Ferromagnetic Spin Alignment in Molecular Systems: An Orbital Approach

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Most stable organic and organometallic molecules are diamagnetic with a closed-shell configuration, such that electron pairing is often considered as one of the fundamental rules of molecular chemistry. For the great majority of molecular chemists, magnetism is a far-off science which has nothing to do with their own field of research. The situation is obviously different for both coordination chemists working with transition metal ions and organic chemists interested in free radicals. The entities they are dealing with may have an open-shell configuration. However, the interactions between unpaired electrons either within the molecular unit (intramolecular) or between molecular units (intermolecular) are most often of the up–down type.

Nature has a pronounced predilection for such antiferromagnetic interactions. The reason for this is well understood; when two singly occupied localized orbitals are close to each other, they tend to overlap, favoring the formation of a delocalized bonding orbital in which the two electrons pair, and a delocalized antibonding orbital which remains empty in the ground state. It is, for example, what happens when two hydrogen atoms, each of them with the $1s^1$ configuration, move to each other and eventually form a diamagnetic dihydrogen molecule. Such behavior is actually the cornerstone of the chemical bond. In a certain sense, antiferromagnetism may be considered as the borderline case of a very weak chemical bond. One uses the concept of antiferromagnetism when the interaction is so weak that not only the up–down spin ground state but also the up–up spin excited state is thermally populated, which leads to a characteristic temperature dependence of the magnetic susceptibility.

The parallel spin alignment, or ferromagnetic interaction, remains exceptional in molecular chemistry and requires that quite peculiar conditions be fulfilled. That is why we may assert that molecular ferromagnetism is a challenge.[1] The pioneering work along this line must be ascribed to McConnell, who in the 1960s proposed two mechanisms to achieve intermolecular ferromagnetic interactions between organic radicals[2,3] which we will discuss later on. The second mechanism

was reformulated by Breslow.[4] Much at the same time, several Japanese groups initiated a long-standing effort to design high-spin organic molecules using the concept of topological degeneracy in alternant hydrocarbons.[5-11] The final goal, which consists of assembling these molecules within the crystal lattice in a ferromagnetic fashion, has not yet been reached. However, purely organic species with ground-state spins as large as $S = 6$ have been synthesized and characterized.[10] During the 1970s and the early 1980s, several other groups succeeded in designing molecules in which the spin carriers were ferromagnetically coupled.[12-14] In the late 1980s several genuine molecular-based magnets were described.[15-24]

In this Account we will explore the various orbital patterns which favor a ferromagnetic interaction between two open-shell molecular units, A and B. We will show that these patterns may be classified into two main categories: those based on spin exchange which do not require any electron transfer between A and B and those in which the parallel spin alignment arises from configurational mixing between the ground con-

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(2) McConnell, H. M. *J. Chem. Phys.* **1963**, *39*, 1910.

(3) McConnel, H. M. *Proc. Robert A. Welch Found. Conf. Chem. Res.* **1967**, *11*, 144.

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(10) Nakamura, N.; Inoue, K.; Iwamura, H.; Fujioka, T.; Sawaki, Y. *J. Am. Chem. Soc.* **1992**, *114*, 1484.

(11) Iwamura, H. *Adv. Phys. Org. Chem.* **1990**, *26*, 179.

(12) See, for example: *Magneto-Structural Correlations in Exchange Coupled Systems*; Willett, R. D., Gatteschi, D., Kahn, O., Eds.; NATO ASI Series; Reidel: Dordrecht, 1985.

(13) (a) Kahn, O. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 834. (b) Kahn, O. *Struct. Bonding (Berlin)* **1987**, *68*, 89.

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(16) Miller, J. S.; Calabrese, J. C.; Rommelmann, H.; Chittipeddi, S. R.; Zhang, J. H.; Reiff, W. M.; Epstein, A. J. *J. Am. Chem. Soc.* **1987**, *109*, 769.

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figuration AB and charge-transfer configurations of the type A^+B^- or A^-B^+.

This contribution is particularly aimed at synthetic chemists interested in the field of molecular magnetism. Our objective is to provide an overview of the various strategies for the design of molecular-based magnets.

Ferromagnetic Interaction without Electron Transfer

We distinguish two cases. First, we consider the exchange interaction between unpaired spins on different centers with a positive sign of the spin density on each center. Electron transfer between different centers is not contained in this approach. Note that in our case the different centers carrying unpaired spins are not restricted to transition metal atoms or ions as in the "classical" ferromagnetism of transition metals or transition metal oxides. Rather the spins can be delocalized over extended molecular units. The second case refers to systems in which spin densities of opposite sign occur in well-separated spatial regions. This leads to a modification of the usual exchange mechanism which has been presented by McConnell.[2] He suggested that negative spin densities arising from the spin polarization effect might play a crucial role for the exchange interaction between molecular units.

Intermolecular Exchange Based on Spin Delocalization. Let us consider two molecular units, A and B, each carrying an unpaired electron in the singly occupied molecular orbitals (SOMOs) a and b, respectively. The method to be used derives from valence bond theory introduced by Heitler and London for H_2. It can be generalized to extended systems[25] leading to the well-known Heisenberg Hamiltonian:

$$\hat{H} = -2 \sum_{i<j} \sum J_{ij} \hat{S}_i \hat{S}_j \qquad (1)$$

J_{ij} is the exchange coupling constant between centers i and j. The spins on centers i and j align parallel or antiparallel for $J_{ij} > 0$ or $J_{ij} < 0$, respectively. The exchange interaction in our AB system leads to singlet ($S = 0$) and triplet ($S = 1$) states with a singlet–triplet gap of $2J$. J has basically the following form in the simple Heitler–London model:[26]

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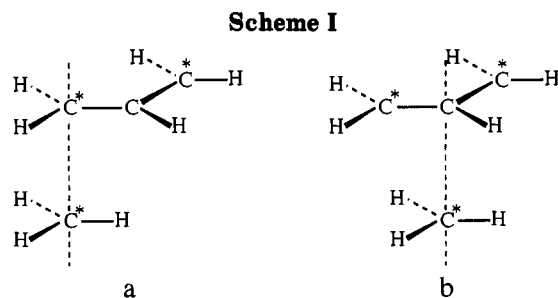
(26) Note that eq 2 does not represent the complete exchange coupling constant for spin exchange because it does not take into account the dependency of the normalization constant of the two-electron wave function on the spin quantum number S which leads to additional terms not contained in eq 2. A more detailed discussion can be found in refs 27 and 28.

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(28) Kollmar, C.; Kahn, O. *J. Chem. Phys.* 1993, *98*, 453.

$$J = 2\beta S + K \qquad (2)$$

with

$$S = \int a\,b\,dv$$

$$\beta = \int a\,\hat{h}\,b\,dv \qquad (3)$$

$$K = \int a(1)\,b(2)\,\frac{e^2}{r_{12}}\,a(2)\,b(1)\,dv_1\,dv_2$$

Equation 2 contains two terms of opposite sign, namely, the two-electron exchange integral K, which is necessarily positive, and the product of a resonance integral β with an overlap integral S. These two factors are of opposite sign so that their product becomes negative. Thus, one can denote $2\beta S$ and K as antiferromagnetic and ferromagnetic contributions, respectively, to the exchange coupling constant. In general, $2\beta S$ dominates. Ferromagnetic interaction is obtained if the overlap integral S vanishes, i.e., if a and b are orthogonal. Therefore the most obvious strategy leading to ferromagnetic interaction between two molecular units A and B is to achieve a spatial arrangement of molecular units such that the two SOMOs a and b are orthogonal (or quasi-orthogonal). In a few cases, the orthogonality can be accidental; in general, however, it arises from the different symmetries of a and b. An accidental orthogonality is obviously much more difficult to control than the strict orthogonality. A zero overlap integral does not necessarily provide a strong stabilization of the parallel spin state; in addition, the two-electron exchange integral K must be large, which is realized when the product ab of the two SOMOs (i.e., the overlap density) is important in some regions of intermolecular space. Note that there are cases where orthogonality is not sufficient to provide ferromagnetic interaction, e.g., twisted ethylene with D_{2d} symmetry which has a singlet ground state in violation of Hund's rule.[29]

Intermolecular Exchange Interaction Including the Spin Polarization Effect. Now let us turn to a type of spin exchange which involves the spin polarization effect in open-shell systems and is often denoted as McConnell mechanism I.[2] The basic idea behind this model was also recognized at about the same time by Anderson.[30] It is based on the fact that there may be regions with negative spin densities in an extended open-shell system.

We consider again two neighboring molecular units A and B with unpaired spins, but now each of them exhibits both positive and negative spin densities. The region where the spin densities of the two units have a strong overlap is crucial for the intermolecular exchange interaction. The most common situation will be that the spin densities of two nearest neighbors both have a positive sign in this region, which most often favors antiferromagnetic spin alignment. However, if it were possible to arrange two neighboring molecular units in such a way that we would have a particularly favorable overlap of regions with opposite sign of the spin density, we would expect ferromagnetic interaction.[2]

(29) Kollmar, H.; Staemmler, V. *Theor. Chim. Acta* 1978, *48*, 223.

(30) Anderson, P. W. In *Magnetism*; Rado, G. T., Suhl, H., Eds.; Academic Press: New York, 1963; Vol. 1, p 25.

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Scheme I


a   b

McConnell developed his idea in the context of alternant hydrocarbon radicals stacked along an axis perpendicular to their molecular plane. In this type of molecule the carbon atoms forming the conjugated π system are divided into two sets, starred and unstarred atoms, in such a way that starred atoms are adjacent only to unstarred atoms and vice versa.[31,32] In a simple Hückel MO picture, the spin density on the unstarred carbons would be 0. Taking into account the spin polarization effect, we obtain positive and negative spin densities on the starred and unstarred C atoms, respectively. If those radicals are stacked in such a way that carbon sites with spin density of opposite sign are in registry on nearest neighbors, one can expect ferromagnetic coupling.

As the most simple model system of this kind let us consider the coupling of an allyl radical with a neighboring methyl radical.[33] Two stacking modes are shown in Scheme I. In allyl, there is a positive spin density on the outer (starred) carbons and there is a negative spin density on the central (unstarred) carbon.[31,32] The spin density on the methyl carbon is positive and localized in the p_z orbital perpendicular to the molecular plane. Thus, there is an alignment of sites with positive spin density in part a of Scheme I and of sites with spin density of opposite sign in part b of Scheme I leading to antiferromagnetic and ferromagnetic coupling, respectively. This has been confirmed by ab initio calculations.[33]

The first McConnell mechanism falls under the category of spin exchange, but it requires the inclusion of excited configurations within each subunit, thus going beyond the Hartree–Fock level. The calculation of the exchange coupling constant J including spin polarization leads to an expression similar to eq 2 but with all signs inverted. In particular, the term governed by the overlap integral which favored antiferromagnetic interaction in the spin delocalization mechanism now favors ferromagnetic interaction.[28]

As a first example for a real system we consider two neighboring diphenylcarbenes incorporated in a paracyclophane skeleton as shown in Figure 1.[34] Thus, the stacking mode for the two units can be fixed in a controlled fashion. A quintet ground state for the pseudoortho and pseudopara arrangement and a singlet ground state for the pseudometa compound have been found in EPR experiments.[34] This is in line with the hypothesis of McConnell, because in the former cases

pseudoortho   pseudometa   pseudopara
S = 2   S = 0   S = 2
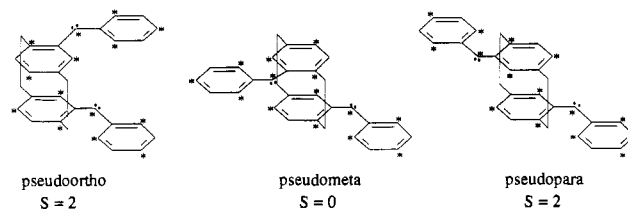
Figure 1. Two diphenylcarbene units connected by a paracyclophane skeleton in different relative positions. The radical electrons of the carbenes are indicated by dots. We also marked the starred and unstarred carbons of these alternant hydrocarbons.
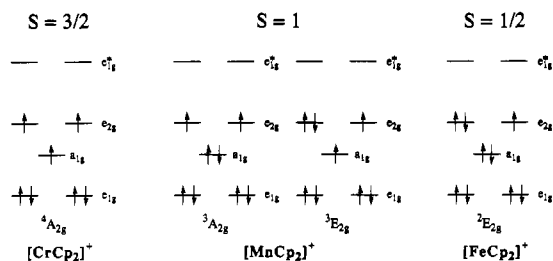
Figure 2. Ground configurations of chromocenium, manganocenium, and ferrocenium in a MO diagram. The ground state of manganocenium is $^3A_{2g}$ or $^3E_{2g}$. Only MOs with considerable metal 3d contributions are shown.

Scheme II
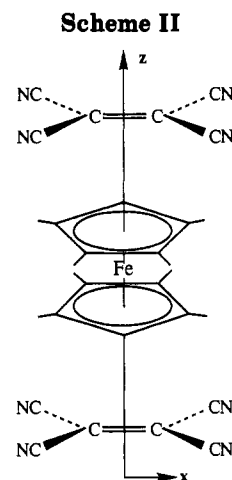
we have an alignment of sites with spin density of opposite sign, contrary to the latter case. Theoretical calculations are in agreement with the experimental observations.[35]

An important class of molecular ferromagnets emerged with the discovery of a ferromagnetic decamethylferrocenium tetracyanoethenide (DMFc TCNE) complex by Miller et al.[15,16] with an alternating arrangement of DMFc donors and TCNE acceptors as shown schematically in Scheme II. Subsequently, other metallocenium complexes with the same structural motif and interesting magnetic properties have been synthesized.[15,16,19,20]

This class of compounds represents the second example to which we would like to apply the first McConnell mechanism.[33,36] The MO scheme for the donor MCp_2^+ with M = Cr, Mn, Fe is given in Figure 2. Its qualitative shape is the same for all of these

(31) Salem, L. *The Molecular Orbital Theory of Conjugated Systems*; W. A. Benjamin Inc.: New York, 1966.
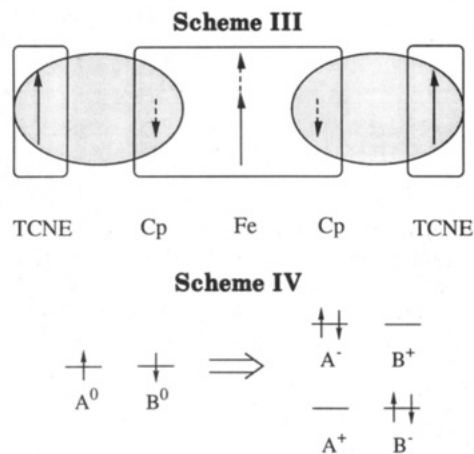
(32) Coulson, C. A.; Rushbrooke, G. S. *Proc. Cambridge Philos. Soc.* **1940**, *36*, 193.

(33) Buchachenko, A. L. *Russ. Chem. Rev.* **1990**, *59*, 307.

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(35) (a) Yamaguchi, K.; Toyoda, Y.; Fueno, T. *Chem. Phys. Lett.* **1989**, *159*, 459. (b) Yamaguchi, K.; Namimoto, H.; Fueno, T. *Mol. Cryst. Liq. Cryst.* **1989**, *176*, 151.

(36) (a) Kollmar, C.; Couty, M.; Kahn, O. *J. Am. Chem. Soc.* **1991**, *113*, 7994. (b) Kollmar, C.; Kahn, O. *J. Chem. Phys.* **1992**, *96*, 2988.

Scheme III

TCNE   Cp   Fe   Cp   TCNE

Scheme IV

Figure 3. Energy level system for ground and charge-transfer states of a donor–acceptor pair for the most common case with a charge transfer between nondegenerate orbitals.

compounds. The a_{1g} and e_{2g} orbitals, which are very close in energy, are of almost pure metal character with very small contributions from the Cp ligands. The higher-lying $e_{1g}*$ orbital pair is also mainly metal but has a considerable antibonding contribution from the Cp ligands (thus the asterisk). Correspondingly, the low-lying e_{1g} orbitals are mainly ligand with some bonding contribution from the metal. A common feature of all configurations shown in Figure 2 is that the unpaired electrons are localized in MOs with almost pure metal character (a_{1g} or e_{2g}). Now the analogy to the previously discussed allyl radical becomes obvious. In allyl the radical electron localized on the outer carbon atoms induced a negative spin density on the central carbon via the spin polarization effect; in the same way the unpaired electrons of the metallocenium ions localized on the metal induce a negative spin density on the Cp rings.[36] This result is supported by earlier proton[37] and ^{13}C[38] NMR data, but it has been only recently that conclusive experimental evience has been provided.[39]

What are the consequences of this spin polarization effect for the spin coupling with the neighboring acceptor? The acceptor, no matter if it is TCNE or TCNQ, carries one unpaired electron resulting from the charge transfer into the $\pi*$ LUMO of the formerly neutral acceptor molecule. The spatial arrangement of the spins is illustrated in Scheme III, where we show one decamethylferrocenium ion and its two nearest TCNE neighbors. The regions of strong overlap of the spin densities are indicated by the shaded areas. The spin densities without spin polarization and the additional spin densities induced by spin polarization are symbolized by solid and dashed arrows, respectively. The ferromagnetic coupling then arises from an exchange effect between the negative spin density on the Cp ring and the positive spin density on the neighboring $TCNE^-$ unit. The direct exchange between the spin on the metal and the one of $TCNE^-$ can be neglected due to the larger distance between the metal and TCNE as compared to the distance Cp–TCNE.
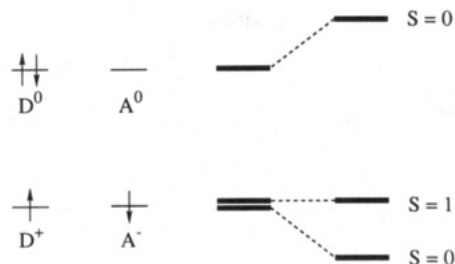
Note that this model describes only the ferromagnetic coupling within the stack and does not account for the three-dimensional ferromagnetic behavior observed

experimentally. It is, however, possible to give plausible hypotheses concerning the interstack coupling as well.[36,40]

Ferromagnetic Interaction Requiring Charge-Transfer States

The considerations in the previous section have been entirely based on a valence-bond-like approach, i.e., configurations which involve a transfer of unpaired electrons from one molecular unit to another have been excluded. It is evident that these charge-transfer states may also give a contribution to the exchange coupling constant of eq 1.

To elucidate this point let us again consider two molecular units A and B with one unpaired electron each. In addition to the covalent configuration A^0B^0 there are also the charge-transfer configurations A^+B^- and A^-B^+ (Scheme IV). In the case of nondegenerate SOMOs the Pauli principle requires singlet character for the charge-transfer states. The mixing with the ground state therefore stabilizes the singlet thus adding another antiferromagnetic term to the exchange coupling constant. However, it is interesting to look for possible exceptions, i.e., for charge-transfer mixing which might favor the ferromagnetic state. We will discuss two approaches.
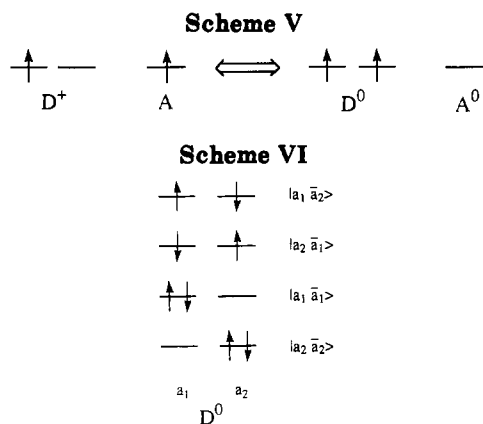
Charge Transfer Involving Degenerate SOMOs. Let us consider a one-dimensional stack of alternating donor and acceptor units $...D^+A^-D^+A^-...$ with one unpaired electron per unit. We single out one pair, D^+A^-, from the stack and consider the backward charge transfer from the acceptor to the donor. If the orbitals involved in the charge transfer are nondegenerate, we find a singlet state for the excited configuration D^0A^0 in analogy to Scheme IV as indicated in Figure 3. The energy stabilization of the singlet ground configuration D^+A^- by mixing with D^0A^0 is described by a second order perturbation theory term:

$$\Delta E = \beta^2/U \tag{4}$$

β is a mixing matrix element the magnitude of which depends on the overlap between the orbitals involved in the charge transfer. U is the energy necessary to transfer an electron from A^- back to D^+.

The situation might be different if, for example, the donor has two degenerate SOMOs. In this case the neutral donor D^0 has in general a triplet instead of a singlet ground state in accordance with Hund's rule because there are two degenerate SOMOs occupied by two electrons (Scheme V). The interaction between the two triplet states arising from the D^+A^- and D^0A^0

(37) (a) McConnell, H. M.; Holm, C. H. *J. Chem. Phys.* 1957, 27, 314. (b) McConnell, H. M.; Holm, C. H. *J. Chem. Phys.* 1958, 28, 749.

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(39) Blümel, J.; Hebendanz, N.; Hudeczek, P.; Köhler, F. H.; Strauss, W. *J. Am. Chem. Soc.* 1992, 114, 4223.

(40) Tchougreef, A. L. *J. Chem. Phys.* 1992, 96, 6026.
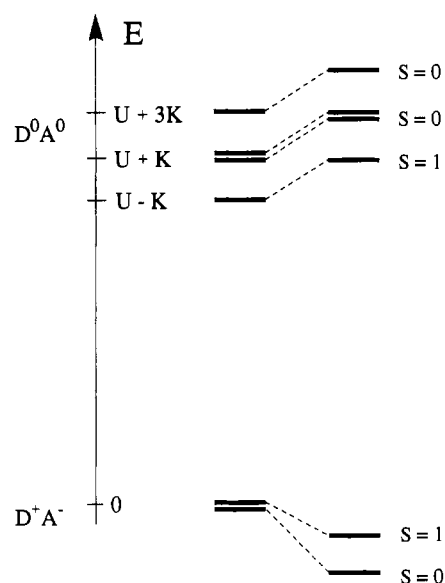
Scheme V

Scheme VI

configurations should stabilize the low-lying triplet which led McConnell to the conclusion that the orbital orbital pattern of Scheme V should result in ferromagnetic spin alignment.[3]

This is in fact an oversimplified picture.[41] To illustrate our point we consider the configuration of D^0 with degenerate SOMOs a_1 and a_2 occupied by two electrons. There are four possible microstates with the magnetic quantum number $M_S = 0$ as shown in Scheme VI. They may be combined to form *three* singlets and *one* triplet. As a consequence there are three energy stabilization terms of the type given in eq 4 for the singlet but only one for the triplet as illustrated in Figure 4. One of the singlet levels is in general degenerate[42] so that there are three energy levels for the charge-transfer configuration D^0A^0 separated by $2K$ with K being an intramolecular exchange integral. For $K \ll U$, as assumed in Figure 4, the ground state of the donor–acceptor pair is a singlet, contrary to the assumption of McConnell, even if the energetically lowest state of the configuration D^0A^0 is actually a triplet. Only if the small intramolecular exchange integral K is of about the same magnitude as the charge-transfer energy U, the difference in the energy denominator of eq 4 favoring the triplet might be large enough to overcome the larger numerator of the stabilization term for the singlet, thus leading to a triplet ground state.[41] Since such a situation will rarely be encountered, this mechanism cannot be considered as an appropriate guideline in the synthesis of molecular ferromagnets. Even highly sophisticated experimental efforts based on this mechanism have been unsuccessful so far.[4]

The second McConnell mechanism has been invoked for the explanation of the ferromagnetism of metallocenium charge-transfer complexes.[15,16] After the discovery of a ferromagnetic chromocenium complex[19b] this view could no longer be upheld.

Charge Transfer from the SOMO to an Empty Orbital (or from a Doubly Occupied Orbital to the SOMO). The charge transfers considered so far involved singly occupied molecular orbitals (SOMOs) on both units. One could, however, think of charge transfers that involve an empty or a doubly occupied orbital. This is indicated in Scheme VII, where we show the next highest doubly occupied molecular orbital (NHOMO) and the lowest unoccupied molecular orbital

(41) Kollmar, C.; Kahn, O. *J. Am. Chem. Soc.* **1991**, *113*, 7987.

(42) If the point group of the molecule contains a rotation or rotation-reflexion axis of order $4n$ with n being an integer, there exist degenerate orbital pairs for which the states obtained from proper linear combinations of the microstates shown in Scheme VII are all nondegenerate.

Figure 4. Energy level scheme for $K \ll U$ corresponding to the orbital configuration of Scheme V but taking into account all charge-transfer states arising from proper linear combinations of the microstates shown in Scheme VI. Note that this energy level scheme is somewhat simplified. Without donor–acceptor interaction there is an additional degeneracy of both the singlet and the triplet state of the ground configuration D^+A^-, because the unpaired electron of D^+ can be in either of the orbitals a_1 or a_2. This degeneracy is lifted by the donor–acceptor interaction resulting in two singlet and two triplet states of which only the energetically lower ones are shown.
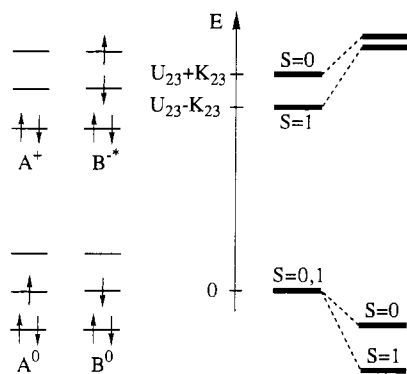
Scheme VII
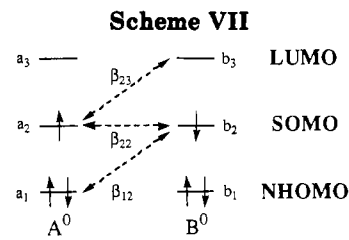
(LUMO) for both units in addition to the SOMOs. The SOMO–SOMO transfer (transfer integral β_{22}) has already been discussed (Scheme IV) and stabilizes the antiferromagnetic state. Additional charge transfers are possible from, for example, the SOMO of A to the LUMO of B (transfer integral β_{23}) and from the NHOMO of A to the SOMO of B (transfer integral β_{12}) leading to the excited configurations A^+B^{-*} and $A^{+*}B^-$, respectively. Note that these charge transfers involve excited states of the individual donor (A^{+*}) or acceptor (B^{-*}). Contrary to the SOMO–SOMO transfer that requires a singlet for the configuration A^+B^- due to the Pauli principle, the configurations A^+B^{-*} or $A^{+*}B^-$ allow both singlet and triplet states with the latter being lower in energy according to Hund's rule. Thus the mixing of the ground configuration A^0B^0 with the excited configurations A^+B^{-*} or $A^{+*}B^-$ stabilizes the triplet more strongly than the singlet. These two types of charge transfer were first introduced by Goodenough[43] and have been invoked recently to justify the ferromagnetism of the β phase of p-nitrophenyl nitroxyl nitroxide.[44]

(43) Goodenough, J. B. *Magnetism and the Chemical Bond*; Interscience Publishers: New York, 1963; p 167.

(44) Turek, P.; Nozawa, K.; Shiomi, D.; Awaga, K.; Inabe, T.; Maruyama, Y.; Kinoshita, M. *Chem. Phys. Lett.* **1991**, *180*, 327.

Figure 5. Energy level scheme for the the charge transfer from the SOMO of A to the LUMO of B. We show the corresponding states with the spin component $M_S = 0$ on the left.

Figure 6. Charge transfer from the π^* orbital, i.e., the SOMO, of TCNE$^-$ to the LUMO of ferrocenium (a) or to an open-shell orbital (e_{1g}^*) of nickelocenium (b).

An energy level scheme for the charge-transfer SOMO–LUMO is shown in Figure 5. An analogous scheme holds for the transfer NHOMO–SOMO. We recognize that the singlet and triplet charge-transfer states are separated by $U_{23} + K_{23}$ and $U_{23} - K_{23}$, respectively, from the ground state. K_{23} is an intramolecular exchange integral involving the orbitals b_2 and b_3 (see Scheme VII) and determines the singlet–triplet gap of the excited configuration B^{-*}, whereas U_{23} is the energy cost for the SOMO–LUMO transfer, which is higher than the corresponding energy cost for the SOMO–SOMO transfer. When the interaction between the two units is switched on, the energies are shifted as indicated in Figure 5. In general, however, the SOMO–SOMO transfer prevails, favoring antiferromagnetic coupling. Only if the mixing matrix element β_{22} for the SOMO–SOMO transfer vanishes or is much smaller than the corresponding matrix elements for the SOMO–LUMO or NHOMO–SOMO transfer, the latter will lead to ferromagnetic alignment of the spins.

The charge-transfer mechanism considered in this section has been implemented by Tchougreef[40] for the metallocenium charge-transfer complexes. He considered a backward charge transfer from the acceptor to the donor resulting in the neutral species, e.g., DMFc$^+$TCNE$^-$ → DMFc TCNE for the decamethylferrocenium compound. The SOMO–SOMO backward charge transfer, i.e., the one from the π^* orbital of TCNE$^-$ back to one of the e_{2g} orbitals of decamethylferrocenium (see Figure 6a), plays no role because the overlap between these orbitals is negligibly small. Remember that the e_{2g} orbitals have almost no contribution from the Cp ligand. On the other hand, the e_{1g}^* orbitals have the strong ligand contribution needed for a large overlap and thus a strong mixing matrix element. Hence, instead of the SOMO–SOMO transfer it is the transfer from the SOMO of TCNE$^-$ (π^*) to the LUMO of decamethylferrocenium (e_{1g}^*) that is crutical for the magnetic interaction.[40] This is illustrated in Figure 6a. Although the LUMO is now degenerate, the analogy to Figure 5 is evident.

The metallocenium complexes considered so far were ferromagnets. It is illustrative to consider the nickelocenium TCNE complex, which shows antiferromagnetic coupling.[15] The MO scheme is shown in Figure 6b. It can be seen that the unpaired electron of nickelocenium now occupies one of the e_{1g}^* MOs which have a strong Cp contribution. Thus, contrary to the compounds shown in Figure 2 with their spins localized
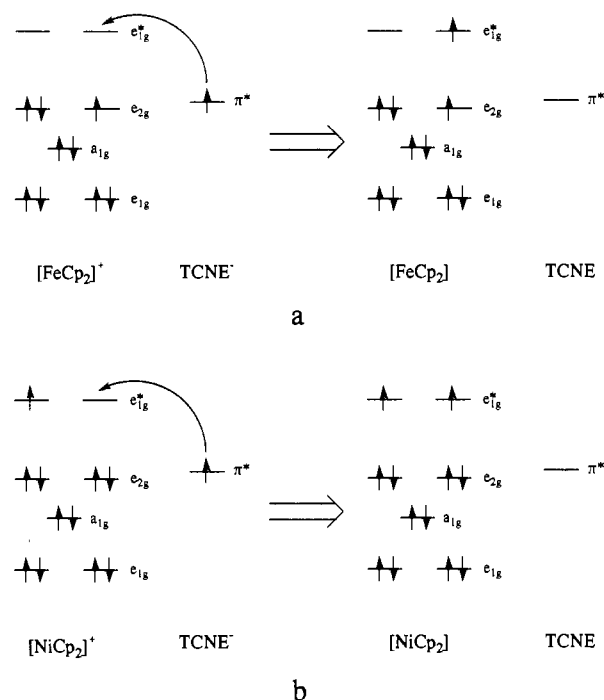
on the metal, there is a direct spin delocalization to the Cp ligand which results in a positive spin density of Cp. The usual Heitler–London spin exchange therefore yields antiferromagnetic coupling, as is observed experimentally. Thus, the sign of the spin density on the Cp rings is crucial for the spin coupling. Negative and positive signs lead to ferromagnetic and antiferromagnetic couplings, respectively.

Now let us again consider the charge transfer back to the e_{1g}^* orbitals for the nickelocenium TCNE complex as shown in Figure 6b. A comparison to Scheme V shows us that this corresponds exactly to the situation envisaged by McConnell in his second mechanism. According to his argument, one should obtain ferromagnetic coupling contrary to the experimental observations! This supports our argument concerning the failure of this mechanism.

Conclusion

To what extent can the ideas presented in this Account help synthetic chemists in their search for molecular ferromagnets? The first strategy coming to mind to obtain a ferromagnetic interaction between two molecular units A and B is the orthogonality of the two SOMOs a and b. To our knowledge this has only been achieved by controlling the geometry through the use of bridges connecting the spin carriers.

The second approach consists of assembling the molecular units in such a way that a weak negative spin density on one unit interacts preferably with a large positive spin density on the neighboring unit. This approach is rather demanding for the synthetic chemist who must both design units with regions of negative spin density and then assemble these units in a proper fashion. Negative spin density is found in quite a few species, like alternant hydrocarbons, or transition metal compounds where the unpaired electrons occupy non-

bonding metal orbitals. In this latter case, the interaction between the ground configuration and excited configurations in which an electron has been transferred from a low-lying metal–ligand bonding orbital toward a high-lying metal–ligand antibonding orbital induces a negative spin density on the ligands, which is not compensated by the positive spin density due to spin delocalization. In addition to the metallocenium cations with M = Cr, Mn, and Fe that we have already discussed, any octahedral low-spin complex of configuration d^n, $n \leq 5$, might show such a negative spin density in the ligand σ orbitals.

Until now, the most thoroughly explored idea to favor a ferromagnetic interaction is the coupling between ground and A → B (or B → A) charge-transfer configurations. An essential result arising from this work is that *most often charge transfer favors anti-ferromagnetic interaction, even when the state of lowest energy arising from the charge-transfer excited state is high-spin.* There is, however, one type of charge transfer which may favor ferromagnetic interaction, namely, the transfer of an electron from the SOMO of one unit to an empty orbital of the other (or, which, is strictly equivalent, from a doubly occupied orbital of one unit to the SOMO of the other). The stabilization of the high-spin state, however, is 1 order of magnitude smaller than the stabilization of the low-spin state due to SOMO–SOMO charge transfer. It is only in the case

in which the overlap integral between the SOMOs is negligible that this charge transfer involving an excited local configuration might determine the nature of the interaction.

What is important to stress is that the strategies based on the stabilization of the ferromagnetic state through a coupling with a charge-transfer high-spin excited state might not be as efficient as it has been assumed by many synthetic chemists so far. In order for such an approach to lead to ferromagnetic interactions, some severe requirements must be fulfilled, which seems to be difficult to control. On the other hand, the orbital approaches based on the orthogonality of orbitals on the one hand and on the spin polarization effect on the other hand might be easier to achieve. This second approach is particularly attractive. Indeed, it respects the strong tendency of nature to favor local spin interactions of the up–down type.

To conclude, we would also like to stress that the through-space interactions on which we have focused in this Account are generally weak except when p atomic orbitals belonging to adjacent molecules point to each other. A way to increase the interaction is by linking the molecular units by closed-shell bridges. Such an approach also allows one to control the relative orientations of the units and therefore to impose the relative symmetries of the interacting orbitals.