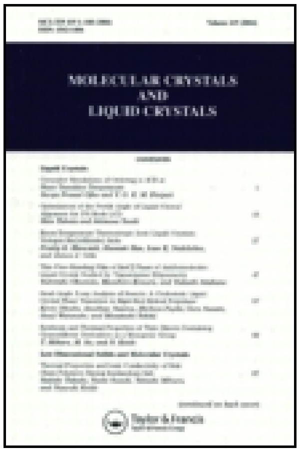

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Orbital Interaction Analysis of McConnell's Model for Through-Space Magnetic Coupling

Kazunari Yoshizawa [a] [b] [c] , Tokio Yamabe [a] [b] [c] & Roald Hoffmann [a] [b] [c]

[a] Department of Molecular Engineering, Kyoto University, Sakyo-ku, Kyoto, 606-01, Japan

[b] Institute for Fundamental Chemistry, 34-4 Takano-Nishihiraki-cho, Sakyo-ku, Kyoto, 606, Japan

[c] Department of Chemistry, Cornell University, Ithaca, New York, 14853-1301, U.S.A.

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ORBITAL INTERACTION ANALYSIS OF McCONNELL'S MODEL FOR THROUGH-SPACE MAGNETIC COUPLING

KAZUNARI YOSHIZAWA, TOKIO YAMABE, and ROALD HOFFMANN
Department of Molecular Engineering, Kyoto University, Sakyo-ku, Kyoto 606-01, Japan, Institute for Fundamental Chemistry, 34-4 Takano-Nishihiraki-cho, Sakyo-ku, Kyoto 606, Japan, and Department of Chemistry, Cornell University, Ithaca, New York 14853-1301, U.S.A.

Abstract McConnell's model for through-space magnetic interaction can be interpreted from the vantage point of molecular orbital interactions. Intermolecular magnetic interactions are analyzed in several stacking modes of diphenylmethyl radical. The nodal properties which lead to the overlap (or lack of it) of the singly occupied molecular orbitals in this system play an essential role in the ferromagnetic coupling of molecules in extended systems. These nodal characteristics, and the overlaps governing orbital interaction are as important as the spin-polarization effects.

INTRODUCTION

Since the 1960s there has been much interest in the design and characterization of ferromagnetic materials based on extended arrays of molecules and macromolecules.[1-7] Observations of ferromagnetism in several nitroxide crystals is of great interest.[8-10] Although the relationship between *intra*molecular magnetic interactions in organic materials and molecular topology is well understood,[11-15] it is difficult to control magnetic interactions through the bulk. In 1963 McConnell[16] suggested that the exchange interaction between two aromatic radicals could be approximated by the following Heisenberg-type Hamiltonian

$$H^{AB} = -\sum_{i,j} J_{ij}^{AB} S_i^A \cdot S_j^B = -S^A \cdot S^B \sum_{i,j} J_{ij}^{AB} \rho_i^A \rho_j^B \tag{1}$$

where J_{ij}^{AB} is the exchange integral between atom i of molecule A and atom j of molecule B; S_i^A is the electron spin density on atom i of molecule A, and S_j^B is that on atom j of molecule B; S^A and S^B are the total spin operators for A and B; ρ_i^A and ρ_j^B are the spin densities on atom i of molecule A and atom j of molecule B, respectively.

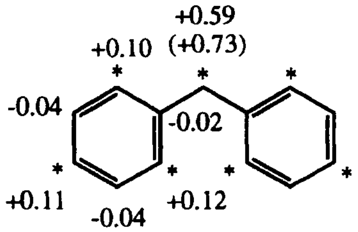
Since J_{ij}^{AB} (evaluated in the context of valence bond theory) is usually negative, the effective exchange interaction between two radicals can be ferromagnetic if the spin-density product $\rho_i^A \rho_j^B$ $(i \neq j)$ is negative. Since in certain organic radicals there exist alternating large positive and negative spin densities, these radicals can in principle be ferromagnetically coupled through the exchange interaction between atoms of positive spin density and those of negative spin density.

The applicability of McConnell's first model of magnetic interaction through space was nicely confirmed by Iwamura et al.[3,17] for the case of diphenylmethylenes with a [2,2]paracyclophane-type structure. Molecular orbital (MO) calculations have also been carried out for these and related systems. Yamaguchi et al.[18] showed that the effective exchange integral is positive for the *ortho*- and *para*-stacking modes of phenylmethylenes, while it is negative for the *geminal*- and *meta*-stacking modes. Buchachenko[19] showed that the effective exchange integral is positive when the methyl radical is aligned with the central carbon of an allyl radical. In addition to these calculations, important analytical studies of McConnell's first[16] and second[20] models for magnetic interaction have been published by Kollmar and Kahn.[21]

The purpose of this paper is to demonstrate that McConnell's first model of magnetic interaction through space may be easily interpreted on the basis of MO interactions. There are important orbital interactions behind McConnell's first model. In this paper, our previous work[22] is reviewed and new calculational results are also presented.

MAGNETIC COUPLING BETWEEN OPEN-SHELL MOLECULES

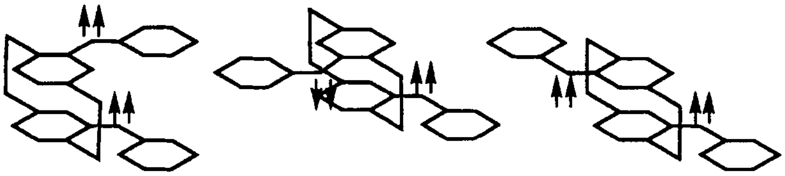
Let us first look at the intermolecular magnetic coupling between two open-shell molecules such as diphenylmethylene. It has large positive spin density on the central carbon and alternating positive and negative spin densities on the two phenyl rings,[3] as indicated in **1**.



1

The σ-spin density at the divalent carbon is shown in parentheses.

Let us look at several stacking modes of two diphenylmethylene radicals, following Iwamura's work.[3,17] In each, one phenyl ring of one radical is in π-contact with its neighbor, but differing in the relative orientations of the remainder of the molecule. The disposition of neighbors in this model is governed by a rotational angle θ defined in **2**. Ferromagnetic coupling can appear if the stacking angle θ is 60° and 180°, while antiferromagnetic coupling is likely for $\theta = 0°$ (not shown here) and 120°. From the spin polarization indicated in **1**, we find that two radicals can be ferromagnetically coupled when starred atoms of one molecule are interacted with unstarred atoms of another molecule.



2

McConnell's first model is clearly based on the spin-polarization of π-electrons. The importance of spin polarization was stressed in a careful analysis of the zero-field splittings of triplet trimethylenemethane by McConnell himself.[23] A recent study by Zheludev et al.[24] showed that the density functional method can predict well the experimentally determined (though small) negative spin density at the unstarred atoms. In this way the spin-polarization mechanism provides us with a useful strategy for predicting intra- and intermolecular magnetic coupling.

ORBITAL INTERACTIONS IN MAGNETIC COUPLING

Having described McConnell's first model phenomenologically, let us now consider intermolecular magnetic coupling in organic molecular assemblies in terms of orbital interaction. Suppose one has two singly occupied molecular orbitals (SOMOs) a and b, which interact weakly. The well-known Heitler-London-type singlet and triplet wave functions are written in the form of Eq. (2)

$$^{1}\Psi = \frac{a(1)b(2)+b(1)a(2)}{\sqrt{2+2S_{ab}^{2}}}\frac{1}{\sqrt{2}}\{\alpha(1)\beta(2)-\beta(1)\alpha(2)\}$$

$$^{3}\Psi = \frac{a(1)b(2)-b(1)a(2)}{\sqrt{2-2S_{ab}^{2}}}\begin{cases}\alpha(1)\alpha(2)\\ \dfrac{\alpha(1)\beta(2)+\beta(1)\alpha(2)}{\sqrt{2}}\\ \beta(1)\beta(2)\end{cases}, \tag{2}$$

where S_{ab} is the overlap between a and b. The triplet-singlet separation is

$$^{1}E-{}^{3}E = \frac{1}{1-S_{ab}^{4}}\left\{-2h_{aa}S_{ab}^{2}-2h_{bb}S_{ab}^{2}+4h_{ab}S_{ab}-2(aa|bb)S_{ab}^{2}+2(ab|ba)\right\}. \tag{3}$$

where

$$h_{ab} = \int a^{*}(1)h(1)b(1)d\tau(1),$$

and the Coulomb integral $(aa|bb)$ and exchange integral $(ab|ba)$ are

$$(aa|bb) = \iint a^{*}(1)a(1)\frac{1}{r_{12}}b^{*}(2)b(2)d\tau(1)d\tau(2)$$

$$(ab|ba) = \iint a^{*}(1)b(1)\frac{1}{r_{12}}b^{*}(2)a(2)d\tau(1)d\tau(2).$$

Since the intermolecular overlap S_{ab} is small,

$$^{1}E-{}^{3}E \cong -2(h_{aa}+h_{bb})S_{ab}^{2}+4h_{ab}S_{ab}-2(aa|bb)S_{ab}^{2}+2(ab|ba). \tag{4}$$

This equation provides us with the exchange constant (J) between two open-shell molecules A and B in the context of a Heisenberg-type Hamiltonian; triplet coupling ($J > 0$) is the necessary precondition for ferromagnetism. The first term in Eq. (4) is positive. On the other hand, the sign of the second term is minus in general. That term is also of the order S_{ab}^{2}, if we assume the Wolfsberg-Helmholz relation of Eq. (5).

$$h_{ab} = K S_{ab}(h_{aa}+h_{bb}). \tag{5}$$

Assuming the extended Hückel method's value of K (1.75), we obtain a very simple expression for the exchange constant between two open-shell molecules in terms of the SOMO-SOMO interactions

$$J \cong 5(h_{aa} + h_{bb})S_{ab}^2 - 2(aa|bb)S_{ab}^2 + 2(ab|ba) \tag{6}$$

This formulation is of course a result of neglecting ionic configurations, which may stabilize a singlet state in delocalized π-electronic systems, as discussed by Girerd et al.[25]

The first and second terms of Eq. (6) are typically negative, thus favoring antiferromagnetic interaction. The third term may lead to net ferromagnetic coupling. The sign of J ultimately depends on magnitudes of h_{aa}, h_{bb}, S_{ab}^2, $(aa|bb)$, and $(ab|ba)$. We think that one may control S_{ab}^2 most easily among these parameters, by considering the geometrical arrangement of molecules, and this will ultimately form the basis of our analysis.

The first consequence of the general expression we have derived is that the triplet state is stabilized when the overlap is small. If orbital overlap is large, inevitably a singlet state will be prevail. A precondition for effective ferromagnetic coupling between two open-shell molecules is to arrange the molecules in such a way that the two SOMOs are orthogonal or as nearly so as possible. Since organic molecules have at most $2p$ atomic orbitals, the detailed geometrical arrangement of the SOMOs is important for the cancellation of overlap.

Second, to achieve the situation of a triplet well below a singlet, it is essential that the interacting orbitals be noded, and arranged in very specific ways. It is best if the relevant orbitals are in same region of space (as in methylene and dioxygen), so as to maximize the exchange integral $(ab|ba)$. To put it simply, the SOMOs of two open-shell molecules must be highly overlapped, although their net overlap must cancel. Skillful control of geometry (assuming that control is in our hands) is needed to engineer this.

The general "two-electron-two-level" problem, in the context of stabilizing singlet states, has been discussed by one of us ealier.[26] If SOMO a of molecule A is degenerate with SOMO b of molecule B, the MOs after interaction defined in Eq. (7)

$$\begin{aligned} \varphi_+ &= (a+b)/\sqrt{2+2S_{ab}} \\ \varphi_- &= (a-b)/\sqrt{2-2S_{ab}}. \end{aligned} \tag{7}$$

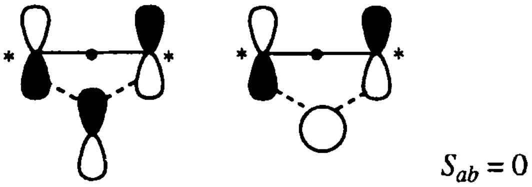
These MOs have first-order one-electron energies given by

$$\begin{aligned}\varepsilon_+ &= \varepsilon_0 + (H_{ab}' - \varepsilon_0 S_{ab}) \\ \varepsilon_- &= \varepsilon_0 - (H_{ab}' - \varepsilon_0 S_{ab}),\end{aligned} \tag{8}$$

where H_{ab}' is the perturbation matrix element, approximately proportional to the overlap in general. H_{ab}' has the opposite sign to the overlap; that is, H_{ab}' is negative for positive S_{ab}, positive for negative S_{ab}.[26] This of course means that positive overlap implies stabilization or bonding. We can choose as a primary measure of orbital interaction the energy splitting between two orbitals after interaction compared with that before interaction. When S_{ab} is zero or nearly zero, however, ε_+ and ε_- are degenerate even after interaction; therefore the triplet state can lie below the singlet state, as Hund's rule implies.

ORBITAL INTERACTION ANALYSIS OF McCONNELL'S MODEL

The important triplet state of the methylene has one electron in the conjugated π-system, just as the diphenylmethyl radical. The methylenes also may be imagined to stack; several kinds of stacking modes of two diphenylmethyl radicals are thus also good models for the experiments of Iwamura et al.[3,17] The SOMOs of odd-numbered alternant hydrocarbons are, within the Hückel MO theory, nonbonding MOs (NBMOs) with energy α, corresponding to the energy of the atomic orbital (AO) of an isolated carbon atom. The most interesting property of the NBMO is that the NBMO coefficients at all the unstarred positions are zero; thus in the NBMO there are nodes at all the unstarred positions. To put it in another way, the signs of the coefficients at the starred positions flanking both sides of every unstarred position are always plus and minus, respectively. This can lead to the cancellation of partial orbital overlaps, as indicated in **3**.



3

Now we consider the orbital interactions between two diphenylmethyl radicals. The amplitude of the Hückel SOMO of diphenylmethyl radical is, of course, largest at the central carbon and smaller at the alternate starred carbons on the two benzene rings. Two types of antiferromagnetic couplings between the SOMOs are illustrated in Figure 1. In these the wave functions φ_+ and φ_- are stabilized and destabilized, respectively. For a stacking rotation angle of $\theta = 0°$ the overlap is complete, especially at the central carbons. Therefore the energy splitting at $\theta = 0°$ should be larger than that at $\theta = 120°$.

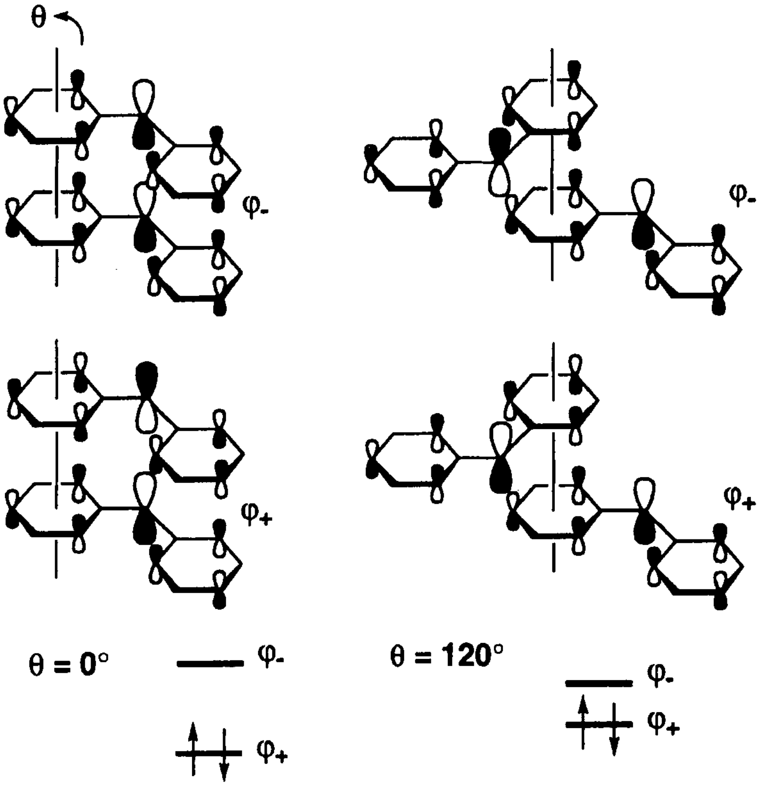


FIGURE 1. Orbital interactions in the magnetic coupling of diphenylmethyl radicals for $\theta = 0$ and 120°.

On the other hand, ferromagnetic coupling is favored at $\theta = 60°$ and 180° (as shown in Figure 2), for at these θ φ_+ and φ_- are nearly degenerate. We see again that the partial overlaps are almost canceled in these stacking modes, due to the nodal structure of the SOMO. Thus control of molecular arrangement is important for creating ferromagnetic intermolecular coupling.

In the Hückel SOMO of diphenylmethyl $|c_c| = 2|c_p|$, where $|c_c|$ is the absolute value of orbital coefficient on the central carbon and $|c_p|$ is those on the two phenyl rings. Thus, the partial orbital overlaps between intermolecular nearest neighbor sites are nearly completely canceled, like the zero overlap in **3**.

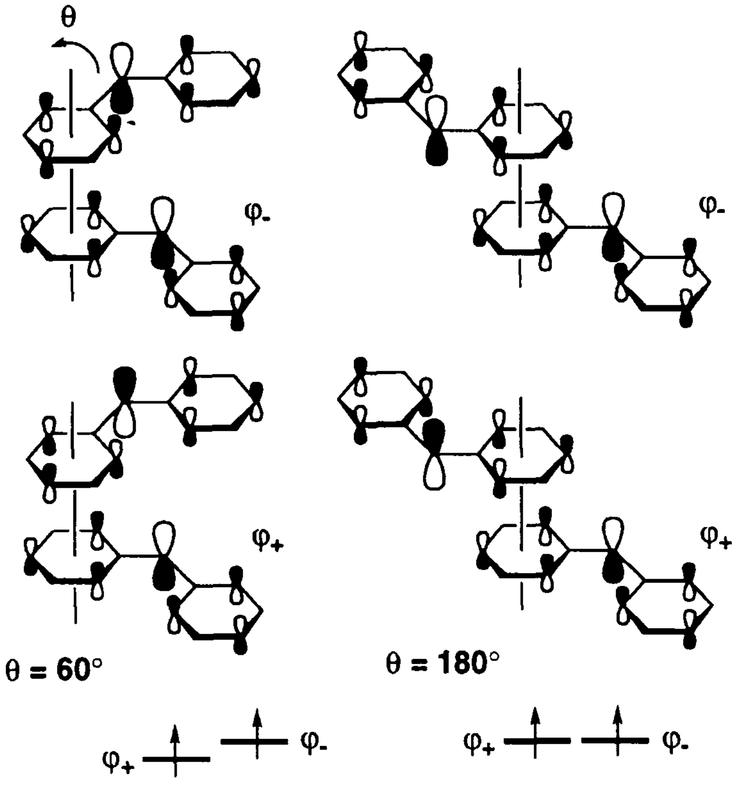


FIGURE 2. Orbital interactions in the magnetic coupling of diphenylmethyl radicals for $\theta = 60$ and 180°.

A Walsh-type diagram for energy of the frontier orbitals of the diphenylmethyl dimer is shown in Figure 3, as a function of rotation angle θ. The distance between the stacked benzene rings is assumed as 2.5 Å in this dimer model. As clearly seen from this diagram, the energies of the HOMO and LUMO are largely dependent on θ. When $\theta = 0$, the HOMO and LUMO are split substantially in energy because the SOMO-SOMO overlap is large, as shown in Figure 1 (left). Therefore we can expect that the singlet state is well below the corresponding triplet state in this stacking mode. On the other hand, when θ is nearly equal to 50 and 160°, the HOMO-LUMO gap is extremely small, so that ferromagnetic coupling can appear in these stacking modes. When $\theta = 120°$, the HOMO-LUMO gap is not small. Thus this configuration is likely to favor an antiferromagnetic interaction.

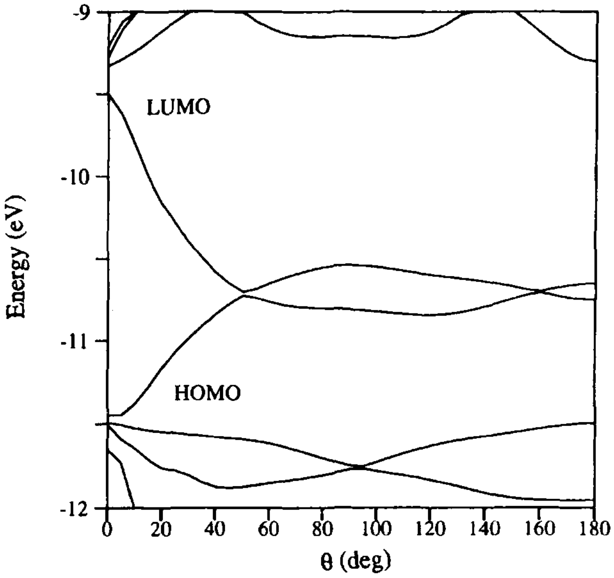


FIGURE 3. Walsh-type diagram for the frontier orbitals of diphenylmethyl dimer as a function of θ.

The essence of these calculational results can be derived easily from orbital interactions between the SOMOs of diphenylmethyl, as shown in Figures 1 and 2. Thus, our qualitative analysis is consistent with the prediction from McConnell's model of through-space magnetic interaction. We think that the well-known spin-polarization mechanism and our orbital interaction analysis are complementary viewpoints in the analysis of magnetic coupling of molecules.

SUMMARY

This paper has been concerned with the qualitative MO analysis of ferromagnetic coupling in molecular assemblies, especially in diphenylmethyl. We have demonstrated that McConnell's model of through-space magnetic interaction, based on spin-polarization, may also be interpreted from a starting point of specific SOMO-SOMO interactions. The nodal properties of the SOMOs are essential for the cancellation of partial overlaps, creating the necessary preconditions for maximizing ferromagnetic intermolecular coupling. We think that the concept of zero or minimal overlap between the SOMOs should play a more fundamental role in the optimization of ferromagnetism. The well-known spin-polarization mechanism and our orbital interaction analysis are complementary viewpoints in the analysis of magnetic coupling of molecules. For realization of higher Curie temperature in molecular systems, the SOMOs must be highly overlapped in space to increase exchange interactions, while their net overlap must be nearly zero. To achieve and optimize interesting magnetic properties one must control the geometrical arrangement of molecules by introducing appropriate substituents, taking proper cognizance of the nodal properties of the SOMOs.

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