

The Role of Orbital Interactions in Determining Ferromagnetic Coupling in Organic Molecular Assemblies

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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 allyl, diphenylmethyl, and nitroxide radical systems. The nodal properties which lead to the overlap (or lack of it) of the singly occupied molecular orbitals in these systems 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, we argue, as the spin-polarization effects from electron correlation.

Introduction

Cooperative magnetic properties are traditionally and importantly exhibited by inorganic solids such as metals and alloys. Since the 1960s there has been much interest in the design and characterization of ferromagnetic materials based on extended arrays of molecules and macromolecules.^{1–6} Recent observations of bulk ferromagnetic properties in several nitroxide crystals^{7–10} and TDAE-C₆₀, where TDAE is tetrakis(dimethylamino)ethylene,^{11–14} are of great interest because these compounds are composed only of light elements such as H, C, N, and O.

Although the relationship between intramolecular magnetic interactions in organic materials and molecular topology is well understood,^{15–22} it is difficult to control magnetic interactions

through the bulk. In 1963 McConnell²³ suggested that the exchange interaction between two aromatic radicals could be approximated by the following Heisenberg-type Hamiltonian

$$H^{AB} = -\sum_{ij} J_{ij}^{AB} S_i^A S_j^B = -S^A \cdot S^B \sum_{ij} J_{ij}^{AB} \rho_i^A \rho_j^B \quad (1)$$

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 ; and 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.

In 1967 McConnell proposed a second model for ferromagnetic spin alignment.²⁴ Although our present study is mainly concerned with his first model, it is important to mention this model here. McConnell's second proposal is that if an ionic charge-transfer pair (D^+A^-) could be built with a donor molecule whose neutral ground state is a triplet, then the $D^+A^-D^+A^- \cdots$ array would show ferromagnetic interaction, due to mixing of the charge-transfer state with the ground state. This model has been extended in various ways by Breslow.²⁵

The applicability of McConnell's first model of magnetic interaction through space was nicely confirmed by Iwamura et

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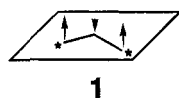
al.^{26,27} for the case of diphenylcarbenes with a [2.2]paracyclophane-type structure in 1985. Molecular orbital (MO) calculations have also been carried out for these and related systems. Thus Yamaguchi et al.²⁸ showed that the effective exchange integral is positive for the *ortho*- and *para*-stacking modes of phenylcarbenes, while it is negative for the *geminal*- and *meta*-stacking modes, and Buchachenko²⁹ showed that the effective exchange integral is positive when the methyl radical is aligned with the central carbon of an allyl radical. Crystal orbital calculations of one-dimensional chains of diphenylcarbene in various stacking modes were carried out by Tanaka et al.³⁰

In addition to these calculations, important detailed analytical studies of McConnell's first²³ and second^{24,25} models for magnetic interaction have been published by Kollmar and Kahn.³¹⁻³⁴ The role of the spin-polarization effect in McConnell's model has been stressed by these authors.²⁶⁻³⁴ Moreover, Kollmar and Kahn in their investigation of McConnell's second model showed that the singlet state may be stabilized, in contrast to McConnell's proposal, if higher-order charge-transfer mixing terms are taken into account. Another mechanism for effective spin interaction of organometallic charge-transfer ferromagnets has been discussed by Tchougreff.³⁵

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 study we place special emphasis on a qualitative understanding of the ferromagnetic interactions in organic molecular assemblies, not on the quality of the computation. We thus mainly use Hückel MOs, which capture the essence of the effect.

Magnetic Coupling between Two Open-Shell Molecules

Let us first look at the intermolecular magnetic coupling based on eq 1 between two open-shell molecules such as allyl and diphenylmethyl radicals. Allyl radical, an alternant hydrocarbon³⁶ (where the conjugated atoms are alternately labeled as "starred" and "unstarred", such that no two atoms of the same label are directly linked), is a classic spin-polarized system. As indicated in 1, in this radical there are substantial positive spin



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densities on the terminal starred carbons and small negative spin density on the central unstarred carbon. The length of the arrows is just an iconic representation of the magnitude of the density. This has been known for some time and is due to the spin-polarization effect.

Now imagine a stack of allyl radicals. We assume a typical π -stacking "geometry" with the radicals in roughly parallel planes. The three configurations shown in Figure 1 indicate approximately the topological range of contact geometries

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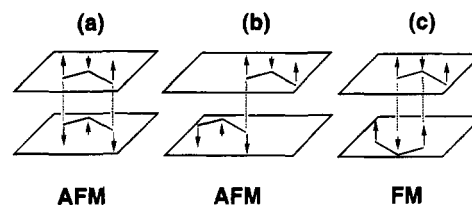


Figure 1. Ferromagnetic (FM) and antiferromagnetic (AFM) couplings of two allyl radicals based on a spin-polarization mechanism.

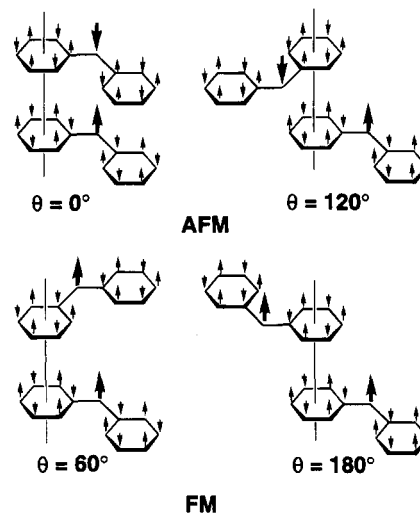
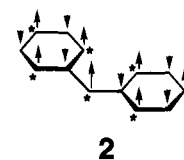


Figure 2. Ferromagnetic (FM) and antiferromagnetic (AFM) couplings of two diphenylmethyl radicals based on a spin-polarization mechanism.

through singling out a pair of neighbor radicals. We see from Figure 1 that ferromagnetic coupling should appear when the large positive spin density on the atom of one molecule is coupled with the small negative spin density on the atom of another molecule, *i.e.*, coupling mode (c). To put it another way, if starred atoms of one molecule are interacted with unstarred atoms of another molecule, the coupling between two radicals can be ferromagnetic. In the other cases, (a) and (b), McConnell's model indicates antiferromagnetic coupling.

Diphenylmethyl is another interesting radical,³⁷ with the spin distribution shown in 2. It has large positive spin density on



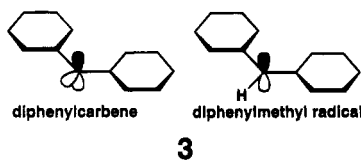
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the central carbon and alternating positive and negative spin densities on the two phenyl rings. The real molecular structure does not have the phenyl rings coplanar with the central carbons, for steric reasons, so the planar system we discuss here serves just as a theoretical model.

Let us assume several stacking modes of two diphenylmethyl radicals. 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 Figure 2. Ferromagnetic coupling can appear if the stacking angle θ is 60° and 180° , while antiferromagnetic coupling is likely for $\theta = 0^\circ$ and 120° . Also in these geometries, we find that two radicals can be ferromagnetically coupled when starred atoms of one molecule are interacted with unstarred atoms of another molecule.

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The π -electronic structure of diphenylcarbene is very much like that of diphenylmethyl, as indicated in **3**. Again, we assume



the phenyl rings are coplanar with the carbene center; they are actually kept nearly so in the paracyclophanes for which this carbene is a model. The important triplet state of the carbene has one electron in the conjugated π -system, just as the diphenylmethyl radical. The carbenes also may be imagined to stack; the four kinds of stacking modes of two diphenylmethyl radicals shown in Figure 2 are thus also good models for the experiments of Iwamura et al.^{26,27}

As indicated above, 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.³⁸ Dowd³⁹ confirmed this effect and observed large ESR proton splittings related to the negative spin density on the central carbon of trimethylenemethane. Ramasesha and Soos⁴⁰ successfully evaluated negative spin densities using diagrammatic valence bond theory. A recent study by Zheludev et al.⁴¹ 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 Intermolecular Ferromagnetic 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 functions⁴² are written in the form of eq 2

$$\begin{aligned}
 {}^1\Psi &= \frac{a(1)b(2) + b(1)a(2)}{\sqrt{2 + 2S_{ab}^2}} \frac{1}{\sqrt{2}} \{ \alpha(1)\beta(2) - \beta(1)\alpha(2) \} \\
 {}^3\Psi &= \frac{a(1)b(2) - b(1)a(2)}{\sqrt{2 - 2S_{ab}^2}} \begin{cases} \alpha(1)\alpha(2) \\ (1/\sqrt{2})(\alpha(1)\beta(2) + \beta(1)\alpha(2)) \\ 2\beta(1)\beta(2) \end{cases} \quad (2)
 \end{aligned}$$

where S_{ab} is the overlap between a and b . The corresponding total energies are

$${}^1E = \{h_{aa} + h_{bb} + 2S_{ab}h_{ab} + (aa|bb) + (ab|ba)\}/(1 + S_{ab}^2)$$

$${}^3E = \{h_{aa} + h_{bb} - 2S_{ab}h_{ab} + (aa|bb) - (ab|ba)\}/(1 - S_{ab}^2) \quad (3)$$

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

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

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

The triplet-singlet separation is then

$$\begin{aligned}
 {}^1E - {}^3E &= \frac{1}{1 - S_{ab}^4} \{ -2h_{aa}S_{ab}^2 - 2h_{bb}S_{ab}^2 + 4h_{ab}S_{ab} - \\
 &\quad 2(aa|bb)S_{ab}^2 + 2(ab|ba) \} \quad (4)
 \end{aligned}$$

Since the intermolecular overlap S_{ab} is small

$${}^1E - {}^3E \approx -2(h_{aa} + h_{bb})S_{ab}^2 + 4h_{ab}S_{ab} - 2(aa|bb)S_{ab}^2 + 2(ab|ba) \quad (5)$$

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 5 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 6.

$$h_{ab} = KS_{ab}(h_{aa} + h_{bb}) \quad (6)$$

K is an adjustable parameter; within the widely used extended Hückel theory⁴³ this expression has found some success, with K typically 1.75. Assuming the extended Hückel method's value of K , we obtain a very simple expression for the exchange constant between two open-shell molecules in terms of the SOMO-SOMO interactions

$$J \approx 5(h_{aa} + h_{bb})S_{ab}^2 - 2(aa|bb)S_{ab}^2 + 2(ab|ba) \quad (7)$$

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.⁴⁴ However, the contribution of ionic configurations seems small in intermolecular interactions, as suggested in several treatments of the hydrogen molecules.⁴⁵

The first and second terms of eq 7 are typically negative, thus favoring antiferromagnetic interaction. The third term may lead to net ferromagnetic coupling. The sign of J ultimately depends on the 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 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

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so as possible. In traditional inorganic magnets, the nodal properties of d or f atomic orbitals would lead to the cancellation of overlap in their crystals. 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,⁴⁶ and arranged in very specific ways. It is best if the relevant orbitals are in the same region of space (as in a carbene), 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. 1s-type wave functions cannot lead to a triplet state below a singlet state, because they have no nodes.⁴⁷

The general "two-electron two-level" problem, in the context of stabilizing singlet states, has been discussed by one of us earlier.⁴⁸⁻⁵³ If SOMO *a* of molecule A is degenerate with SOMO *b* of molecule B, the MOs after interaction are defined in eq 8

$$\begin{aligned}\varphi_+ &= (a + b)/\sqrt{2 + 2S_{ab}} \\ \varphi_- &= (a - b)/\sqrt{2 - 2S_{ab}}\end{aligned}\quad (8)$$

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

$$\begin{aligned}\epsilon_+ &= \epsilon_0 + (H_{ab}' - \epsilon_0 S_{ab}) \\ \epsilon_- &= \epsilon_0 - (H_{ab}' - \epsilon_0 S_{ab})\end{aligned}\quad (9)$$

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} and positive for negative S_{ab} .⁵² 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.⁵² 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.⁵⁴ A discussion of the singlet-triplet splitting on the basis of a localized MO picture has been given in ref 55.

The SOMOs of odd-numbered alternant hydrocarbons are, within the Hückel MO theory, nonbonding MOs (NBMOs)³⁶ 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

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(47) The triplet state of the H₂ molecule has a very small potential minimum at about $R = 8$ au, due to van der Waals interactions. See: (a) Hirschfelder, J. O.; Linnert, J. W. *J. Chem. Phys.* **1950**, *18*, 130. (b) Kolos, W.; Wolniewicz, L. *J. Chem. Phys.* **1965**, *43*, 2429.

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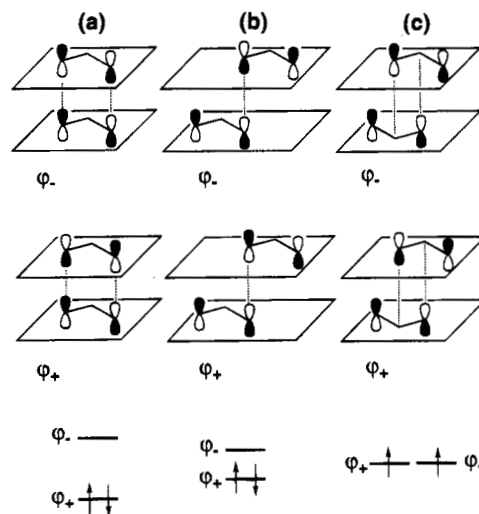


Figure 3. Orbital interactions in the magnetic coupling of two allyl radicals.

leads to interesting intermolecular magnetic coupling, as described below.

Let us first look at the orbital interactions between two allyl radicals. Figure 3 shows the three types of stacking modes between the two SOMOs of allyl radicals *a* and *b*. φ_+ and φ_- signify respectively the bonding and antibonding combinations between the two SOMOs after interaction. In stacking modes (a) and (b), the overlap is not zero; therefore the wave function φ_+ is stabilized and φ_- is destabilized. We can gauge the energy splitting between the two orbitals after interaction on the basis of the orbital phases or orbital coefficients; since the two SOMOs are maximally overlapping in mode (a), while their overlap is small in (b), the energy splitting should be larger in (a), as shown in Figure 3. Under certain specific symmetry conditions (in a spiro system) there may also occur other small through-space interactions between allyls.⁴⁸

On the other hand, in stacking mode (c) (see Figure 3) the overlap between the two SOMOs almost vanishes, at least in the Hückel approximation. A semiquantitative discussion of the orbital orthogonality will be given below. We see that the node on the central carbon in the SOMO of the allyl radical plays an important role in the cancellation of the partial overlaps in this stacking mode. The energy splitting after interaction is therefore nearly zero. As a result the triplet state should lie below the corresponding singlet state, following Hund's rule.⁵⁴

Next we consider the orbital interactions between two diphenylmethyl radicals, a more realistic model for the experiments of Iwamura et al.^{26,27} The amplitude of the Hückel SOMO of the 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 4. In these the wave functions φ_+ and φ_- are stabilized and destabilized, respectively. For a stacking rotation angle of $\theta = 0^\circ$ the overlap is complete, especially at the central carbons. Therefore the energy splitting at $\theta = 0^\circ$ should be larger than that at $\theta = 120^\circ$.

On the other hand, ferromagnetic coupling is favored at $\theta = 60^\circ$ and 180° (as shown in Figure 5), 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.⁵⁶ Thus control of molecular arrangement is important for creating ferromagnetic intermolecular coupling.

(56) 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.

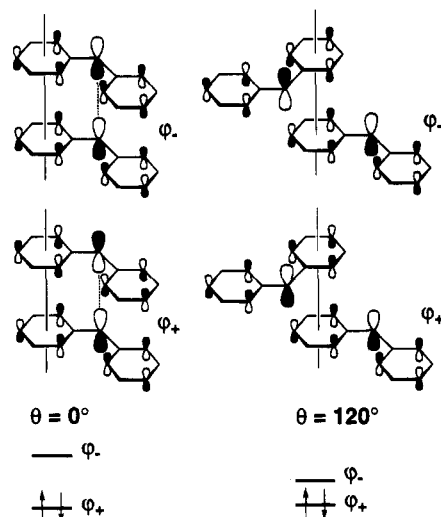


Figure 4. Orbital interactions in the magnetic coupling of diphenylmethyl radicals, for $\theta = 0$ and 120° .

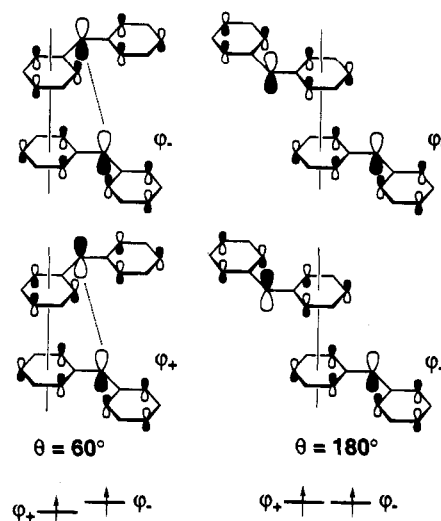


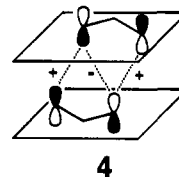
Figure 5. Orbital interactions in the magnetic coupling of diphenylmethyl radicals, for $\theta = 60$ and 180° .

The through-space interaction between the central carbons of both molecules cannot be entirely neglected at $\theta = 60^\circ$, as indicated in Figure 5. As a result there is some small bonding in the stacking mode at $\theta = 60^\circ$, and a consequent magnetic level splitting. The ideal ferromagnetic stacking in this case is for $\theta = 180^\circ$. In the stacking of diphenylcarbenes, the observed quartet-triplet splitting at $\theta = 180^\circ$ is 110 cm^{-1} , while that at $\theta = 60^\circ$ is reduced to 60 cm^{-1} .^{26,27} These experimental results can now be easily understood on the basis of our qualitative analysis of the orbital interactions.

As discussed above, a nearly orthogonal arrangement of SOMOs is important for achieving ferromagnetic coupling of open-shell molecules. It may be useful to define a measure of orthogonality through eq 10:

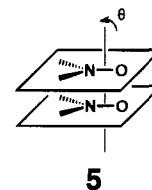
$$\gamma = \frac{|\sum_{\langle i,j \rangle} c_{1i} c_{2j} S|}{\sum_{\langle i,j \rangle} |c_{1i}| |c_{2j}| |S|} \quad (10)$$

where c_{1i} and c_{2j} are expansion coefficients of SOMO 1 and 2, respectively; $\langle i,j \rangle$ specifies nearest neighbor interactions; and S is the overlap integral, as indicated in 4. For example, in stacking mode (c) of allyl radicals (Figure 3), $\gamma = 1/3$. On the other hand, $\gamma = 1/5$ in the stacking mode for $\theta = 180^\circ$ of diphenylmethyl radicals (Figure 5). Consequently, the partial overlaps are more efficiently canceled in the latter stacking mode of diphenylmethyl radicals.

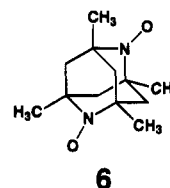


Although the two examples discussed above have dealt with pairs of identical open-shell molecules, such ferromagnetic intermolecular coupling is also possible between different odd-numbered alternant hydrocarbons. One example is the pair of perinaphthyl and benzyl radicals. Since the two SOMOs have the nonbonding energy α in the Hückel model, they are degenerate. The ferromagnetic coupling between these radicals, based on McConnell's first model and our orbital interaction model, is shown in Figure 6. We do not repeat the detailed analysis here, but the reader can see that the characteristic nodal properties of these SOMOs lead to zero overlap. Since the γ value is 0 in this pair, the orthogonality of the SOMOs is complete, within the framework of the Hückel method. Thanks are due to one of the reviewers of this paper for suggesting to us that the model also applies to a pair of different open-shell molecules.

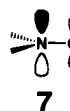
Finally let us consider the through-space magnetic coupling between two nitroxides, because several organic molecular ferromagnets composed of light elements have been realized in this system.⁷⁻¹⁰ There is a variety of potentially coupled orientations of nitroxides in discrete molecules or extended structures; perhaps it is easiest to define the extremes once again by a rotational angle θ , as in 5. Yamaguchi et al.⁵⁷ calculated



with the UHF-based Møller-Plesset perturbation method that the effective exchange integral is positive in the *anti* stacking mode ($\theta = 180^\circ$) whereas it is negative in the *syn* stacking mode ($\theta = 0^\circ$). Ferromagnetic coupling is realized in the *anti* stacking mode, consistent with the crystal structure of an adamantane-type dinitroxide ferromagnet **6**.⁹ Our orbital interaction analysis should explain why ferromagnetic coupling appears in the *anti* stacking mode of two nitroxides.



The characteristic feature of nitroxides is that the SOMO is an antibonding π^* , *i.e.*, the MO housing the odd electron has a node between nitrogen and oxygen, as indicated in 7. The



SOMO of nitroxide may be written as $c_N \chi_N - c_O \chi_O$, where χ_N and χ_O are 2p atomic orbitals of nitrogen and oxygen,

(57) Yamaguchi, K.; Okumura, M.; Maki, J.; Noro, T.; Namimoto, H.; Nakano, M.; Fueno, T.; Nakasuji, K. *Chem. Phys. Lett.* **1992**, *190*, 353.

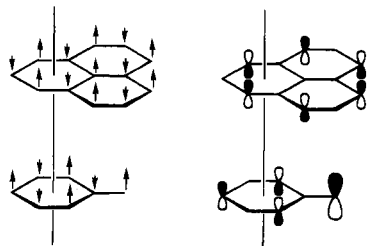


Figure 6. Ferromagnetic coupling between perinaphthyl and benzyl radicals, based on the spin-polarization and orbital-interaction mechanisms.

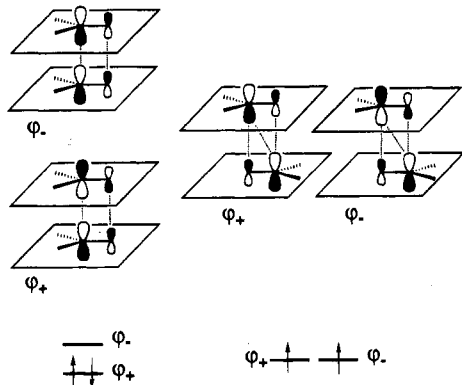


Figure 7. Orbital interactions in *syn* and *anti* stacking modes of nitroxides.

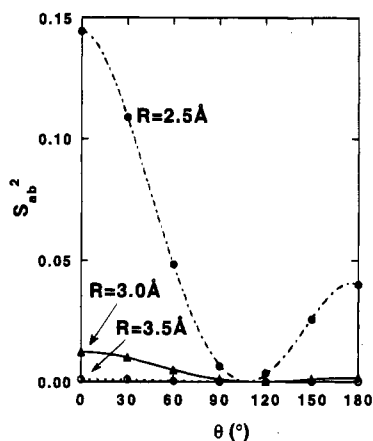


Figure 8. S_{ab}^2 of two nitroxides as a function of stacking rotation angle θ (degrees).

respectively, and c_N and c_O are positive orbital coefficients. Since oxygen is more electronegative than nitrogen, the π orbital is localized more on oxygen, and the π^* here relevant more on nitrogen. Thus in the π^* SOMO $c_N > c_O$.

Consider the two extremes of nitroxide stacking shown in Figure 7. Clearly, the overlap is large in the *syn* stacking mode, leading to a level splitting. The singlet state will be consequently stabilized, compared to the corresponding triplet state, in this geometry. On the other hand, the radical–radical overlap in the *anti* stacking mode has σ and π components in it; the “cross” N–N interactions (see Figure 7) cannot be neglected, since $c_N > c_O$. The N–N ($\sigma + \pi$) interactions are of opposite sign to two N–O (both σ) interactions; the net overlaps are likely to be small.

We may estimate the actual SOMO–SOMO overlaps by means of an FMO (fragment molecular orbital) analysis, based on the extended Hückel method.⁴³ Figure 8 shows the computed S_{ab}^2 of the SOMOs of two nitroxides as a function of stacking

angle θ . In fact the overlaps are very small in actual molecular crystals, in which individual molecules are separated by at least a typical π van der Waals contact of 3.05 Å. S_{ab}^2 is maximum at $\theta = 0^\circ$ (*syn* stacking) and minimum at $\theta = 110^\circ$. S_{ab}^2 at $\theta = 180^\circ$ (*anti* stacking) is about one-fourth of that in *syn* stacking, as expected from a qualitative MO analysis described above. Thus, the overlap becomes small in the *anti* stacking mode of two nitroxides, due to the nodal properties of the π^* SOMO. In the *syn* stacking mode, in contrast, it is large.

Ferromagnetic coupling has a chance of being realized in the *anti* stacking mode of nitroxides. It could be optimized still further, our considerations suggest, if one could engineer a stacking with θ near 110° . One might note that this type of magnetic interaction cannot be easily rationalized by McConnell’s model, because in the N–O bond there is no spin polarization, on which McConnell’s model is based.

As mentioned above, Rassat et al.⁹ prepared and characterized the adamantane-type dinitroxide *N,N'*-dioxo-1,3,5,7-tetramethyl-2,6-diazaadamantane (**5**), which shows the highest Curie temperature (1.48 K) known to date within the ferromagnetic nitroxide family. This molecule is nicely designed because the two nitroxides are arranged in such a way that they are orthogonal within a single molecule, producing triplet coupling. In addition to this *intramolecular* ferromagnetic coupling, two nitroxides are coupled in a nearly *anti* stacking mode between neighboring molecules. The four methyl groups attached to the adamantane skeleton shown in **5** lead to this ideal stacking mode in the crystal structure. Thus the interesting bulk magnetic properties of this material may be ascribed to both the *intra*- and *intermolecular* ferromagnetic couplings.

Summary

This paper has been concerned with the qualitative MO analysis of ferromagnetic coupling in molecular assemblies, especially in organic materials. 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. Hückel MOs can be easily derived and used in the synthetic and crystal design of molecular ferromagnets. 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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