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SEMIEMPIRICAL MOLECULAR ORBITAL (MO) CALCULATIONS OF THE EFFECTIVE EXCHANGE INTEGRALS FOR SANDWICH DIMERS OF FREE RADICAL SPECIES.
ANTI- AND FERROMAGNETIC SPIN COUPLINGS OF ORGANIC FREE RADICALS

Kizashi YAMAGUCHI,* Takayuki FUENO, Kazuhiro NAKASUJI,† and Ichiro MURATA†
Department of Chemistry, Faculty of Engineering Science, Osaka University,
Toyonaka, Osaka 560
†Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka 560

The effective exchange integrals (Jab) for magnetically coupled organic systems are divided into two different contributions, (i) orbital-overlap and (ii) spin-density-product terms. MO calculations have shown that the former term overweighs the latter in the case of free radical dimers, leading to the negative Jab values, a trend which is compatible with observations.

It has been known that the effective exchange interactions (Jab) between free radicals are negative in sign in many cases.[1-4] Therefore,free radical dimers and clusters usually have low-spin ground states, in contrast to the cyclophane-type carbene dimers[5] examined in Ref. 6. We here wish to consider the reason why the free radical dimers should generally have negative Jab values and to discuss the possibility of reversion in sign of their Jab values on the basis of the molecular orbital (MO) calculations.

The effective exchange integrals (Jab) calculated by the ab-initio GMO method[5] are here assumed to be divided into two different contributions as[7]

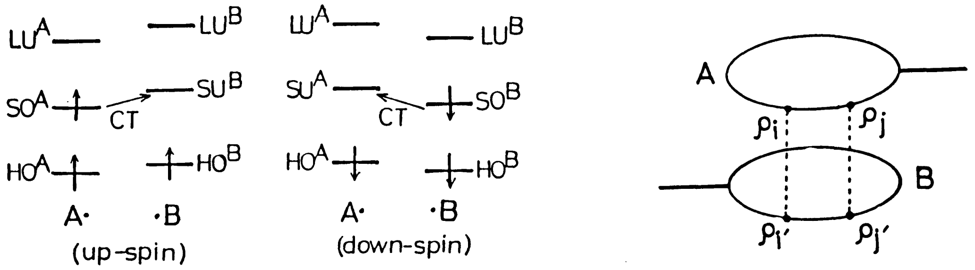
$$\mathrm{Jab} = \mathrm{Jab(OO)} + \mathrm{Jab(SDP)} \qquad (1)$$

where Jab(OO) and Jab(SDP) denote the orbital-overlap and spin-density-product (SDP) terms, respectively. Other terms such as the spin dipolar term were neglected. The orbital-overlap term is responsible for the electron delocalization as illustrated in Fig. 1A and is governed by the sum, S(OO), of orbital overlaps $<\phi_p|\phi_q>$ between the magnetic (radical) orbitals of radical components. For free radical dimers, it is approximately given by the UHF SOMO-SUMO orbital overlaps

$$\mathrm{Jab(OO)} = \sum_p^A \sum_q^B J_{pq}^{AB}(\mathrm{OO})<\phi_p^A|\phi_q^B>^2 \cong J(\mathrm{OO})S(\mathrm{OO}), \quad J(\mathrm{OO})=J_{\mathrm{SO-SU}}^{AB}, \qquad (2a)$$

$$S(\mathrm{OO}) = \{\sum_i C_{i,\mathrm{SO}}^A(\uparrow)C_{i,\mathrm{SU}}^B(\uparrow)\}^2 + \{\sum_i C_{i,\mathrm{SO}}^B(\downarrow)C_{i,\mathrm{SU}}^A(\downarrow)\}^2 \qquad (2b)$$

where $C_{i,p}(\uparrow)$ denotes the LCMO coefficient of orbital p for the up-spin. $J_{pq}^{AB}(\mathrm{OO})$ are regarded as the intermolecular orbital effective exchange constants, which are responsible for the transfer (resonance) integrals.[8] On the other hand, the SDP



(A) Charge-transfer interactions between the frontier orbitals of the up- and down-spins, which are responsible for the orbital-overlap term (Eq. 2).

(B) Spin densities (ρ_j) induced by the spin polarization effect, which are responsible for the spin-density-product (SDP) term (Eq. 3).

Fig. 1. Schematic illustration of the orbital-overlap and spin-density-product terms.

term is approximately given by the product S(SDP) of spin densities ρ_i^X (X=A or B) on the aromatic rings as illustrated in Fig. 1B[1])

$$Jab(SDP) = \sum_i^A \sum_j^B J_{ij}^{AB}(SDP)\, \rho_i^A \rho_j^B \cong J(SDP)S(SDP) , \tag{3a}$$

$$S(SDP) = \sum_{(i,i')} \rho_i^A \rho_{i'}^B , \quad J(SDP) = J_{ii'}^{AB}(SDP) \quad (i,i' : \text{paired}) \tag{3b}$$

where J_{ij}^{AB}(SDP) denote the effective exchange constants for the spin moments induced by the spin polarization effects.[8]) Both exchange integrals can be calculated using the LCAO coefficients for the magnetic orbitals and spin densities on the aromatic ring for component radicals A and B, provided the exchange constants J(OO) and J(SDP) are known. These constants were determined so that the present LCMO procedure can reproduce the values of Jab, already obtained in the preceding ab-initio GMO calculations for the para and meta cyclophane-type carbene dimers,[6]) which were 288.9 and -297.0 cm^{-1}), respectively. They have come out to be J(OO)= -37.7 and J(SDP)=-67.8 cm^{-1}. Incidentally, these constants, when combined with the S(OO) and S(SDP) values resulting from the STO-3G UHF treatment of phenylcarbene monomer, gave the Jab value of 289.6 cm^{-1} for the ortho carbene dimer,[6]) in line with the high-spin (quintet) ground state reported.[5]) This in turn supports the decomposition defined by Eq. 1.

Equations 1 to 3 are used here to calculate the effective exchange integrals

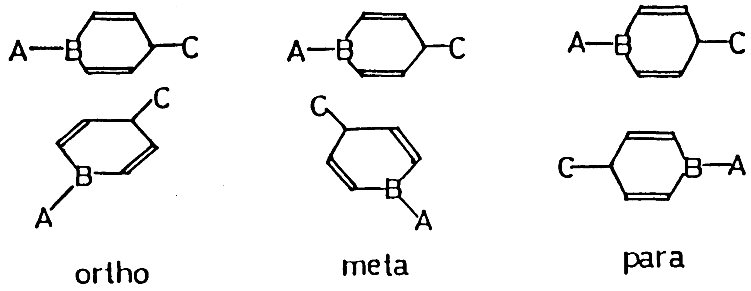


Fig. 2. Face-to-face dimers constructed of the free radicals shown in Fig. 3. Ortho, meta,and para denote the conformations of the face-to-face dimers examined.

for the face-to-face dimers of several free radicals. The three spatial arrangements, ortho, meta, and para, were examined for each dimer, as illustrated in Fig. 2. Five different types of free radicals I-V shown in Fig. 3 were considered as component radicals, for which the LCAO MO coefficients and spin densities were determined by the INDO method for the sake of computational economy. Table 1 summarizes the calculated results.

The data given in Table 1 reveal the following :

(1) The effective exchange integrals (Jab) for the free radical dimers are

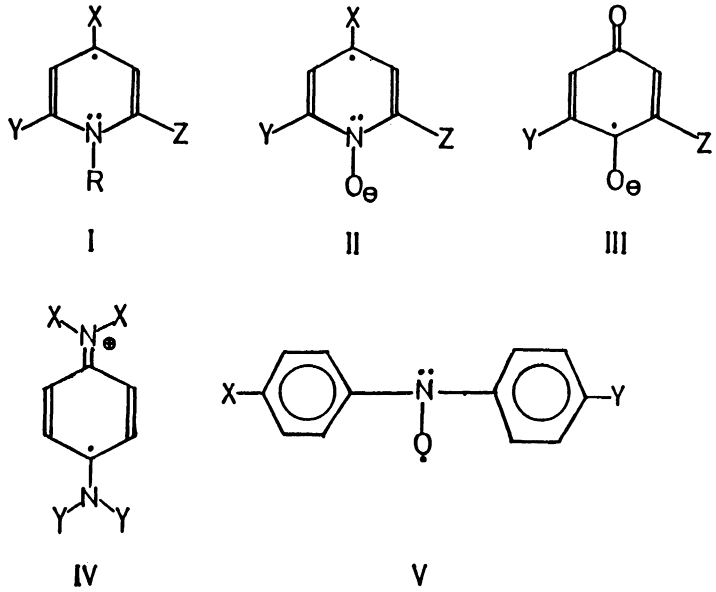


Fig. 3. **Free radical species (I-V) used to construct the face-to-face dimers in the ortho-, meta-, and para-type forms in Fig. 2. The interface distance was assumed to be 3.0 Å.**

Table 1. Orbital overlaps S(OO), spin density product S(SDP), and the effective exchange integrals for free radical dimers

System	R	X	Y	Z	ortho			meta			para		
					S(OO)	S(SDP)	Jab	S(OO)	S(SDP)	Jab	S(OO)	S(SDP)	Jab
Ia	H	H	H	H	0.447	-0.088	-10.9	0.353	0.150	-23.4	1.275	0.006	-48.4
Ib	H	CN	H	H	0.340	-0.059	-8.79	0.323	0.251	-29.1	1.176	0.036	-46.8
Ic	H	X[a)]	H	H	0.319	-0.033	-9.77	0.334	0.209	-26.8	1.169	0.071	-48.9
Id	Me	CN	CN	CN	0.321	-0.056	-8.31	0.193	0.180	-19.5	0.816	0.026	-32.5
Ie	Me	CN	NH_2	NH_2	0.339	-0.072	-7.83	0.285	0.229	-26.3	1.046	0.037	-41.9
IIa		CN	H	H	0.176	-0.074	-1.66	0.276	0.056	-14.2	0.994	0.163	-48.5
IIb		CN	CN	CN	0.313	0.062	-16.0	0.325	0.074	-17.2	1.246	0.423	-75.7
IIIa			H	H	0.029	-0.009	-0.48	0.028	-0.010	-0.38	0.596	0.029	-24.4
IIIb			CN	CN	0.014	-0.020	0.77	0.014	-0.015	0.48	0.501	0.036	-21.3
IIIc			NH_2	NH_2	0.045	-0.001	-1.66	0.032	-0.001	-1.12	0.529	0.013	-20.8
IVa			H	H	0.126	0.026	-6.51	0.125	0.026	-6.48	0.686	0.031	-28.0
Va			H	H	0.004	-0.007	0.32	0.009	0.007	-0.80	0.005	-0.007	0.27

a) X=$COOCH_3$.

negative in sign in the majority of cases, showing that the singlet state should generally be more stable as compared with the triplet state. This indicates that the antiferromagnetism should be observed for the free radical salts even if the magnetic orderings are truely accomplished.1-4)

(2) In meta and para dimers, both the orbital-overlap (Eq. 2a) and spin-density-product (Eq. 3b) terms tend to be negative in sign, thus favoring the singlet state concurrently.

(3) For most of the ortho dimers, the orbital overlap factor S(OO) is positive in sign while the spin density factor S(SDP) is negative. The contribution of the former factor to Jab overshadows that of the latter, so that the total effective exchange integrals Jab are mostly negative in sign.

(4) The MO overlap factors S(OO) for some of IIb and Va are nearly zero, while the spin-density-product factors S(SDP) are evidently negative in sign. The net effect is that the total effective exchange integrals Jab(SDP) is positive, indicating the possibility of the ferromagnetic spin coupling in the ground state.

The present MO calculations show that the effective exchange integrals (Jab) for free radical pairs are usually negative in sign, in agreement with the observations.1-4) This is primarily because the orbital-overlap terms outweigh the spin-density-product terms. The generalization now suggests that there may be two ways to reverse the sign of the Jab-values. (i) One is to reduce the orbital-overlap term by preventing the face-to-face orbital overlap between free radicals. This could be accomplished by changing crystal structures of free radical salts with the introduction of appropriate substituents.9) (ii) The other is to increase the contribution of the spin-density-product term by an enhancement of the spin polarization effect. One of such methods is to introduce other radical sites which can enhance the spin polarization of π-electrons. The triplet diphenyl carbene5) corresponds to this case. Similar enhancements are expected for the $n-\pi^*$ excited piperidine N-oxide (VI) and related species. In fact, the calculated Jab value for the para dimer of VI is 2.74 cm^{-1}, indicating the ferromagnetic spin coupling, while the Jab values for the anion radicals of piperidine N-oxides (II) are all negative as shown in Table 1.

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