric geometries, and the sensitivity of the results to the choice of the density functional is illustrated.

Keywords DFT calculations · Double exchange · Parameter extraction · Magnetic systems · Theory of magnetism

Dedicated to the memory of Professor Jean-Pierre Daudey and published as part of the Daudey Memorial Issue.

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1 Introduction

The main characteristics of magnetic systems reside in their intrinsic multireference character that comes from the existence of weakly coupled unpaired electrons. Their theoretical study requires highly correlated treatments and the modelization of their properties usually relies on model Hamiltonians, such as Heisenberg Hamiltonians, t-J models or double exchange models. Ab initio calculations may help to understand the microscopic origin of their macroscopic properties and are often used to evaluate quantitatively the interactions of these model Hamiltonians. Two different strategies have been successfully used:

i. The calculation of the lowest energy spectrum using correlated methods. This approach is generally computationally expensive, but it provides the energies and wave functions of the lowest spin states with a good accuracy. It enables one to calculate the model interactions from ab initio information, since the energies of the correlated computed states can be directly assimilated to the eigenvalues of the model Hamiltonian. The first evaluations were perturbative [1–4]; then variational truncated Configuration Interaction, especially the Difference Dedicated Configuration Interaction [5–8], has been preferred, providing very accurate results.[1] Combining these correlated ab initio calculations with the use of the Effective Hamiltonian Theory (EHT) [10] permits to appreciate the validity of the model Hamiltonian and sometimes enables one to improve the model Hamiltonian [11, 12]. Indeed, the amplitude of the projections of the correlated wave functions onto the model space gives a direct evaluation of the physical content of the

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[1] See a non-exhaustive list of references to successful applications in [9].

model Hamiltonian. Moreover, the numerical determination of the model Hamiltonian matrix owing to the EHT method directly evidences the missing interactions when the Hamiltonian is not appropriate. Following this strategy, it has been possible to show the limits of validity of Heisenberg Hamiltonian in spin $S = 1/2$ [13, 14] and $S = 1$ systems [15–17], *t–J* models [18] and double exchange Hamiltonian [18–23]. The determination of complex interactions, such has three-body interactions in spin $S = 1$ Heisenberg model [16, 17], three-body interactions in *t–J* model [18] and four-body interactions in spin $S = 1/2$ Heisenberg model [13, 14] are straightforward in this procedure. In all the mentioned cases these interactions were crucial for an accurate reproduction of the properties of the systems.

ii. The calculation of several broken symmetry (BS) solutions using Density Functional Theory [24–27]. Since only single determinant calculations can be performed in this methodology, it is no more possible to assimilate the computed energies to those of the spin Hamiltonian. The procedure here consists in assimilating the calculated energies to the diagonal elements of the model Hamiltonian. For instance, in the case of a Heisenberg Hamiltonian, the computed energies will be assimilated to the energies of an Ising Hamiltonian. Although these solutions are a priori not orthogonal, this procedure has shown to produce accurate magnetic couplings provided that a correct percentage of Fock exchange is used. The main advantage of this procedure is due to the low computational cost of DFT in comparison to highly correlated methods. Calculations can be performed for high-spin and high-nuclearity systems which are not accessible using correlated treatments. For spin ½ systems it is possible to extract four-body operators amplitudes from the multiplicity of DFT solutions, corresponding to different spin distributions, even in periodic calculations [28]. However, unless the lowest DFT solutions show a completely different electronic structure than the one predicted by the model Hamiltonian, this approach does not permit to estimate the validity of the model Hamiltonian. It is actually not possible to have access to the projections of the multiconfigurational wave functions onto the model space and the extraction of complex interactions such as those mentioned above are not trivial.

Recently, it has been shown that an accurate extraction of the interactions of a generalized Hubbard Hamiltonian could be performed by assimilating the DFT solutions to the determinants of the model space of a Hubbard Hamiltonian [29]. Then, since it is possible to derive analytically the simpler spin Hamiltonian from a Hubbard Hamiltonian, the interactions of the spin Hamiltonian can be determined from those of the Hubbard one. This technique has been successfully used to extract biquadratic exchange and the amplitude of three-body interactions in spin $S = 1$ systems. One should, however, mention the problem which we face in these systems when working with BS solutions which do not have the same spin polarisation.

The present paper considers the possible extraction of double exchange interactions. This phenomenon occurs in mixed valence compounds having several open-shells per centre. The phenomenon has received several modelizations of various complexities [19–23, 30–35]. Two electron populations coexist: The delocalized electrons are characterized by an inter-site hopping integral between the local orbitals having the largest overlap while the localized electrons interacting through an inter-site magnetic coupling, often antiferromagnetic, occupy the less overlapping local orbitals. The magnitude of the hopping integral governs the magnetic behaviour which generally happens to be ferromagnetic. Contrary to the previous purely magnetic cases, the use of broken-symmetry solutions is here more problematic, since the solutions may differ from each other by their spatial configuration and by both their specific spin and the charge polarizations. The extractions of the interactions of the model from symmetry-adapted and/or broken-symmetry solutions should carefully be analysed.

2 Modelization of the physics of the double exchange phenomenon from an extended Hubbard Hamiltonian

2.1 A simple model problem

In order to define adequate magnetic orbitals, we shall consider first a complex involving two equivalent metal ions, each of them bearing two unpaired electrons in two magnetic orbitals. While in a real complex, inner closed shells are present, their effect will not explicitly be considered at this stage and we shall only treat the magnetic orbitals and the magnetic electrons. The ground state of these metal ions is triplet, according to the Hund's rule. Let us assume that the two sites are equivalent and symmetrical with respect to a symmetry centre or plane. Let us also assume that an additional symmetry element of the geometrical structure of the complex, for instance a plane, enables one to distinguish the spatial symmetries of the two atom-centred magnetic orbitals, for instance $dx^2{-}y^2$ and dz^2. For convenience we will refer to symmetry A (or B) the combinations of the orbitals a (or b, respectively). The on-site magnetic orbitals will be noted a_1 and b_1 on site 1, a_2 and b_2 on site 2.

We may assume, without loss of generality, that these orbitals are orthogonal, i.e. obtained from the restricted open-shell calculation of the Ms = 2 component of the quintet state of the complex, for instance. The single-determinantal wave function of this quintet state is

$$^{(2)}\Phi_g = |a_1 b_1 a_2 b_2| = |g_a u_a g_b u_b| \tag{1}$$

where the upper index indicates the M_s value of the determinants and not its spin multiplicity, and

$$\begin{aligned} g_a &= (a_1 - a_2)/\sqrt{2}, \\ u_a &= (a_1 + a_2)/\sqrt{2} \end{aligned} \tag{2}$$

are symmetry-adapted MOs for the symmetry A, with similar definitions of g_b and u_b as functions of b_1 and b_2 for the symmetry B. The phase combinations depend on the nature of the atomic orbitals. Since the numerical example will concern 2p type atom-centred magnetic orbitals, the gerade MO is the out of phase combination of the atomic orbitals.

Let us introduce a simple Hamiltonian which models the essential physics of the so-defined minimal valence space. It would be valid for an arbitrary number of electrons. This Hamiltonian is a generalized Hubbard Hamiltonian. It involves monoelectronic and bielectronic operators:

$$\hat{H} = \hat{H}_1 + \hat{H}_2 \tag{3}$$

The monoelectronic energies of the atom-centred orbitals are ε_a and ε_b for the orbitals of symmetry A and B, respectively. The monoelectronic operator $\hat{H}_1$ also involves intersite hopping integrals t_a and t_b between the orbitals of the same symmetry:

$$\hat{H}_1 = \sum_i \varepsilon_i (a_i^+ a_i) + \sum_{i \neq j} t_{ij} (a_i^+ a_j) \tag{4}$$

In the typical double-exchange systems, one of the hopping integrals is significantly larger than the other(s), reflecting the difference of overlap between the underlying purely atomic orbitals. This is the case, for instance if the orbitals a are p_z orbitals interacting through a σ overlap, which leads to a positive sign of t_a. The orbitals b interact through a π or δ overlap resulting in a negative sign of t_b. In the following we shall consider $|t_a| \gg |t_b|$.

The bielectronic operator $\hat{H}_2$accounts for the electron–electron repulsion and the spin-exchange on each centre. Let us first consider a centre bearing two electrons. The bielectronic energy of its triplet ground state (the three Ms = 1, Ms = −1 and Ms = 0 components of which are, respectively a_1a_2, $\bar{a}_1\bar{a}_2$ and $\left(a_1\bar{b}_1 - b_1\bar{a}_1\right)/\sqrt{2}\right)$, is taken as the zero of the one-centre bielectronic energies. The open-shell excited singlet state is

$$S = (a_1\bar{b}_1 + b_1\bar{a}_1)/\sqrt{2} \tag{5}$$

Its bielectronic energy is positive, and equal to 2K, where K is the exchange integral between the a_1 and b_1 orbitals, $K = K_{a1b1} = K_{a2b2}$. If the two electrons occupy the same orbital, as in $a_1\bar{a}_1$ or $b_1\bar{b}_1$, the bielectronic energy will be assumed to be equal to 3K. This equality is grounded on the asymptotic degeneracy between the two lowest singlet states of the atom $\left|a_1\bar{b}_1\right| + |b_1\bar{a}_1|/\sqrt{2}$ and $|a_1\bar{a}_1| - \left|b_1\bar{b}_1\right|/\sqrt{2}$, which occurs when the magnetic orbitals, a and b, are of the same nature (for instance 2p orbitals).

Let us now consider determinants in which the number of electrons on the centre is different from two. The one-centre bielectronic energy is equal to U when the centre bears three electrons.

In the double-exchange mechanism, the bi-metallic complex is a mixed valence system. Let us establish the matrix elements for the single determinants of the three-electron problem in four atomic orbitals. The Ms = 3/2 determinants in which the hole is located in the a-type orbitals, as indicated in upper-index, are

$$^{(3/2)}\phi_2^a = |a_1 b_1 b_2| \tag{6}$$

$$^{(3/2)}\phi_1^a = |a_2 b_1 b_2| \tag{7}$$

where the indexes 1 and 2 refer to the centre in which the hole is located. Their monoelectronic energy is $\varepsilon_a + 2\varepsilon_b$. The determinants in which the hole is located in the b-type orbitals

$$^{(3/2)}\phi_2^b = |a_1 b_1 a_2| \tag{8}$$

$$^{(3/2)}\phi_1^b = |a_2 a_1 b_2| \tag{9}$$

have the monoelectronic energy $\varepsilon_b + 2\varepsilon_a$. In the Ms = 1/2 subspace, the energies of the three-open-shell determinants in which the hole is located in the a-type orbitals are

$$E\left(\left|a_1 b_1 \bar{b}_2\right|\right) = E\left(\left|a_2 \bar{b}_1 b_2\right|\right) = \varepsilon_a + 2\varepsilon_b \tag{10}$$

$$\begin{aligned} E\left(\left|a_1 \bar{b}_1 b_2\right|\right) &= E(|\bar{a}_1 b_1 b_2|) = E\left(\left|a_2 b_1 \bar{b}_2\right|\right) = E(|\bar{a}_2 b_1 b_2|) \\ &= \varepsilon_a + 2\varepsilon_b + K \end{aligned} \tag{11}$$

while the energies of the one-open-shell determinants are

$$E\left(\left|a_1 b_2 \bar{b}_2\right|\right) = E\left(\left|a_2 b_1 \bar{b}_1\right|\right) = \varepsilon_a + 2\varepsilon_b + 3K \tag{12}$$

Similar expressions are obtained for the determinants having the hole located in the b-type orbitals. Their monoelectronic energy is $\varepsilon_b + 2\varepsilon_a$. For the sake of simplicity, we shall no longer distinguish the orbital energies in the two symmetries and consider that the monoelectronic energy is 3ε, with $\varepsilon = \varepsilon_a = \varepsilon_b$, and is incorporated in the reference zero-energy. For symmetry reasons, there is no interaction between the states where the number of electrons in a-type orbitals is odd (family of states A), and those where it is even, which belong to family B.

2.2 Approximate solutions of the Hubbard Hamiltonian for the three-electron problem

The eigenstates in the $Ms = 3/2$ subspace are easily obtained. For the A symmetry there are only two determinants, $|a_1b_1b_2|$ and $|a_2b_1b_2|$, interacting through the integral t_a, so that the eigenstates and eigenenergies are

$$\begin{aligned} {}^{(3/2)}\Psi_{ag} &= |u_a g_b u_b| = \frac{1}{\sqrt{2}}(|a_1b_1b_2| + |a_2b_1b_2|), \\ E_{ag}^{3/2} &= \varepsilon_a + 2\varepsilon_b + t_a \end{aligned} \tag{13}$$

$$\begin{aligned} {}^{(3/2)}\Psi_{au} &= |g_a g_b u_b| = \frac{1}{\sqrt{2}}(|a_1b_1b_2| - |a_2b_1b_2|), \\ E_{au}^{3/2} &= \varepsilon_a + 2\varepsilon_b - t_a \end{aligned} \tag{14}$$

It is important to notice that these wave functions may be written as single determinants, the $|b_1b_2|$ antisymmetrized product being identical to the $|g_b u_b|$ one.

The $Ms = 1/2$ components of the quartet states have of course the same energies. Then the energies of the quartet states are

$$\begin{aligned} E_{au}^{3/2} &= -t_a \\ E_{ag}^{3/2} &= t_a. \end{aligned} \tag{15}$$

The situation is more complex for the doublet states developed on the previously expressed determinants which interact either through the on-site exchange integral or through the hopping integrals t_a or t_b, when they differ by one orbital only. Considering symmetry combinations of these determinants, the size of the Hamiltonian matrix is 4 and no straightforward analytical solution is accessible.

Relevant approximations have been proposed in the past. They all assume that the hopping integral t_b is weak, smaller than t_a, and much smaller than the on-site exchange integral K and the on-site repulsion integral U. This means that the two electrons in the b orbitals are strongly correlated and their distribution is dominated by the neutral forms $|b_1\bar{b}_2|$ and $|b_2\bar{b}_1|$, the ionic distributions $|b_1\bar{b}_1|$ and $|b_2\bar{b}_2|$ acting only as perturbers. The most rigorous derivation [19, 20] obtained at the second order of perturbations leads to the following expression of the eigenenergies:

$$E_{au}^{1/2} = K - \sqrt{(K^2 + t_a(t_a - K))} - \frac{3}{4}t_b^2\left(\frac{1}{2K} + \frac{1}{U}\right) \tag{16}$$

$$E_{ag}^{1/2} = K - \sqrt{(K^2 + t_a(t_a + K))} - \frac{3}{4}t_b^2\left(\frac{1}{2K} + \frac{1}{U}\right) \tag{17}$$

This derivation has been generalized [19–23] to the situations where the centres bear more than two magnetic orbitals. The above expressions treat both the effect of the hole delocalization, including through the local excited non-Hund states (here the singlet), and the effect of the weak delocalization in the b-type orbitals. They lead to a better description of the spectrum than the one obtained either from Zener [30], Anderson and Hazegawa [31] (which accounts for the effect of the non-Hund states) or from the model Hamiltonian proposed by Girerd et al. [32–35] in which the energies of the doublet are given by

$$E_g^{1/2} = -t_a/2 - 3J_b/2 \tag{18}$$

$$E_u^{1/2} = +t_a/2 - 3J_b/2, \tag{19}$$

where the exchange integral J_b describes the energetic effect of the delocalization between the two electrons in the b orbitals:

$$J_b = \frac{1}{2}t_b^2\left(\frac{1}{2K} + \frac{1}{U}\right). \tag{20}$$

If t_a is much smaller than K, a power development in terms of t_a/K of Eqs. 16 and 17 leads to Girerd's expression.

The special feature of double exchange systems is their energy ordering. In most cases, both the ground state and the upper state have the highest spin multiplicity, while the intermediate spin multiplicity states lie in this interval. In the specific case studied here, as soon as $|t_a| > 3J_b$, the energy ordering is expected to be

$$E_{au}^{3/2} < E_{ag}^{1/2} < E_{au}^{1/2} < E_{ag}^{3/2}. \tag{21}$$

This energy ordering contrasts with the expected energy ordering in which the lowest orbitals are filled with electron pairs, automatically leading to a doublet ground state.

Of course there exist similar solutions for the family of states in which the hole is located in the b-type orbitals. But if $|t_a| \gg |t_b|$, then $|t_b|$ will become smaller than J_a, and the doublet states may be at lower energies than the quartet states:

$$E_{bg}^{1/2} < E_{bu}^{1/2} < E_{bu}^{3/2} < E_{bg}^{3/2}. \tag{22}$$

As shown in a stretched N_2^+ molecular ion model study [36], intermediate energy orderings may occur.

2.3 Comparison with the space symmetry-adapted single determinant energies

While the extraction of the interactions of the model is straightforward from the multireference state energies obtained from a correlated ab initio calculation, it happens to be more complicated for the energies of simple single determinants. A representation of the determinants and their energy are given in Fig. 1. The energies of the Au space symmetry-adapted single determinants having $Ms = 1/2$ are the following:

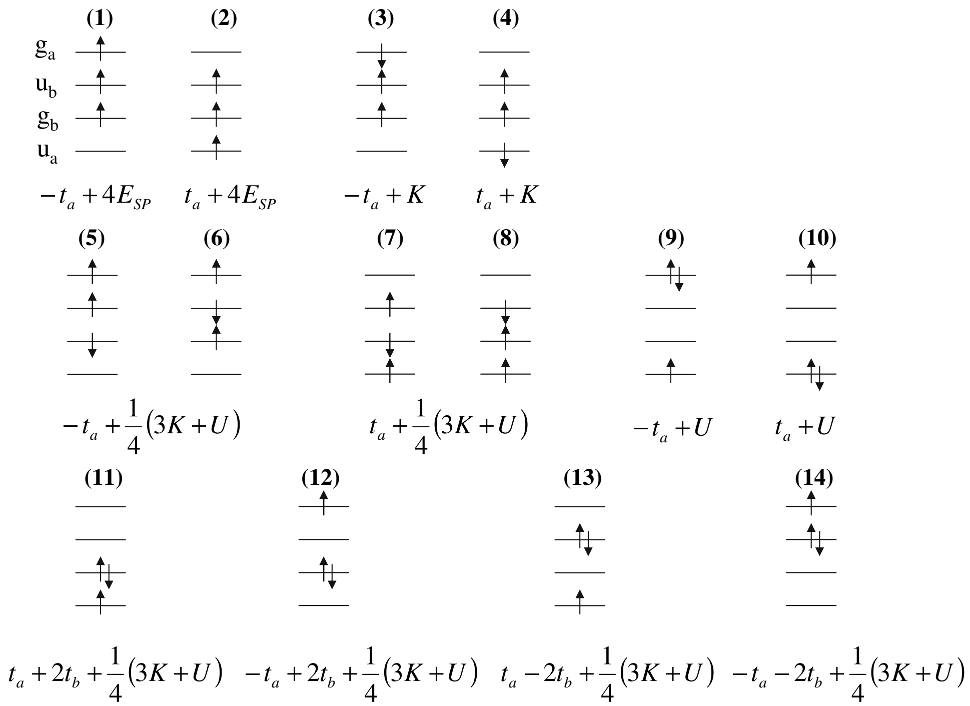

Fig. 1 Schematic representation of the determinants and their analytical unrestricted energy

$$^{(1/2)}\Phi^3_{\mathrm{au}} = |\bar{\mathrm{g}}_\mathrm{a}\mathrm{g}_\mathrm{b}\mathrm{u}_\mathrm{b}|, \quad \mathrm{E}^3_{\mathrm{au}} = -t_\mathrm{a} + \mathrm{K} \tag{23}$$

$$^{(1/2)}\Phi^5_{\mathrm{au}} = |\mathrm{g}_\mathrm{a}\bar{\mathrm{g}}_\mathrm{b}\mathrm{u}_\mathrm{b}| \text{ and } {}^{(1/2)}\Phi^6_{\mathrm{au}} = |\mathrm{g}_\mathrm{a}\bar{\mathrm{u}}_\mathrm{b}\mathrm{g}_\mathrm{b}|, \quad \mathrm{E}^5_{\mathrm{au}} = \mathrm{E}^6_{\mathrm{au}} = -t_\mathrm{a} + \frac{1}{4}(3\mathrm{K} + \mathrm{U}) \tag{24}$$

$$^{(1/2)}\Phi^{11}_{\mathrm{au}} = |\mathrm{u}_\mathrm{a}\bar{\mathrm{g}}_\mathrm{b}\mathrm{g}_\mathrm{b}|, \quad \mathrm{E}^{11}_{\mathrm{au}} = t_\mathrm{a} + 2t_\mathrm{b} + \frac{1}{4}(3\mathrm{K} + \mathrm{U}) \tag{25}$$

$$^{(1/2)}\Phi^{13}_{\mathrm{au}} = |\mathrm{u}_\mathrm{a}\bar{\mathrm{u}}_\mathrm{b}\mathrm{u}_\mathrm{b}|, \quad \mathrm{E}^{13}_{\mathrm{au}} = t_\mathrm{a} - 2t_\mathrm{b} + \frac{1}{4}(3\mathrm{K} + \mathrm{U}) \tag{26}$$

$$^{(1/2)}\Phi^9_{\mathrm{au}} = |\mathrm{u}_\mathrm{a}\bar{\mathrm{g}}_\mathrm{a}\mathrm{g}_\mathrm{a}|, \quad \mathrm{E}^9_{\mathrm{au}} = -t_\mathrm{a} + \mathrm{U}. \tag{27}$$

where the upper index refers to the label number of the determinants represented in Fig. 1 and where the zero of energy is taken as the mean energy of the two quartet states of the A symmetry. Similar expressions may be obtained for the determinants of Ag symmetry. The first of the above solutions, which is not an eigenfunction of S^2, has a much higher energy than the doublet eigenstate (see Eq. 16) since K is a large positive integral. The determinants in which two electrons occupy the same b orbital are eigenfunction of S^2, but their energy is also very high since they involve ionic components of energy U. None of these solutions can be assimilated to the desired doublet state. Similar conclusions would be reached concerning the Ag symmetry solutions, i.e. there is no possibility to identify the energy of a symmetry-adapted Ms = 1/2 single determinant to the energy of the low-lying doublet states, due to the intrinsic multireference character of these eigenstates.

2.4 Broken-space-symmetry single determinantal solutions

Let us first consider the following determinant:

$$^{(1/2)}\Phi_{\mathrm{a}1} = \left|\mathrm{a}_1\mathrm{b}_1\bar{\mathrm{b}}_2\right| \tag{28}$$

It is a product of the local ground state triplet on site 1 and the local ground state doublet on site 2 and its orbitals are strongly localized as they were optimized for the highest spin state. Its energy, which is zero according to our zero energy definition, is lower than those (Eqs. 23–27) of the symmetry-adapted determinants as soon as $\mathrm{K} > |t_\mathrm{a}|$, since it satisfies the Hund's rule on site 1. Lower energy Ms = 1/2 single determinants having a broken-space-symmetry may therefore be obtained in such correlated systems by an orbital optimization. Since the resulting optimized spatial and spin electronic structures have no left–right symmetry, the gerade and ungerade labels referring to the symmetry centre are no longer relevant. The optimization of the orbitals introduces the intersite delocalization in the MOs of A and B symmetries.

In full generality a symmetry-broken single determinantal solution may be expressed as

$$^{(1/2)}\Phi'_{\mathrm{a}1} = \left|\mathrm{a}'_1\mathrm{b}'_1\bar{\mathrm{b}}'_2\right| \tag{29}$$

where the MOs have a large coefficient on one site and optimized delocalization tails on the other:

$$\mathrm{a}'_1 = \mathrm{a}_1\cos\varphi + \mathrm{a}_2\sin\varphi \tag{30}$$

$$b_1' = b_1 \cos\theta + a_2 \sin\theta \quad (31)$$

$$b_2' = b_2 \cos\chi + b_1 \sin\chi \quad (32)$$

The three angles of mixing are small and different. Actually the delocalization between the orbitals of symmetry B has no reason to be the same for up and down spins. It is possible to express the energy of ${}^{(1/2)}\Phi'_{a1}$ as a function of these angles and to minimize this energy with respect to the three angles. A set of three coupled equations is obtained:

$$\tan 2\varphi = \frac{2t_a}{K(\sin^2\theta - \sin^2\chi) + (U - 2K)(\cos^2\chi - \sin^2\theta)} \quad (33)$$

$$\tan 2\theta = \frac{2t_b}{2K(\sin^2\varphi - \sin^2\chi) + (U - K)(\cos^2\chi - \sin^2\varphi)} \quad (34)$$

$$\tan 2\chi = \frac{2t_b}{2K(\sin^2\theta - \sin^2\varphi) + U(\cos^2\varphi - \sin^2\theta)}. \quad (35)$$

In the double exchange regime, the ratios K/|*t*| and U/|*t*| are significantly larger than one. It is therefore possible to analytically determine the energy of the broken symmetry solution ${}^{(1/2)}\Phi'_{a1}$ at the second order of perturbation. Starting from ${}^{(1/2)}\Phi_{a1}$, the delocalization of the up spin in the A symmetry gives a second-order correction to the energy equal to $-t_a^2/K$, the delocalization of the up spin electron in the B symmetry stabilizes by the quantity $-t_b^2/3K$, and that of the down spin by $-t_b^2/U$. The so-obtained energy of the broken-symmetry solution is

$$E_a' = -t_a^2/K - t_b^2/3K - t_b^2/U\,. \quad (36)$$

The symmetry breaking is expected to occur when the parameters are such that

$$K - t_a > -t_a^2/K - t_b^2/3K - t_b^2/U \quad (37)$$

which is always the case when K > |t_a|. The other broken-symmetry solution, having the hole in the B symmetry has the energy

$$E_b' = -t_b^2/K - t_a^2/3K - t_a^2/U \quad (38)$$

The intrinsic instability of the symmetry-adapted solutions has important consequences:

- It is not possible to have a direct access to the exact energy of the doublet states from broken-symmetry solutions.
- In cases of non-symmetric compounds, the only solutions that can be calculated from mean-field approaches are always the broken-symmetry ones. The study of geometrical deformations would always present a discontinuity of the potential energy curves at the symmetric point.

3 Indirect extraction of the double-exchange interactions from single-determinantal energies

3.1 The three-electron problem model case

Let us first remain in the simple model which only considers three electrons in four orbitals. The basic integrals of the Hubbard Hamiltonian can be extracted from the symmetry-adapted single determinant energies. The energies of the two solutions ${}^{(3/2)}\Phi_{au}$ and ${}^{(3/2)}\Phi_{ag}$ give an evaluation of t_a:

$$-t_a = (E_{au}^{3/2} - E_{ag}^{3/2})/2. \quad (39)$$

The hopping integral t_b would be obtained similarly from the energies of the quartet states of symmetry B. Taking the reference energy as

$$E_0 = (E_{au}^{3/2} + E_{ag}^{3/2})/2 \quad (40)$$

the on-site exchange integral K is extracted from the energy of the lowest in energy Ms = 1/2 determinant (Eq. 23), which has three singly occupied MOs:

$$K = E_{au}^{3} + t_a. \quad (41)$$

From the energy of the Ms = 1/2 single determinant (Eq. 25) having a double occupancy in the g_b MO, one may extract the on-site repulsion integral U:

$$U = 4(E_{au}^{11} - E_0) - 4t_a - 8t_b - 3K. \quad (42)$$

Finally, the spectrum can be modelled from these four quantities, using Eqs. 16 and 17. Notice that the amplitudes of these interactions could have been obtained from the energy of other solutions. One may for instance extract t_b from the energy difference between E_{4au} and E_{5au}, or use these energies to evaluate U. Nevertheless, the energy E_{1au} is compulsory to fix K. The consistency of the extraction can be checked by comparing the magnitude of the interactions obtained from various solutions.

3.2 Spin and charge polarization

The real systems are not reducible to their active magnetic electrons; they have a core, made of doubly occupied MOs in restricted open-shell pictures. If the symmetry adapted solutions can be obtained in an unrestricted formalism, then the magnetic electrons spin-polarize the core electrons and different MOs are obtained for the up and down spins. This phenomenon is called the spin polarization effect. However, many codes do not allow imposing freely the orbital occupancies per symmetry and the obtained solutions are not symmetry adapted, i.e. the hole is localized on one of the two centres. In such cases, both the spin and the charge polarizations are present.

3.2.1 *Spin polarization effects*

Since the numbers of α and β magnetic electrons are not equal, these electrons will induce an exchange field on the core electrons and polarize differently the α and β core MOs. The spin polarization is larger in the Ms = 3/2 solutions than in the Ms = 1/2 ones, since the exchange field is larger in the former ones. This subsection evaluates the difference of spin polarization in the two spin determinants.

Since the spin polarization is essentially local, let us first evaluate the spin polarization of a single magnetic centre bearing one unpaired electron. Starting from a determinant expressed in the strongly localized orbitals (a_1, a_2, b_1 and b_2) and having one unpaired electron in the b_1 orbital, the polarization of its core orbitals σ due to the single excitation σ to σ^* stabilizes its energy by

$$E_{sp} = \frac{\Sigma_{\sigma,\sigma^*}\langle\sigma|K_{b_1}|\sigma^*\rangle\langle\sigma^*|K_{b_1}|\sigma\rangle}{\varepsilon_\sigma - \varepsilon_{\sigma^*}} \qquad (43)$$

where K_{b1} is the exchange operator relative to the b_1 orbital. For the determinants having two unpaired up electrons in the a_1 and b_1 orbitals, the contribution to the spin polarization energy is four times the previous quantity while it is zero if the two spins are antiparallel.

Starting from the Ms = 3/2 determinant of Eq. 29 the optimization of its orbital in symmetry adapted way leads to the solution

$$^{(3/2)}\psi'_{ag} = \left|u'_a g'_b u_{b'}\right| \qquad (44)$$

Since one may write

$$K_{u'_a} = (K_{a_1} + K_{a_2})/2 \qquad (45)$$

$$K_{g'_b} + K_{u'_b} = K_{b_1} + K_{b_2} \qquad (46)$$

the spin-polarization energy, calculated at the second-order perturbation, involves two on-site exchange operators 3K/2, one around each site, polarizing the MOs of its own environment. It is therefore equal to

$$E_{sp}\left(M_S = \frac{3}{2}\right) = \frac{\Sigma_{\sigma_1,\sigma_1*}\langle\sigma_1|3K_1/2|\sigma_1^*\rangle\,\langle\sigma_1^*|3K_1/2|\sigma_1\rangle}{\varepsilon_{\sigma_1} - \varepsilon_{\sigma_1*}} + \frac{\Sigma_{\sigma_2,\sigma_2*}\langle\sigma_2|3K_2/2|\sigma_2^*\rangle\,\langle\sigma_2^*|3K_2/2|\sigma_2\rangle}{\varepsilon_{\sigma_2} - \varepsilon_{\sigma_2*}}$$

$$E_{sp}\left(M_S = \frac{3}{2}\right) = \frac{9}{2}E_{sp} \qquad (47)$$

On all the Ms = 1/2 solutions, since the on-site exchange operator is K/2, the same equations lead to a spin polarization equal to

$$E_{sp}\left(M_S = \frac{1}{2}\right) = \frac{1}{2}E_{sp} \qquad (48)$$

One should notice here the difference between double-exchange compounds and purely magnetic compounds. In the latter, the UDFT solutions which are commonly used in the extraction of the magnetic exchange integral have the same spin polarization since they are always product of the local high-spin states which have the same number of electrons on each site. In contrast, in double exchange compounds, the spin polarization is different in the several calculated solutions and a proper evaluation of this quantity is required for a rigorous extraction of the interaction of the model from unrestricted solutions as illustrated in the following section.

3.2.2 *Charge polarization effects*

An additional physical effect must be considered, even for left–right symmetric complexes, namely the charge localization of the self-consistent solution due to the charge polarization of the inactive orbitals. This problem is rather well documented in the simplest (non-magnetic) mixed-valence problem. The localization of the charge on one site induces a static charge polarization of the core electrons. In a symmetry-adapted $M^{+1/2}$ … $M^{+1/2}$ charge distribution the inactive MOs are optimized in the field of an average charge distribution and are therefore not optimal neither for the M^+ …M distribution nor for the M…M^+ one. If the hole is localized on one site, leading to a M^+…M distribution, the energetic benefit of its delocalization to the other site is lost, but the self-consistent calculation which relaxes the inactive MOs under this electrostatic field lowers its energy. The inactive MOs tend to go closer to the positively charged centre and further from the neutral one. A variational mean-field UHF calculation which does not keep the left–right symmetry of the MOs leads to a charge-localized spatially broken-symmetry solution. This occurs as soon as the hopping integral between the two magnetic atom-centred orbitals becomes sufficiently small with respect to the energy stabilization brought by the charge polarization of the core electrons. The single determinantal treatments of double exchange systems will necessarily face the same phenomenon of charge–symmetry breaking as soon as the hopping integral t_a will become sufficiently small. Since it is also true for the state of highest spin multiplicity, the charge polarization prevents us from identifying this single determinant to an eigenstate.

Hence a possible spatial localization of the charge and of the spins in the mean-field single determinantal calculations may be induced by both the spin polarization and the charge polarization of the inactive electrons, the extraction of the spectrum of the system becomes difficult. One should, however, notice, that while these charge and spin-polarized UHF solutions can easily been computed, the UDFT ones remain delocalized in many systems due to the self-interaction error [37]. This defect, manifested by the artificial stabilization of delocalized states in mixed-valence systems at large interatomic distances, of course affects the double exchange systems [38]. Since this error essentially concerns the open-shell MOs, it may act differently on the determinants which involve three-open shells (Ms = 3/2) and those which only involve one (Ms = 1/2), biasing therefore their energy difference. This is a supplementary problem faced by DFT calculations on double-exchange systems.

3.3 Methodological conclusions

Let us formulate here the main conclusions reached by the preceding discussion:

- An estimate of energy spacings in double exchange systems from single-determinant variational calculations is only possible when the geometry of the system exhibits a left–right symmetry and if the MOs are compelled to keep this symmetry.
- Only the symmetry-adapted determinant of highest spin-multiplicity can be assimilated to an eigenstate. From their energy difference the amplitude of the hopping integral in the most delocalized subsystem, t_a, sometimes labelled B in the literature, can be determined. Contrary to the simplest purely magnetic cases, solutions “à la Noodleman” cannot be defined. This is certainly a major drawback of a few previous attempts [39–41] to use UDFT calculations to determine the parameters of the Girerd model Hamiltonian. The choice of the doublet state determinant is not clear, and the estimates of the parameters J and t_a may be rather inconsistent (for instance, they have the same order of magnitude in Ref. 40, while J, reflecting the delocalization effect between highly correlated electrons, should be much smaller).
- In order to calculate the energy of the lower spin-multiplicity states, it seems compulsory to calculate the double-exchange interactions, and an estimate of the low-energy spectrum, from a preliminary determination of the interactions of a Hubbard model. This extraction, although indirect, is possible from single determinant energies, but faces some difficulties concerning differences in spin-polarization and self-interaction errors,
- even in symmetric cases the spin-polarization of unrestricted HF or DFT solutions raises methodological difficulties. Restricted open-shell solutions should be preferred. Unfortunately, the calculation of several open-shells solutions of low Ms values is not always available in the standard codes.

4 A numerical test study

The low-energy spectrum of a model double exchange system, namely the cation of a dimer of NH molecules, i.e. the $(NH)_2^+$ molecular ion, has been studied as a numerical illustration. The NH molecule has a triplet ground state, with two magnetic electrons in two magnetic 2p orbitals which are orthogonal to the NH axis. A planar trans-geometry was considered, the two NH bonds being orthogonal to the N…N axis. In this geometry the in-plane magnetic 2p orbitals have a larger overlap than those which are perpendicular to the plane. The interaction between the former ones (labelled a_1 and a_2 in the previous section) leads to two σ-type MOs, here, respectively, labelled g_a and u_a according to their the gerade and ungerade symmetry with respect to the symmetry centre, while the weak interactions between the latter ones (labelled b_1 and b_2) give two π-type MOs, here labelled g_b and u_b. Two families of states, referred to as family A or B, which differ by the position of the hole, either in the σ or in the π orbitals, respectively, are computed.

Symmetry-adapted unrestricted UDFT calculations have been performed using the MOLCAS [42], MOLPRO [43] and GAUSSIAN [44] codes while restricted RDFT calculations were obtained using the MOLPRO code. All computations were done using a B3LYP functional which happens to be different in the three codes. Double Zeta plus Polarization (DZP) basis sets were used in these DFT calculations. Some of the calculations were performed using a different percentage of exact Fock exchange with the GAUSSIAN code.

At large enough distances, the system should exhibit the double-exchange features, and we decided to concentrate on the 5 Å distance for a study of the ability of spatially symmetric UDFT and RDFT calculations to provide, at least indirectly, reasonable estimates of the spectrum of the system.

Before extracting values of the various Hubbard Hamiltonian interactions from UDFT calculations, the amplitude of the spin polarization should be evaluated. From unrestricted and restricted open-shell DFT calculations, performed with the MOLPRO package on both Ms = 3/2 determinants ((**1**) and (**2**) in Fig. 1), the same value of the quantity $E_{sp} = -11.4$ meV is obtained.

From the energy difference between determinants (**1**) and (**3**) which is equal to $K - 4\,E_{sp}$, it is possible to extract a value of the on-site exchange integral, $K = 604$ meV, which is a reasonable value.

The amplitude of the hopping integrals t_a and t_b may be extracted from several equations, depending on the Ms value of the obtained UDFT solutions. Table 1 reports the values calculated from the energy differences between several solutions.

Finally, the on-site repulsion U can be calculated from the energies of Ms = 1/2 determinants having one single open-shell. Depending on the solutions which are used for the extraction, the values varies slightly around 11 eV which is also a reasonable value.

Table 1 Values (in meV) of the hopping integrals extracted from energy differences between different UDFT determinants

t_a from (1) and (2)	13.9
t_a from (13) and (14)	14.1
t_a from (3) and (4)	15.8
t_b from (12) and (14)	−1.6
t_b from (11) and (13)	−1.4

The labels of the determinants are indicated in parenthesis

The exact spectrum of the two families of states may be calculated from the so-obtained values of the matrix elements of the Hubbard Hamiltonian, and they are reported in Table 2. The $t_a = 13.9$ meV value extracted from the Ms = 3/2 solutions and the mean value $t_b = -1.5$ meV between the two extracted ones were used for the determination of the spectrum.

The relative position of the two families of states, i.e. the energy difference (ΔE_{A-B}) between the two mean values of the quartet states of each family, can be calculated from the energy differences between the Ms = 3/2 determinants differing by the position of the hole, either in the σ or π MOs. In a simple single-electronic picture, this energy difference, which is found to be 0.03 meV, can be related to the MOs energy such as

$$\Delta E_{A-B} = \frac{1}{2}\left(\varepsilon_{g_b} + \varepsilon_{u_b} - \varepsilon_{u_a} - \varepsilon_{g_a}\right)$$

The two interactions of the double-exchange model, namely the hopping integrals and the magnetic couplings, have been calculated for the two families of states, from the interactions of the Hubbard Hamiltonian. They are reported in Table 3.

The relative magnitude of the magnetic couplings fulfils our expectation, since J_b is governed by the weak delocalization in the π MOs while J_a is governed by the larger delocalization in the σ MOs. One may notice that since the interactions have been extracted from a general Hubbard model, no assumption was done in the determination of the double exchange interaction. Contrarily to what has been observed in several previous studies of double exchange compounds, the obtained spectrum verifies the expected energy spacings of the Girerd Papaefthymiou model and negligible deviations from this model is obtained. The family A almost presents a purely Zener double-exchange spectrum due to the very small value of the magnetic coupling J_b.

Table 2 Energies (in meV) of the states of the two double-exchange families of states calculated from the extracted interactions (see text) of the Hubbard Hamiltonian

$E^{3/2}_{au}$	$E^{1/2}_{ag}$	$E^{1/2}_{au}$	$E^{3/2}_{ag}$	$E^{1/2}_{bg}$	$E^{1/2}_{bu}$	$E^{3/2}_{bu}$	$E^{3/2}_{bg}$
+13.9	−7.1	+6.8	13.9	−0.9	0.6	−1.5	1.5

The mean value of the energies of the quartet states is taken as the zero of energy for both families

Table 3 Amplitudes of the interactions of the double-exchange model calculated from the interactions of the Hubbard Hamiltonian (see text) for the two families of states

t_a	J_b	t_b	J_a
+13.90	0.0016	−1.50	0.1331

The amplitudes of these interactions are different according to the percentage of exact Fock exchange used in the DFT calculations. In order to estimate the effect of this degree of freedom, several calculations using three different percentages were performed using the GAUSSIAN code. The amplitudes of the Hubbard Hamiltonian interactions are reported in Table 4.

The *t* values are decreased while K and U are increased by a quite large amount. This trend is perfectly consistent with what is known for the calculation of the magnetic constant in magnetic dimers, namely a reduction of its amplitude when increasing the Fock exchange percentage, correlated to a decrease of the inter-site hopping integral [11–14]. The increase of the Fock exchange percentage would induce smaller values of the magnetic couplings of the double-exchange model for both families. Since both the hopping integrals and the magnetic couplings are decreasing, the resulting double-exchange spectrum width would be reduced. It is important to note the high sensitivity of the parameters and therefore the spectrum to this quantity. Actually one should notice that the above-reported values of the hopping integrals obtained from the Gaussian code are about one half of those obtained from the MOLCAS code, due to a small difference in the exchange correlation parameters. We must add that high-accuracy ab initio MR SDCI calculations give a value of t_a equal to 23 meV at this distance, i.e. a doubled width of the spectrum with respect to the DFT one obtained from the MOLCAS code. The corresponding value for t_b is −2.2 meV. A lot of test calculations have to be performed to establish the reliability of density functional for such problems.

Table 4 Values of the Hubbard Hamiltonian parameters as functions of the percentage of exact Fock exchange considered in the UDFT calculations

Percentage of Fock exchange	t_a	t_b	K	U
0.2	6.79	−0.5	653	10.7
0.25	5.20	−0.45	913	14.7
0.3	5.05	−0.45	974	16.6

5 Conclusion

The calculation of the properties of magnetic materials, especially in coordination chemistry, is a real challenge for theoreticians. The near-degeneracy of the low-lying states and the intrinsic multireference or multi-open shell character of these systems generate specific methodological difficulties. In principle, strict ab initio correlated methods are required for their correct description. They furnish accurate results when applicable [9, 11–23], but they are computationally expansive and limited, especially when variational methods are used. Even second-order perturbative evaluations may become prohibitive when the number of unpaired electrons increases and when the ligands are large (for such a study of a double-exchange system [42]). In this context the use of the much less expansive DFT tools is tempting. The present work discusses the possible use of single determinant energies, namely Kohn–Sham DFT energies, to calculate the low-energy spectrum of double-exchange compounds. These systems are mixed-valence magnetic complexes, and one might hope that the Unrestricted DFT calculations could be as useful and successful as they are for the evaluation of magnetic coupling constants between homo-valence magnetic ions. For the latest magnetic materials, the energies calculated for determinants of different M_s values may be exploited easily. Provided that one takes into account the fact that the solutions for which $|M_s| < |M_s|_{max}$ are not eigenfunctions of the $\mathbf{S}^2$ operator, and correcting the energies of spin-contaminated solutions, physically grounded estimates of spin couplings are easily obtained. The quantitative agreement with experiment depends dramatically on the density functional, and especially on the percentage of Fock exchange introduced in the exchange–correlation operator [28], but empirical values of this ratio have been proposed. The method has been used to obtain not only magnetic coupling between adjacent sites, but also couplings between next nearest neighbour sites, as well as four-body operator interactions between $M_s = 1/2$ magnetic sites [28]. It has been shown recently that they may be used as well to evaluate biquadratic exchanges and three-body operator interactions in systems of spin $S = 1$ [29].

A few previous works [39–41] have assumed that double-exchange systems might be treated in a similar manner, i.e. assimilating the energies of single determinants to the diagonal energies of some functions on which the model Hamiltonian is assumed to be defined. The main conclusion of the present analysis is that such an assumption is not physically grounded in double exchange systems. Single determinant solutions having the highest $|M_s|$ value provide a value of the hopping integrals of the model. But the energies of the lower spin-multiplicities states are not directly accessible. To get reliable double exchange interactions, several calculations of independent solutions are required to determine the amplitudes of the interactions of a generalized Hubbard Hamiltonian, namely, hopping integrals, on-site exchange integrals and effective electron–electron repulsions. The analytical relations between these interactions and those of the double-exchange model enable one to finally calculate the double-exchange interactions and the spectrum. Owing to the generality of the Hubbard model, the so-calculated spectrum does not suffer from any assumptions regarding either the effect of the non-Hund states or those of the ionic forms responsible for the magnetic couplings. As a consequence, deviations to the Zener [30], Anderson–Hazegawa [31] and Girerd–Papaefthymiou [32–35] models can be appreciated. One should, however, note that, due to the sensibility of the parameters to the percentage of Fock exchange operator in the exchange–correlation operator, a preliminary determination of the adequate percentage from wave-function based calculations is recommended to get reliable values of the interactions. But there is no guarantee that the functionals which are efficient in magnetic systems are equally reliable in double-exchange ones.

The present work, which is essentially methodological, has stressed on the importance of dealing with symmetry-adapted MOs, while both spin and charge-polarization may make these symmetry-adapted solutions unstable with respect to partial localization of the magnetic MOs. The fact that symmetry-adapted single determinant solutions remain more stable than localized ones in many DFT calculations minimizes this risk, but this feature is known to be an artefact, due to the self-repulsion error. This defect may also result in a severe numerical problem in the study of double-exchange systems, when one wants to use the energy differences between determinants with different numbers of singly occupied MOs for the highest and lower values of Ms, since the error essentially concerns the singly occupied MOs. This problem adds a supplementary difficulty for the use of DFT calculations for these kinds of systems.

The analysis has only been performed for a mixed-valent dimer of $S = 1$ spins. It should be extended to trimers (to establish the possible occurence of three-body operators, analogous to those which appear in homo-valent systems of $S + 1/2$ spins), and to systems of spins larger than 1. Finally the sensibility of the results to the choice of the exchange potential, self-repulsion treatment, and other approximations, should require further numerical studies.

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