Lithium Corp. and was titered prior to use by the method of Suffert.[11] The 2-iodo-3-formylquinoline was prepared according to literature procedures[4] and was recrystallized from ethanol prior to use. All other reagents were obtained from commercial sources and used without purification unless otherwise noted. Reactions were carried out with standard Schlenk glassware and techniques.

Preparation of 2-Iodo-3-(hydroxymethyl)quinoline (4). To a solution of 2-iodo-3-formylquinoline (2.10 g, 7.40 mmol) and 1 drop of 20% NaOH solution in 150 mL of methanol cooled to 0 °C was added 0.15 g of $NaBH_4$ in small portions. The reaction was then stirred at 0 °C for 15 min, during which time a precipitate formed. The reaction was poured onto ice and filtered to yield a tan solid, which was recrystallized from ethanol to yield 1.68 g (5.88 mmol, 79%) of **4** as a light tan solid, mp 183–184 °C. The material gave ^{1}H and ^{13}C NMR spectra consistent with those reported previously.[3] Anal. Calcd for $C_{10}H_8INO$: C, 42.13; H, 2.83; N, 4.91; I, 44.51. Found: C, 42.40; H, 2.83; N, 4.92; I, 44.21.

Representative Preparation and Reaction of 2-Iodo-3-(deuteriooxymethyl)quinoline (1) with *n*-BuLi, Followed by CH_3OH Quenching. A solution of **4** (0.1377 g, 0.483 mmol) in 5 mL of dry THF and 5 mL of CH_3OD was stirred for 8 h, and then the solvents were removed in vacuo. Additional THF and CH_3OD (5 mL each) were added, and the reaction was stirred for 10 h followed by removal of the solvents in vacuo. The sample was kept under high vacuum for 48 h, and then 9.5 mL of dry THF was added and the solution cooled to −78 °C. *n*-BuLi (0.97 mmol, 1.4 M, 0.69 mL) was added dropwise, and the reaction was stirred at −78 °C for 10 min and then quenched by addition of CH_3OH (0.8 mL). The reaction was warmed to room temperature, poured into NH_4Cl solution, and extracted three times with Et_2O. The combined organic layers were dried over $MgSO_4$, filtered, and the solvents removed in vacuo. Purification by reverse-phase HPLC (50% CH_3OH/H_2O) provided 0.0533 g (0.335 mmol, 69%) of a mixture of the deuterated and undeuterated 3-(hydroxymethyl)quinolines **2** and **3** as a white solid, mp 82–83 °C. FIMS analysis of the product relative to an undeuterated standard indicated a deuterium content of 32%.

Representative Reaction of 2-Iodo-3-(hydroxymethyl)quinoline (4) with *n*-BuLi, Followed by CH_3OD Quenching. To a solution of **4** (0.1547 g, 0.543 mmol) in 11 mL of dry THF cooled to −78 °C under N_2 was added *n*-BuLi (1.1 mmol, 1.4 M, 0.78 mL) dropwise. The reaction was stirred at −78 °C for 15 min, and then 0.8 mL of CH_3OD was added. The reaction was stirred at −78 °C for 15 min and then warmed to room temperature and poured into a saturated NH_4Cl solution. The mixture was extracted with Et_2O three times, the combined organic layers were dried over $MgSO_4$ and filtered, and the solvent was removed in vacuo. Purification by reverse-phase HPLC (50% CH_3OH/H_2O) provided 0.0652 g (0.408 mmol, 76%) of **2** and **3** as a white solid, mp 81–82 °C. FIMS analysis indicated a deuterium incorporation of 60%.

Preparation of 2-Deuterio-3-(hydroxymethyl)quinoline (2) for Use as a Deuterated Standard. Starting from 0.2258 g (0.792 mmol) of **4**, the O-deuterated quinoline **1** was prepared as described above and then dissolved in 15 mL of dry THF. To this solution was added *n*-BuLi (1.65 mmol, 1.5 M, 1.1 mL) dropwise. The reaction was stirred for 15 min and then quenched by addition of 1.0 mL of CH_3OD. The reaction was stirred for 15 min at −78 °C and warmed to room temperature. The reaction mixture was poured into saturated NH_4Cl and extracted three times with Et_2O. The combined extracts were dried over $MgSO_4$ and filtered, and the solvent was removed in vacuo. Purification by HPLC (50% CH_3OH/H_2O) provided 0.896 g (0.560 mmol, 71%) of **2** as a white solid: mp 80–82 °C; ^{1}H NMR ($CDCl_3$) δ 4.39 (b, 1 H), 4.83 (s, 2 H), 7.48 (t, 1 H), 7.62 (t, 1 H), 8.00 (d, 1 H), 8.06 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 62.27, 126.78, 127.67, 127.83, 128.54, 129.31, 133.85, 133.92, 146.97, 149.52 (t, J_{C-D} = 27.1 Hz). FIMS analysis relative to a undeuterated standard indicated a deuterium incorporation of >95%.

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Is the McConnell Mechanism a Suitable Strategy for the Design of Molecular Ferromagnets?

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Abstract: We present a qualitative discussion of a mechanism ascribed to McConnell that is supposed to predict ferromagnetic behavior for certain orbital configurations of the molecules in a stack of alternating donor and acceptor units. We examine in detail the possible mixing of ground and charge-transfer configurations of a donor–acceptor pair for both singlet and triplet states. It is shown that more charge-transfer mixing terms are available for the stabilization of the singlet as compared to the triplet. In contrast to McConnell's assumption, this will result in a singlet ground state if the Hubbard-like charge-transfer parameter Δ is much larger than the singlet–triplet splitting of the charge-transfer configurations governed by an exchange integral, K. In addition, a modification of McConnell's mechanism for uniform stacks is discussed. In this case, a triplet ground state of the dimer might be obtained only for a highly symmetrical arrangement of the molecules in the stack.

1. Introduction

Molecular ferromagnets have been a challenge to both experimentalists and theorists for some time. Different strategies have evolved for the design of these materials.

On the basis of the existence of high-spin organic molecules, some models for purely organic ferromagnetic polymers with a conjugated π system have been suggested.[1] The ferromagnetic behavior of these hypothetical compounds is a consequence of the topology of their π electron network, which gives rise to degenerate nonbonding orbitals in accordance with the Coulson–Rushbrooke theorem.[2] Hund's rule then suggests a parallel alignment of the spins of the radical electrons in these singly occupied orbitals. Although tetracarbene and pentacarbene molecules with nonet and decet ground states, respectively, could be synthesized,[3] no real polymeric material of this kind is known as yet. A related concept also based on the topology of conjugated polymers suggests a ferromagnetic coupling of polarons.[4]

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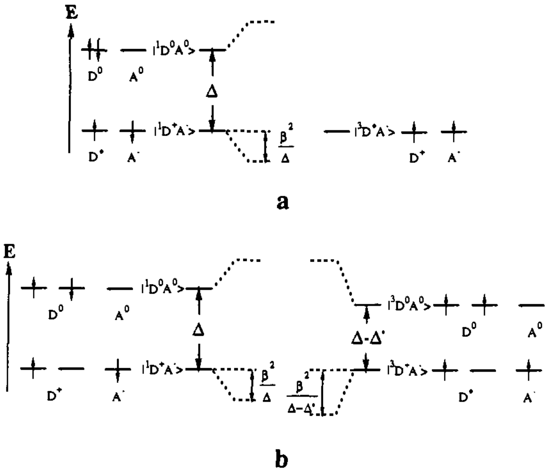

Figure 1. Energy level scheme for ground and charge-transfer states of a donor–acceptor pair. (a) shows the most common case with a singlet state for both the neutral donor and acceptor. (b) refers to the situation considered by McConnell with a triplet ground state for the neutral donor. Δ is the charge-transfer energy. It is diminished by Δ' for the triplet.

Another model for designing molecular-based systems with a spontaneous magnetization has been presented by one of us.[5] Bimetallic units with an antiparallel alignment of spins of different magnitude (e.g., Mn(II) or Fe(III) with $S = {}^5/_2$ and Cu(II) with $S = {}^1/_2$) are coupled. The spins of different units then couple ferromagnetically, resulting in a ferrimagnet.

The mechanism most frequently invoked, however, is based on an idea of McConnell.[6] He considers charge-transfer salts consisting of stacks of alternating donor and acceptor molecules $D^+A^-D^+A^-$... Let us take a single donor–acceptor pair within such a stack. Its ground state will be dominated by the electronic configuration D^+A^- with one radical electron on the donor and one on the acceptor. But there is some configurational mixing with charge-transfer states, either obtained by backward charge transfer (D^0A^0) or further forward charge transfer ($D^{2+}A^{2-}$), which stabilizes the ground state. In general, the charge-transfer states have singlet character and therefore stabilize the singlet of D^+A^- as shown in Figure 1a for the backward charge transfer leading to D^0A^0. No such mixing is available for the triplet at least if we consider only the charge-transfer states lowest in energy. The question that arises is the following: Is there a configurational mixing that stabilizes the triplet state of the two radical electrons of D^+A^- more than the singlet? What kind of orbital pattern is then needed? McConnell suggested a neutral donor, D^0, with a triplet instead of a singlet ground state. The corresponding orbital configuration consists of a 2-fold degenerate HOMO occupied by two electrons. Hund's rule then provides for a triplet ground state. This is illustrated in Figure 1b. Of course, a singlet state is also available for the neutral donor D^0. But the mixing of the singlet charge-transfer configuration with the singlet ground configuration is smaller than that of the corresponding triplet because the former is higher in energy.

It should be noted that we are dealing with molecular crystals where the distances between neighboring molecules are large compared to the intramolecular distances between neighboring atoms. Thus, the overlap between donor and acceptor orbitals is small, resulting in a small mixing of ground and charge-transfer configurations. It is therefore justified to describe the energy stabilization by simple perturbation theory terms:

$$\Delta E = \frac{|\langle \mathrm{GS}|\hat{H}|\mathrm{CT}\rangle|^2}{\Delta} \qquad (1)$$

In the nominator, we have the interaction matrix element between

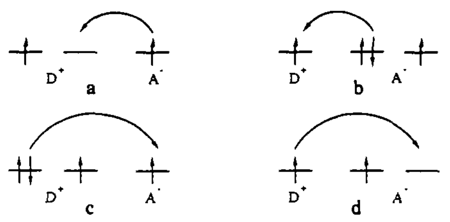

Figure 2. Orbital configurations suitable for the McConnell mechanism. The relevant charge transfers are indicated by the arrows. We have the following cases: (a) triplet ground state for D^0 obtained by backward charge transfer, (b) triplet ground state for A^0 obtained by backward charge transfer, (c) triplet ground state for D^{2+} obtained by further forward charge transfer, and (d) triplet ground state for A^{2-} obtained by further forward charge transfer.

the ground state (GS) and the charge-transfer state (CT) denoted as β in the following. Δ is the energy necessary to transfer an electron back from the acceptor to the donor. Apart from the difference between the ionization potential and the electron affinity of the donor and acceptor, respectively, the charge-transfer energy Δ also contains the Madelung energy, which plays an important role for the relative stability of neutral and ionic phases.[7] Following McConnell, Δ is supposed to be lower for the triplet charge-transfer state, which is therefore more strongly stabilized than the singlet in accordance with eq 1 and as shown in Figure 1b. A word with respect to the terminology is necessary at this point in order to avoid confusion. We will denote the configuration D^+A^- as the ground state in the following. The neutral state D^0A^0 then corresponds to a charge-transfer state contrary to what one might expect from looking at the charges. Our assignment is based on the presumed energetical sequence of the states.

How can we infer ferromagnetic behavior for the whole stack from the triplet state of a single pair? If we have a ferromagnetic coupling for one donor–acceptor pair, it will occur for any such pair of neighboring donors and acceptors and, thus, throughout the stack. It should be noted that there are other orbital configurations than just the one shown in Figure 1b which allow for the same mechanism. Thus, a triplet ground state for the neutral acceptor instead of the donor will do as well. Moreover, one could think of forward charge-transfer states, which would also stabilize the triplet. We have summarized the corresponding orbital configurations in Figure 2. A more comprehensive list has been given by Miller et al.[8]

A modification of the McConnell mechanism has been presented by Torrance et al.[9] They consider a uniform stack of singly charged aromatic molecules, say M^-. Again we single out one pair, M^-M^-. The charge transfer now corresponds to a disproportionation of the charge in either direction, leading to $M^{2-}M^0$ or M^0M^{2-}. Now we can apply the same argument as before; if the two additional electrons of M^{2-} in the charge-transfer configuration are placed in two degenerate orbitals, we obtain a triplet in accordance with Hund's rule. Thus, the triplet state of the ground configuration M^-M^- will be stabilized most strongly. The consequences are the same as described above.

Despite many theoretical and experimental efforts, it has been only recently that charge-transfer salts exhibiting ferromagnetic behavior have been reported in the literature.[8,10] A pioneering role in this context can be ascribed to the decamethylferrocenium tetracyanoethenide (DMFcTCNE) compound synthesized and investigated by Miller et al.[8] The orbital pattern for this compound meets the conditions for the McConnell mechanism and corresponds to Figure 2c. It is therefore tempting to invoke this concept

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in order to explain the ferromagnetism of DMFcTCNE as has been done by Miller. We will give an account of the ferromagnetic coupling in this complex in a subsequent paper. More recently similar organometallic complexes with ferromagnetic behavior have been reported.[10] Their number can be expected to grow in the near future. It seems to have become common practice to a posteriori invoke the McConnell mechanism for an explanation of the ferromagnetism of these compounds in lack of another suitable theory.

Indeed, the orbital patterns of most of these compounds fit the configurations suggested by McConnell. There is one notable exception, however. This is the compound $[Cr(C_6Me_6)_2]^+$-$[TCNE]^-$.[10b] The experiments suggest ferromagnetic coupling for this compound whereas the McConnell mechanism would predict antiferromagnetic coupling as has been noted by Miller et al.[10b] This is due to the $^2A_{1g}$ ground state of $[Cr(C_6Me_6)_2]^+$ corresponding to the electronic configuration $e_{2g}{}^4a_{1g}{}^1$ with the nondegenerate HOMO a_{1g}. Miller et al. try to save the McConnell mechanism by invoking an electron transfer from the next highest occupied e_{2g} orbital instead of the a_{1g} HOMO without giving any specific reason for this choice. Thus, without having examined the mechanism in detail, one would say that the applicability of the McConnell mechanism to this particular compound is rather obscure. At least it casts some doubt on the predictive power of this model.

In this contribution, we will focus on the McConnell mechanism in a quite general fashion, writing down the correct symmetry-adapted wave functions of the states involved and examining the mixing matrix elements in some more detail. This seems worthwhile because highly sophisticated experimental efforts focusing a priori on the McConnell mechanism have been pursued,[11] so far to no avail. Our main objective is to discuss the McConnell mechanism in its original form, i.e., the spin coupling arising from mixing with charge-transfer states in a one-dimensional heterostack of alternating donor and acceptor units. The modification of the mechanism introduced by Torrance et al.[9] in order to deal with homomolecular stacks has already been discussed by Bagus and Torrance[12] who performed a calculation for a benzene anion dimer. They showed that the mechanism works when a highly symmetrical arrangement of the benzene molecules (D_{6h} symmetry for the dimer) is retained. In an additional section, we will therefore examine in a qualitative fashion the effect of symmetry lowering. Finally, it should be noted that all considerations that follow refer to the coupling in one-dimensional chains. We do not discuss the coupling in three dimensions, which is necessary to obtain bulk ferromagnetism.

2. The McConnell Mechanism for Mixed Donor–Acceptor Stacks

Let us return to Figure 1b. This crude picture certainly needs some refinement, because it does not include all the states obtained by placing two electrons in three orbitals (two donor and one acceptor orbitals in the case of Figure 1b). Altogether we obtain eight electronic configurations consisting of four ground-state and four charge-transfer-state configurations. Without donor–acceptor interaction, the four ground-state wave functions (two singlets and two triplets) are degenerate. This is not the case for the charge-transfer states (three singlets and one triplet) as we will discuss in the following.

It can be seen from Figure 2 that all charge-transfer configurations obtained by shifting the electrons according to the arrows involve a degenerate pair of orbitals occupied by two electrons. It is therefore essential to examine this orbital configuration in some more detail. Since we will focus on the configuration of Figure 2a in the following, the degenerate orbitals will be donor orbitals. Let us assume that the degeneracy of these orbitals is not accidental but a result of symmetry, i.e., we have a rotation or rotation–reflexion axis higher than 2-fold. This is a reasonable assumption although a degeneracy can also result from the topology of a molecule as is well known for conjugated alternant hydrocarbons.[2]

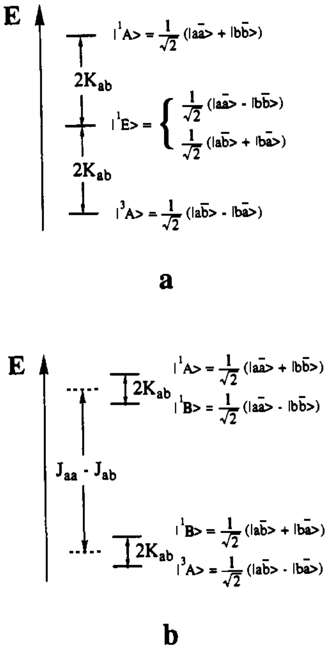

Figure 3. Energy level scheme for a degenerate HOMO belonging to an e irreducible representation and occupied by two electrons. We also show the corresponding wave functions, which are denoted by their symmetry labels. (a) shows the most common case, which is valid for all e representations of all groups except for some particular e representations of the groups C_{4n}, D_{4n}, etc. but also, e.g., of D_{2d} (see text). These cases are represented in (b).

We will denote the degenerate orbitals belonging to an irreducible representation, e, as a and b in the following. With two electrons in these orbitals, we have to form the product representation e ⊗ e for a basis $|a\bar{a}\rangle$, $|a\bar{b}\rangle$, $|b\bar{a}\rangle$, $|b\bar{b}\rangle$. This four-dimensional representation is reducible and, with some exceptions discussed below, contains the following irreducible representations:

$$e \otimes e = a + a + e \qquad (2)$$

It should be noted that the a representations on the right-hand side of eq 2 are different in general and that the e representations on the right- and left-hand sides need not be the same. The labels or primes attached to these representations depend on the point group of the molecule in question. Equation 2, however, does not; a reducible product representation, e ⊗ e, in most cases contains one e and two a irreducible representations. An exception from this scheme is given by the groups containing axes of the order $4n$ (C_{4n}, D_{4n}, etc., with n being an integer, but also, e.g., D_{2d}, which contains a 4-fold rotation–reflexion axis). But for the moment let us focus on the more general case of eq 2. The irreducible product basis consists of three singlets (e and one of the a representations) and one triplet (the remaining a representation). This is in contrast to the simple picture of Figure 1b, which takes into account only one triplet and one singlet state for the charge-transfer configurations. Figure 3a shows the energetical sequence of the states corresponding to the irreducible product basis obtained by linear combinations of $|a\bar{a}\rangle$, $|a\bar{b}\rangle$, $|b\bar{a}\rangle$, and $|b\bar{b}\rangle$. The energies of these states are the following:

$$\begin{aligned} E(^1A) &= E_0 + J_{ab} + 3K_{ab} \\ E(^1E) &= E_0 + J_{ab} + K_{ab} \qquad (3) \\ E(^3A) &= E_0 + J_{ab} - K_{ab} \end{aligned}$$

with the Coulomb and exchange integrals defined as

$$J_{ab} = [aa|bb] = \int a^*(1)a(1)\frac{e^2}{r_{12}}b^*(2)b(2)\,dv_1\,dv_2$$

$$K_{ab} = [ab|ba] = \int a^*(1)b(1)\frac{e^2}{r_{12}}b^*(2)a(2)\,dv_1\,dv_2 \qquad (4)$$

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E_0 contains the energy terms resulting from the one-electron part of the Hamiltonian and the Coulomb and exchange terms for the electron–electron interaction involving orbitals other than a and b. Let us call the electrons in these orbitals core electrons in the following. Although this separation is somewhat arbitrary, it is convenient with respect to the notation that otherwise would involve the full Slater determinant. Equations 3 can be verified by using the following relation between the Coulomb and exchange integrals:

$$J_{ab} = J_{aa} - 2K_{ab} \tag{5}$$

This relation is also a consequence of symmetry and is, of course, not valid in general but only for the orbitals a and b of an e irreducible representation, the product of which can be decomposed according to eq 2.

Now let us discuss the exceptions mentioned above, i.e., the groups C_{4n}, D_{4n}, C_{4nh}, etc. with axes of order $4n$. Any such group contains one or two series of doubly degenerate representations E_1, E_2...E_{2n-1} to which additional labels (g,u or ′,″) may be attached according to the particular point group in question. Within this series, it is just *one* representation, the *n*th E_n, to which the scheme of Figure 3a does not apply. What happens is essentially the following: The states that were of ^1E symmetry in Figure 3a are no longer degenerate, and we end up with two ^1B states instead.[13] Hence, instead of eq 2, we obtain the following decomposition of the reducible product representation:

$$e \otimes e = a + a + b + b \tag{6}$$

The corresponding energy level scheme is given in Figure 3b. It should be noted that eq 5, which allowed us some simplification in the calculation of the energy expression 3, no longer holds. The energies corresponding to Figure 3b are the following:

$$\begin{aligned} E(^1A) &= E_0 + J_{aa} + K_{ab} \\ E(^1B) &= E_0 + J_{aa} - K_{ab} \\ E(^1B) &= E_0 + J_{ab} + K_{ab} \\ E(^3A) &= E_0 + J_{ab} - K_{ab} \end{aligned} \tag{7}$$

A well-known example to which the present scheme applies is square-planar cyclobutadiene. This molecule belongs to the group D_{4h}, and its HOMO is of e_g symmetry. It is important to note that the exchange integral K_{ab} is particularly small in this case. In fact, if we neglect the differential overlap between orbitals on different atoms as is the case in all semiempirical SCF-MO methods (CNDO, INDO, etc.), it even vanishes. Thus, the singlet and triplet ground states $^1B_{2g}$ and $^3A_{2g}$ of cyclobutadiene are degenerate in this approximation. Taking into account electron correlation by configuration interaction pushes the singlet below the triplet.[14] Thus, it looks as if Hund's rule is violated, a phenomenon that can be explained qualitatively by "dynamic spin polarization".[14] In this case, we can forget the McConnell mechanism right from the start. Another well-known example with a singlet instead of a triplet ground state that also corresponds to the energy level scheme of Figure 3b is twisted ethylene with D_{2d} symmetry.[14c] Of course, we cannot conclude from these two examples that a CI calculation will always invert the energy sequence of singlet and triplet states for a molecule corresponding to the energy level scheme of Figure 3b, but we have seen that K_{ab} is sufficiently small that this effect will occur at least in some cases. The singlet and triplet states will therefore always be very close in energy. Thus, molecules corresponding to Figure 3b are no good candidates for the McConnell mechanism even if we cannot exclude that, in some cases, they might have a triplet ground state which is a necessary prerequisite for the McConnell model. In addition, such molecules might be rare in practice. Hence, we will focus on the more common case of Figure 3a in the following.

Why this little digression into some of the more basic notions of group theory? Looking at Figure 1b, we recognize that the energy sequence of the charge-transfer states is essential for McConnell's argument. We have just seen that this energy sequence is completely determined by symmetry if we disregard the effects of CI and just use the symmetry-adapted configurations of Figure 3. It is important to notice that Figure 3 and the corresponding energy expressions 3 and 7 *do not depend on the actual point group of the molecule* if there only is a higher than 2-fold axis and two electrons in two degenerate HOMO's belonging to an e irreducible representation, just the electronic configuration involved in the McConnell mechanism.

In general, the performance of a CI calculation, i.e., the inclusion of electron correlation, will lower the energy of the singlet state more strongly than that of the corresponding triplet and therefore tend to diminish the singlet–triplet energy gap or, as we have seen, even invert the sequence of the energy levels. This is due to the fact that electron correlation of electrons with parallel spins is already included in the Hartree–Fock scheme without CI, which therefore gives a more accurate description of the high-spin as compared to the corresponding low-spin state. Due to symmetry, the exchange integral K_{ab} in Figure 3a has a finite positive value even in an approximation neglecting differential overlap on different atoms and can be assumed to be larger than the corresponding value in Figure 3b, leading to a larger singlet–triplet splitting. Thus, we expect that the performance of a CI calculation will not change the qualitative energy sequence of Figure 3a. Since CI works in favor of the singlet, we will stick to the picture of Figure 3a, which actually favors the McConnell mechanism that we want to argue against.

These symmetry considerations refer to the symmetry of the donor only. The presence of the acceptor will disturb the symmetry of the donor and, in principle, lift the degeneracy of the e orbitals. However, since we have assumed that the donor and acceptor are sufficiently far apart from each other to interact only slightly, the properties of the individual molecules are basically retained and our approach remains a good approximation.

After these introductory remarks, we want to take a closer look at the matrix elements between the different ground and charge-transfer states. We will use the configuration of Figure 2a, but the arguments for the other configurations of Figure 2 are completely analogous. The degenerate donor orbitals are labeled a and b, and the acceptor orbital involved in the charge transfer is labeled c.

We will consider the triplet first. We have already seen that one of the singlet charge-transfer states is degenerate (the ^1E and state of D^0, Figure 3a). The undisturbed ground state of the donor D^+ is also degenerate because the single electron can be in either of the orbitals a and b (^2E for D^+). Omitting the core electrons, we have the following triplet wave functions for the ground and charge-transfer states of the combined donor–acceptor system:

$$\begin{aligned} |^3D^+A_1^-\rangle &= |ac\rangle \\ |^3D^+A_2^-\rangle &= |bc\rangle \\ |^3D^0A^0\rangle &= |ab\rangle \end{aligned} \tag{8}$$

In contrast to Figure 3 where we have chosen the triplet wave function with $M_S = 0$, we use here the one with $M_S = 1$ for computational convenience. We will assume for the moment that all the orbitals are orthogonal. This is an idealization because there is an overlap between donor and acceptor orbitals; otherwise there could be no matrix element between ground and CT states. But this idealization allows us to use the Slater–Condon rules for the evaluation of the matrix elements that otherwise get messy. It should also be noted that we use the same orbitals for the ground and charge-transfer states, thus neglecting orbital reorganization that inevitably takes place if one removes or adds an electron to a molecule. For the matrix element between the first of the ground states and the charge-transfer state in eqs 8, we obtain

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$$\langle {}^3\mathrm{D}^+\mathrm{A}_1^-|\hat{H}|{}^3\mathrm{D}^0\mathrm{A}^0\rangle = \langle \mathrm{c}|\hat{F}_{\mathrm{core}} + \hat{J}_{\mathrm{a}} - \hat{K}_{\mathrm{a}}|\mathrm{b}\rangle \tag{9}$$

with

$$\hat{F}_{\mathrm{core}} = \hat{h} + \hat{J}_{\mathrm{core}} - \hat{K}_{\mathrm{core}} \tag{10}$$

$\hat{h}$ is the one-electron part of the Hamiltonian, whereas $\hat{J}_{\mathrm{core}}$ and $\hat{K}_{\mathrm{core}}$ are sums of the Coulomb and exchange operators for the core electrons. $\hat{J}_{\mathrm{a}}$ and $\hat{K}_{\mathrm{a}}$ are the Coulomb and exchange operators, respectively, for orbital a. They are defined in the usual way:

$$\hat{J}_{\mathrm{a}}(1)\psi(1) = \int \mathrm{d}v_2\, \mathrm{a}^*(2)\mathrm{a}(2)\frac{e^2}{r_{12}}\psi(1)$$

$$\hat{K}_{\mathrm{a}}(1)\psi(1) = \int \mathrm{d}v_2\, \mathrm{a}^*(2)\Psi(2)\frac{e^2}{r_{12}}\mathrm{a}(1) \tag{11}$$

Please note that the Fock Hamiltonian of eq 9 refers to the combined donor–acceptor system whereas the orbitals themselves are assumed to have been determined self-consistently for the individual donor and acceptor molecules.

Now let us consider the singlet states. Whereas we had only one triplet charge-transfer state, we have three singlets (Figure 3). Note that the two ^{1}E states, although degenerate for the individual donor, are not equivalent if we consider their mixing with the ground state because in this case it is the symmetry of the combined donor–acceptor system that matters. We obtain the following states:

$$|{}^1\mathrm{D}^+\mathrm{A}_1^-\rangle = \frac{1}{\sqrt{2}}(|\mathrm{a}\bar{\mathrm{c}}\rangle + |\mathrm{c}\bar{\mathrm{a}}\rangle)$$

$$|{}^1\mathrm{D}^+\mathrm{A}_2^-\rangle = \frac{1}{\sqrt{2}}(|\mathrm{b}\bar{\mathrm{c}}\rangle + |\mathrm{c}\bar{\mathrm{b}}\rangle)$$

$$|{}^1\mathrm{D}^0\mathrm{A}_1^0\rangle = \frac{1}{\sqrt{2}}(|\mathrm{a}\bar{\mathrm{b}}\rangle + |\mathrm{b}\bar{\mathrm{a}}\rangle) \tag{12}$$

$$|{}^1\mathrm{D}^0\mathrm{A}_2^0\rangle = \frac{1}{\sqrt{2}}(|\mathrm{a}\bar{\mathrm{a}}\rangle - |\mathrm{b}\bar{\mathrm{b}}\rangle)$$

$$|{}^1\mathrm{D}^0\mathrm{A}_3^0\rangle = \frac{1}{\sqrt{2}}(|\mathrm{a}\bar{\mathrm{a}}\rangle + |\mathrm{b}\bar{\mathrm{b}}\rangle)$$

Again we consider the first ground state. The corresponding matrix elements are

$$\langle {}^1\mathrm{D}^+\mathrm{A}_1^-|\hat{H}|{}^1\mathrm{D}^0\mathrm{A}_1^0\rangle = \langle \mathrm{c}|\hat{F}_{\mathrm{core}} + \hat{J}_{\mathrm{a}} + \hat{K}_{\mathrm{a}}|\mathrm{b}\rangle$$

$$\langle {}^1\mathrm{D}^+\mathrm{A}_1^-|\hat{H}|{}^1\mathrm{D}^0\mathrm{A}_2^0\rangle = \langle \mathrm{c}|\hat{F}_{\mathrm{core}} + \hat{J}_{\mathrm{a}} - \hat{K}_{\mathrm{b}}|\mathrm{a}\rangle \tag{13}$$

$$\langle {}^1\mathrm{D}^+\mathrm{A}_1^-|\hat{H}|{}^1\mathrm{D}^0\mathrm{A}_3^0\rangle = \langle \mathrm{c}|\hat{F}_{\mathrm{core}} + \hat{J}_{\mathrm{a}} + \hat{K}_{\mathrm{b}}|\mathrm{a}\rangle$$

We have three singlet charge-transfer states to mix with one of the ground states but only one triplet. Obviously this simple fact has been overlooked so far. It will certainly have an impact on the energy stabilization and change the oversimplified picture of McConnell (Figure 1b). Let us write down the energy stabilization for the singlet and the triplet by using the perturbation theory term of eq 1. We can see from eqs 9 and 13 that the Fock operators in the one-electron matrix elements differ by some exchange terms. The influence of these terms on the magnitude of the matrix elements can be assumed to be small, and for reasons of lucidity we will assume a common Fock operator, $\hat{F}$, for all matrix elements in the following. The energy separations of the charge-transfer states from the ground state occurring in the denominator of eq 1 can be inferred from Figure 3a. We obtain

$$U({}^3\mathrm{D}^0\mathrm{A}^0) = \Delta - K$$

$$U({}^1\mathrm{D}^0\mathrm{A}_1^0) = \Delta + K \tag{14}$$

$$U({}^1\mathrm{D}^0\mathrm{A}_2^0) = \Delta + K$$

$$U({}^1\mathrm{D}^0\mathrm{A}_3^0) = \Delta + 3K$$

These values correspond to the wave functions of eqs 8 and 12. With the simplified Fock operator and using eqs 1, 9, 13, and 14,

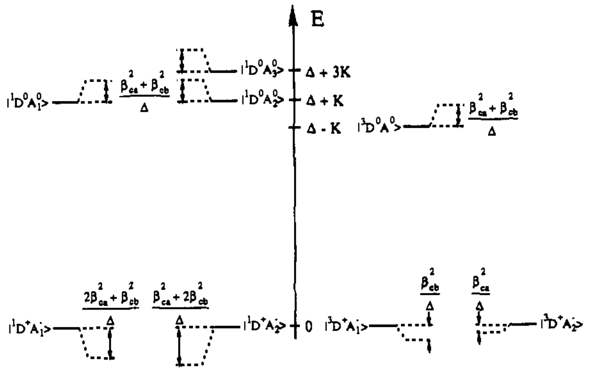


Figure 4. Energy level scheme for $K \ll \Delta$ corresponding to the same orbital configuration as Figure 1b but taking into account all possible ground and charge-transfer states. The singlet states are shown on the left-hand side of the energy axis whereas the triplet states are shown on the right. The energy shifts due to the mixing of ground and charge-transfer states are indicated by dashed lines.

we obtain the following energy stabilizations for the singlet and the triplet states:

$$\Delta E_{\mathrm{T}}^1 = \frac{|\langle \mathrm{c}|\hat{F}|\mathrm{b}\rangle|^2}{\Delta - K}$$

$$\Delta E_{\mathrm{S}}^1 = \frac{|\langle \mathrm{c}|\hat{F}|\mathrm{b}\rangle|^2}{\Delta + K} + \frac{|\langle \mathrm{c}|\hat{F}|\mathrm{a}\rangle|^2}{\Delta + K} + \frac{|\langle \mathrm{c}|\hat{F}|\mathrm{a}\rangle|^2}{\Delta + 3K} \tag{15}$$

This is the energy stabilization for the first of the two degenerate ground states, namely, the one with the single donor electron of D$^+$ in orbital a. The procedure for the second state with the single electron in orbital b is completely analogous to the one just described; all we have to do is to interchange the labels a and b in eqs 8–15. Thus, we end up with the following expression for the energy stabilization of the second ground state:

$$\Delta E_{\mathrm{T}}^2 = \frac{|\langle \mathrm{c}|\hat{F}|\mathrm{a}\rangle|^2}{\Delta - K}$$

$$\Delta E_{\mathrm{S}}^2 = \frac{|\langle \mathrm{c}|\hat{F}|\mathrm{a}\rangle|^2}{\Delta + K} + \frac{|\langle \mathrm{c}|\hat{F}|\mathrm{b}\rangle|^2}{\Delta + K} + \frac{|\langle \mathrm{c}|\hat{F}|\mathrm{b}\rangle|^2}{\Delta + 3K} \tag{16}$$

The exchange integral K is in general a small quantity; it is less than 1 eV in most cases. Δ on the other hand denotes the energy necessary to transfer an electron back from the acceptor to the donor in our case. This quantity can and in many cases will be quite large, amounting to several eV's. Then all the denominators occuring in eqs 15 and 16 will have similar values, and the additional terms for the singlet energy will weigh in favor of a singlet ground state. That means that the McConnell mechanism does not work if we assume that Δ is sufficiently large as compared to K. It should be noted that the matrix elements in eqs 15 and 16 do not all involve the same orbitals. The triplet and one of the singlet matrix elements in eqs 15 is formed between orbitals b and c, whereas the remaining two singlet matrix elements involve a and c. One could imagine that the combined donor–acceptor system still has some symmetry, e.g., a mirror plane. If orbitals b and c are of the same symmetry with respect to this symmetry element but a and c are not, the second and third term for the singlet in eqs 15 vanish. In this case, it is the singlet of eqs 16 that will be the lowest state because it contains two terms with the matrix element $\langle \mathrm{c}|\hat{F}|\mathrm{b}\rangle$.

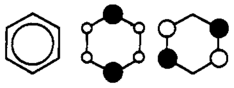
We are now able to present a more accurate picture than that of Figure 1b, at least for $K \ll \Delta$. This is done in Figure 4 where we use an abbreviated notation for the matrix elements, e.g., $\langle \mathrm{c}|\hat{F}|\mathrm{b}\rangle = \beta_{\mathrm{cb}}$. The figure is based on eqs 15 and 16. It would be interesting to support this merely qualitative picture by a quantitative calculation for a hypothetical model system.

3. A Modification of the McConnell Mechanism for Uniform Stacks

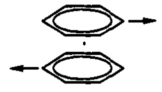
We already mentioned that the McConnell mechanism can be also considered for a uniform stack, e.g., of aromatic molecules with one radical electron per site corresponding to a negative charge. This modification has been introduced by Torrance et al.[9] It has been discussed later by Bagus and Torrance[12] who performed a calculation for a hypothetical benzene anion dimer. Torrance's modification of the McConnell mechanism is illustrated in Figure 5, picking again a dimer from the one-dimensional stack. The degenerate orbital pairs on molecules A and B are denoted as a_A, b_A and a_B, b_B, respectively. A and B are of course the same molecules.

Unfortunately, the number of electronic configurations is now twice as large as before; we have sixteen of them. They consist of eight ground-state configurations (four singlets and four triplets) and eight charge-transfer configurations (six singlets and two triplets). Correspondingly, there are a lot of possibilities for mixing, and the situation is therefore not very transparent. One could imagine that there is a symmetry operation which interchanges the two molecules, e.g., an inversion center, a reflection plane, or a C_2 axis, a situation perhaps not too unlikely for a dimer in a uniform stack. In this case, we can distinguish states with g and u symmetry, which of course cannot mix with each other. Thus, we have a less complicated mixing pattern. We will come back to this below, but let us start with an even more symmetrical situation by choosing the model system of Bagus and Torrance.[12] This is the hypothetical benzene anion dimer with one negative charge per benzene molecule.

Our discussion of this compound will be qualitative and is mainly based on symmetry considerations. The orbital pattern corresponds to Figure 5, with a and b now being the e_{2u} orbitals of benzene (**1**). We assume an eclipsed configuration as in ref 12 (**2**). Thus, the D_{6h} symmetry is retained for the dimer, and we can classify the states according to this symmetry group. It can be shown that, in this case, all ground-state configurations are symmetry distinct and that the same holds for the charge-transfer configurations. Thus, each ground-state configuration has maximally one charge-transfer partner to mix with and vice versa. Some states have no partner at all as we will see below.



1



2

Finding the symmetry-adapted product functions for the dimer is an exercise in group theory, and we give only the final result:

$$|^1E_{2g}^{CT}\rangle = \begin{cases} {}^1/_2(|a_A\bar{a}_A\rangle - |b_A\bar{b}_A\rangle + |a_B\bar{a}_B\rangle - |b_B\bar{b}_B\rangle) \\ {}^1/_2(|a_A\bar{b}_A\rangle + |b_A\bar{a}_A\rangle + |a_B\bar{b}_B\rangle + |b_B\bar{a}_B\rangle) \end{cases}$$

$$|^1E_{2g}^{GS}\rangle = \begin{cases} {}^1/_2(|a_B\bar{a}_A\rangle - |b_B\bar{b}_A\rangle + |a_A\bar{a}_B\rangle - |b_A\bar{b}_B\rangle) \\ {}^1/_2(|a_B\bar{b}_A\rangle + |b_A\bar{a}_B\rangle + |a_A\bar{b}_B\rangle + |b_B\bar{a}_A\rangle) \end{cases}$$

$$|^1A_{1g}^{CT}\rangle = {}^1\!/_2(|a_A\bar{a}_A\rangle + |b_A\bar{b}_A\rangle + |a_B\bar{a}_B\rangle + |b_B\bar{b}_B\rangle)$$

$$|^1A_{1g}^{GS}\rangle = {}^1\!/_2(|a_B\bar{a}_A\rangle + |b_B\bar{b}_A\rangle + |a_A\bar{a}_B\rangle + |b_A\bar{b}_B\rangle)$$

$$|^3A_{2g}^{CT}\rangle = {}^1\!/_2(|a_A\bar{b}_A\rangle - |b_A\bar{a}_A\rangle + |a_B\bar{b}_B\rangle - |b_B\bar{a}_B\rangle)$$

$$|^3A_{2g}^{GS}\rangle = {}^1\!/_2(|a_B\bar{b}_A\rangle - |b_A\bar{a}_B\rangle + |a_A\bar{b}_B\rangle - |b_B\bar{a}_A\rangle) \qquad (17)$$

$$|^1E_{2u}^{CT}\rangle = \begin{cases} {}^1/_2(|a_A\bar{a}_A\rangle - |b_A\bar{b}_A\rangle - |a_B\bar{a}_B\rangle + |b_B\bar{b}_B\rangle) \\ {}^1/_2(|a_A\bar{b}_A\rangle + |b_A\bar{a}_A\rangle - |a_B\bar{b}_B\rangle - |b_B\bar{a}_B\rangle) \end{cases}$$

$$|^1A_{1u}^{CT}\rangle = {}^1\!/_2(|a_A\bar{a}_A\rangle + |b_A\bar{b}_A\rangle - |a_B\bar{a}_B\rangle - |b_B\bar{b}_B\rangle)$$

$$|^1A_{2u}^{GS}\rangle = {}^1\!/_2(|a_B\bar{b}_A\rangle + |b_A\bar{a}_B\rangle - |a_A\bar{b}_B\rangle - |b_B\bar{a}_A\rangle)$$

$$|^3E_{2u}^{GS}\rangle = \begin{cases} {}^1/_2(|a_B\bar{a}_A\rangle - |b_B\bar{b}_A\rangle - |a_A\bar{a}_B\rangle + |b_A\bar{b}_B\rangle) \\ {}^1/_2(|a_B\bar{b}_A\rangle - |b_A\bar{a}_B\rangle - |a_A\bar{b}_B\rangle + |b_B\bar{a}_A\rangle) \end{cases}$$

$$|^3A_{1u}^{GS}\rangle = {}^1\!/_2(|a_B\bar{a}_A\rangle + |b_B\bar{b}_A\rangle - |a_A\bar{a}_B\rangle - |b_A\bar{b}_B\rangle)$$

$$|^3A_{2u}^{CT}\rangle = {}^1\!/_2(|a_A\bar{b}_A\rangle - |b_A\bar{a}_A\rangle - |a_B\bar{b}_B\rangle + |b_B\bar{a}_B\rangle)$$

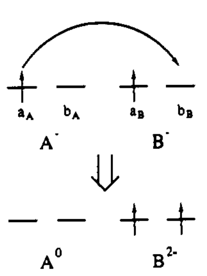


Figure 5. Orbital configuration for a dimer of a uniform stack. The HOMO of each molecule is degenerate, with the corresponding orbitals of molecule A and B denoted as a_A,b_A and a_B,b_B, respectively. We have indicated the charge transfer for one of the triplet configurations.

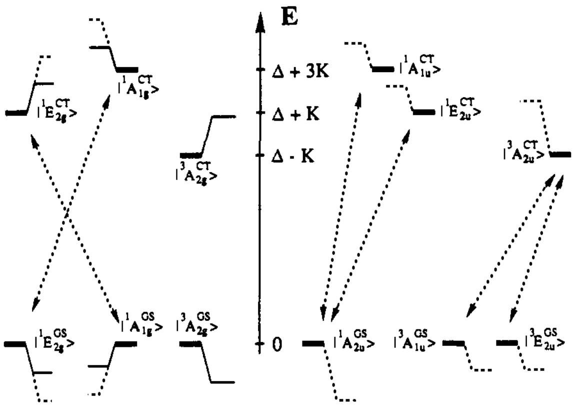


Figure 6. Energy level scheme of a benzene anion dimer. The states with g symmetry with respect to the inversion center are shown on the left of the energy axis whereas the u states can be found on the right. It should be noted that this energy level scheme is of general validity as far as the undisturbed ground and charge-transfer states are concerned. The symmetry labels, however, refer to our specific situation of the benzene anion dimer with D_{6h} symmetry. The energy shifts due to the mixing of ground and charge-transfer states for the latter case are indicated by full lines. The dashed arrows and lines show additional mixing possibilities and the corresponding additional energy shifts, respectively, if we remove the D_{6h} symmetry but retain the inversion center.

The indices GS and CT refer to ground state and charge-transfer state, respectively. Equations 17 are not transparent, either. It is much more illustrative to depict the states of eqs 17 in an energy level diagram as shown in Figure 6. This figure should be compared to Figure 1 of ref 12. Now we can see more clearly what happens; the states with symmetry u with respect to the inversion center shown on the right of the energy axis in Figure 6 differ either by spin or by their spatial symmetry so that they cannot mix at all for D_{6h} symmetry. The situation is different for the g states where there is a corresponding charge-transfer state for each ground state of a certain spin and symmetry. The energy shifts due to the mixing of these states are indicated by the full lines in Figure 6. We can see that McConnell's argument applies in this case; the lowest state will be a triplet of A_{2g} symmetry in accordance with the quantitative results of Bagus and Torrance.[12]

Now we want to consider a lowering of the symmetry of the dimer. It is illustrative to do this in such a way that the inversion center is retained. This can be achieved by shifting the benzene molecules out of registry while keeping their molecular planes parallel. The displacement is indicated by the arrows in **2** where we also marked the inversion center. The energy level scheme of Figure 6 remains valid in this case for the undisturbed ground and charge-transfer states. The symmetry labels in the figure however loose their meaning except for the g and u indices attached to them. These indices refer to the inversion center we retain. As a consequence of the loss of symmetry, more states can mix. The additional mixing possibilities are indicated by the dashed arrows in Figure 6. The triplet g state, which was the lowest one before, however, still has only one charge-transfer state to mix with. The singlet g states, on the other hand, acquire additional

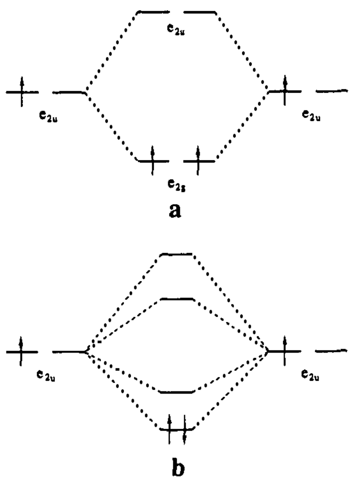


Figure 7. Schematical MO interaction diagram for the interaction of the e_{2u} orbitals of two benzene anions combined to a dimer. In (a), the two molecules are in an eclipsed position, thus retaining the D_{6h} symmetry and the orbital degeneracy. In (b), this symmetry is removed for the dimer. Hence, the degeneracy is lifted.

energy stabilization terms, which are indicated schematically by dashed lines in Figure 6. It should be noted that we have drawn only one state for the two degenerate E_{2g} states in Figure 6. Lowering of the symmetry will lead to additional cross-term mixing between the former E_{2g} ground and charge-transfer states, which is not visible in Figure 6. There is now also some mixing for the u states, which remained pure for D_{6h} symmetry. Again the number of charge-transfer states available for mixing is higher for the singlet than for the triplet ground states as can be seen from Figure 6.

So far we still retained the inversion center as a symmetry element. If the dimer has no symmetry at all, any singlet and triplet ground state can mix with any singlet and triplet charge-transfer state, respectively, and vice versa. The situation is complicated, but it is obvious from Figure 6 that the singlet states have more possibilities for mixing and, thus, more energy stabilization terms available than the triplets.

Of course, we cannot say that the additional mixing possibilities will shift one or more of the singlets below the triplet in any case if we just remove the D_{6h} symmetry. This will depend on the actual geometry of the dimer, and no predictions are possible on the qualitative level of our discussion. What seems clear, however, is that the highly symmetrical molecular arrangement chosen by Bagus and Torrance for their calculation favors the triplet. Moreover, the configuration space of their calculation involves only electron shifts within the orbitals shown in Figure 5. We already mentioned that a more extensive CI will lower the energy gaps between the singlet and triplet states of $C_6H_6^{2-}$ (see footnote 9 of ref 12). Thus, both the assumed geometry and the lack of electron correlation in the calculation of Bagus and Torrance are in favor of the triplet.

It is interesting to note that the symmetry argument stressed above applies also to an MO picture. We want to emphasize that this picture is certainly not appropriate in the case of the benzene anion dimer given the large distance between the benzene molecules. Nevertheless, it is illustrative to consider the MO interaction diagram for a benzene anion dimer with and without D_{6h} symmetry. Such a diagram is shown schematically in Figure 7. It can be seen that, for the symmetrical situation, the HOMO of the dimer consists of two degenerate e_{2g} orbitals (Figure 7a). Placing two electrons in these orbitals results in a triplet state according to Hund's rule. If we remove the D_{6h} symmetry, the degeneracy is lifted as shown in Figure 7b. Now the ground state can be expected to be a singlet if the HOMO-LUMO splitting is sufficiently large.

4. Discussion and Conclusions

In the preceding sections, we have shown that the idea of McConnell for ferromagnetic coupling in molecular compounds is too simple because it does not take into account the whole multitude of electronic configurations arising from the orbital pattern involved in the mechanism. The least one can say is that the mechanism is not of the general validity assumed so far. We cannot rule out the mechanism completely, but its application might be restricted to special circumstances. Those are encountered when the charge-transfer energy Δ is small, i.e., of the same order of magnitude as the exchange integral K. In this case, the differences in the energy stabilization terms for the singlet and the triplet are dominated by the denominators of the perturbation theory terms of eqs 15 and 16 rather than by the matrix elements in the nominators.

For the benzene dianion dimer, the values $\Delta = 6.7$ eV and $K = 0.37$ eV are given by Bagus and Torrance.[12] This is in accordance with our assumption $K \ll \Delta$. Experimentally determined Δ values for stacks of tetrathiafulvalenium (TTF$^+$) or tetracyano-*p*-quinodimethane (TCNQ) are smaller, only $\sim$1–1.5 eV.[15] But even this value is larger than any reasonable value for the exchange integral K in aromatic molecules. Charge-transfer energies for a variety of mixed stack organic CT compounds can also be found in the literature.[7] They range from $\sim$1 to 3 eV. Calculations like the one of Bagus and Torrance for the benzene anion dimer might also help to determine such values. In the solid state, additional effects like Madelung corrections have to be included. Nevertheless, the requirement of small Δ values places a serious restriction on the McConnell mechanism.

Another open question concerns the assumption of orthogonal orbitals. This facilitates the calculation of the matrix elements considerably, leading to the simple terms 9 and 13. Of course one could assume that the orbitals are Löwdin-orthogonalized.[16] But it is not a priori clear whether this is an admissible procedure in our case. Our approach is in some sense similar to a valence bond approach where the wave functions comprise electrons in localized orbitals rather than delocalized ones. The localized orbitals in our case are not AO's but the MO's of either the donor or the acceptor. Performing a Löwdin orthogonalization will delocalize the orbitals; i.e., an orbital on the donor will acquire some contribution from the acceptor and vice versa. This delocalization will be small due to the small overlap of donor and acceptor orbitals, but the same small overlap also provides for a small charge-transfer mixing, which is the crucial effect. Although the calculation of the matrix elements is therefore obscured by the problem of overlap, it is not clear if a correct inclusion of the overlap integrals would favor the triplet. In any case, our main argument that there are more singlet than triplet charge-transfer states available for mixing with the corresponding ground states remains unaffected. It is this argument that casts doubt on the oversimplified picture of McConnell.

The McConnell mechanism is based on the mixing with charge-transfer states. Of course there is also a singlet–triplet energy splitting if we consider the ground-state configurations alone in analogy to the Heitler–London method for the hydrogen molecule, which does not include charge-transfer (ionic) states. But the calculation of Bagus and Torrance for the benzene anion dimer shows that this contribution is small and that the singlet–triplet splitting is really dominated by the mixing with charge-transfer states, thus justifying this aspect of McConnell's idea. We are therefore faced with a kind of paradox: Whereas in our case (e.g., the benzene anion dimer) the mixing with charge-transfer states is small due to the large distance of the molecules (leading to a small matrix element in the nominator of eq 1), it is nevertheless this small mixing that dominates the singlet–triplet splittings. For the H_2 molecule, on the other hand, the ionic states contribute considerably, but one can obtain a reasonably good description of the singlet–triplet splitting by omitting them (in fact, the Heitler–London method is superior to the MO method of Hund and Mulliken, which exaggerates the role of the

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(15) (a) Torrance, J. B. *Acc. Chem. Res.* **1979**, *12*, 79. (b) Torrance, J. B.; Scott, B. A.; Welber, B.; Kaufman, F. B.; Seiden, P. E. *Phys. Rev. B* **1979**, *19*, 730.

(16) Löwdin, P. O. *J. Chem. Phys.* **1950**, *18*, 365.

J. Am. Chem. Soc. 1991, 113, 7994–8005

charge-transfer states). The contribution of the ground state alone to the singlet–triplet splitting will favor the singlet in most cases, except if the overlap integral between the orbitals containing the radical electrons vanishes for symmetry reasons.[17]

The so-called McConnell mechanism has been mentioned in a quite inaccessible source[6] in a short section without being elaborated in detail. It is surprising that such a more or less spontaneous idea could give rise to such extensive experimental efforts without being checked thoroughly. Maybe our arguments will give second thoughts to experimentalists working along this line. It is already difficult enough to prepare molecules with a stable triplet ground state.[11] The additional requirement of a very small charge-transfer parameter, Δ, in order for the McConnell mechanism to work will further compound the experimental difficulties. As to the modification of the mechanism introduced by Torrance et al.,[9] it seems that it can work in principle but rests on a highly symmetrical arrangement of the molecules in the stack. It may be very difficult to achieve such an arrangement in a real system.

A word seems also in place with respect to the invokation of the McConnell mechanism for some recently discovered organometallic complexes that exhibit ferromagnetic behavior.[8,10] We do not believe that the McConnell mechanism can provide for an explanation of the ferromagnetism in any of these cases. In a subsequent paper, we will present evidence that it does not for the DMFcTCNE complex. An alternative model for the ferromagnetism of this complex will also be proposed in this paper.

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[17] Kahn, O.; Charlot, M. F. In *Valence Bond Theory and Chemical Structure*; Klein, D. J., Trinastic, N., Eds.; Elsevier: Amsterdam, 1990; p 489.

A Mechanism for the Ferromagnetic Coupling in Decamethylferrocenium Tetracyanoethenide

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Abstract: We discuss a model for the ferromagnetic coupling in a stack of alternating $[Fe(C_5Me_5)_2]^+$ and $[TCNE]^-$ ions. We present evidence against the proposed mechanism based on a model suggested by McConnell in which the ferromagnetism arises from configurational mixing of a virtual triplet excited state ($D^{2+}A^{2-}$) with the ground state D^+A^- ($D = Fe(C_5Me_5)_2$, A = TCNE). Instead, we point to a different kind of configurational mixing that involves a singly excited configuration on ferrocenium. The excitation arises from a transition between orbitals of two e_{1g} sets, which are the only ones with considerable covalent character. First, we set up the symmetry-adapted $^2E_{2g}$ ground- and excited-state wave functions for a single ferrocenium ion and discuss their mixing. It is shown that this mixing gives rise to an important spin correlation effect inducing negative spin densities on the Cp rings. Then the ferrocenium doublet wave functions are coupled to the TCNE doublet to form singlet and triplet wave functions for a donor–acceptor pair. The resulting singlet–triplet energy difference can be interpreted as an exchange effect between the negative spin density on the Cp rings and the radical electron density on TCNE in complete analogy to the Heitler–London model for the H_2 molecule. We obtain a term comprising a two-electron exchange integral and products of overlap and resonance integrals. Due to the negative sign of the spin density on the Cp rings, the signs of these contributions and, thus, the sign of the singlet–triplet energy splitting are inverted in our case as compared to the Heitler–London model, resulting in a triplet ground state for a donor–acceptor pair and, thus, ferromagnetic coupling. The exchange between the spin density on Fe and the one on TCNE can be neglected because the corresponding overlap densities are very small due to the large distance between Fe and TCNE (5 Å as compared to 3.5 Å for the distance Cp–TCNE). Our model corresponds to another coupling mechanism suggested by McConnell, which has nothing to do with the configurational mixing of donor–acceptor charge-transfer states.

1. Introduction

Molecular ferromagnets, both organic and organometallic, have aroused a lot of interest in recent times.[1] This is due to the ease of synthesis of organic materials. It is expected that the magnetic properties of these compounds can be tuned over a wide range by simple manipulations of the organic constituents. This would make these materials interesting for future technical applications, particularly in magnetooptics.

Different strategies, both theoretically and synthetically, have been pursued for the design of these materials. One of them is based on high-spin organic molecules, e.g., polycarbenes. Tetracarbenes with a nonet ground state[2] and pentacarbenes with $S = 5$[3] have been synthesized, but no real polymeric material of this kind is known as yet. Theoretically, many one- and two-dimensional hypothetical organic polymers with a conjugated π system and ferromagnetic coupling of their radical electrons have been suggested.[4] The ferromagnetism of these molecules results from the topology of their π electron networks in accordance with the Coulson–Rushbrooke theorem.[5] Even if these polymers with intramolecular ferromagnetic coupling could be synthesized, an intermolecular coupling mechanism would be needed in order to achieve bulk ferromagnetism. It is indeed well established that there is no one- or two-dimensional magnetic ordering.[6] Such an intermolecular coupling mechanism for conjugated π radicals has been suggested by McConnell.[7] This mechanism is based

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