On the Validity of the McConnell-I Model of Ferromagnetic Interactions: The [2.2]Paracyclophane Example

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A formal comparison between a rigorous implementation of a Heisenberg Hamiltonian model in a VB space with the McConnell-I model shows that the validity of the McConnell model rests upon a heuristic one-to-one correspondence between spin density products in the latter with the difference of the spin exchange density matrix elements in the former. Using a rigorous Heisenberg Hamiltonian, a numerical model computation of the singlet/quintet stability for pseudoortho, pseudometa, and pseudopara bis(phenylmethylenyl)-[2.2]paracyclophanes (modeled with the correponding singlet/triplet bis(methyl)[2.2]paracyclophanes) shows that the McConnell model makes the correct prediction of low and high spin stability only because the contributions from "closest contact" carbon atoms that are not directly aligned is rather small. In systems where the alignment is not perfect, this cancelation may not hold. The association between spin density products in the McConnell model with the difference of the spin exchange density matrix elements in the VB Heisenberg Hamiltonian is shown to be valid because the McConnell model correctly predicts the leading configuration terms in the VB expansion.

Introduction

The design of purely organic magnetic materials has been the subject of considerable recent research.[1] These materials require the presence of a persistent free radicals,[2] and the formation of crystals made of these radicals showing spontaneous magnetization below a certain critical temperature T_c. Many examples of such magnetic crystals are found in the family of the so-called α-nitronyl nitroxide radicals.[1,3] Some of them present bulk ferromagnetism, although up to now, only at low critical temperatures.

The fact that different crystal phases of the same radical give rise to different magnetic properties, suggests that molecular magnetism in a crystal is strongly related to the relative geometrical arrangement of the radicals within the crystal.[1] Thus, as a first step toward the rational design of purely organic magnetic materials with higher critical temperatures, one requires theories relating the magnetism with the crystal structure. Rational design could be founded on a model or a magnetostructural correlation, based on the observation of known structures. Once the geometrical arrangements of the molecules capable of producing ferromagnetic interactions are known, one has to learn how to control the presence of these arrangements in the packing of the crystal.

There are many models aimed at rationalizing magnetism-structure correlations and in current use.[1a,4] Many of these models are designed to explain the magnetism in polynuclear derivatives of transition metal compounds. This "through bond" magnetism was first rationalized in a qualitative form by the models of Anderson,[5] Kahn,[1b] and Hay−Thibeault−Hoffmann.[6] The latter two approaches give similar results and successfully predict the presence of ferro and antiferromagnetic interactions, and have been useful to establish qualitative magnetism-correlation relationships.[7] However, such approximations lack the electron correlation effects required to properly describe some of the properties of magnetic compounds, as those observed in dinuclear compounds made of different magnetic centers.[8] This has prompted to the development of more accurate approaches to these systems, aimed at the quantitative study of the magnetic properties. Such methods have been based on perturbation methods[9] and on configuration interaction methods such as the difference dedicated configuration interaction method.[10] The broken symmetry approach introduced by Noodleman, in the context of the density functional methodology,[11] also seems to give reasonable results in some cases.[12] Methods used to explain the high spin−low spin ordering of states in diradical molecules[13,14] are closely related.

Of particular interest are models[1,2,15−20] designed to explain the magnetism in purely organic molecular systems via the so-called "through-space" magnetism (to distinguish it from the previous "through bond" magnetism). The most widely used methods for magnetism in molecular crystals are based on the models proposed by McConnell (also known as McConnell-I[15] and -II[16] models or mechanisms). The McConnell-II mechanism is a charge-transfer model that was shown not to work in a detailed work by Kollmar and Kahn.[20] Thus, we will focus our attention in the first model.

The McConnell-I model is based on a Heisenberg spin Hamiltonian and predicts the presence of intermolecular ferromagnetic interactions only when short intermolecular contacts are found in the crystal between atoms i, j bearing considerable spin population $\rho_i\rho_j$ of opposite sign. Accordingly, the magnetic behavior of a given molecular crystal can be rationalized by

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computing the spin distribution on the atoms of its constituent molecules, a property available from experiment[2,21] or from theoretical computations.[21,22]

In spite of its popularity, the validity of the McConnell-I model has never been demonstrated in a rigorous theoretical way. Nevertheless, there is a good agreement between observed magnetism and the predictions of the McConnell theory, based upon accurate ab initio computations of spin densities for simple model systems.[23−24] The often quoted example is the singlet vs quintet stability of the pseudoortho, -meta, and -para [25] bis(phenylmethylenyl)[2.2]paracyclophane isomers. Here, the predicted singlet vs quintet stability of the linked dimers is in excellent agreement with the observed ESR experiments.

However, some experimental magnetostructural relationships are difficult to explain by a straightforward application of the McConnell-I model, raising doubts on its validity and range of applicability. In this paper, we show that one may derive a rigorous Heisenberg Hamiltonian in the context of a VB wave function. Comparison with the McConnell theory, shows that the product of the spin densities $\rho_i\rho_j$ of the two molecular fragments used in the McConnell theory must be taken in one-to-one correspondence with two electron exchange density matrix elements. A numerical computation on paracyclophane compounds with the rigorous Heisenberg Hamiltonian shows that this association has numerical validity. However, this correct agreement is partly "accidental" and leads to a conceptual interpretation that is not correct. As we shall demonstrate, high spin stability is associated with the fact that "closest contact" sites are always ferromagnetically coupled and that the "closest contact" sites for the singlet state must be more strongly ferromagnetically coupled than for the triplet state.

Theory

Heisenberg Hamiltonians. A general Heisenberg spin-exchange Hamiltonian can be written as follows

$$\hat{H}^{S} = Q - \sum_{i,j} J_{ij}(2\hat{\boldsymbol{S}}_i\cdot\hat{\boldsymbol{S}}_j + {}^{1}/_{2}\hat{I}_{ij}) \qquad (1)$$

where $\hat{\boldsymbol{S}}_i$ is the spin operator associated with the ith site, and $\hat{I}_{ij}$ is the identity spin operator. In the $\hat{H}^S$ operator defined in eq 1, the complexities of the wave function are absorbed into parameters Q and J_{ij} and one associates an electron with each site i [for a discussion see ref 26]. The expectation value of the spin scalar product $\langle 2\hat{\boldsymbol{S}}_i\cdot\hat{\boldsymbol{S}}_j\rangle$ is just $S(S+1) - {}^{3}/_{2}$. A two-electron example clarifies the meaning of eq 1. The expectation value of $\langle\hat{\boldsymbol{S}}_i\cdot\hat{\boldsymbol{S}}_j\rangle$ for singlet and triplet states gives $-{}^{3}/_{4}$ and $+{}^{1}/_{4}$. Therefore, from eq 1, for singlet and triplet two-electron states we have the familiar result

$$E^{S/T} = Q \pm J_{12} \qquad (2)$$

since for two electrons we have

$$-\langle(2\hat{\boldsymbol{S}}_i\cdot\hat{\boldsymbol{S}}_j + {}^{1}/_{2}\hat{I}_{ij})\rangle^{S/T} = \pm 1 \qquad (3)$$

In the application of Heisenberg Hamiltonians, the exchange coupling parameter J_{ij} is interpreted in terms of the electron distribution as the Heitler−London exchange

$$J_{ij} = [ij|ij] + 2s_{ij}\,\langle i|h|j\rangle \qquad (4)$$

where $[ij|ij]$ is the small positive two electron exchange energy, and $\langle i|h|j\rangle$ is dominated by the nuclear electron attraction being large and negative. Thus J_{ij} is negative in general. The quantity s_{ij} is the overlap of the orbitals i and j, so that J_{ij} becomes positive only when the orbital overlap becomes very small. Clearly, in making such an interpretation one is also associating an electron i on site i with an atomic orbital (AO) on center i.

At this stage one must stress the fact that eq 1 corresponds to a "model" with empirical parameters that reduces the problem of chemical binding to coupling of electron spins. There is no real physical coupling between the electron spins (except for relativistic terms which are assumed to be negligible). Thus the problem of constructing an ab initio quantum chemistry theory that yields such a model requires some careful consideration. Anderson[27a] was the first to recognize that Heisenberg Hamiltonians might be understood as effective Hamiltonians computed from an exact full CI Hamiltonian using a model space of neutral VB determinants formed from n electrons in n AO. The use of such spaces in quantum chemistry was first proposed in this context by the Toulouse School,[27] and we have successfully implemented a scheme[28] where the Q and J parameters are derived from CASSCF computations. Clearly, in a rigorous (i.e., faithful) implementation of eq 1 one must be able to associate an electron i on site i with an AO on center i. This implies that the orbitals are localized on atomic sites (i.e., localized AO). Further, $\hat{H}^S$ is only defined on a space of many electron functions spanned by a basis where the space part of all the configurations is the same and the configurations differ only in the spin part. This implies that the space on which $\hat{H}^S$ acts is the space of VB determinants where each spatial orbital occurs once (i.e., neutral VB determinants).

Now, we must write eq 1 in a form suitable for implementation in quantum chemistry. We assume that we have an orbital basis of AO that can be identified with sites i and j in eq 1. The second quantized form of eq 1 then takes the form

$$\hat{H}^{S} = Q - \sum_{i,j}^{N} J_{ij}\Big\langle i(1)\,j(2)\Big|\hat{\boldsymbol{S}}(1)\cdot\hat{\boldsymbol{S}}(2) + \frac{1}{4}\hat{I}(1,2)\Big|i(1)\,j(2)\Big\rangle a_i^{+}\,a_j^{+}a_ja_i \qquad (5)$$

where $i(1)$ and $j(2)$ are AO localized in sites i and j and a_i^{+},a_i are creation and annihilation operators. For practical purposes, the Hamiltonian 5 can be rewritten [see, for example, ref 28a] in terms of the standard generators $\hat{E}_{ij}^{\sigma\sigma} = a_{i\sigma}^{+}a_{j\sigma}$ of the unitary group $U(n)$ in the form where $\sigma = \alpha,\beta$

$$\hat{H}^{S} = Q + \sum_{i,j}^{M} J_{ij}\frac{1}{2}(\hat{E}_{ij}^{\alpha\alpha}\,\hat{E}_{ji}^{\beta\beta} + \hat{E}_{ij}^{\beta\beta}\,\hat{E}_{ji}^{\alpha\alpha} + [\hat{E}_{ij}^{\alpha\alpha}\,\hat{E}_{ji}^{\alpha\alpha} - \hat{E}_{ii}^{\alpha\alpha}] + [\hat{E}_{ij}^{\beta\beta}\,\hat{E}_{ji}^{\beta\beta} - \hat{E}_{ii}^{\beta\beta}]) \qquad (6)$$

Now eq 6 forms the basis of a quantum chemistry implementation of eq 1 since the expectation values of the bilinear forms in eq 6 are just standard two-particle density operators ("symbolic" density matrices) for a CI computation. It is also obvious that the operators in eq 6 only connect configurations where the space part of configurations is the same and the configurations differ only in the spin part. Thus, the Heisenberg Hamiltonian acts on the space of VB determinants where each spatial orbital occurs once. As we have demonstrated elsewhere,[28b] any full CI Hamiltonian can be projected onto such a space and a subset of the eigenvalues can be reproduced exactly. Therefore, the matrix representation of eq 6 on the space of neutral VB determinants forms a completely rigorous implementation of a Heisenberg Hamiltonian.

For subsequent comparison with the McConnell-I theory it is convenient to introduce the spin exchange density matrix P_{ij} [see ref 28c]. We can write the energy as the expectation value in the form

$$\langle \hat{H}^{\mathrm{S}} \rangle = Q + \sum J_{ij} P_{ij} \tag{7}$$

The exchange density matrix P_{ij} can in turn be written either as

$$P_{ij} = \left\langle -\left(2\hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j + \frac{1}{2}\hat{I}_{ij} \right) \right\rangle \tag{8}$$

or (for practical purposes) as

$$P_{ij} = \left\langle \frac{1}{2}(\hat{E}_{ij}^{\alpha\alpha}\,\hat{E}_{ji}^{\beta\beta} + \hat{E}_{ij}^{\beta\beta}\,\hat{E}_{ji}^{\alpha\alpha} + [\hat{E}_{ij}^{\alpha\alpha}\,\hat{E}_{ji}^{\alpha\alpha} - \hat{E}_{ij}^{\beta\beta}\,] + [\hat{E}_{ij}^{\beta\beta}\,\hat{E}_{ji}^{\beta\beta} - \hat{E}_{ii}^{\beta\beta}]) \right\rangle \tag{9}$$

Equation 9 is just a two-particle density matrix element [see, for example, ref 28a] that can be obtained from any CI computation. The exchange density must satisfy the relationship[29]

$$S(S+1) = -\frac{1}{4}N(N-4) - \sum_{i,j} P_{ij} \tag{10}$$

where N is the number of electrons.

This exchange density P_{ij} obtained from a computation using neutral VB determinants has a simple interpretation and is indicative of the nature of the spin coupling between electrons in orbitals i and j. Using a single configuration perfectly paired VB wave function (i.e., a Rumer function[30]), the P_{ij} have values $+1$ for paired spins coupled antiparallel to a singlet, -1 for two electrons coupled parallel to a triplet, and $-{}^1/_2$ for uncoupled spins (i.e., i and j belong to *different* "spin-paired" functions) [see perfect pairing formula in ref 30]. Of course, the P_{ij} computed from eq 9 will differ from these "ideal" values because of configuration interaction. Thus, from a numerical point of view, after configuration interaction, we cannot distinguish between "triplet coupled" and "uncoupled spins". Thus from this point onward we shall refer to positive P_{ij} as "singlet coupled" and negative P_{ij} as "triplet coupled". Since J_{ij} is usually negative, the negative P_{ij} (triplet or uncoupled electrons) are obviously associated with destabilizing interactions via eq 7.

McConnell's Heisenberg Hamiltonian. In 1963, McConnell[15] suggested that the magnetic interaction between two aromatic radicals A and B could be approximated by a Heisenberg Hamiltonian of the following form:

$$\hat{H}^{\mathrm{AB}} = -\sum_{i \in A, j \in B} J_{ij}^{\mathrm{AB}}\, \hat{\mathbf{S}}_i^{\mathrm{A}} \cdot \hat{\mathbf{S}}_j^{\mathrm{B}} \tag{11}$$

in which J_{ij}^{AB} are two-center exchange integrals, and $\hat{\mathbf{S}}_i^{\mathrm{A}} \cdot \hat{\mathbf{S}}_j^{\mathrm{B}}$ is the product of the spin operators on atoms i, j of fragments A and B. One can easily cast this Hamiltonian into the form of eq 5. Clearly, aside from the identity operator (corresponding to a change in the zero of the energy), this Hamiltonian neglects the intrafragment terms in eq 5. *Thus the first fundamental assumption in the McConnell-I theory is that the intrafragment contributions are the same for each state on which the Hamiltonian acts.*

However, the Hamiltonian corresponding to eq 11 has never been used in this form, but is replaced by an "ad hoc" simplification given as

$$\hat{H}^{\mathrm{AB}} = -\hat{\mathbf{S}}^{\mathrm{A}} \cdot \hat{\mathbf{S}}^{\mathrm{B}} \sum_{i \in A, j \in B} J_{ij}^{\mathrm{AB}}\, \rho_i^{\mathrm{A}}\, \rho_j^{\mathrm{B}} \tag{12}$$

in which J_{ij}^{AB} are two-center exchange integrals, and $\rho_i^{\mathrm{A}}, \rho_j^{\mathrm{B}}$ are spin densities on atoms i, j of fragments A and B. The $\hat{\mathbf{S}}^{\mathrm{A}}, \hat{\mathbf{S}}^{\mathrm{B}}$ are the total spin operators for fragments A, B, and the expectation value of the product is given by

$$\langle \hat{\mathbf{S}}^{\mathrm{A}} \cdot \hat{\mathbf{S}}^{\mathrm{B}} \rangle = \frac{1}{2}[S(S+1) - S_{\mathrm{A}}(S_{\mathrm{A}}+1) - S_{\mathrm{B}}(S_{\mathrm{B}}+1)] \tag{13}$$

At this stage it is important to stress that the Hamiltonian given in eq 12 acts only on a model space (usually two-dimensional) spanned by states of different spin multiplicity (e.g., a singlet and a triplet), and thus has only diagonal elements. Further, eq 12 is purely phenomenological. There is no systematic set of approximations that gives eq 12 from eq 11.

For a two-level many-electron problem (i.e., two doublets coupled to a triplet or singlet) one has $\langle \hat{S}^{\mathrm{A}} \cdot \hat{S}^{\mathrm{B}} \rangle^{\mathrm{T}} = {}^1/_4$ and $\langle \hat{S}^{\mathrm{A}} \cdot \hat{S}^{\mathrm{B}} \rangle^{\mathrm{S}} = -{}^3/_4$, respectively, so that

$$E^{\mathrm{S/T}} = \begin{Bmatrix} {}^3/_4 J \\ -{}^1/_4 J \end{Bmatrix} \tag{14}$$

This result is the same as eq 2 except for the change of energy zero. The effective coupling constant J is given as

$$J = \sum_{i \in A, j \in B} J_{ij}^{\mathrm{AB}}\, \rho_i^{\mathrm{A}}\, \rho_j^{\mathrm{B}} \tag{15}$$

It remains now to relate the theory suggested by eq 11 with the rigorous Heisenberg Hamiltonian model embodied in eq 1.

Comparison between McConnell-I Model with the Rigorous Heisenberg Hamiltonian Model. To make a comparison between McConnell-I model with the rigorous Heisenberg development, one must consider energy differences. An example where we consider the energy difference between a singlet and triplet clarifies the main ideas. Thus for a singlet and triplet, from eq 14 (McConnell-I model) we have

$$E^{\mathrm{S}} - E^{\mathrm{T}} = \sum_{i \in A, j \in B} J_{ij}^{\mathrm{AB}}\, \rho_i^{\mathrm{A}}\, \rho_j^{\mathrm{B}} \tag{16}$$

In contrast, from eq 7 (Heisenberg Hamiltonian model) we have

$$E^{\mathrm{S}} - E^{\mathrm{T}} = \sum_{i,j} J_{ij} \Delta P_{ij} \tag{17}$$

where the ΔP_{ij} is defined as

$$\Delta P_{ij} = P_{ij}^{\mathrm{S}} - P_{ij}^{\mathrm{T}} \tag{18}$$

We emphasize that P_{ij}^{S} and P_{ij}^{T} are the singlet and triplet exchange density matrixes obtained from singlet and triplet eigenvectors (i.e., separate computations on the singlet and triplet state). In contrast $\rho_i^{\mathrm{A}}\, \rho_j^{\mathrm{B}}$ is the product of the difference of spin densities evaluated from two doublet fragments. Upon comparing eqs 16 and 17, it is clear that the McConnell relationship is valid only if we make the association

$$\Delta P_{ij} \Leftrightarrow \rho_i^{\mathrm{A}}\, \rho_j^{\mathrm{B}} \tag{19}$$

There is no obvious reason why $\rho_i^{\mathrm{A}}\, \rho_j^{\mathrm{B}}$ and ΔP_{ij} should be related to each other than heuristically. This association thus constitutes the most fundamental assumption of McConnell-I model which has never been tested numerically.

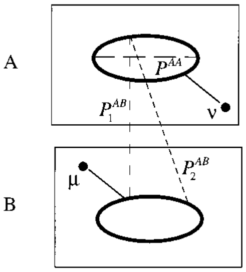


Figure 1. A schematic representation of the partition of the exchange density for two aromatic doublet structures.

For triplet stability effective coupling constant J in eq 15 must be positive. Thus, since the set of J_{ij}^{AB} are assumed to be negative, then $\rho_i^{\mathrm{A}}\,\rho_j^{\mathrm{B}}$ must be negative. *(Note that in eq 16 one MUST take the fragments A and B so that $S_z^A = 1/2$, $S_z^B = 1/2$).* However, there is a severe conceptual difficulty here. The case where $\rho_i^{\mathrm{A}}\,\rho_j^{\mathrm{B}}$ is negative is usually associated with "ferromagnetic coupling". As we shall see in the Results and Discussion section, a negative ΔP_{ij} (corresponding to triplet stability) for the "shortest contact" or interfragment sites arises from the case where P_{ij}^{S} and P_{ij}^{T} are both negative but $|P_{ij}^{\mathrm{S}}|\rangle|P_{ij}^{\mathrm{T}}|$. Therefore, *the "shortest contact" sites in the singlet are more strongly triplet coupled than the "shortest contact" sites in the triplet. Thus the association of negative $\rho_i^A\,\rho_j^B$ with the concept of ferromagnetic coupling is dubious from a conceptual point of view.*

A Practical Scheme for a McConnell-Like Decomposition of the Singlet/Triplet Energy Separation. It is convenient to illustrate the approach we will use by considering the spin coupling of two doublet fragments A and B with radical centers ν and μ as shown in Figure 1. In general, there are two types of interfragment interactions, a first set which consists of the "close contact atoms" and a second set consisting of the remaining interactions. In the model shown in Figure 1, the first set corresponds to the direct interactions between aligned carbon atoms and the second to indirect interactions between nonaligned carbon atoms. This partition will be useful for the bis(phenylmethylenyl)[2.2]paracyclophane isomers we will discuss later. However, such a division must depend in general on the system being studied.

The summation in eq 16 is restricted to interfragment interactions $i \in A$, $j \in B$, while the summation in eq 17 extends over all atoms. Thus, to compare the predictions obtained from eq 17 with the McConnell's theory, we must partition the sum in eq 17 in which both indexes are restricted to be on the same fragment A, i.e., $\{\Delta P_{ii'}\}_{ii'\in A}$, and interfragment contributions $\{\Delta P_{ij}\}_{i\in A, j\in B}$. We now consider this point in more detail.

The P_{ij} and ΔP_{ij} in eq 18, can be divided into an intrafragment set $\{\Delta P^{\mathrm{AA}}\} = \{\Delta P_{ii'}\}_{ii'\in A}$ and an interfragment set $\{\Delta P^{\mathrm{AB}}\} = \{\Delta P_{ij}\}_{i\in A, j\in B}$. It is then convenient to divide the interfragment set into 3 contributions: (i) $\{P_1^{\mathrm{AB}}\}$ and $\{\Delta P_1^{\mathrm{AB}}\}$, the set of direct interactions between aligned carbon atoms, (ii) $\{P_2^{\mathrm{AB}}\}$ and $\{\Delta P_2^{\mathrm{AB}}\}$, the set of indirect interactions between nonaligned carbon atoms, and (iii) $\{P_3^{\mathrm{AB}}\}$ and $\{\Delta P_3^{\mathrm{AB}}\}$, the set of interfragment couplings of the radical centers ν, μ themselves together with the coupling of the radical centers ν with the centers on fragment B, and the coupling of the radical centers μ with the centers on fragment A. Thus $\{\Delta P_3^{\mathrm{AB}}\} = \{\Delta P_{i\mu} \cup \Delta P_{j\nu} \cup \Delta P_{\mu\nu}\}_{i\in A, j\in B, j\neq\mu, i\neq\nu}$.

We now introduce some notation to simplify the presentation. We shall use $\{P_r^{\mathrm{AB}}\}$, $\{\Delta P_r^{\mathrm{AB}}\}$ to refer to a set of density matrix elements and density difference matrix elements of type r ($r =$ 1,2,3). We then use P_r^{AB} and ΔP_r^{AB} to denote the sum of the quantities contained in the sets $\{P_r^{\mathrm{AB}}\}$ and $\{\Delta P_r^{\mathrm{AB}}\}$. The corresponding contributions to the energy will be written as ΔE_r^{AB}. For example, if $r = 3$, then

$$\Delta P_3^{\mathrm{AB}} = \sum_{\substack{i\in A, j\in B,\\ j\neq\mu, i\neq\nu}} (\Delta P_{i\mu} + \Delta P_{j\nu} + \Delta P_{\mu\nu}) \qquad (20)$$

$$\Delta E_3^{\mathrm{AB}} = \sum_{\substack{i\in A, j\in B,\\ j\neq\mu, i\neq\nu}} (J_{i\mu}\Delta P_{i\mu} + J_{j\nu}\Delta P_{j\nu} + J_{\mu\nu}\Delta P_{\mu\nu}) \qquad (21)$$

Finally we use ΔP and ΔE to denote the summation over all contributions.

With these definitions to hand, there are some approximate relationships that must hold if the McConnel-I model is to have qualitative validity. First, the intrafragment spin coupling should correspond to a doublet (i.e., the S^2 eigenvalue is $3/4$). Thus, from eq 10, the following relationship should hold approximately for fragment A (or B)

$$S_{\mathrm{A}}(S_{\mathrm{A}} + 1) = -\frac{N_{\mathrm{A}}(N_{\mathrm{A}} - 4)}{4} - \sum_{ii'\in A} P_{ii'} = -\frac{N_{\mathrm{A}}(N_{\mathrm{A}} - 4)}{4} - P^{\mathrm{AA}} \approx \frac{3}{4} \qquad (22)$$

Here N_{A} is the number of electrons associated with fragment A. Second, the McConnell-I theory neglects the intrafragment coupling. Thus, all the elements of the set $\{\Delta P^{\mathrm{AA}}\}$ should be approximately zero and consequently $\Delta E^{\mathrm{AA}} = 0$. Thus, if the McConnell-I model is to have quantitative validity, the $\rho_i^{\mathrm{A}}\,\rho_j^{\mathrm{B}}$ and the ΔP_{ij} must behave in a qualitatively similar fashion and the set $\{\Delta P^{\mathrm{AA}}\}$ must be approximately zero.

In the limit where the fragments do not interact, there are two *localized* electrons in radical centers ν and μ, these two electrons can either couple to singlet or triplet. Thus, according to the perfect pairing formula,[30] the value of $\Delta P_{\mu\nu}$ is given as

$$\Delta P_{\mu\nu} = P_{\mu\nu}^{\mathrm{S}} - P_{\mu\nu}^{\mathrm{T}} = 1 - (-1) = 2.0 \qquad (23)$$

Further, the set of $\{\Delta P_1^{\mathrm{AB}}\}$ and $\{\Delta P_2^{\mathrm{AB}}\}$, and all the contributions due to $\{\Delta P_3^{\mathrm{AB}}\}$, will be zero if there is no interaction between the fragments except those arising from $P_{\mu\nu}$ on the *localized* electrons in radical centers ν and μ. When the fragments interact, $\Delta P^{\mathrm{AA}} = 0$ and $\Delta P^{\mathrm{AB}} \approx 2$, we have

$$\Delta P_3^{\mathrm{AB}} \approx 2 - \delta \qquad (24)$$

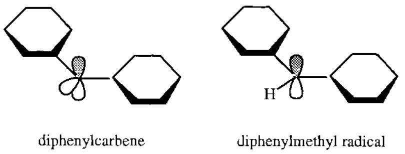
and

$$\Delta P_{1+2}^{\mathrm{AB}} \approx \Delta P_1^{\mathrm{AB}} + \Delta P_2^{\mathrm{AB}} \approx \delta \qquad (25)$$

where δ is a small positive quantity which arises from the interaction of the fragments A, B.

However, the McConnell-I model is always used qualitatively. The individual J_{ij}^{AB} are never evaluated (but assumed to be negative) and only the $\rho_i^{\mathrm{A}}\,\rho_j^{\mathrm{B}}$ are used to make predictions. Thus, there are some additional assumptions, relating to individual J_{ij}^{AB} that are inherent in even the qualitative application of the McConnell-I model. First, the contributions from nonaligned "closest contact" sites, the $\{\Delta P_3^{\mathrm{AB}}\}$, are completely ignored. However, the $\{\Delta P_3^{\mathrm{AB}}\}$ are expected to be large (see eq 24) so that the validity of McConnell's approach

SCHEME 1



diphenylcarbene diphenylmethyl radical

depends on all the members of the set $J_{\mu\nu}, \{J_{i\mu} \cup J_{j\nu}\}_{i\in A, j\in B, j\neq\mu, i\neq\mu}$ being zero (which is reasonable provided the radical centers are far apart). Secondly, in qualitative applications of the McConnell-I theory for aromatic molecules that are pancaked on top of one another in crystals, one focuses on the contribution from the aligned centers $\{\Delta P_1^{AB}\}$ and the contribution from $\{\Delta P_2^{AB}\}$ is ignored so that McConnell's theory effectively makes a qualitative estimate of ΔE_1^{AB}. From eq 25, it is clear that ΔP_{1+2}^{AB} is a small number δ that results from sum of ΔP_1^{AB} and ΔP_2^{AB}. Thus, it is clear that ΔP_1^{AB} and ΔP_2^{AB} must have a similar magnitude but opposite sign. Therefore, qualitative applications are only valid if the corresponding J_{ij} that are combined with the $\{\Delta P_2^{AB}\}$ terms are very small. If these conditions hold, the geometry and the relative singlet/triplet ordering will be controlled by the $\{\Delta P_1^{AB}\}$ elements. Thus, if the $\{\Delta P_1^{AB}\}$ are all negative the spin coupling will be triplet in agreement with McConnell-I theory, which requires $\rho_i^A\,\rho_j^B < 0$. Further, the J_{ij} corresponding to $\{\Delta P_1^{AB}\}$ will be very sensitive to distance because of the direct overlap of the carbon atom p^π orbitals.

Computational Details

The [2.2]paracyclophanedicarbenes (e.g., pseudoortho, pseudometa, and pseudopara bis(phenylmethylenyl)[2.2]-paracyclophane (bPhMenyl) isomers) have been proposed to provide a reasonably good model for examining the intermolecular magnetic interaction in reference to McConnell-I model,[25] since the spin-containing benzene rings of two diphenylcarbene molecules are pancaked on top of one another in the [2.2]paracyclophane skeleton. Experimental data available for the bPhMenyl system shows that, among the three isomers with different orientation of the two phenylmethylenyl substituents, only the pseudoortho and pseudopara isomers present a quintet ground state, while the singlet is the ground state in the pseudometa stacking mode.[25] However, strictly speaking, the model is far from ideal: the two benzene rings incorporated in the [2.2]paracyclophane structure are not planar but bent into a boat form with interring distances not even (~2.8−3.1 Å), and the two rings are deeclipsed by 3.2° to avoid the ethano-type eclipsing in the side chains.[31]

A recent study[32] showed that the π-electronic structure of diphenylcarbene is very much like that of diphenylmethyl radical, as indicated in Scheme 1. The important triplet state of the carbene has one electron in the conjugated π-system. Accordingly, it is sensible to model this system with a methyl radical rather than carbene unit. Therefore, one would obtain for bis(phenylmethyl)[2.2]paracyclophanes, a singlet ground state for the pseudometa stacking mode and triplet ground state for the pseudoortho and pseudopara ones. Further, the phenylmethyl radical can be replaced by a simple methyl radical, thus giving rise to bis(methyl)[2.2]paracyclophane (namely, bMe), since the phenyl attached to the methyl is not involved in the π-electron reorganization related to singlet/triplet states.[32]

Energies and geometry optimization of the pseudoortho, pseudometa, and pseudopara bMe model systems were carried out by means of the Molecular Mechanics−Valence Bond (MMVB) method. MMVB[28] is a hybrid method, which uses the MM2 potential[33] to describe the inert molecular σ-bonded framework and a Heisenberg Hamiltonian,[27] parametrized against CASSCF computations, to represent electrons on sp^2/sp^3 carbon atoms which are involved in π-conjugation or new σ-bond formation. The Heisenberg Hamiltonian implemented in MMVB is a faithful representation of eqs 5 and 6 and acts on a basis set of neutral many-electron VB states constructed from active orbitals which are singly occupied. The P_{ij} matrix elements are obtained from the CI vectors of the MMVB Hamiltonian[28c] and provide a partition of $\hat{S}(1)\cdot\hat{S}(2)$ into interactions between these sites.

The fundamental principles behind the parametrization of MMVB via an effective Hamiltonian have been discussed in ref 28b. The important point is the exchange parameters are fitted to a CASSCF effective Hamiltonian. In ref 28b, we show that these parameters can be interpreted in terms of an expansion involving powers of the overlap. However, no overlap integrals are ever computed in pratice. Thus, eq 4 is used for interpretative purposes only. The exchange parameters contain higher powers of the overlap implicitly. Further, by construction, the CASSCF effective Hamiltonian reproduces neutral covalent states of all spin multiplicies, so there is no explict spin dependence of the paremetrization.

Results and Discussion

For the bis(methyl)[2.2]paracyclophane (later on, bMe) model system, the MMVB optimization [28] of the pseudoortho, pseudometa, and pseudopara isomers was carried out for both the singlet and the triplet states. In addition, the singlet/triplet crossing geometries were characterized and located. The geometries for minima and the singlet/triplet crossing geometries are shown in Figure 2 [Cartesian coordinates for all critical points are available in Table 1S (Supporting Information)]. At the lowest energy optimized structures (triplet in the case of the pseudoortho and -para structures, and singlet in the case of the pseudometa structure), a decomposition of the singlet/triplet energy difference was carried out in terms of the $\{\Delta P_r^{AB}\}$. These data are presented in Tables 1 and 2 [the $P_{ij}^{S/T}$ contributions to ΔP for all three bMe isomers evaluated at the ground-state geometry are listed in Tables 2S (Supporting Information), and the corresponding J_{ij} are in Table 3S (Supporting Information)].

The relative ordering of the singlet and triplet states is indicated in column 2 of Table 1 and is in agreement with that observed experimentally for the low-spin meta and high-spin ortho/para isomers of bis(phenylmethylenyl)[2.2]paracyclophane (later on, bPhMenyl).[25] The absolute value of the energy difference between singlet and triplet states at the optimized geometries is similar for all three isomers (3 kcal mol^{-1}). To confirm that the conclusions regarding triplet versus singlet stability arise mainly from the stacking orientation of the benzyl groups in the paracyclophane, we also carried out a series of computations with two planar benzyl radicals placed 3 Å apart in the ortho, meta, and para orientations. The results are qualitatively similar to the results on the optimized paracyclophanes and will not be included here.

We begin with a brief discussion of the optimized geometries in Figure 2. The geometries for the singlet and triplet states differ only by ca. 0.001−0.07 Å with respect to interfragment C−C bond lengths. Thus, the main factors that control singlet/triplet stability are electronic in origin rather than geometric. This conclusion is reinforced by a consideration of the geometries where singlet and triplet states cross. In each case, the

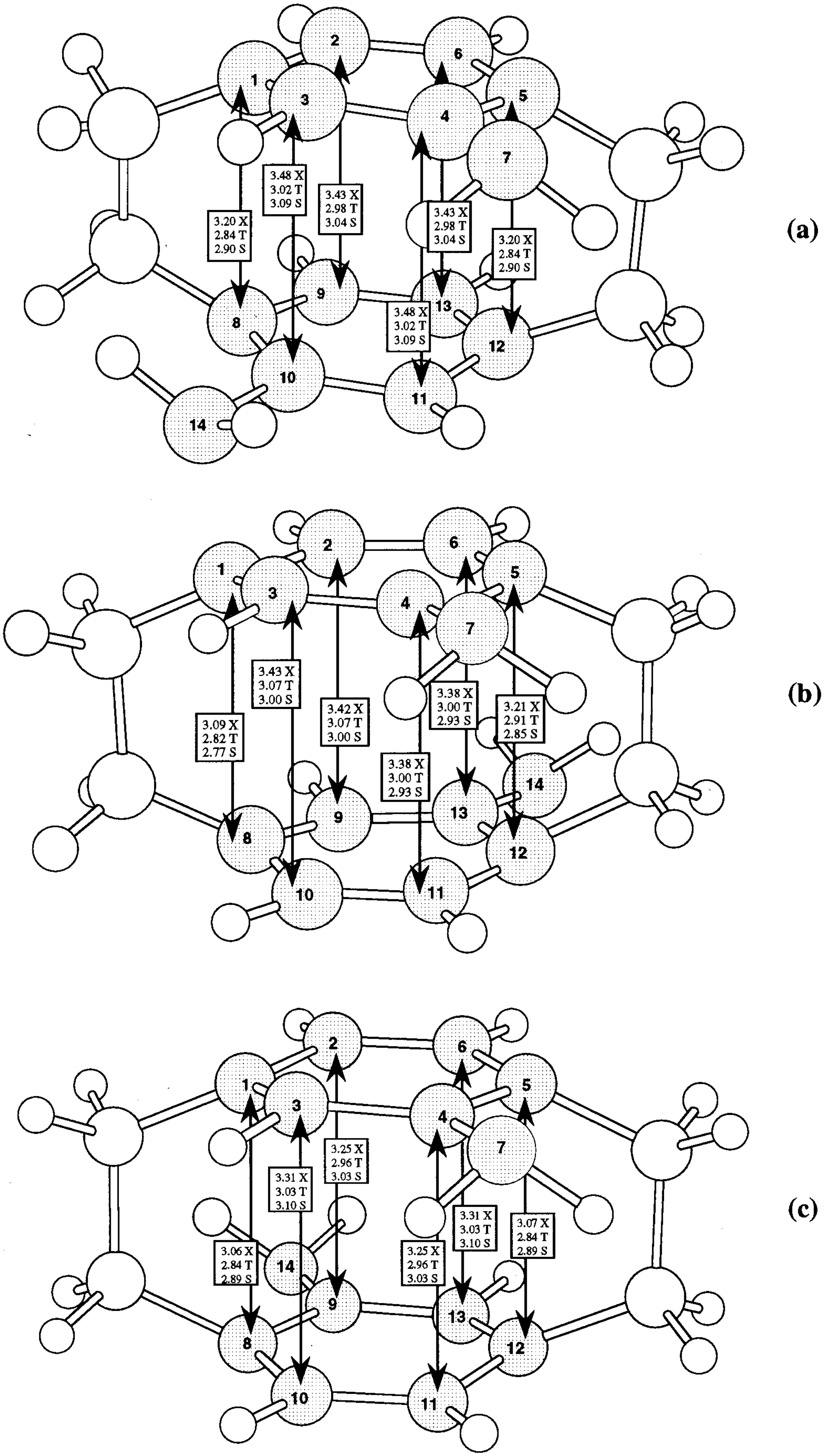


Figure 2. The optimized MMVB interfragment distances for pseudo- (a) ortho-, (b) meta-, and (c) para-bis(methyl)[2.2]paracyclophane (S = singlet, T = triplet, X = surface crossing).

crossing occurs when the interfragment bond distances are increased from ca. 2.9 Å to ca. 3.3 Å so that the interfragment J_{ij} falls to near zero. Therefore, the relative stability of singlet and triplet persists as the interfragment distances are increased

TABLE 1: Interfragment Exchange Density Matrices Differences ΔP_r^{AB} and Contributions to the Total Energy ΔE_r^{AB}. All Energy Differences in kcal mol^{-1}

isomer	stucture	ΔE^{AB}	ΔP_3^{AB} ΔE_3^{AB}	ΔP_1^{AB} ΔE_1^{AB}	ΔP_2^{AB} ΔE_2^{AB}	ΔP_{1+2}^{AB}
pseudoortho	T_{min}	2.9493	1.834	−1.355	1.508	0.153
			0.3765	3.7651	−1.1923	
pseudometa	S_{min}	−2.1963	1.666	1.264	−0.942	0.322
			−0.1255	−3.5768	1.5060	
pseudopara	T_{min}	2.6983	1.831	−1.370	1.525	0.155
			0.0000	4.0161	−1.3178	

TABLE 2: Interfragment Exchange Density Matrices Differences {ΔP^{AB}} for the Minima[a]

atom number	1	2	3	4	5	6	7
(a) Pseudoortho (Triplet Minimum)							
8	−***.236***	.320	.326	−.299	.388	−.231	**.609**
9	.137	−***.198***	−.194	.175	−.231	.138	−**.356**
10	.175	−.245	−***.258***	.230	−.299	.175	−**.467**
11	−.190	.267	.273	−***.258***	.326	−.194	**.509**
12	.132	−.188	−.190	.175	−***.236***	.137	−**.352**
13	−.188	.262	.267	−.246	.320	−***.198***	**.497**
14	−**.352**	**.496**	**.509**	−**.467**	**.609**	−**.355**	**.957**
(b) Pseudometa (Singlet Minimum)							
8	***.121***	−.172	−.171	.146	−.198	.116	−**.292**
9	−.171	***.270***	.259	−.221	.303	−.174	**.445**
10	−.172	.263	***.269***	−.225	.306	−.174	**.359**
11	.116	−.174	−.174	***.158***	−.205	.119	−**.301**
12	−.198	.307	.303	−.264	***.370***	−.205	**.531**
13	.146	−.226	−.221	.192	−.264	***.158***	−**.387**
14	−**.292**	**.452**	**.445**	−**.387**	**.531**	−**.301**	**.785**
(c) Pseudopara (Triplet Minimum)							
8	−***.239***	.326	.329	−.305	.397	−.233	**.613**
9	.176	−***.260***	−.249	.230	−.305	.179	−**.465**
10	.137	−.192	−***.199***	.179	−.233	.137	−**.356**
11	−.190	.267	.268	−***.260***	.326	−.192	**.501**
12	.132	−.190	−.189	.176	−***.239***	.137	−**.351**
13	−.189	.268	.268	−.250	.329	−***.199***	**.503**
14	−**.350**	**.501**	**.502**	−**.465**	**.613**	−**.356**	**.948**

[a] ΔP_1^{AB} bold italic; ΔP_2^{AB} plain type; ΔP_3^{AB} bold. Atom numbers correspond to Figure 2.

until the interfragment interactions fall to zero. The interfragment−ring distances for the singlet and triplet states agree with the available experimental data (2.8 and 3.1 Å in bPhMenyl[31]). Thus, the bMe model system appears to be a good model of the bPhMenyl system (as expected since none of the phenyls attached to the methylenyl is involved in the π-electron reorganization[25]).

We now turn our attention to the analysis of the singlet/triplet energy difference ΔE^{AB} in terms of the components of ΔP^{AB} given in Table 1. The individual components of ΔP^{AB} for all the interfragment interactions are collected in Table 2. One must stress that this analysis is only sensible if $\Delta E^{AA} = \Delta E^{BB} = 0$. In all examples, this contribution computed to be less than 0.2 kcal mol^{-1}. Moreover, for each fragment, the computed intrafragment P^{AA} and P^{BB} are −6.0 (corresponding to a doublet in eq 22 with $N_A = N_B = 7$), irrespective of whether the overall spin coupling is triplet or singlet so that $\Delta P^{AA}(\Delta P^{BB})$ is zero.

The $\rho_i^A \rho_j^B$[25] are negative for the pseudoortho and -para species and positive for the pseudometa species according to the McConnell model, and thus, triplet ground states are predicted for the former and singlet for the latter. The computed values of $\{\Delta P_1^{AB}\}$ collected in the diagonal elements (bold) of Table 2 are in remarkable agreement with the qualitative model of McConnell. Thus the $\{\Delta P_1^{AB}\}$ components are negative for the pseudoortho and -para species (which have triplet ground states), and positive for the pseudo-meta species (which has a singlet ground state). Thus eq 19 appears to hold numerically.

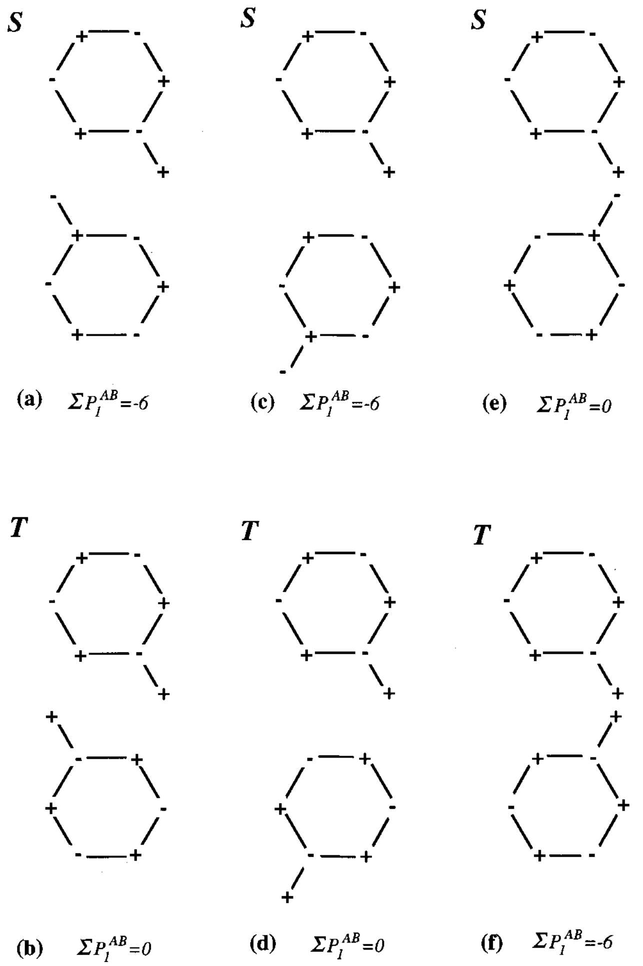
Now let us examine some other aspects of the McConnell-I model that are necessary for reliable predictions. The $\{\Delta P_2^{AB}\}$ and $\{\Delta P_3^{AB}\}$ are ignored in the McConnell model; however, the $\{\Delta P_2^{AB}\}$ and $\{\Delta P_3^{AB}\}$ in Table 2 are clearly not zero. Rather they have large positive and negative elements. First, as predicted in eq 24, $\Delta P_3^{AB} \approx 2$. However, because the corresponding J_{ij} elements (see Table 3S) are all small we have $\Delta E_3^{AB} \approx 0.0$ (Table 1), so this term does not contribute to singlet versus triplet stability. Second, from Table 1, $\Delta P_{1+2}^{AB} \approx \delta$ (as suggested in eq 25) because ΔP_2^{AB} and ΔP_1^{AB} have opposite sign. However, ΔE_2^{AB} is not negligible. Thus, the singlet versus triplet stability results from a competition between ΔE_1^{AB} and ΔE_2^{AB}. For all the examples studied $|\Delta E_1^{AB}| > |\Delta E_2^{AB}|$, so that ΔE_1^{AB} alone gives a qualitative prediction that is in agreement with McConnell-I model. This situation arises because the magnitudes of J_{ij} (see Table 3S) that are combined with the $\{\Delta P_2^{AB}\}$ are in general smaller than the magnitudes of J_{ij} that are contracted with the $\{\Delta P_1^{AB}\}$.

Conclusions

If one compares eqs 16 and 17, it is clear that singlet/triplet stability depends on the sign and magnitude of $\rho_i^A \rho_j^B$ or ΔP_{ij}, and on the magnitude of the J_{ij} that are combined with the $\rho_i^A \rho_j^B$ or ΔP_{ij}. In this work we have included both effects on the bMe model system that is related to the bPhMenyl standard normally used to test the validity of the McConnell-I relationship. Remarkably, the predictions obtained from our Heisenberg Hamiltonian defined in eq 17, are in complete agreement with the qualitative predictions from eq 16 because of fortuitous cancelations. This agreement arises because the signs of $\rho_i^A \rho_j^B$ and ΔP_{ij} are the same and many J_{ij} are zero. We now discuss the origin of this effect in more detail.

It is clear that the agreement of the predictions of the McConnell-I model (eq 16) and our Heisenberg Hamiltonian (eq 17) arises because the partition into $\{\Delta P_1^{AB}\}$, $\{\Delta P_2^{AB}\}$, and $\{\Delta P_3^{AB}\}$ is possible, and the contribution from $\{\Delta P_1^{AB}\}$ dominates. The individual $\{\Delta P_2^{AB}\}$ and $\{\Delta P_3^{AB}\}$ are large and contain both positive and negative elements; however, this contribution is not important because the corresponding J_{ij} are very small. Thus, the McConnell-I model makes a correct prediction for our paracyclophane model by the lucky chance that $|\Delta E_1^{AB}| > |\Delta E_2^{AB}|$. In general, when the atoms are not perfectly aligned, one can expect that the ΔE_2^{AB} will not be negligible. In this case, a qualitative prediction using the McConnell model is impossible without an a priori knowledge of the J_{ij}. Further, it is clear the J_{ij} have strong orientational and directional properties. Thus, when ΔE_1^{AB} and ΔE_2^{AB} have similar magnitude (but opposite sign), the question of singlet/triplet stability will depend on subtle details of orientation manifested in the behavior of the J_{ij}.

The preceding discussion masks a severe conceptual problem. The computed "closest contact" couplings $\{P_1^{AB}\}$ (see Table 2S) are *always* negative, irrespective of whether the ground state is triplet or singlet. Thus, a negative ΔP_1^{AB} (corresponding to triplet stability) can be obtained if $|P_1^{AB}|^S > |P_1^{AB}|^T$. (In the "ideal" case where the wave function is just a simple Rumer function the P_{ij} have values −1 for two electrons coupled parallel to a triplet, and $-{}^1/_2$ for uncoupled spins, i.e., *i* and *j* belong to *different* "spin-paired" functions). Since the dominant Rumer function in the wave function must involve intrafragment



(a) $\Sigma P_1^{AB}=-6$ (c) $\Sigma P_1^{AB}=-6$ (e) $\Sigma P_1^{AB}=0$

(b) $\Sigma P_1^{AB}=0$ (d) $\Sigma P_1^{AB}=0$ (f) $\Sigma P_1^{AB}=-6$

Figure 3. A schematic representation of the leading determinants in the singlet and triplet wave functions used to compute the P_{ij} for the pseudo-ortho-(a/b), para-(c/d), and meta- (e/f) bis(methyl) [2.2]paracyclophane isomers.

spin coupled pairs, the interfragment coupling is mainly that of uncoupled electrons. Therefore, we expect that the P_{ij} for the "closest contact" sites should be ca. $-{}^{1}/_{2}$. In fact, the MMVB "closest contact" couplings are all negative and range from about -0.3 to -0.6, which is in agreement with this observation. According to McConnell-I, the case where $\rho_i^{\mathrm{A}}\,\rho_j^{\mathrm{B}}$ is negative is usually associated with "ferromagnetic coupling". Similarly a negative ΔP_1^{AB} is associated with triplet stability. Thus, we are left with the difficulty of explaining why the triplet stability implies that the "closest contact" sites are more strongly ferromagnetically coupled (i.e., with a negative P_1^{AB}) in the singlet state than in triplet state for the case where the ground state is a triplet. The answer turn out to be remarkably simple as we now discuss.

In Figure 3 we show the leading determinants in the singlet and triplet wave functions that were used to compute the P_{ij}. The $+$ and $-$ in the figure indicate the spin (α or β) of the orbital on the corresponding site for singlet (S) and triplet (T). Remarkably, the spin arrangements for the triplet ($|S_z| = 1$) are in agreement with those suggested by the McConnell model (Figure 3b, d, f). From eq 9 for a single determinant, $P_{ij} = -1$ for electrons of same spin and $P_{ij} = 0$ for different spin. We have given the value of the sum of the ideal "closest contact" P_{ij} values as $\sum P_1^{\mathrm{AB}}$ in Figure 3. Clearly, for the first term in the wave function the "closest contact" P_{ij} for the singlet in the case of a triplet ground state (Figure 3 a/b and c/d) are negative, while the situation is inverted for the case of the singlet ground state (Figure 3 e and f). Thus, as said before, triplet stability implies that the "closest contact" sites are more strongly ferromagnetically coupled in the singlet state than in triplet state for the case where the ground state is a triplet. Therefore, the McConnell model appears to correctly predict the stability of the leading term in the VB wave function. The magnitudes of the ΔP_1^{AB} are predictable crudely from the leading term in the wave function. However, there is no reason to expect this situation to hold in general.

Thus, the McConnell-I model gives the correct prediction of singlet/triplet stability for the bis(methyl)[2.2]paracyclophane example because many contributions are small and the association $\Delta P_{ij} \Leftrightarrow \rho_i^{\mathrm{A}}\,\rho_j^{\mathrm{B}}$ is sensible. Further, the McConnell model seems to predict the leading determinants in the wave function correctly. However, the predictive value of the McConnell model must be limited in general because the orientational dependence of the model via the J_{ij} is never studied.

Finally, we believe that the methods used in this study are quite generally applicable to other related problems in magnetism. An example is the related problem of ferrimagnetism which arises form the coupling of two spins of different magnitudes in such a way, that one never has an $S = 0$ coupling. McConnell I is a through space mechanism while ferrimagnetism is often through-bond in polymetalates. But the formalism descibed in ths work is equally applicable. Another example of a through-bond mechanism is the Dougherty model.[2c] An application to this problem is published elsewhere.[34]

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Supporting Information Available: Cartesian coordinates for the MMVB optimized singlet, triplet, and surface crossing geometries for the ortho-, meta-, and para-bis(methyl)[2.2]-paracyclophane isomers in Table 1S, the individual $P_{ij}^{\mathrm{S/T}}$ contributions to ΔP for all three bis(methyl)[2.2]paracyclophane isomers evaluated at the ground-state geometry in Tables 2S, and the corresponding J_{ij} in Table 3S (11 pages). Ordering information is given on any current masthead page.

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