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Invited Review

Magnetic Orbitals and Mechanisms of Exchange II. Superexchange

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Summary. In a first step, we examine the concept of *magnetic orbital* which is very useful to treat the mechanism of *superexchange*. After that, we recall the general broad lines of the first historical model proposed by *Anderson*. In a second step, we develop a new general treatment for superexchange, in the case of the centrosymmetrical model *AXB*, where *A* and *B* are metal cations and *X* a common bridging ligand (with here, for simplification, $A = B$, without transfer between cations). It allows one to retrieve the expression of exchange energy *J vs.* key molecular integrals, as respectively proposed by several authors such as *Anderson* on the one hand, *Hay*, *Thibeault*, and *Hoffmann* on the other one, and, finally, *Kahn* and *Briat*. This model may be easily generalized to the case where a transfer does exist between both cations, with $A = B$ or $A \neq B$.

Keywords. Magnetic orbital; Superexchange; *Anderson* model; *Goodenough-Kanamori* rules; *Hay-Thibeault-Hoffmann* model; *Kahn-Briat* model.

The Concept of Magnetic Orbital [1]

Let us consider the simplest case of an *A*–*B* bimetallic system in which *A* and *B* are metal ions surrounded by their ligands, with a common ligand between *A* and *B*. In addition the ground states of *A* and *B* are both characterized by one unpaired electron. Thus, the interaction between the single-ion doublet states gives rise to molecular singlet and triplet states, respectively, and the singlet-triplet energy gap is *J*. *J* is a physical observable and not a parameter closely linked to the phenomenological model used to interpret experimental data. Under these conditions, we can write the general *phenomenological Hamiltonian* (Eq. (1)).

$$H_{\text{phen}} = -J\boldsymbol{S}_{\text{A}} \cdot \boldsymbol{S}_{\text{B}} + \boldsymbol{S}_{\text{A}}(\Lambda)\boldsymbol{S}_{\text{B}} + \boldsymbol{D} \cdot (\boldsymbol{S}_{\text{A}} \times \boldsymbol{S}_{\text{B}}) + \cdots \qquad (1)$$

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J is a scalar, (Λ) is the anisotropy tensor, and $\boldsymbol{D}$ is the well-known *Dzialoshinski-Moriya* vector. Thus, the first term in Eq. (1) leads to a singlet–triplet splitting, the second term splits the triplet state, and the third one couples the singlet and triplet states. As previously seen, *the phenomenological Hamiltonian* given by Eq. (1) *shows eigenvalues which correspond to the experimental low-lying states but does not provide any information on the microscopic mechanisms really involved so that it has no predictive character.*

As a consequence, it becomes necessary to use a *microscopic Hamiltonian*, *i.e.*, an Hamiltonian taking into account the kinetic energy of the unpaired electrons T_i on A and B, the electron-cores potential energies V_i, and the electrostatic interaction between the electrons of the system (Eq. (2)) where $r_{ij} = |\boldsymbol{r}_i - \boldsymbol{r}_j|$ is an interelectronic distance and h_{so} is the spin-orbit coupling Hamiltonian (*cf.* Eq. (75) in I).

$$H_{\mathrm{micro}} = \sum_{i=1}^{n} (T_i + V_i) + \sum_{i=1}^{n} \sum_{i<j} \frac{e^2}{4\pi\varepsilon_0 r_{ij}} + h_{\mathrm{so}} \tag{2}$$

In this article, we shall consider $h_{\mathrm{so}} = 0$. Of course, this Hamiltonian seems less easy to handle than the phenomenological one given by Eq. (1). However, the idea of comparing the eigenvalues of H_{micro} and H_{phen} may be maintained owing to justified approximations. In other words, each orbital model employed for finding the eigenvalues of H_{micro} must be precisely characterized by the nature of the chosen approximations.

When A and B are without interaction, the wave functions describing A and B are simply given by Eq. (3) where + holds for the singlet and − for the triplet.

$$\Phi_{\pm}(\boldsymbol{r}_1, \boldsymbol{r}_2) = \frac{1}{\sqrt{2}} [\Phi_A(\boldsymbol{r}_1)\Phi_B(\boldsymbol{r}_2) \pm \Phi_A(\boldsymbol{r}_2)\Phi_B(\boldsymbol{r}_1)] \tag{3}$$

When the interaction between A and B is no longer zero but remains weak enough, the *Heitler-London* [2] function $\Phi_{\pm}(\boldsymbol{r}_1, \boldsymbol{r}_2)$ given by Eq. (3) is a good first-order approximation to describe the two low-lying states thermally populated and the overlap $S = \langle \Phi_A(\boldsymbol{r}_1) | \Phi_B(\boldsymbol{r}_1) \rangle$ may appear in the normalization coefficient. Then, the semi-localized orbitals Φ_A and Φ_B, which will describe the magnetic properties of A–B, are called *magnetic orbitals*. They are, in principle, non-orthogonal and the overlap S plays a key role in the description of the interaction between A and B. These non-orthogonal magnetic orbitals (NMO) have been said *natural* by *Girerd et al.* [3]. For most of authors, the magnetic orbitals may be rigorously orthogonal by construction (OMO) [4]. In the case on which we focus, non-orthogonal magnetic orbitals (NMO) will be denoted Φ_A and Φ_B whereas orthogonal magnetic orbitals will be Φ'_A and Φ'_B.

Φ_A and Φ_B are chosen as the highest occupied molecular orbitals for the A (or B) fragment. Thus, Φ_A and Φ_B are nothing but the eigenfunctions of one-electron local Hamiltonians [5, 6]. By definition, they are centred on each metal ion and partially delocalized towards the surrounding ligands.

When Φ_A and Φ_B are orthogonalized through a *Löwdin* procedure [7] Eq. (4) is obtained.

$$\begin{pmatrix} \Phi'_A \\ \Phi'_B \end{pmatrix} = \begin{pmatrix} 1 & S \\ S & 1 \end{pmatrix}^{-1/2} \begin{pmatrix} \Phi_A \\ \Phi_B \end{pmatrix} \tag{4}$$

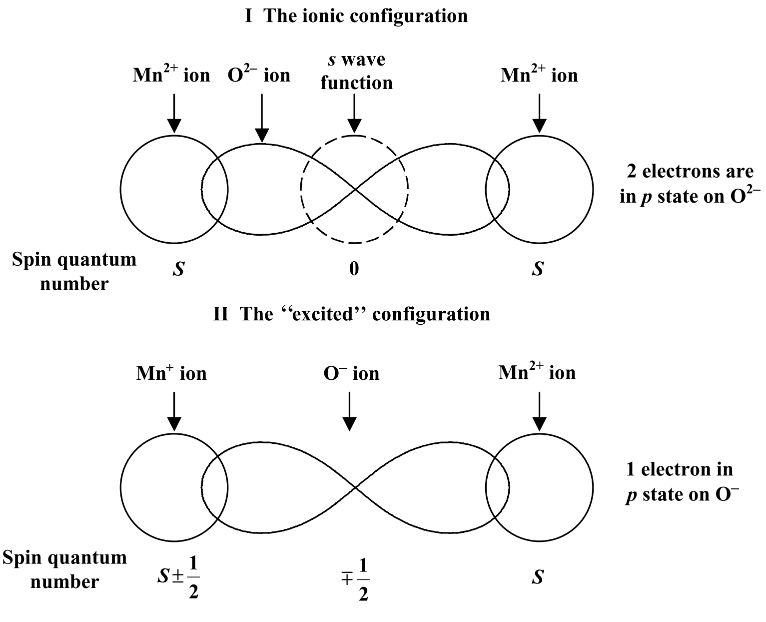
Φ'_A is still localized on centre A, with a residual contribution on centre B, outside the bridging region common to A and B, and increasing with the overlap [3]. Φ'_A and Φ'_B may be derived by another process. We start from the two-highest singly occupied molecular orbitals φ_+ and φ_- for the low-lying triplet state of A–B. When $A = B$, then Φ'_A and Φ'_B are given by Eq. (5) [4].

$$\Phi'_A = \frac{1}{\sqrt{2}}(\varphi_+ + \varphi_-), \qquad \Phi'_B = \frac{1}{\sqrt{2}}(\varphi_+ - \varphi_-) \tag{5}$$

They are equivalent to the *Wannier* functions used by *Anderson* for periodic lattices (see below) [4]. Under these conditions, OMOs derived by Eqs. (4) and (5) are not strictly equivalent, simply due to the fact that the one-electron Hamiltonian of A–B is not the sum of the local Hamiltonians for A and B, considered separately. However, both types of OMOs show the same defect of localization. In addition, from a practical point of view, the OMO approach leads to much simpler calculations, as shown by *Anderson* [4] whereas the NMO approach is closer to the real mechanism involved in the nature of interaction and will favour the use of more realistic molecular integrals. From now and for clarity, magnetic orbitals will be written without the prime (′) notation.

Anderson Model for Superexchange

According to *Anderson* [4] *superexchange acquired its name because of the relatively large distances, occupied by normally diamagnetic ions, radicals or, molecules, over which the exchange effect often was found to act*. In other words (i) the overlap of the wave functions associated with the two magnetic centres separated



$$\psi(S_{\mathrm{tot}}) = a\psi_{\mathrm{ionic}}(S_{\mathrm{tot}}) + b\psi_{\mathrm{excited}}(S_{\mathrm{tot}})$$

Fig. 1. "Ground" and "excited" configurations in the original superexchange process, for the sequence Mn–O–Mn appearing in the crystallized compound MnO (from Ref. [4])

by a non-magnetic bridge (or ligand) is quasi negligible [8]; (ii) the ligand wave function is slightly modified by the presence of the magnetic ions; and (iii) the corresponding modification confers a magnetic character which may give exchange interactions with other ions. Under these conditions, *Anderson* [9] has considered the simplest modification: the transfer of one of the ionic ligand electrons into the external shell of the magnetic ion. For instance, in the well-known case of *d* shells, this transfer could only take place into an empty *d* orbital. This transfer notion has been illustrated by measurements of the hyperfine interaction of the ligand nuclear spin with the electronic spins of the "magnetic" ion. Indeed these results have allowed to demonstrate graphically that the ligand wave function is partially magnetic, with the expected degree [10–13].

Before interacting with the electron of the ligand orbital, each unpaired electron *d* belonging to each magnetic centre is artificially characterized by a spin parallel to the corresponding spin of ligand. Both electrons *d* finally interact on each side of ligand *via* this bridge by an assumed antiferromagnetic mechanism, thus giving rise to antiferromagnetism. The diagram of Fig. 1 gives an illustration of the process leading to superexchange.

1. Description of Anderson Model

Of course, for treating analytically superexchange, the choice of wave functions is fundamental and finally conditions the important aspect of overlap. The whole problem concerns the interaction of an electron with the rest of the lattice. This aspect is taken into account through the ligand field theory. As experimentally shown by the comparative study of hyperfine interactions with ligand ion nuclei between dilute and concentrated versions of the same compound, the exchange effects between one magnetic ion and the other ones do not strongly disturb the ligand field wave function. Thus, there is a well-defined wave function characterizing each magnetic ion, not changed drastically by its magnetic surrounding.

As a consequence, *Anderson* has chosen two levels of sophistication for treating the electrons belonging to the magnetic ions and the ligand, respectively. The first level consists in treating the extra electrons in terms of simple one-electron *Hartree-Fock* functions while the second is treating them as excitations of a many-body system. Thus, *Anderson* considers a periodic potential due to the nuclei and the "core" electrons, whose wave functions may be taken as given quantities, not expected to change very much as excitations occur in the "magnetic" electron system. Such core electrons (including those of the involved ligand) play two important roles: (i) they contribute to the self-consistent field and (ii) the "magnetic electrons" wave functions must be orthogonalized to all the cores. At this step, one must note that true spin polarization of the cores is considered as a minor effect, in contrast to the situation of the free (or "*s*") electrons in the *Zener-Ruderman-Kittel* exchange *via* free electrons in metals.

Under these conditions, the *Coulomb* interaction between the electrons involved in the collective wave function is introduced by the bias of a mean-field approximation (*Hartree-Fock approximation*). As previously seen in introduction, an assumption concerning the starting magnetic configuration is required: *Anderson* has chosen a ferromagnetic configuration. This aspect could be questionable but *Kondo* has shown that there are no pernicious effects [14]. Then the secular problem may be solved self-consistently. Thus, the ligand field wave function $\varphi_i(\boldsymbol{r})$ is assumed to be a solution of the *Hartree-Fock* equations (Eq. (6)).

$$-\frac{\hbar^2}{2m}\boldsymbol{\nabla}^2\varphi_i(\boldsymbol{r}) + \left[\left(V(\boldsymbol{r}) + \sum_j \frac{e^2}{4\pi\varepsilon_0}\int d\boldsymbol{r}'\,\frac{|\varphi_j(\boldsymbol{r}')^2|}{|\boldsymbol{r}-\boldsymbol{r}'|}\right)\varphi_i(\mathbf{r}) - \frac{e^2}{4\pi\varepsilon_0}\sum_j\left(\int d\boldsymbol{r}'\,\frac{\varphi_j^*(\boldsymbol{r}')\varphi_i(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}\right)\varphi_j(\mathbf{r})\right] = \in_i\varphi_i(\boldsymbol{r}) \qquad (6)$$

Note that the integrals are also spin sums and the j sums may extend over all occupied functions including i. At this step, due to the experimental reasons previously evoked, we may recall that one can neglect the relative arrangement of the ‘‘magnetic’’ electrons. In this purpose *Anderson* has adopted the *Wigner-Seitz* scheme of removing the ‘‘magnetic’’ electron charge from the cell in which it finds itself (this scheme must be understood as a ‘‘trick’’ to find usable wave functions). Then the equation for the ligand field wave function may be simply rewritten artificially as Eq. (7).

$$-\frac{\hbar^2}{2m}\boldsymbol{\nabla}^2\varphi_{\boldsymbol{k}}(\boldsymbol{r}) + V(\boldsymbol{r})\varphi_{\boldsymbol{k}}(\boldsymbol{r}) + \frac{e^2}{4\pi\varepsilon_0}\left(\sum_{\boldsymbol{k}'}\int d\boldsymbol{r}'\,\frac{|\varphi_{\boldsymbol{k}'}(\boldsymbol{r}')|^2}{|\boldsymbol{r}-\boldsymbol{r}'|}\right)_{\substack{\boldsymbol{r}\text{ and }\boldsymbol{r}'\text{ not in}\\ \text{the same cell}}}\varphi_{\boldsymbol{k}}(\boldsymbol{r}) + \frac{e^2}{4\pi\varepsilon_0}\sum_j\left(\int d\boldsymbol{r}'\,\frac{|\varphi_j(\boldsymbol{r}')|^2}{|\boldsymbol{r}-\boldsymbol{r}'|}\varphi_{\boldsymbol{k}}(\boldsymbol{r}) - \int d\boldsymbol{r}'\,\frac{\varphi_j^*(\boldsymbol{r}')\varphi_{\boldsymbol{k}}(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}\varphi_j(\boldsymbol{r})\right)_{\substack{\text{ligands}\\ \text{and cores}}} = \in(\boldsymbol{k})\varphi_{\boldsymbol{k}}(\boldsymbol{r}) \qquad (7)$$

Since Eq. (7) has the periodicity of the lattice, its solutions are *Bloch* waves $\varphi_{\boldsymbol{k}}$ with wave vectors $\boldsymbol{k}$. The most important properties of these functions are deducible from the quantity $\in(\boldsymbol{k})$. It contains both the crystal field effects and the kinetic energy. To each d band labelled m, non-degenerate and well separated with respect to the other bands, corresponds a particular energy spectrum $\in_m(\boldsymbol{k})$. Since $\in_m(\boldsymbol{k})$ is periodic it may be expanded in a *Fourier* series (Eq. (8)) where the $\boldsymbol{\tau}$s are fundamental translations of the lattice.

$$\in_m(\boldsymbol{k}) = a_m + \sum_{\boldsymbol{\tau}} b_m(\boldsymbol{\tau})\exp(-i\boldsymbol{k}\cdot\boldsymbol{\tau}) \qquad (8)$$

Now the final *Bloch* solutions of Eq. (7) may be unitary transformed to a new orthonormal set composed of *Wannier* functions (Eq. (9)) where N is the number of lattice sites involved.

$$\varphi_m(\boldsymbol{r}-\boldsymbol{n}) = \frac{1}{\sqrt{N}}\sum_{\boldsymbol{k}}\varphi_{\boldsymbol{k}}^m(\boldsymbol{r})\exp(i\boldsymbol{k}\cdot\boldsymbol{n}) \qquad (9)$$

Thus, the effect of the self-consistent field on the localized functions φ_m is obtained by applying Eqs. (8) and (9) in the following *Schrödinger* equation (Eq. (10)).

$$H_{Sch}\varphi_m(\boldsymbol{r}-\boldsymbol{n}) = a_m\varphi_m(\boldsymbol{r}-\boldsymbol{n}) + \sum_{\boldsymbol{\tau}} b_m(\boldsymbol{\tau})\varphi_m(\boldsymbol{r}-(\boldsymbol{n}+\boldsymbol{\tau})) \qquad (10)$$

a_m represents the crystal field parameter, this crystal field separating the different d levels m. $b_m(\tau)$ appears as a transfer integral representing the effect of the kinetic energy (responsible of the electron motion through the lattice). A more rigorous discussion [15] has allowed to take into account other d bands m' and Eq. (10) may be simply generalized as Eq. (11) where now the transfer integral $b_{mm'}(\tau)$ is given by Eq. (12).

$$H_{Sch}\varphi_m(\boldsymbol{r}-\boldsymbol{n}) = a_m\varphi_m(\boldsymbol{r}-\boldsymbol{n}) + \sum_{m',\tau} b_{mm'}(\tau)\varphi_{m'}(\boldsymbol{r}-(\boldsymbol{n}+\tau)) \tag{11}$$

$$b_{mm'}(\tau) = \int d\boldsymbol{r}\varphi_m^*(\boldsymbol{r}-\boldsymbol{n})(T+V)\varphi_{m'}(\boldsymbol{r}-(\boldsymbol{n}+\tau)) \tag{12}$$

m and m' thus label the corresponding orbitals, each one containing one electron. *Anderson* has designated this contribution to exchange coupling as *kinetic exchange*, simply due to the fact that, during the formation of the weak chemical bond characterized by an antiferromagnetic effect, there is a gain in kinetic energy.

Interactions between *magnetic* electrons on the same ion core interact very strongly and may show three forms:

(i) Two electrons belonging to the same ion may repel each other with an average *Coulomb* energy called U which does not depend on their relative orbital or spin functions (for d electrons $U \approx 10\,\text{eV}$ [16]). U is nothing but the energy which keeps the electrons localized. In other words, each electron stays on its own core exactly and the difference between the first excited state and the ground one is precisely U.

(ii) When the unpaired electrons are in orthogonal orbitals the spins are coupled parallel and the contribution to the exchange coupling is given by Eq. (13).

$$J_{mm'}(\text{potential}) = \int d\boldsymbol{r}\,d\boldsymbol{r}'\varphi_m^*(\boldsymbol{r}-\boldsymbol{n})\varphi_{m'}^*(\boldsymbol{r}-\boldsymbol{n})\frac{e^2}{4\pi\varepsilon_0|\boldsymbol{r}-\boldsymbol{r}'|}\varphi_{m'}(\boldsymbol{r}'-\boldsymbol{n})\varphi_m(\boldsymbol{r}'-\boldsymbol{n}) \tag{13}$$

It is *attractive* because two electrons described by similar wave functions tend to avoid each other through the *Fermi hole* which occurs when spins are parallel, this hole being less repulsive when electrons are closer to each other. *Anderson* has designated this contribution as *potential exchange*. In next subsection we shall give physical comments concerning the labels *kinetic* and *potential exchanges*.

(iii) Small differences in the repulsive energies may also occur due to the relative orientations of the orbitals involved, i.e., as shown by Eq. (14).

$$\int d\boldsymbol{r}\,d\boldsymbol{r}'|\varphi_{m_1}(\boldsymbol{r}-\boldsymbol{n})|^2\frac{e^2}{|\boldsymbol{r}-\boldsymbol{r}'|}|\varphi_{m_2}(\boldsymbol{r}'-\mathbf{n})|^2 \neq \int d\boldsymbol{r}\,d\boldsymbol{r}'|\varphi_{m_3}(\boldsymbol{r})|^2\frac{e^2}{|\boldsymbol{r}-\boldsymbol{r}'|}|\varphi_{m_4}(\boldsymbol{r}')|^2 \tag{14}$$

These differences are the well-known *Slater* integrals which determine how the orbital moments orient themselves, for a free ion. In a real crystal, there will always exist a competition between the crystal field parameters (described by the a_ms) and integrals like those appearing in Eq. (14) which will condition the ionic state.

Thus, superexchange occurs because the best *Hartree-Fock* orbitals are not the *Wannier* functions of Eq. (9) when some of the spins are antiparallel to others. As *Anderson* noted [4], when two neighbouring spins are parallel, their orbitals must of course be orthogonal; when they are antiparallel, their spin functions are automatically orthogonal and the orbitals may overlap each other. The gain of energy has been calculated by *Anderson* [16] and *Kondo* [14], owing to perturbation theory. For two antiparallel neighbours at a distance $\boldsymbol{\tau}$ we have from Eq. (11), Eq. (15) where $U > 0$ is the *Coulomb* repulsion energy so that, for a single pair of spins, Eq. (16) is obtained.

$$\begin{aligned} \varphi_m(\boldsymbol{r}-\boldsymbol{n}) &\rightarrow \varphi_m(\boldsymbol{r}-\boldsymbol{n}) + \sum_{m'} \frac{b_{mm'}(\boldsymbol{\tau})}{U} \varphi_{m'}(\boldsymbol{r}-\boldsymbol{n}-\boldsymbol{\tau}) \\ \varphi_{m'}(\boldsymbol{r}-\boldsymbol{n}-\boldsymbol{\tau}) &\rightarrow \varphi_{m'}(\boldsymbol{r}-\boldsymbol{n}-\boldsymbol{\tau}) + \sum_{m} \frac{b_{mm'}(\boldsymbol{\tau})}{U} \varphi_m(\boldsymbol{r}-\boldsymbol{n}) \end{aligned} \tag{15}$$

$$\Delta E_{(\text{parallel/antiparallel})} = -\frac{2b_{mm'}(\boldsymbol{\tau})^2}{U} \tag{16}$$

The effect is always antiferromagnetic and depends on the presence of half-filled orbitals on the two involved ions, with non-vanishing $b_{mm'}$s. Finally, *Kondo* [14] and *Anderson* [16] have separately shown that, in spite of the fact that superexchange differs from true usual exchange, it is equivalent to an $\boldsymbol{s}_1 \cdot \boldsymbol{s}_2$ coupling, (Eq. (17)) so that the "kinetic" contribution to the exchange integral is given by Eq. (18) and is characterized by a negative sign.

$$\Delta H = \sum_{\substack{m,m',\\ \boldsymbol{n},\boldsymbol{\tau}}} \frac{b_{mm'}(\boldsymbol{\tau})^2}{U} \left(-\frac{1}{2}\mathbf{1} + 2\boldsymbol{s}_{\boldsymbol{n}}^{m} \cdot \boldsymbol{s}_{\boldsymbol{n}+\boldsymbol{\tau}}^{m'} \right) \tag{17}$$

$$J_{mm'(\text{kinetic})} = -\frac{2b_{mm'}(\boldsymbol{\tau})^2}{U} \tag{18}$$

It means that the energies of parallel spins (ferromagnetic arrangement) are not affected but those of antiparallel spins (antiferromagnetic arrangement) are lowered. This is opposite to the true exchange effect where antiparallel spins are not affected. The total exchange is finally $J = J_{mm'(\text{potential})} + J_{mm'(\text{kinetic})}$, the conventional writing of exchange Hamiltonian being $-2J\boldsymbol{S}_{\text{A}} \cdot \boldsymbol{S}_{\text{B}}$.

2. *Physical Comments and Improvements of the Model*

We have just seen that *Anderson* has suggested that the ferromagnetic part be called *potential exchange* and the antiferromagnetic one *kinetic exchange* [16]. These terms are only partially adequate. The first one takes into account the *Coulomb* potential energy which plays a major role in this mechanism but ignores the fact that the extension of the *Fermi* hole is governed by the smoothness of the wave functions which find their origin in the kinetic energy term. For the second label, despite the contribution to the energy lowering which results from a partial electron delocalization, it must be recalled that this comes in fact from the non-vanishing term $b_{mm'}(\tau)$ which contains both kinetic and potential contributions.

These remarks allow one to point out the fundamental complexity of the exchange problem. Indeed we deal with tiny (or at least very small) energy terms, generally accessible through a chain of perturbation process. In addition, since any modification of the wave functions simultaneously affects most of the contributions to the Hamiltonian, it is not possible to strictly separate them *via* a variational process and to specifically attribute to one of them any energy lowering. Finally, it must be emphasized that $b_{mm'}(\tau)$ contains the *Coulomb* electron-electron interactions as well as the one-electron energy terms, since the self-consistent Hamiltonian involves the two-particle energy through the effective mean-field interaction potential.

After the publication of *Anderson*'s initial model [9], experimental works [17] have pointed out that superexchange could also lead to purely ferromagnetic spin arrangements between magnetic centres. A first improvement to *Anderson*'s model has consisted in considering the true polarization effects [18]. In addition, the perturbation expansion has been examined at higher orders, in particular the case of a delocalized orbital containing the unpaired electron and overlapping with an empty orbital on a second metal ion. Intra-atomic coupling of the electrons in the orthogonal metal orbitals leads to a ferromagnetic spin arrangement. This contribution to the exchange integral is given by Eq. (19).

$$J'_{mm'(\text{potential})} = \left(\frac{b_{mm'}(\tau)}{U}\right)^2 J_{(intra\text{-}atomic)} \tag{19}$$

Calculations have given $|J_{mm'(\text{kinetic})}| >> J_{mm'(\text{potential})}$ so that, when both kinetic and potential exchanges co-exist, the kinetic contribution is usually the largest one and the resultant exchange coupling is antiferromagnetic. Ferromagnetic interactions have been considered as resulting from the operation of *Hund*'s rules where the unpaired electrons are delocalized into orthogonal orbitals on a common bridging ligand. Only the exchange pathways involving overlaps between non-orthogonal orbitals give rise to antiferromagnetism.

It early appeared that qualitative rules allowing the prediction of the nature of the interaction between two magnetic centres A and B should be proposed according to the symmetry of the AXB entity. From *Anderson*'s first paper [9], it was suggested that superexchange between ions with d shells half filled or more might be antiferromagnetic, with less ferromagnetic. However experimental contradictions have rapidly appeared (for instance, with compounds containing Cr^{3+} ions which are almost uniformly antiferromagnetic, with a d shell less than half full [17]). A first step proposed by *Anderson* has involved the orientation of magnetic orbitals in the entity AXB. *Anderson's rules suggest that there is a stronger interaction between two spins with a ligand directly between them in 180° position than at right angles with respect to the ligand ion.*

However a considerably more satisfactory system of semi-empirical rules has been developed in the second part of the fifties by *Goodenough* [19] and most clearly stated by *Kanamori* [20]. These rules take into account the occupation of the various d levels as recommended by ligand field theory. They are related to *Anderson*'s prescription about the sign of superexchange energy. Finally, *the angular relationship to the intermediate ligand ion does not play a major role*. Under these conditions the *Goodenough-Kanamori* rules are [4]:

(i) When the two ions have lobes of magnetic orbitals pointing toward each other in such a way that the orbitals would have a reasonably large overlap integral, the exchange is antiferromagnetic. There are several subcases:

1. When the lobes are d_{z^2}-type orbitals in the octahedral case, particularly in the "180° position" in which these lobes point directly toward a ligand and each other, one obtains a large superexchange energy.
2. When d_{xy} orbitals are in the 180° position to each other, so that they interact *via* $p\pi$ orbitals on the ligand, one again obtains antiferromagnetic superexchange.
3. In a 90° ligand situation, when one ion has a d_{z^2} occupied and the other a d_{xy}, the $p\pi$ for one is the $p\sigma$ for the other and one expects a strong overlap and thus antiferromagnetic exchange.

(ii) When the orbitals are arranged in such a way that they are expected to be in contact but to have no overlap integral – most notably a d_{z^2} and a d_{xy} in 180° position where the overlap is zero by symmetry – the rule gives ferromagnetic interaction (not as strong as the antiferromagnetic one in absolute value).

These two rules have explained almost the complete gamut of spin arrangements encountered in a wide variety of compounds. At this step we may make the following comments. (i) Antiferromagnetic superexchange effect can only arise between two orbitals having a finite transfer integral b connecting them and the exchange energy is proportional to b^2 (*cf.* Eq. (18)). In other words, the two orbitals must have the same symmetry in the region of overlap. (ii) If the orbitals do not have the same symmetry so that $b = 0$ (orthogonality by symmetry), one can expect a ferromagnetic exchange. Important applications have been achieved for verifying these rules [21] as well as numerous regularities suggested by theory [4].

A New General Treatment for the Superexchange Mechanism

In this part we develop a general formalism for the *AXB* centrosymmetrical model system, where A and B are two magnetic centres with one unpaired electron each, and X is a closed-shell diamagnetic bridge (or ligand). A first approach has been previously given by *Georges* [22]. Under these conditions, let us start with the two-particle Hamiltonian (Eq. (20)).

$$H = T_1 + V_1 + T_2 + V_2 + \frac{e^2}{4\pi\varepsilon_0 r_{12}}, \quad r_{12} = |\boldsymbol{r}_1 - \boldsymbol{r}_2| \tag{20}$$

The potentials $V_1 = V(\boldsymbol{r}_1)$ and $V_2 = V(\boldsymbol{r}_2)$ include all the nucleus and extra electron contributions to the *Coulomb* field acting on electrons 1 and 2. In other words, we operate in the framework of the *Hartree-Fock approximation*, *i.e.*, the action of extra electrons over electrons 1 and 2 is taken into account through a *mean-field approximation*.

1. Basic Assumptions

The potential operator $\mathscr{V}(\boldsymbol{r})$ commutes with any symmetry operator Φ. Φ forms a double group $\mathscr{G}$ with the identity operation $\mathbf{1}$. Thus, as we deal with a two-electron problem on both sides of ligand X, separately, the two low-lying states of the bonds A–X and X–B are a spin singlet and a spin triplet of respective irreducible representations (irreps) ${}^1\Gamma_\mathrm{g}$ and ${}^3\Gamma_\mathrm{u}$. They are close enough in energy to both be populated at room temperature. In Fig. 2 we have reported the general shape of $V(\boldsymbol{r})$ as well as the energy diagram for the AXB model. The three atomic orbitals involved are Φ_A and Φ_B centred on A and B, respectively, and Φ_X centred on the bridge X (the corresponding states are $|A\rangle$, $|B\rangle$, and $|X\rangle$). Φ_A, Φ_B, and Φ_X are assumed to be real and are considered as starting (non-disturbed) wave functions, *i.e.*, free atomic wave functions which give a spatial description of each of the states $|A\rangle$, $|B\rangle$, or $|X\rangle$. *For instance,* Φ_A *and* Φ_B *are cationic d-orbitals and* Φ_X *is an anionic (s or p) orbital.*

We have the following conventions based on the symmetry problem, notably on the fact that A and B are far apart and without interaction:

(i) The states are normalized but not orthogonal (except $|A\rangle$ and $|B\rangle$) (Eq. (21)).

$$\langle A|A\rangle = 1, \qquad \langle B|B\rangle = 1, \qquad \langle X|X\rangle = 1, \qquad \langle A|B\rangle = \langle B|A\rangle = 0 \tag{21}$$

The fact that $|A\rangle$ and $|B\rangle$ are orthogonal (*i.e.*, without overlap) simply means that there is no bond between A and B (but this could be taken into account in the present model). As noted after Eq. (20), only two unpaired electrons belonging respectively to cations A and B participate to the creation of a bond on each side of the central ligand X, the other electrons being considered as passive. This is the *active-electron approximation* which is plainly justified from an experimental point of view. Indeed, for numerous compounds (for instance, for oxo- or fluoro-bridged compounds), the highest-occupied molecular orbitals of the bridging ligands that interact with the metal ions are low in energy compared to the cationic d orbitals. In addition they are well separated from other metal or ligand occupied orbitals.

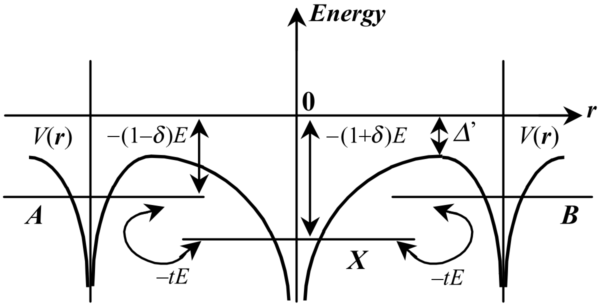


Fig. 2. Energy diagram for the periodic AXB model in the particular case of similar magnetic centres ($A = B$) on both sides of ligand X

(ii) The overlap between A and X on the one hand, X and B on the other one, are equal (Eq. (22)) in the particular case where $A{=}B$ (without changing the generality of the model).

$$\langle A|X\rangle = \langle X|B\rangle = s, \quad s>0 \tag{22}$$

(iii) The magnetic centres A and B have the same cationic energy level higher than the anionic one, as is generally the case for transition metal compounds; the energy difference between these two levels is $2\delta E$, with $E>0$, so that Eq. (23) is obtained.

$$\begin{aligned}&\langle A|(T_1+V_1)|A\rangle = \langle B|(T_1+V_1)|B\rangle = -(1-\delta)E,\\&\langle X|(T_1+V_1)|X\rangle = -(1+\delta)E, \quad E>0\end{aligned} \tag{23}$$

δ is lower than unity but not necessarily small; $\delta>0$ is a very usual case and $\delta<0$ corresponds to the particular case of hydrogen molecule.

(iv) The transfer integrals between $|A\rangle$ and $|X\rangle$ on the one hand, $|X\rangle$ and $|B\rangle$ on the other one, are equal (Eq. (24)).

$$\langle A|(T_1+V_1)|X\rangle = \langle X|(T_1+V_1)|B\rangle = -tE, \qquad \langle A|(T_1+V_1)|B\rangle = 0, \quad t>0 \tag{24}$$

The last equation which states that there is no transfer between A and B but exclusively between A and X or X and B is a consequence of condition (i). However, as previously noted, the case $\langle A|(T_1+V_1)|B\rangle \neq 0$ could be introduced in a more general model, without difficulty.

(v) s and t are small compared to unity and t is mainly related to the potential interaction between the anion and the cation so that Eq. (25) is valid where Δ' is defined in Fig. 2.

$$-tE \approx -s\Delta' < -s(1-\delta)E \tag{25}$$

2. Construction of the Intermediate Cationic States

In the absence of direct overlap and transfer between A and B, any exchange interaction between electrons belonging to the magnetic centres A and B must automatically occur through the anionic intermediate bridge X. In a first step we diagonalize the one-particle Hamiltonian $T_i + V_i\ (i=1, 2)$ in the reduced basis $\{|A\rangle, |X\rangle\}(i=1)$ or $\{|X\rangle, |B\rangle\}(i=2)$, separately. The goal of such an operation is to obtain the new cationic (antibonding) normalized eigenstates $|A\rangle$ and $|B\rangle$ such as given by Eq. (26) where α and β are real numbers. As we deal with a weak chemical bond between A and X or X and B, β must remain small. Then, using condition (i) of the previous subsection, *i.e.*, the normalization condition $\langle A|A\rangle = \langle B|B\rangle = 1$, as well as condition (ii), the new normalization condition $\langle A|A\rangle = \langle B|B\rangle = 1$ leads to the Eq. (27) characterized by the solutions $1-\alpha = -\beta s \pm \sqrt{1-\beta^2+(\beta s)^2}$.

$$|A\rangle = (1-\alpha)|A\rangle + \beta|X\rangle, \qquad |B\rangle = \beta|X\rangle + (1-\alpha)|B\rangle \tag{26}$$

$$(1-\alpha)^2 + 2\beta s(1-\alpha) + \beta^2 - 1 = 0 \tag{27}$$

If we define the new direct overlap $S = \langle A|B\rangle = \langle B|A\rangle$ we derive Eq. (28) so that by reporting in Eq. (27) we have Eq. (29).

$$S = 2\beta s(1-\alpha) + \beta^2 > 0 \tag{28}$$

$$1-\alpha = \pm\sqrt{1-S} \tag{29}$$

From now, the sign + will be conventionally adopted. The new energy is given by Eq. (30).

$$\mathcal{E} = \langle A|(T_1+V_1)|A\rangle = \langle B|(T_1+V_1)|B\rangle \tag{30}$$

It characterizes a degenerate state; but, if $A \neq B$ (general case), the system is non-degenerate. Introducing the definition of $|A\rangle$ and $|B\rangle$ given by Eq. (26) we may write Eq. (31).

$$\mathcal{E} = -[(1-\alpha)^2 + \beta^2](1-\delta)E - 2\beta t(1-\alpha)E \tag{31}$$

The undetermined parameter β may now be chosen so that $\mathcal{E}$ is minimum, *i.e.*, owing to Eq. (31), the equation $\partial\mathcal{E}/\partial\beta = 0$ gives after few calculations β (Eq. (32)).

$$\beta = \pm(1-\alpha) = \pm\sqrt{1-S} \tag{32}$$

Thus, β and $1-\alpha$ may show the same sign or opposite signs: if $\beta > 0$ (respectively, $\beta < 0$) the state $|A\rangle$ or $|B\rangle$ will be represented by a spatially symmetrical wave function (respectively, spatially antisymmetrical). In addition, as β is small, $1-\alpha$ is small too and α is close to unity. Then, using the particular value of β given by Eq. (32), the ground state energy is described by Eq. (33).

$$\mathcal{E} = -(1-\delta)E \pm 2(1-S)(s[1-\delta]-t)E \tag{33}$$

As we have $t > s(1-\delta)$ (*cf.* Eq. (25)), according to the chosen sign $+(\beta>0)$ or $-(\beta<0)$, we shall have $\mathcal{E} < -(1-\delta)E$ or $\mathcal{E} > -(1-\delta)E$. Of course the previous conditions mainly depend on the nature of ligand X.

We finally define the transfer integral $\mathcal{T}$ as shown by Eq. (34).

$$\mathcal{T} = \langle A|(T_1+V_1)|B\rangle = \langle B|(T_1+V_1)|A\rangle \tag{34}$$

Proceeding as for S and $\mathcal{E}$ we derive Eq. (35).

$$\mathcal{T} = -2\beta t(1-\alpha)E - \beta^2(1+\delta)E \tag{35}$$

and by using the particular value of β given by Eq. (32) we have Eq. (36) where the sign + holds for $\beta > 0$ and – for $\beta < 0$.

$$\mathcal{T} = -(1-S)(1+\delta \pm 2t)E \tag{36}$$

As $E > 0$, $1-S > 0$, $1+\delta > 0$ whatever the sign of δ and $t << 1$, $\mathcal{T}$ is *negative*. Thus, before constructing the collective states, it is clear that S, $\mathcal{E}$, *and* $\mathcal{T}$ *appear as the basic parameters of the bond* A–X or X–B *and finally characterize the collective states of AXB*. In some cases, the cationic orbitals directly overlap and some kind of direct exchange may occur. Under these conditions, one may use the present formalism with slight modifications: $|A\rangle$ and $|B\rangle$ appear as the cationic (bonding) states themselves, S and $\mathcal{T}$ are the direct overlap and transfer integrals, respectively. Finally, it must be noticed that the potential energy between entities *A* and *X* or *X* and *B* may be higher than close to them (for instance in the molecule H_2). In that very particular case δ becomes negative (see Fig. 2).

3. Construction of the Collective States

The cationic states $|A\rangle$ and $|B\rangle$ may now give rise to four cationic spin-orbital states: $|A,+\rangle$, $|A,-\rangle$, $|B,+\rangle$, and $|B,-\rangle$ from which we may construct, in a first step, four molecular states adapted to the $\mathcal{G}$ symmetry group molecular orbitals. Notably, owing to their behaviour under the interchange of $|A\rangle$ and $|B\rangle$, we may call them "gerade" (unchanged) or "ungerade" (sign change). Thus we may write Eq. (37) for the "gerade" and "ungerade" states, respectively labelled *g* and *u*.

$$\begin{aligned}|g,\sigma\rangle &= \frac{1}{\sqrt{2(1+S)}}(|A,\sigma\rangle + |B,\sigma\rangle),\\ |u,\sigma\rangle &= \frac{1}{\sqrt{2(1-S)}}(|A,\sigma\rangle - |B,\sigma\rangle), \quad \sigma = \pm\end{aligned} \tag{37}$$

The coefficients $[2(1 \pm S)]^{-1/2}$ are self-evident normalizing factors and $\sigma = \pm$ recalls the nature of the corresponding spin state ("up" or "down"). Then it is easily shown that the related energies are given by Eq. (38) where $\mathcal{E}$ and $\mathcal{T}$ are given by Eqs. (33) and (36), respectively, and the difference of energy between the "gerade" and "ungerade" states is described by Eq. (39),

$$\mathcal{E}_g = \frac{\mathcal{E}+\mathcal{T}}{1+S}, \qquad \mathcal{E}_u = \frac{\mathcal{E}-\mathcal{T}}{1-S} \tag{38}$$

$$\mathcal{E}_g - \mathcal{E}_u = 2\frac{\mathcal{T} - S\mathcal{E}}{1-S^2} \tag{39}$$

i.e., as β, s, t, and S are small, as shown by Eq. (40).

$$\mathcal{E}_g - \mathcal{E}_u \approx -2\beta^2(1+\delta)E \tag{40}$$

Thus, $\mathcal{E}_g - \mathcal{E}_u$ is independent of the sign of β, as expected, remains very small, as β is small, and negative.

With two electrons and four available spin orbitals, 2^4 determinantal collective states may be then built. However, *Pauli*'s exclusion principle coupled to the notion of particle indiscernibility contributes to reduce this number to 6. Let us label $|X_{S,S^z}\rangle$ the collective states: X=U (ungerade) or X=G (gerade) refers to the symmetry of the orbital part with respect to the interchange of $|A\rangle$ and $|B\rangle$; S and S^z describe the total spin configuration. We shall denote $|P,\sigma;P',\sigma'\rangle$ the *Slater* determinant (Eq. (41)).

$$|P,\sigma;P',\sigma'\rangle = \frac{1}{\sqrt{2}}\begin{vmatrix}|P(r_1)\sigma(s_1)\rangle & |P'(r_1)\sigma'(s_1)\rangle\\ |P(r_2)\sigma(s_2)\rangle & |P'(r_2)\sigma'(s_2)\rangle\end{vmatrix} \tag{41}$$

It is then easy to understand that a combination of a *g*-type orbital and a *u*-type one allows one to obtain a *U*-type collective state, whereas combining two *g*- or two *u*-orbitals gives rise to a *G*-type orbital. As a consequence we may build the six following collective states (Eq. (42)).

$$\begin{aligned}
|U_{1,1}\rangle &= |u,+;g,+\rangle,\\
|U_{1,0}\rangle &= \frac{1}{\sqrt{2}}(|u,+;g,-\rangle + |u,-;g,+\rangle),\\
|U_{1,-1}\rangle &= |u,-;g,-\rangle,\\
|U_{0,0}\rangle &= \frac{1}{\sqrt{2}}(|u,+;g,-\rangle - |u,-;g,+\rangle),\\
|G^{g}_{0,0}\rangle &= |g,+;g,-\rangle,\\
|G^{u}_{0,0}\rangle &= |u,+;u,-\rangle
\end{aligned} \tag{42}$$

Their spin characters may be simply verified by applying to each of the previous collective states the convenient total spin operator. Then, introducing the expressions previously obtained for the molecular spin-orbital states, we derive Eq. (43).

$$\begin{aligned}
|U_{1,1}\rangle &= \frac{1}{\sqrt{1-S^2}}|A,+;B,+\rangle,\\
|U_{1,0}\rangle &= \frac{1}{\sqrt{2(1-S^2)}}(|A,-;B,+\rangle + |A,+;B,-\rangle),\\
|U_{1,-1}\rangle &= \frac{1}{\sqrt{1-S^2}}|A,-;B,-\rangle,\\
|U_{0,0}\rangle &= \frac{1}{\sqrt{2(1-S^2)}}(|A,+;A,-\rangle - |B,+;B,-\rangle),\\
|G^{g}_{0,0}\rangle &= \frac{1}{2(1+S)}(|A,+;A,-\rangle + |A,+;B,-\rangle + |B,+;A,-\rangle + |B,+;B,-\rangle),\\
|G^{u}_{0,0}\rangle &= \frac{1}{2(1-S)}(|A,+;A,-\rangle - |A,+;B,-\rangle - |B,+;A,-\rangle + |B,+;B,-\rangle)
\end{aligned} \tag{43}$$

Concerning these latter states, it is useful to notice that they may be also expressed by means of the polar and non-polar normalized (but non strictly orthogonal) states $|G^{p}_{0,0}\rangle$ and $|G^{np}_{0,0}\rangle$, respectively, Eq. (44) with conditions being given by Eq. (45).

$$\begin{aligned}
|G^{g}_{0,0}\rangle &= \frac{\sqrt{1+S^2}}{\sqrt{2}(1+S)}(|G^{p}_{0,0}\rangle + |G^{np}_{0,0}\rangle),\\
|G^{u}_{0,0}\rangle &= \frac{\sqrt{1+S^2}}{\sqrt{2}(1-S)}(|G^{p}_{0,0}\rangle - |G^{np}_{0,0}\rangle)
\end{aligned} \tag{44}$$

$$\begin{aligned}
|G^{p}_{0,0}\rangle &= \frac{1}{\sqrt{2(1+S^2)}}(|A,+;A,-\rangle + |B,+;B,-\rangle),\\
|G^{np}_{0,0}\rangle &= \frac{1}{\sqrt{2(1+S^2)}}(|A,+;B,-\rangle + |B,+;A,-\rangle)
\end{aligned} \tag{45}$$

4. Hamiltonian Matrix and Energy Spectrum

The last step consists in evaluating the elements of the Hamiltonian matrix in the new basis $\{|G^g_{0,0}\rangle, |G^u_{0,0}\rangle, |U_{0,0}\rangle, |U_{1,1}\rangle, |U_{1,0}\rangle, |U_{1,-1}\rangle\}$. The non-vanishing terms are those ones existing between states belonging to the same irreducible representation (irrep) of the orbital ($\mathscr{G}$) and spin ($\mathscr{R}$) symmetry groups. As a consequence one may expect: (i) diagonal and off-diagonal terms between $|G^g_{0,0}\rangle$ and $|G^u_{0,0}\rangle$; (ii) only diagonal terms for the states $|U_{S,S^z}\rangle$ with $S=0$ ($S^z=0$) and $S=1$ ($S^z=0, \pm1$); (iii) finally all the diagonal terms of the states $|U_{1,S^z}\rangle$ are equal because we deal with the irrep $\mathrm{D}_1 \otimes {}^3\Gamma_\mathrm{u}$. Under these conditions, the Hamiltonian matrix is given by Eq. (46) with conditions being given by Eq. (47).

$$H = \begin{pmatrix} E_0^{Gg} & K & 0 & 0 & 0 & 0 \\ K & E_0^{Gu} & 0 & 0 & 0 & 0 \\ 0 & 0 & E_0^U & 0 & 0 & 0 \\ 0 & 0 & 0 & E_1^U & 0 & 0 \\ 0 & 0 & 0 & 0 & E_1^U & 0 \\ 0 & 0 & 0 & 0 & 0 & E_1^U \end{pmatrix} \tag{46}$$

$$\begin{aligned} E_0^{Gg} &= \langle G^g_{0,0}|H|G^g_{0,0}\rangle, \qquad K = \langle G^g_{0,0}|H|G^u_{0,0}\rangle = \langle G^u_{0,0}|H|G^g_{0,0}\rangle, \\ E_0^{Gu} &= \langle G^u_{0,0}|H|G^u_{0,0}\rangle, \qquad E_0^U = \langle U_{0,0}|H|U_{0,0}\rangle, \\ E_1^U &= \langle U_{1,1}|H|U_{1,1}\rangle = \langle U_{1,0}|H|U_{1,0}\rangle = \langle U_{1,-1}|H|U_{1,-1}\rangle \end{aligned} \tag{47}$$

At this step we introduce the following quantities (Eq. (48)) with Eq. (49) where $r_{12} = |\boldsymbol{r}_1 - \boldsymbol{r}_2|$.

$$\begin{aligned} U &= \langle A|\langle A|U_{1,2}|A\rangle|A\rangle = \langle B|\langle B|U_{1,2}|B\rangle|B\rangle, \\ C &= \langle A|\langle B|U_{1,2}|B\rangle|A\rangle, \\ \gamma_1 &= \langle A|\langle B|U_{1,2}|A\rangle|B\rangle, \qquad \gamma_2 = \langle A|\langle A|U_{1,2}|A\rangle|B\rangle \end{aligned} \tag{48}$$

$$\langle W|\langle X|U_{1,2}|Y\rangle|Z\rangle = \int d\boldsymbol{r}_1\, d\boldsymbol{r}_2 \Phi_W^*(\boldsymbol{r}_1)\Phi_X^*(\boldsymbol{r}_2)\frac{e^2}{4\pi\varepsilon_0 r_{12}}\Phi_Y(\boldsymbol{r}_2)\Phi_Z(\boldsymbol{r}_1) \tag{49}$$

The physical meaning of parameters U, C, γ_1, and γ_2 is simply the following one: (i) U is the *Coulomb* energy for an electron pair occupying the same site; (ii) C is the *Coulomb* energy for two electrons occupying neighbouring sites; (iii) γ_1 is the *Coulomb* self-energy of the exchange charge distribution $-e\Phi_\mathrm{A}(\boldsymbol{r})\Phi_\mathrm{B}(\boldsymbol{r})$ and is thus referred to as the exchange integral; (iv) γ_2 appears as the *Coulomb* energy between the exchange charge distribution and an electron charge localized on one site. In other words γ_2 is a transfer integral between two cationic orbitals, resulting from the effective *Coulomb* potential created by the charge of another electron involved in the secular problem.

Under these conditions, the matrix elements given by Eq. (47) may be easily calculated (Eqs. (50)–(52)) where $\mathcal{E}_g$ and $\mathcal{E}_u$ are given by Eq. (38) and U, C, γ_1, and γ_2 by Eq. (48).

$$E_0^{Gg} = 2\mathcal{E}_g + \frac{U+C+2\gamma_1+4\gamma_2}{2(1+S)^2}, \qquad E_0^{Gu} = 2\mathcal{E}_u + \frac{U+C+2\gamma_1-4\gamma_2}{2(1-S)^2}, \tag{50}$$

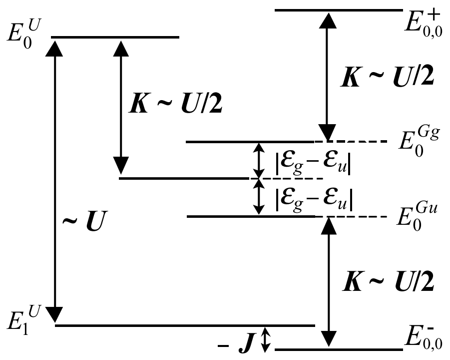


Fig. 3. Description of the energy level scheme for the *AXB* centrosymmetrical model system; the difference $|\mathcal{E}_g - \mathcal{E}_u|$ has been artificially zoomed for clarity

$$K = \frac{U - C}{2(1 - S^2)}, \tag{51}$$

$$E_0^U = \mathcal{E}_g + \mathrm{E}_u + \frac{U - \gamma_1}{1 - S^2}, \qquad E_1^U = \mathcal{E}_g + \mathcal{E}_u + \frac{C - \gamma_1}{1 - S^2} \tag{52}$$

In addition, by diagonalizing the upper 2×2 matrix in Eq. (46), we have the following eigenvalues (Eq. (53)) as well as the diagonal energy terms E^p and E^{np} for $|G_{0,0}^p\rangle$ and $|G_{0,0}^{np}\rangle$, respectively (Eq. (54)).

$$E_{0,0}^{\pm} = \frac{1}{2}\left(E_0^{Gg} + E_0^{Gu} \pm \sqrt{(E_0^{Gg} - E_0^{Gu})^2 + 4K^2}\right) \tag{53}$$

$$E^p = \frac{2(\mathcal{E} + S\mathcal{T}) + U + \gamma_1}{1 + S^2}, \qquad E^{np} = \frac{2(\mathcal{E} + S\mathcal{T}) + C + \gamma_1}{1 + S^2} \tag{54}$$

From the definitions of γ_2, C, γ_1, and U given by Eq. (48), we may deduce the following classification (Eq. (55)), the "physical" values ranging from tenths of eV to a few eV.

$$\gamma_2 \ll C \approx \gamma_1 \ll U \tag{55}$$

The resulting energy level scheme is reported in Fig. 3 and it will be the basis of the physical discussion in next subsection. Most of the considerations will concern the classification of the *Coulomb* terms with respect to the difference $|\mathcal{E}_g - \mathcal{E}_u|$ and the relative positions of the levels characterized by the energies E_1^U and $E_{0,0}^{-}$, their difference giving rise to the expression of J.

Comparison with Previous Models and Illustrations

1. Return on the First Hund's Rule

Let us briefly show that the previous formalism is suitable to establish the first *Hund*'s rule. Here, the orbitals describing the states $|A\rangle$ and $|B\rangle$ belong to the same ion, atom, or molecule. *Since they are solutions of the same secular problem, they* *exhibit vanishing common overlap and transfer integrals*. Thus, the eigenvalues of the upper 2×2 matrix appearing in the Hamiltonian and given by Eq. (53) may be written as Eq. (56) where $\mathcal{E}$ is given by Eqs. (30) and (31) and which must be compared to E_0^U and E_1^U (given by Eq. (52)), respectively close to $2\mathcal{E} + U - \gamma_1$ and $2\mathcal{E} + C - \gamma_1$. In addition, for an atom, $\gamma_2 = 0$ and, for a molecule or a polyatomic ion, $\gamma_2 \neq 0$.

$$E_{0,0}^{+} \approx 2\mathcal{E} + U + \gamma_1 + \frac{4\gamma_2{}^2}{U - C}, \qquad E_{0,0}^{-} \approx 2\mathcal{E} + C + \gamma_1 - \frac{4\gamma_2{}^2}{U - C} \tag{56}$$

Clearly, owing to the previous discussion concerning the order of magnitude of the *Coulomb* terms, the ground level corresponds to the triplet state and appears to be stabilized by about $2\gamma_1$ ($\sim$eV for intra-atomic exchange) with respect to the first excited level. A similar argument may prevail whenever some orbital degeneracy occurs. The ferromagnetic interaction based on the *Coulomb* exchange integral γ_1 is often called *Heisenberg* exchange.

The *Pauli*'s exclusion principle states that two electrons cannot occupy the same spatial position, when showing the same spin, since due to its antisymmetry property, the corresponding wave function then vanishes. This function must vary smoothly, as required for avoiding too large kinetic energy. Thus, it keeps weak values when two electrons characterized by parallel spins are not enough separated. This result also concerns the probability density. As a result a hole appears in the up (down) spin electron distribution in the vicinity of one of them (*Fermi* hole). As a consequence, the larger distance thus maintained between similar spin electrons explains their lower *Coulomb* energy, as compared to antiparallel spin electrons.

2. Molecular Orbital Model

In that case, the *Coulomb* interaction is assumed to play a secondary role. Then, the scheme of energy levels appearing in Fig. 3 becomes that one given in Fig. 4. Clearly, the ground state is one of the singlets $|g, +;\ g, -\rangle$ or $|u, +;\ u, -\rangle$ owing to the relative stability of the orbital states $|g, \sigma\rangle$ and $|u, \sigma\rangle$ (*G*-type collective state). The first excited state is the triplet $|U_{1,S^z}\rangle$, with $S^z = 0,\ \pm 1$.

This approach is relevant when the overlap between orbitals belonging to neighbouring sites is large (for instance in C–C covalent bonds). In case of orbital degeneracy, two low-lying states $|g, \sigma\rangle$ or $|u, \sigma\rangle$ are available for the electron pair which may then form a singlet or a triplet. Of course, the first *Hund*'s rule tells us that the triplet is more stable, as often encountered.

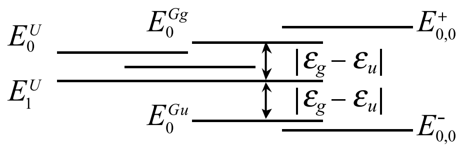


Fig. 4. Description of the energy level scheme for the *AXB* centrosymmetrical model system when *Coulomb* interactions are negligible (molecular orbital model)

3. Comparison with Anderson Model [4]

Anderson model of the isotropic exchange has been proposed for extended systems like oxides and fluorides. In a first step, *Anderson* builds up the molecular orbitals of the A–B system in a triplet state. Then, he determines the orthogonal magnetic orbitals (OMO), as defined in Eq. (5). These functions are the *Wannier* functions (the symmetry group being the crystal translation group). From the ground state (with one unpaired electron per magnetic orbital), it appears a singlet state and a triplet one. One singlet state arises from the excited configurations and may couple with the low-lying singlet state, thus allowing its stabilization. We have seen that the total exchange constant is such as: $J = J_{mm'(\text{potential})} + J_{mm'(\text{kinetic})}$, where $J_{mm'(\text{potential})}$ and $J_{mm'(\text{kinetic})}$, are given by Eqs. (13) and (18). The link between the transfer integral $b_{mm'}(\boldsymbol{\tau})$ defined by Eq. (12) and our model is given by Eq. (57) where $\mathcal{T}$ and γ_2 are given by Eqs. (34) and (48).

$$b_{mm'}(\boldsymbol{\tau}) = \gamma_2 + \mathcal{T} \tag{57}$$

In addition, the *Coulomb* energy U appearing in *Anderson* model corresponds to the quantity $U - C$ in our model. Taking into account the conventional writing of the exchange Hamiltonian ($H_{\text{ex}} = -2J\boldsymbol{S}_{\text{A}} \cdot \boldsymbol{S}_{\text{B}}$) we may write Eq. (58).

$$J_{\text{And}} = \gamma_1 - \frac{2(\gamma_2 + \mathcal{T})^2}{U - C} \tag{58}$$

From the eigenvalues of the upper 2×2 matrix in the Hamiltonian given by Eq. (53), we obtain the lowest eigenvalue (Eq. (59)).

$$E^-_{0,0} \approx 2\mathcal{E} + C + \gamma_1 - \frac{4(\gamma_2 + \mathcal{T})^2}{U - C} \tag{59}$$

We must now compare this value to E^U_1 written in the vanishing-S limit, *i.e.*, Eq. (60).

$$E^U_1 \approx 2\mathcal{E} + C - \gamma_1 \approx 2\mathcal{E} \quad \text{as } C \sim \gamma_1 \tag{60}$$

From the conventional writing of the exchange Hamiltonian we have now $-2J = E^U_1 - E^-_{0,0}$, *i.e.*, Eq. (61) where J is derived from our model.

$$J_{\text{And}} = \gamma_1 - \frac{2(\gamma_2 + \mathcal{T})^2}{U - C} = J \tag{61}$$

4. Comparison with Hay-Thibeault-Hoffmann (HTH) Model [23]

In spite of the fact that the method of calculation is somewhat different, the *HTH* model is very close to *Anderson* one. This model may be seen as the reduction of the homo-(poly)nuclear *Anderson* model to the homo-(bi)nuclear case. The *HTH* model also focuses on the two-singly occupied magnetic orbitals in the triplet state φ_+ and φ_- (*cf.* Eq. (5)), with the energies ε_+ and ε_-. These authors introduce orthogonal magnetic orbitals (OMO) and find J (with, as in *Anderson* model, $H_{\text{ex}} = -2J\boldsymbol{S}_{\text{A}} \cdot \boldsymbol{S}_{\text{B}}$) (Eq. (62)) where we have the following correspondence with our model $K_{ab} = \gamma_1$, $J_{aa} - J_{ab} = U - C$, K_{ab} being the exchange integral, and, J_{aa} and J_{ab}, the one- and two-centre *Coulomb* repulsion integrals.

$$J_{HTH} = K_{ab} - \frac{(\varepsilon_+ - \varepsilon_-)^2}{2(J_{aa} - J_{ab})} \tag{62}$$

Let us make the following comments about Eq. (62): (i) the ground state will be a triplet for the degenerate case $\varepsilon_+ = \varepsilon_-$($J = K_{ab}$, with $K_{ab} > 0$); (ii) the triplet state is destabilized with respect to the singlet state if $\varepsilon_+ \neq \varepsilon_-$; (iii) the difference $|E_{\mathrm{T},0} - E_{\mathrm{S},0}|$ can become vanishingly small for certain values of the integrals and energies which describe the exchange coupling process, but in some cases the paramagnetic centres remain exchange coupled; (iv) for certain values of the integrals and energies, the singlet state may become the ground state [24].

The *HTH* model derives from our general framework by: (i) taking into account the polar state; (ii) neglecting the overlap integral S. This situation is thus formally analogous to that one which prevails in the establishment of the first *Hund*'s rule. The last correspondence with our model concerns the quantity $\varepsilon_+ - \varepsilon_-$: we have $\varepsilon_+ - \varepsilon_- = 2(\gamma_2 + \mathcal{T})$, where $\mathcal{T}$ does not *a priori* vanish between orbitals which are no longer distinct eigenfunctions of the same one-particle effective Hamiltonian. As a consequence, using the same conventional writing of the exchange Hamiltonian as *Anderson*'s one, we have Eq. (63) where J is derived from our model. Thus, the exchange coupling shows a ferromagnetic contribution (basically of *Coulomb-type*) and an antiferromagnetic one (mixing orbital and *Coulomb* processes).

$$J_{HTH} = J_{\mathrm{And}} = J \tag{63}$$

Here the important novelty is that the antiferromagnetic contribution appears even in the case of vanishing overlap. It is related to the possibility of virtual excitation of an electron from one site to another one, without simultaneous reverse motion of the other electron (formation of a polar state). It results from an elementary perturbation theory that such an admixture necessarily pushes down the lowest non-disturbed energy level. In the present framework, since only two orbitals are involved in the mechanism, such polar states are possible only with antiparallel spins. As a consequence, this admixture favours the singlet state.

When orthogonality occurs because the orbitals involved in the mechanism are solutions of the same one-particle Hamiltonian, $\mathcal{T}$ may vanish. In practice, this situation is not often encountered: (i) the intervening orbitals are primarily considered in their own idealized environments and are solutions of *distinct* Hamiltonians; (ii) the effects of the surrounding extra atoms (potential energy contribution, symmetry lowering) introduced when synthetizing the molecule are generally neglected. However, even if $\mathcal{T}$ vanishes, γ_2 remains and favours an antiferromagnetic coupling.

5. Kahn-Briat (KB) Model [25]

Kahn and *Briat* have investigated many molecular systems involving metal cations linked by various organic bridges. The situation is at the opposite of that one which supports the molecular orbital model. The overlap and transfer integrals are small now and the *Coulomb* integrals must no longer be ignored.

Kahn and *Briat* start from the observation that, in this limit, the states $|G^g_{0,0}\rangle$ and $|G^u_{0,0}\rangle$ are nearly degenerate. Thus, the strong off-diagonal term K in the upper 2×2 matrix associated with the Hamiltonian (*cf.* Eq. (46)) strongly mixes them, then giving the eigenstates $|G^{\pm}_{0,0}\rangle \sim |G^g_{0,0}\rangle \pm |G^u_{0,0}\rangle$, which appear to be respectively very close to the polar and non-polar states $|G^p_{0,0}\rangle$ and $|G^{np}_{0,0}\rangle$ (*cf.* Eq. (44) in the vanishing-S limit). *Kahn* and *Briat* exclude the polar state due to its very high energy. As a consequence, the low-lying states are the non-polar triplet and singlet states, *i.e.*, $|U_{1,S^z}\rangle$ (with $S^z=0,\ \pm1$) and $|G^{np}_{0,0}\rangle$. Using the conventional writing of Eq. (1) for the exchange part, also adopted in the *KB* model, we may immediately derive the difference $-J = E^U_1 - E^-_{0,0}$ (up to second order in S and $\mathcal{T}$), with E^U_1 and $E^-_{0,0}$, respectively, given by Eqs. (52) and (53) (Eq. (64)).

$$J = 2(\gamma_1 - CS^2) + 4S(\mathcal{T} - S\mathcal{E}) - 4\frac{[\gamma_2 + \mathcal{T} - S(C+\gamma_1)]^2}{U-C} + \cdots \tag{64}$$

After a convenient translation with the *KB* notation [1, 3, 25], it is easy to show that Eq. (64) exactly coincides with the result obtained by these authors. The first contribution finds its origin in the electron–electron *Coulomb* interaction U_{12}. Since γ_1 and C have been shown to be of the same order of magnitude, γ_1 dominates CS^2. The *Coulomb* contribution remains positive and favours a ferromagnetic coupling. In the second term, the quantity $\mathcal{T} - S\mathcal{E}$ is proportional to the quantity $\mathcal{E}_g - \mathcal{E}_u$ defined by Eq. (39). It emphazises the key role of the overlap in the stabilization of the singlet state. As it is negative (*cf.* Eq. (40)), this term added to the third one describes the antiferromagnetic contribution. Following *Kahn* and *Briat* we define (Eq. (65)) so that J is given by Eq. (66).

$$J_{\uparrow\uparrow} = 2(\gamma_1 - CS^2), \qquad J_{\uparrow\downarrow} = 4S(\mathcal{T} - S\mathcal{E}) - 4\frac{[\gamma_2 + \mathcal{T} - S(C+\gamma_1)]^2}{U-C} + \cdots \tag{65}$$

$$J = J_{\uparrow\uparrow} + J_{\uparrow\downarrow} \tag{66}$$

The ferromagnetic contribution $J_{\uparrow\uparrow}$ dominated by γ_1 is actually a *misadventure* of the first *Hund*'s rule (*Fermi* hole), while the antiferromagnetic one $J_{\uparrow\downarrow}$ is mainly associated with the prohibition for the electrons to occupy the same orbital with the same spin. Both are demonstrations of the *Pauli*'s exclusion principle. The first term of $J_{\uparrow\downarrow}$ vanishes with the overlap, while the second one remains a residual contribution. Thus, in case of orbital orthogonality, we asymptotically deal with the ferromagnetic contribution only.

This has been an important axis of research to elaborate high-spin molecular ferromagnets [26–36]. In this respect, a strategy has been proposed to favour ferromagnetic interactions between nearest magnetic centres, based on the concept of orthogonality of the magnetic orbitals [26–29]. It may be summarized as follows. The starting point concerns an A–B pair, with n_A unpaired electrons on A occupying the a_μ magnetic orbitals, and n_B unpaired electrons on B occupying the b_ν magnetic orbitals. a_μ (respectively, b_ν) transforms as Γ^a_μ (respectively, Γ^b_ν), the irreducible representation (irrep) of the point symmetry group characterizing the A–B pair. The magnetic orbitals are orthogonal if $\Gamma^a_\mu \neq \Gamma^b_\nu$ for any couple (μ, ν). As a consequence, the ground state has the highest spin multiplicity $(n_A + n_B)/2$. Because of the orthogonality of the magnetic orbitals a_μ and b_ν, it is not possible to form low-energy molecular orbitals, delocalized on the whole *A–B* pair, for which the "magnetic" electrons would pair. Under these conditions, *Hund*'s rule holds and one obtains a parallel spin arrangement for the lowest energy state. This strategy has been successfully tested on the copper(II)-orthosemiquinone entity, a copper(II)-vanadyl(II) complex, and a Cr(III)Ni(II)$_3$ tetranuclear species [26].

6. Other Models Illustrating the Charge Transfer Process

Models for organic ferromagnets with unpaired electrons in non-bonded orbitals have been proposed by *Mataga* and *Ovchinnikov* [30]. A model using π electrons in a mixed (...*DADADA*...) stack has been proposed by *Mc Connell* [37] and extended by *Breslow* [38], in the context of charge transfer complexes. It is characterized by the introduction of excited (anomalously polarized) configurations in the Hamiltonian basis, similarly to the polar states introduced in our model. From that point of view, they do not basically differ from that scheme based on the energy lowering term $4(\gamma_2 + \mathcal{T})^2/(U–C)$ involving the transfer integral.

In *Anderson* model (see Fig. 5, case (*a*)), the excited configuration is assumed to be a singlet whereas the ground starting configuration is a triplet, thus contributing to antiferromagnetism. Conversely, *Mc Connell* has pointed out that molecules showing a triplet ground state might be used to construct organic ferromagnets [37]. In this respect, *Mc Connell* considers an ionic molecular crystal D^+A^- characterized by an alternation of species D^+ and A^-, and formed with: (i) a donor molecule D whose neutral ground state is a triplet and a singlet state acceptor

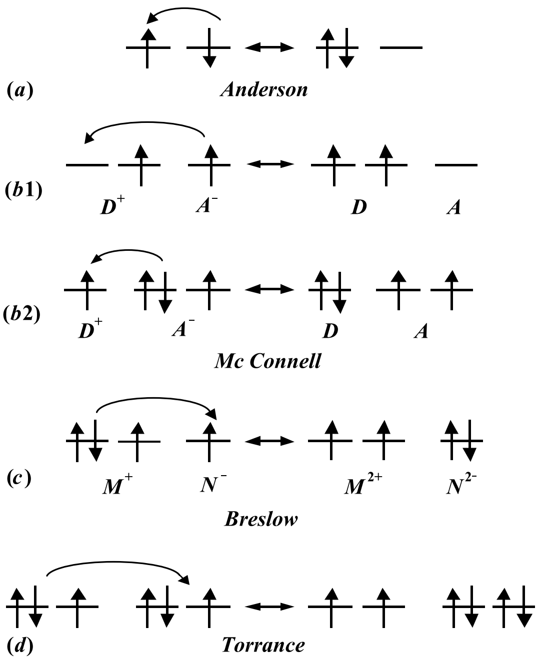


Fig. 5. Various examples of charge transfer models proposed by *Mc Connell* [37], *Breslow* [38], and *Torrance et al.* [39] for explaining ferromagnetic molecular ground states

molecule A (case ($b1$)); (ii) a donor molecule D characterized by a neutral singlet ground state and an acceptor A showing a neutral triplet ground state (case ($b2$)). In both cases a charge transfer mechanism is involved, thus leading to a charge-transferred diradical characterized by a triplet ground state, keeping the spins parallel on both species. The charge transfer can go in either direction: the spin on a given A^- is parallel to the spins on both neighbours D^+ so that ferromagnetic domains may appear in the whole crystal. If the charge transfer is not only linear, one can expect $2D$ or $3D$ domains. Of course, this model does not work if both D and A show a triplet ground state.

A simple change has been proposed by *Breslow* [38]: the triplet species is a dication. In Fig. 5 case (c) shows a version in which species M has fully donated an electron to species N, making the $M^{\overset{+}{\bullet}}/N^{\overset{-}{\bullet}}$ pair. But the charge transfer study indicates that there is a contribution of M^{2+}/N^{2-} to the structure. If M^{2+} has a triplet ground state, N^{2-} being a singlet, the charge transfer then leads to a ferromagnetic coupling. This mechanism also works if N^{2-} is the triplet and M^{2+} the singlet.

Later on, *Torrance et al.* [39] have proposed another model for a segregated stack of radical ions causing a ferromagnetic spin alignment. In this respect, they consider a pair of adjacent radical anions $M_1^{\overset{-}{\bullet}}$ and $M_2^{\overset{-}{\bullet}}$, each species having an unpaired electron delocalised in a π orbital over an aromatic molecule. The ground state of the two molecule dimer may be written as $M_1^{\overset{-}{\bullet}}M_2^{\overset{-}{\bullet}}$ and may be either a singlet or a triplet. The excited state is the one induced by the charge transfer of an electron from one molecule to its neighbour, *i.e.*, $M_1^{2-}M_2^0$ or $M_1^0M_2^{2-}$. The effect of the overlap is to mix ground and excited states. When synthetizing the molecule the aim is to make a triplet with the lowest excited state. This occurs *via Hund*'s rule in case of orbital degeneracy: the two unpaired electrons in the dianion must go into different (but degenerate) orbitals, with their spins parallel. In the case of an aromatic molecule, the orbital degeneracy is caused by the high molecular symmetry; in another molecule, it may arise from appropriate non-bonded orbitals (see Fig. 5, case (d)).

Part of the difficulties arises from the triplet state molecular engineering [40]. As already pointed out incidentally, stabilizing a triplet state generally requires special symmetry properties. These properties are not often met in free molecules due to their own conformation. Electron–phonon coupling itself (*Jahn-Teller* effect) may be quite efficient in reducing the degeneracy of the available orbitals. In addition, the crystallization process may contribute to reduce it again. Although strict degeneracy or orbital orthogonality is not required, molecular crystals showing ferromagnetic couplings are not numerous [31–36].

Conclusion

In this article we have developed a general model in order to describe the superexchange mechanism for the centrosymmetrical system AXB, where A and B are magnetics centres and X is a common bridging ligand. For clarity we have considered the degenerate case $A = B$, where A or B is described by a cationic d-orbital and X by a p (or s) ligand orbital. Of course, the general case $A \neq B$ may be introduced without difficulty. In addition the orbitals describing the states $|A\rangle$ and $|B\rangle$ do not overlap but the important case of overlap between A and B may be also taken into account. However, in both cases, the overlap between $|A\rangle$ and $|X\rangle$ or $|X\rangle$ and $|B\rangle$ is always considered as weak.

Under these conditions, the general treatment which has been set on has allowed to construct an energy level spectrum and the corresponding energies have been derived. Notably, from the singlet-triplet splitting of the low-lying states, a closed-form expression of the exchange energy J may be expressed *vs.* key molecular integrals. The restriction of the present model to the most important cases previously published allows one to exactly retrieve the J expression respectively derived by *Anderson* on the one hand, *Hay-Thibeault-Hoffmann* on the other, or finally by *Kahn* and *Briat*, thus bringing a strong validation to our model.

Important generalizations may be brought. Notably, spin polarization effects may be introduced for the fragment AXB, as well as the spin-orbit coupling. In particular, as this latter contribution must remain small (see article I), the formalism may be slightly altered by replacing the zeroth-order magnetic orbitals by new magnetic orbitals taking into account the spin-orbit perturbation. However, the most important key point concerns the possible generalization of our formalism to any kind of molecule or polyatomic ion.

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