

Heisenberg Hamiltonian for charge-transfer organometallic ferromagnets

A. L. Tchougreeff^{a)}

Department of Chemistry, Cornell University, Ithaca, New York 14853-1301

(Received 25 October 1991; accepted 2 January 1992)

A highly anisotropic Heisenberg spin one-half Hamiltonian is derived for the organometallic charge-transfer ferromagnet DMeFc-TCNE and its effective exchange parameters are estimated. Its relationship to the generally adopted McConnell picture of ferromagnetic interaction in such systems is established and particular charge-transfer states responsible for the ferromagnetic sign of the effective spin-spin interaction are discussed. The model proposed is valid for a number of charge-transfer magnets. Possible effects of high anisotropy on critical temperature in the DMeFc-TCNE ferromagnet are discussed briefly.

I. INTRODUCTION

In recent years, numerous molecular magnets have been synthesized.¹⁻⁴ Among these, the charge-transfer ferromagnets proposed by Miller, Epstein, and co-workers are of particular interest because they realize effectively a simple idea—to construct a ferromagnetic material from separate molecules in the most direct fashion. [The crystals of the Miller-Epstein compounds are assemblies of the separate molecules of the donor (usually metallocenes) and acceptor (usually polycyanolefines) types. Molecules of the both types bear unpaired electrons.] However, a complete theoretical model for the magnetic order in charge-transfer organometallic crystals has not yet been developed. Experimental data on molecular magnets are usually fitted to Heisenberg models with ferromagnetic nearest-neighbor interactions. However, the Heisenberg model is itself semiempirical and its applicability must be confirmed. We need to understand how the effective exchange between the localized spins arises and how this gives rise to ferromagnetic vs antiferromagnetic behavior.

The origin of the effective exchange in the Miller-Epstein magnets is attributed unanimously to charge-transfer states.^{1,2,5} Soos and McWilliams⁵ noticed that the charge-transfer states involving ligand orbitals of the donor molecules are particularly important. Their contribution was taken into account⁶⁻⁸ by the hopping term coupling the singly occupied orbital of the acceptor with the vacant orbital of the donor. No direct interaction is available⁵⁻⁸ between unpaired electrons on the donor and acceptor sites. It has been proposed⁶⁻⁸ that a Kondo type term on the donor site appears to provide the necessary coupling between the localized unpaired electrons in the *d* shell of the metallocene donor molecule and the electron back transferred from the acceptor to the vacant orbital of the donor. This interaction is of the Coulomb origin and the most important contribution to it is the *intraatomic* Heisenberg exchange^{5,9} (i.e., the spin-dependent part of the Coulomb interaction). The same

interaction is responsible for the validity of Hund's rule in atoms.

Recently, a model Hamiltonian has been proposed for the one-dimensional donor-acceptor stack.⁶⁻⁸ It incorporates all of the terms which are necessary to describe a charge-transfer ferromagnet. These include the kinetic energy of electrons (or the electron hopping term), electron-electron repulsion, and the Kondo term describing the spin-dependent part of the electron-electron interaction in the donor molecule. It is worthwhile to note that in contrast to the semiempirical Heisenberg spin-spin interactions, all the interactions mentioned just above are in some sense fundamental ones. They are not introduced *ad hoc*, but are present in the exact electronic Hamiltonian of the crystal.

The model Hamiltonian⁶⁻⁸ was reduced to the ferromagnetic Heisenberg Hamiltonian.⁸ However, the considerations of this paper⁸ contain two interconnected imperfections. They are limited to separate one-dimensional donor-acceptor stacks and the entire treatment is carried out in the framework of the unrestricted Hartree-Fock (UHF) approximation. It is known, however, that the UHF approximation applied to one-dimensional systems always gives a ground state with long-range order, irrespective whether that order really exists or not. Therefore, results derived for the one-dimensional system in the UHF approximation cannot be extended to the three-dimensional system directly. Nevertheless, the form of the effective exchange parameters obtained in Ref. 8 suggests that a satisfactory description could be derived in the framework of a perturbative treatment of the kinetic energy term in the model Hamiltonian.⁶ The perturbative approach can be applied effectively to three-dimensional systems. It usually leads to effective spin Hamiltonians, which are known to give the long-range magnetic order only when the exact solution has the same order.

The purpose of this paper is to derive the Heisenberg Hamiltonian for the whole crystal of the charge-transfer Miller-Epstein compounds, starting from the more general model Hamiltonian.⁶⁻⁸ In this way, we expect to get an effective spin Heisenberg Hamiltonian of the crystal and to estimate its effective exchange parameters. We also hope to avoid the limitations of the UHF approximation and of one dimensionality.

^{a)} On leave from the L. Y. Karpov Institute of Physical Chemistry, Moscow, Russia.

II. THEORY

A. Effective Heisenberg Hamiltonian for the donor-acceptor pair

The Miller-Epstein compounds consist of molecules of two types—donors (D, metallocenes) and acceptors [A, tetracyanethylene (TCNE), tetracyanoquinodimethane (TCNQ), and others of that type]. Normally, their stoichiometry is 1:1. In the crystal, one electron in each DA pair is transferred completely from the donor site to the acceptor site: thus the electronic structure of the entire crystal can be depicted as $\cdots D^+ A^- D^+ A^- D^+ A^- \cdots$. Both the donor and the acceptor sites bear local spins. According to Ref. 8, the following orbitals are to be included in the model in order to describe the effective interactions between local spins: on the acceptor site, one orbital, namely, the lowest unoccupied orbital of the free acceptor molecule, or equivalently the singly occupied one of the radical anion, is considered. This orbital will be referred to as an acceptor orbital. On the donor site, several orbitals must be taken into account. First, there is at least one empty orbital which has a nonvanishing overlap

with the acceptor orbital defined previously (this orbital hereafter will be referred to as a ligand orbital). Other orbitals on the donor sites (d orbitals) are included depending on the particular magnitude of the local spin residing on that site. For example, in the iron derivative containing decamethylferrocene as donor ($D = \text{DMeFc} = \text{FeCp}_2^*$, where Cp^* stands for the permethylated cyclopentadienyl anion), the local momentum residing on the donor site corresponds to $S = 1/2$. Therefore, we include one singly occupied d orbital on each donor site to reproduce this value of the local spin. On the other hand, in the case of the manganese derivative containing decamethyl-manganocene as a donor ($D = \text{MnCp}_2^*$) $S = 1$, at least two singly occupied d orbitals must be included on each donor site. We will consider explicitly the simplest case of the DMeFc-TCNE compound with one d orbital on each donor site. Generalization to cases of larger local spin is obvious.

Let us now consider a donor-acceptor pair ($D^+ A^-$, $D = \text{DMeFc}$, $A = \text{TCNE}$) extracted from the crystal. The Hamiltonian⁸ for such a pair, formulating the above qualitative considerations, has the form

$$\begin{aligned}
 H &= H_0 + H_R, \quad H_0 = - \sum_{\sigma} (\alpha_L \hat{n}_{L\sigma} + \alpha_A \hat{n}_{A\sigma} + W \hat{n}_{d\sigma}) + \gamma_L \hat{n}_{L_1} \hat{n}_{L_1'} + \gamma_A \hat{n}_{A_1} \hat{n}_{A_1'} + U \hat{n}_{d_1} \hat{n}_{d_1'} + K \hat{S}_L \hat{S}_d, \\
 H_R &= -t \sum_{\sigma} (L_{\sigma}^+ A_{\sigma} + A_{\sigma}^+ L_{\sigma}), \quad \hat{n}_{L\sigma} = L_{\sigma}^+ L_{\sigma}, \quad \hat{n}_{A\sigma} = A_{\sigma}^+ A_{\sigma}, \quad \hat{n}_{d\sigma} = d_{\sigma}^+ d_{\sigma}, \\
 \hat{S}_L \hat{S}_d &= 1/2 (S_L^+ S_d^- + S_d^+ S_L^-) + S_L^z S_d^z, \quad S_L^+ = L_1^+ L_1, \quad S_L^- = L_1^- L_1, \\
 S_d^+ &= d_1^+ d_1, \quad S_d^- = d_1^- d_1, \quad S_L^z = 1/2 (\hat{n}_{L_1} - \hat{n}_{L_1'}), \quad S_d^z = 1/2 (\hat{n}_{d_1} - \hat{n}_{d_1'}).
 \end{aligned} \tag{1}$$

Here L_{σ} is the annihilation operator for an electron with spin projection σ on the ligand orbital; A_{σ} and d_{σ} are the same for the acceptor and d orbitals; the spin projection $\sigma = \pm 1/2$ and its positive and negative values are denoted by the $_+$ and $_-$ subscripts, respectively.

In Eq. (1), the first term in H_0 is the energy of attraction of electrons to their sites, the second term describes the on-site Coulomb repulsion in the simplest Hubbard form, and the last term in H_0 , the Kondo term, describes the spin-dependent part of the intramolecular Coulomb interaction (intramolecular exchange) of unpaired d electron with an electron in the ligand orbital. The exchange parameter K is simply the Heisenberg exchange integral for the d and the ligand orbitals at the same site multiplied by -2 [$K = -2(dL|Ld)$]. Thus it has ferromagnetic sign ($K < 0$). The operator H_R is the resonance or hopping operator. It describes one-electron transfers between the acceptor orbital and the ligand orbital.

We will now consider the Hamiltonian H_0 as the zero-order Hamiltonian and the hopping term H_R as a perturbation. According to the generally accepted¹⁻⁴ picture of the electronic structure of the DMeFc-TCNE salt, two unpaired electrons occupy acceptor and d orbitals. All the states of the Hamiltonian H_0 with two unpaired electrons in these two orbitals are degenerate. The perturbation theory in the form

of the Löwdin projection method¹⁰ will be used to find out how the degeneracy is removed by the hopping term.

Let P be the projection operator on the subspace of the entire configurational space of the separate $D^+ A^-$ pair, which is spanned by the two-electron basis states, where unpaired electrons occupy d and acceptor orbitals only. Let Q be the complementary projection operator ($Q = 1 - P$). The effective Hamiltonian acting in the P subspace has the form¹⁰

$$H^{\text{eff}} = PHP + PHQR_Q(E)QHP, \tag{2}$$

where $RQ(E) = (QE - QHQ)^{-1}$ is the resolvent of the operator H in the complementary subspace (Q subspace).

The action of the projection operator P is obvious

$$\begin{aligned}
 L_{\sigma} P &= PL_{\sigma}^+ \equiv 0, \quad PHP = PH_0 P, \quad QHQ = QH_0 Q, \\
 QHP &= QH_R P, \quad PHQ = PH_R Q.
 \end{aligned}$$

All the states of the Hamiltonian H_0 in the P subspace have the same energy $E_0 = -\alpha_A - W$. The states of the Hamiltonian H_0 in the Q subspace are not degenerate. The singlet and triplet states which are produced by transfer of one electron from the acceptor orbital to the ligand orbital have different energies due to the Kondo term.

The projection operator Q is the sum of its singlet and triplet constituents $Q = Q_S + Q_T$. The energies of the sing-

let and triplet back-charge-transfer states measured from the E_0 level are, respectively,

$$\Delta E_{\text{BCT}}^{\text{S}} = \Delta\alpha - K/2, \quad \Delta E_{\text{BCT}}^{\text{T}} = \Delta\alpha + K/2,$$

where $\Delta\alpha = \alpha_A - \alpha_L$. The triplet back-charge-transfer state has lower energy due to the sign of the exchange parameter.

The resolvent becomes

$$R_Q(E_0) = -\frac{Q_S}{\Delta\alpha - K/2} - \frac{Q_T}{\Delta\alpha + K/2}.$$

The projection operators Q_S and Q_T can be readily expressed through the operator of the total spin on the donor site

$$\hat{S}_D = \hat{S}_d + \hat{S}_L, \quad Q_S = 1 - \hat{S}_D^2/2, \quad Q_T = \hat{S}_D^2/2.$$

The operator Q_S removes the triplet states [those with $S_D(S_D + 1) = 2$] and keeps unchanged the singlet ones ($S_D = 0$), whereas Q_T removes singlets and keeps triplets. After some easy algebra, we get

$$R_Q(E_0) = -\frac{1}{\Delta\alpha - K/2} + \frac{\hat{S}_D^2}{2} \frac{K}{(\Delta\alpha)^2 - K^2/4}.$$

Substituting the explicit form of the total spin operator and the eigenvalues of the square spin operators for individual electrons in the ligand and d orbitals ($3/4$), we get

$$R_Q(E_0) = -\frac{\Delta\alpha - K/4}{(\Delta\alpha)^2 - K^2/4} + \frac{K}{(\Delta\alpha)^2 - K^2/4} \hat{S}_d \hat{S}_L.$$

Since the energies of the both charge-transfer states are positive, the denominator in both resolvent terms is positive as well. This expression must be inserted into Eq. (2) for the effective Hamiltonian. Taking into account the abovementioned properties of the projection operators P and Q , we can write

$$H^{\text{eff}} = t^2 \sum_{\sigma, \sigma'} P A_{\sigma}^{\dagger} L_{\sigma} R_Q(E_0) L_{\sigma'}^{\dagger} A_{\sigma'} P.$$

The resolvent comprises two terms—a constant and a spin multiplier term. Therefore, the effective Hamiltonian can also be split into two terms. The spin-independent term is

$$H_1^{\text{eff}} = t^2 \frac{\Delta\alpha - K/4}{(\Delta\alpha)^2 - K^2/4} \sum_{\sigma} \hat{n}_{A\sigma}.$$

It describes a bonding due to weak delocalization of an electron from the acceptor orbital to the ligand orbital. All the effects of magnetic ordering are hidden in the second, spin-dependent term

$$H_2^{\text{eff}} = \frac{t^2 K}{(\Delta\alpha)^2 - K^2/4} \sum_{\sigma, \sigma'} P A_{\sigma}^{\dagger} L_{\sigma} \hat{S}_d \hat{S}_L L_{\sigma'}^{\dagger} A_{\sigma'} P.$$

Inserting the explicit formula (1) for the product of the spin operators and making use of the Fermion anticommutation relations, we transform the above expression in order to place the annihilation operators L_{σ} after all others, but before the projection operator P . The terms containing the $L_{\sigma} P$ multiplier will be vanishing, whereas the nonzero terms can be transformed to

$$H_2^{\text{eff}} = \frac{t^2 K}{(\Delta\alpha)^2 - K^2/4} \hat{S}_d \hat{S}_L.$$

In the P subspace, the number of electrons in the accep-

tor orbitals is constant. Therefore, the first spin-independent term in the effective Hamiltonian also can be omitted. Finally, we can see that the effective Hamiltonian for the donor-acceptor pair has the form of the Heisenberg Hamiltonian for a pair of $1/2$ spins with effective exchange integral

$$H^{\text{eff}} = J \hat{S}_d \hat{S}_L, \quad J = \frac{t^2 K}{(\Delta\alpha)^2 - K^2/4} < 0. \quad (3)$$

This is precisely the form that we wanted to get. Due to the ferromagnetic sign of the intramolecular exchange term ($K < 0$), the total effective exchange interaction J between the electron spins located in the d and in the acceptor orbitals is also ferromagnetic (provided the energies of both the triplet and singlet back-charge-transfer states are positive).

B. Heisenberg Hamiltonian for the entire DMeFc-TCNE crystal

Now we consider the actual crystal structure of the DMeFc-TCNE salt. It is known¹ that in the DMeFc-TCNE salt alternating donor and acceptor molecules are arranged in one-dimensional stacks. The stacks are aligned in the a direction. Each stack has six adjacent ones [Fig. 1(a)], of which four are “out of registry” (i.e., are shifted by $a/2$) and two are “in registry” (not shifted) [Figs. 1(b) and 1(c)].¹ The singly occupied orbital of the acceptor (TCNE) is its b_{3g} orbital. The singly occupied level of the donor is the e_{2g} orbital, formed mainly by the $3d_{x^2-y^2}$ orbital of the Fe^{3+} cation.

According to our above considerations (see also Ref. 8), the ligand (empty) orbital of the donor must have nonvanishing overlap with the singly occupied TCNE orbital. For the idealized geometry of the stacks [Figs. 1(b) and 1(c)] proposed in Ref. 5, only one π orbital of the Cp^* ring overlaps with the b_{3g} orbital of TCNE, i.e., the e_{1x} orbital. It is originally occupied in the Cp^{*-} anion, but due to mixing with the empty d_{xz} orbital of the Fe atom, it contributes to the e'_{1gx} vacant orbital.¹¹ Thus the empty e'_{1gx} orbital of DMeFc^+ overlaps with the singly occupied acceptor orbital. Though the main contribution to e'_{1gx} is given by the $3d_{xz}$ orbital of Fe^{3+} , it will be considered as the ligand orbital irrespective to its actual composition.

Nonvanishing overlap (and thus a nonvanishing hopping integral) occurs between the acceptor and ligand orbitals when the adjacent molecules are either in one stack or in the neighbor out-of-registry stacks [Fig. 1(b)]. The acceptor–ligand hopping integrals in the in-registry pairs vanish due to the large intermolecular separation.¹² Both acceptor–acceptor and ligand–ligand hopping integrals in the in-registry pairs are nonvanishing. The d – d hopping integrals also vanish because of large interstack Fe–Fe distances. In addition, due to symmetry constraints, the interstack hopping integral between d (e_{2g}) and ligand (e'_{1gx}) orbitals in the in-registry donor–donor pairs also vanishes.

To summarize the above considerations based on symmetry constraints and intermolecular separations, we can say that hopping integrals appear only between nearest neighbors and, moreover, the hopping does not involve d orbitals.

Now we consider the effect of nonvanishing hopping

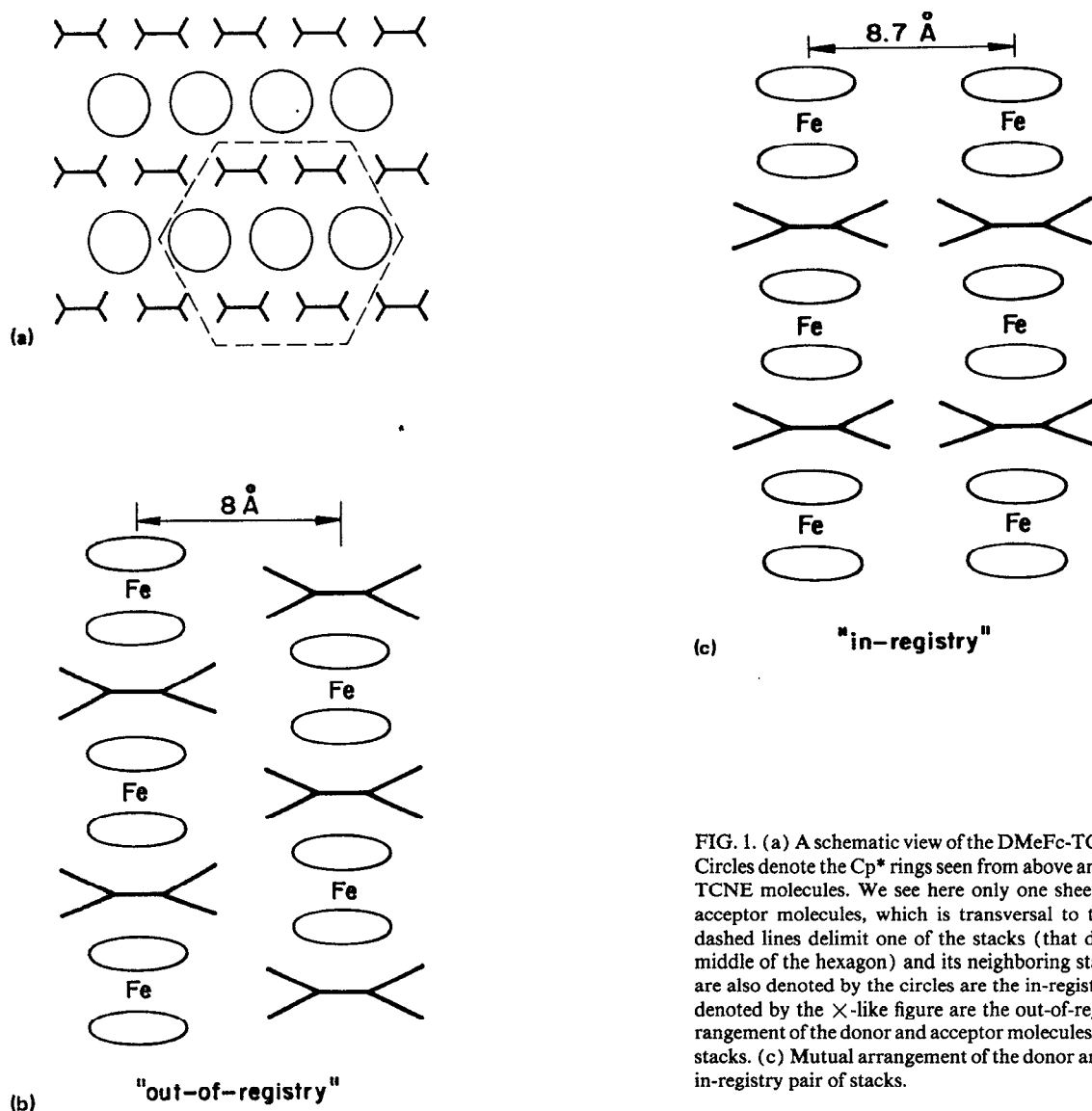


FIG. 1. (a) A schematic view of the DMeFc-TCNE crystal along the a axis. Circles denote the Cp* rings seen from above and \times -like figures present the TCNE molecules. We see here only one sheet formed by the donor and acceptor molecules, which is transversal to the stacking direction. The dashed lines delimit one of the stacks (that denoted by the circle in the middle of the hexagon) and its neighboring stacks. The two stacks which are also denoted by the circles are the in-registry ones; the four which are denoted by the \times -like figure are the out-of-registry ones. (b) Mutual arrangement of the donor and acceptor molecules in the out-of-registry pair of stacks. (c) Mutual arrangement of the donor and acceptor molecules in the in-registry pair of stacks.

integrals of different types upon the electronic structure of the DMeFc-TCNE crystal. According to the previous discussion, both the intrastack and the out-of-registry interstack ligand-acceptor hoppings lead to Heisenberg coupling of a ferromagnetic sign between the local spins in the acceptor and donor sites.

According to general considerations (see Ref. 9), one-electron hopping between two singly occupied acceptor orbitals also gives the Heisenberg coupling between the acceptor spins, but of antiferromagnetic sign. Its effective exchange constant is given by the well-known relation

$$J_{AA} = \frac{2t_{AA}^2}{\gamma_A},$$

where t_{AA} is the acceptor-acceptor hopping integral. It can be proven that any effective interaction between the donor localized spins (i.e., electrons in d orbitals) caused by the

ligand-ligand hopping term in the in-registry pairs does not appear up to fourth order in the intersite hopping integrals. The latter are always small due to large intermolecular separations. For these reasons, we neglect terms of higher orders in hopping integrals and no effective exchange appears between the donor located spins in the in-registry pairs.

Finally, the picture of the effective spin-spin interactions in the DMeFc-TCNE crystal appears as follows: each acceptor site has six neighbors; four of them are donors and two are acceptors. Donor-acceptor Heisenberg interactions are ferromagnetic. The effective intrastack exchange parameter is

$$J_{\parallel} = \frac{t_{\parallel}^2 K}{(\Delta\alpha)^2 - K^2/4},$$

where t_{\parallel} is the intrastack hopping integral. For the inter-

stack donor–acceptor exchange parameter, we have a similar expression

$$J_{\perp} = \frac{t_{\perp}^2 K}{(\Delta\alpha)^2 - K^2/4}.$$

The two remaining neighbors of the given acceptor molecule are also acceptors which will interact antiferromagnetically as described above.

The donor site has effectively (in the sense of magnetic interactions) four neighbors only (two in the same stack and two in the adjacent out-of-registry stacks). They all interact ferromagnetically and the effective exchange parameters are determined above (J_{\parallel} and J_{\perp}).

C. Estimates

In our previous paper,⁸ some estimates were given for the principal parameters of the original model Hamiltonian equation (1). Those estimates touched the intrastack parameters only and were bound strongly to the unrestricted Hartree–Fock (UHF) approximation. Nevertheless, these estimates for $\Delta\alpha$ and K were correct within an order of magnitude. Now we are in a position to estimate all the significant exchange parameters of the given model. The donor–acceptor electron hopping integrals t_{\parallel} are obviously equal to the resonance integrals between the e_{1x} orbital of the Cp* ring (which contributes to the ligand e'_{1gx} orbital of DMeFc) and the acceptor b_{3g} orbital multiplied by the coefficient of the ring orbital in the expansion of the ligand orbital (see also Ref. 13). This coefficient was taken from Ref. 11. The intermolecular resonance integrals between the ring and acceptor π orbitals [the latter were calculated by the standard Pariser–Parr–Pople (PPP) method (see Ref. 14)] were calculated according to the scheme given in Ref. 15. As a result, the longitudinal hopping integral t_{\parallel} amounts to about 900 K.

The intermolecular exchange constant K has been shown in Ref. 8 to be mainly of intra-atomic origin. As was mentioned before $K = -2(dL|Ld)$ and

$$(dL|Ld) = e^2 \int dr \int dr' \psi_d^*(r) \psi_L(r) |r-r'|^{-1} \\ \times \psi_L^*(r') \psi_d(r'),$$

where $\psi_d(r)$ and $\psi_L(r)$ are the coordinate wave functions (orbitals) for the d and ligand orbitals, respectively. Substituting expansions for $\psi_L(r)$ and $\psi_d(r)$ over the Fe atomic orbitals and the ring π orbitals into the formula for K and assuming two-center exchange integrals to be zero (for more details see Ref. 16, where the intermediate neglect of differential overlap (INDO) approximation has been extended to transition metal complexes), we obtain

$$K = -2(dL|Ld) = -2C_{xz}^2 C_{x^2-y^2}^2 (\delta\pi|\pi\delta), \\ (\delta\pi|\pi\delta) = 3F^2(dd)/49 + 20F^4(dd)/441,$$

where $(\delta\pi|\pi\delta)$ stands for the two-electron Coulomb interaction integral between the d_{xz} (d_{π}) and $d_{x^2-y^2}$ (d_{δ}) atomic orbitals, $F^2(dd)$ and $F^4(dd)$ are the Slater–Condon parameters of the intra-atomic Coulomb interaction, and C_{xz} and $C_{x^2-y^2}$ are the coefficients of the d_{xz} and $d_{x^2-y^2}$ orbitals of

the Fe atom in the expansions for the ligand and d orbitals, respectively. The coefficients C_{xz} and $C_{x^2-y^2}$ were taken from Ref. 11 and the values of the Slater–Condon parameters from Ref. 17. Thus K is estimated to be 10^4 K.

The mean energy of the ($d_{\delta} \rightarrow d_{\pi}$) transitions in decamethylferrocene is the lower estimate for $\Delta\alpha$.⁶ To estimate the mean transition energy, we took the energies of allowed singlet–singlet transitions in DMeFc from Ref. 18 and assumed the energies of the triplet states which are not known from the experiment to be smaller than those of the singlets by 5000 cm^{-1} , as was in the case of nonmethylated ferrocene.¹⁹ Thus $\Delta\alpha$ is estimated to be 3.75×10^4 K. Inserting these numbers in the formula for the longitudinal exchange parameter, we obtain $J_{\parallel} = 5.9$ K, which is the upper estimate for this parameter.

The situation with the J_{\perp} exchange parameter is more complicated. For the mutual arrangement of the donor and acceptor moieties shown in Fig. 1(a), both (x and y) components of the degenerate e'_{1g} manifold give nonvanishing resonance integral with the b_{3g} orbitals of adjacent out-of-registry TCNE molecules. Therefore two back-charge-transfer states (from b_{3g} to the x and y components of e'_{1g}) must be taken into account. The two do not interfere in the second order of perturbation theory and the total effective exchange constant is simply a sum of the two partial constants. Inserting the values of the hopping integrals in the formula for J_{\perp} , we get an estimate of about 4×10^{-4} K for this exchange parameter.

We calculated the t_{AA} hopping parameter assuming that it equals the resonance integral between the lowest unoccupied orbitals of two TCNE molecules found in the PPP approximation. Irrespective of the mutual orientation of two TCNE molecules, the hopping integral t_{AA} does not exceed 0.25 K, providing the separation between the centers of the two C = C bonds is maintained at 8.7 Å. The intramolecular electron–electron repulsion parameter γ_A is about 1 eV. Therefore, the J_{AA} exchange parameter does not exceed 10^{-5} K.

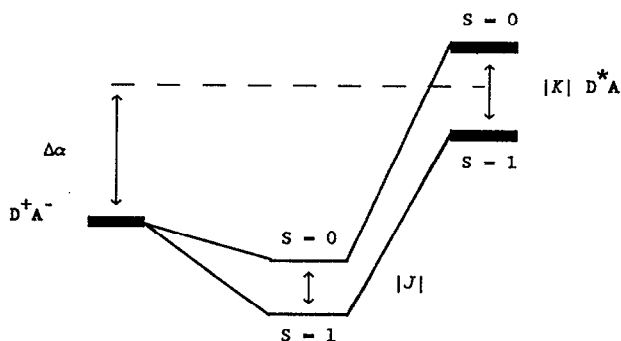
III. DISCUSSION

In the present paper, we derived the Heisenberg type Hamiltonian for a charge-transfer molecular magnet starting from a model Hamiltonian.^{6–8} Earlier, it had been suggested^{1,20} that the effective ferromagnetic exchange appears because the triplet (or more generally, the high spin) component of the $D^+ A^-$ manifold (or, in our language, of the P subspace) acquires more stabilization than the singlet (or the low spin) component from the interaction with states with different charge distribution. This difference can have many origins. The most obvious reason for it is that the energy denominators in the second-order perturbation expressions for the energy corrections for the triplets are smaller than those for the singlets. This mechanism is usually referred to as the second McConnell mechanism.²¹ Miller and Epstein²⁰ (ME) assumed that the triplet states from the $D^2 + A^{2-}$ manifold play the role of the desired triplet states of relatively low energy, and the direct hopping between singly occupied orbitals of the donor and acceptor sites pro-

vides stabilization of the triplet $D^{2+}A^{2-}$ states in the second McConnell mechanism.

Some authors^{5,8,13} have strongly criticized the ME choice of both the $D^{2+}A^{2-}$ states (which should be of high energy) and also the assumption of direct $d-A$ hopping (which should vanish due to symmetry conditions). However, all these objections are not, indeed, directed against the general McConnell idea, but only against its ME implementation.²⁰ The second McConnell mechanism, as described above, generally does not imply either particular charge-transfer states to be admixed or definite interactions to admix them. The problem is to find particular states and interactions which could provide the necessary admixing.

Together with their criticism of the ME implementation, the authors of Refs. 5–8 proposed to take into account charge-transfer states involving the ligands, i.e., Cp^* rings. This idea has been built in the model Hamiltonian,^{6–8} which stresses the role of the acceptor to ligand back-charge-transfer states. In the present paper, in line with previous ideas of Refs. 5 and 8, we use the back-charge-transfer states involving the ligand orbital as the triplet states to be admixed in order to stabilize the triplet component of the P subspace. The ligand–acceptor hopping term admixes the states from the DA manifold into the degenerate ones from the D^+A^- manifold. The accessible part of the DA manifold can be denoted as D^*A in order to stress that the donor molecule is in one of its excited states. The characteristic energy of the D^*A states (back-charge-transfer states) is generally smaller than that of the $D^{2+}A^{2-}$ states (double charge-transfer states) and therefore contribution from the latter (if any exists) can be neglected. The total picture of interactions between charge-transfer states will be like that sketched in a scheme



This scheme obviously presents an implementation of the second McConnell mechanism, but both the states and the interactions differ from those discussed extensively previously in the literature.^{1–4,13,20}

The second McConnell mechanism, modified by the choice of the back-charge-transfer D^*A states instead of the $D^{2+}A^{2-}$ states,²⁰ is successful even in those situations where the previous $D^{2+}A^{2-}$ treatment failed. For example, the ferromagnetic²² $CrCp_2^*-TCNQ$ salt has a d^3 ($a_{1g}^1 e_{2g}^2$) configuration and the acceptor site spin is $3/2$. The forward charge-transfer states invoked in Ref. 20 will have the lower total spin ($S=1$; only two electrons remain in the d shell, and A^{2-} has a closed shell) and their admixture stabilizes

only low spin states from the D^+A^- manifold. The effective interaction will be of antiferromagnetic sign (i.e., it turns out to be ferrimagnetic) in contradiction with experiment.²² This is one of the most important failures of the second McConnell model in the ME implementation. However, the back-charge-transfer states from the D^*A manifold have electron configuration d^4 ($a_{1g}^1 e_{2g}^2 e_{1g}^1$) and the corresponding states of high total spin ($S=2$) will have lower energy than the states of the low total spin. This leads to the ferromagnetic sign for the total effective exchange, in accordance with recent experiments.²²

Ferromagnetic interactions in the $MnCp_2^*-TCNQ$ salt have the same origin as those in the $FeCp_2^*-TCNE$ and $CrCp_2^*-TCNQ$ salts. It can be seen easily from the structure given in Ref. 23 that any direct hopping between occupied orbitals of the Mn^{3+} ion and the singly occupied $TCNQ^-$ orbital is ruled out by symmetry. Therefore ferromagnetic interaction can only arise from the admixture of the back-charge-transfer states. The latter obviously produce effective ferromagnetic interaction, in accordance with experiment.²³

The case of antiferromagnetic $NiCp_2^*-TCNE$ also can be discussed in the framework of the proposed approach. In the $NiCp_2^{*+}$ cation, an unpaired electron occupies one of the degenerate ligand orbitals (x or y components of the e'_{1g} manifold). The x orbital has a nonvanishing hopping integral with the singly occupied orbitals of adjacent acceptors in the same stack. If the unpaired electron occupies the x orbital, that immediately produces an antiferromagnetic effective interaction between the unpaired electrons in the donor and acceptor sites (see above and Ref. 9). If the unpaired electron in $NiCp_2^{*+}$ occupies the y component of the e'_{1g} manifold, the effective interaction will be ferromagnetic.²⁴ Which of the components is actually occupied and what is the sign of the effective exchange depends ultimately on the ratio between the kinetic exchange leading to the antiferromagnetic exchange and the ferromagnetic exchange of the form of Eq. (3).

The form of the effective ferromagnetic exchange parameter obtained in this paper coincides almost completely with that in the effective one-dimensional Heisenberg Hamiltonian obtained in Ref. 8 and with that mentioned recently by Georges.²⁵ This interaction was also listed in the book by Goodenough.²⁶ Unfortunately, Georges discussed that effective interaction only in very general terms and gave no indication of how his general formula relates to the particular problem of the ferromagnetic interaction in the Miller–Epstein compounds and what will be the sign of the effective exchange parameter. Here we present particular states which are involved in the interaction and give estimates of the parameters of the effective Hamiltonian. Indeed, both Ref. 8 and the present one invoke the same states and interactions in order to describe the effective ferromagnetic coupling in the Miller–Epstein compounds. However, we show here the important role of the back-charge-transfer states explicitly. Another significant difference between the present paper and Ref. 8 is that in the present paper, we avoided the UHF approximation and have obtained results valid for the three-dimensional crystal.

The values of the effective exchange parameters obtained in the present paper may be used to estimate the Curie temperature of the Miller–Epstein ferromagnets. Inserting the above values of the exchange parameters into the formula¹² derived in the molecular field approximation, we get the value of the Curie temperature $T_c = 5.8$ K, which is satisfactory when compared with the known¹ experimental value 4.8 K. It should be noted, however, that the formula¹² for T_c is a very rough estimate. It is known²⁷ that for the isotropic three-dimensional Ising model with coordination number 6 (simple cubic lattice), the exact Curie temperature is smaller than the molecular field value by a factor of about 0.75. This is due to fluctuations, which are neglected in the molecular field approach. The fluctuation effects will be significantly stronger for the Heisenberg Hamiltonian and for a highly anisotropic system. Due to fluctuations, antiferromagnetic interactions can affect the Curie temperature stronger than it follows from the molecular field treatment. Indeed, in the spin wave limit,²⁸ we have for the Curie temperature the expression $T_c = 1.556(J_{\parallel}J_{\perp})^{1/2}$. With the parameters of the present paper, it gives us the estimate for T_c of about 10^{-2} K. This is obviously too small. It is not clear, however, if the formula of Ref. 28 applies to the system where the interchain interactions may have different sign [both ferromagnetic and antiferromagnetic (see above)] and if the formulas of Ref. 15 for the resonance integrals (t_{\perp} and t_{AA}) work for the interatomic separations characteristic for the interstack interactions. To summarize, we need some more elaborate theory describing the Curie temperature of the highly anisotropic Heisenberg magnets, as well as describing intermolecular electron hopping at long distances, to make conclusions on compatibility of any estimates of calculated effective exchange parameters with experimental data.

Recently, another mechanism for effective spin interactions in the Miller–Epstein compounds has been proposed.¹³ It is based on interaction between spin densities of the constituent open-shell molecules. The underlying idea is known as the first McConnell mechanism²⁹ and its applicability to the Miller compounds was at first indicated by Buchachenko.³⁰ Although Kahn and Kollmar¹³ as well as Broderick and Hoffman²² considered the failures of the second McConnell model in the ME implementation for CrCp^{*}TCNQ as catastrophic, we have shown that using D^{*}A states one can predict the sign of the effective interaction correctly. Thus, additional experimental and theoretical investigations will be required to distinguish the two mechanisms.

ACKNOWLEDGMENTS

This paper was written during a visit to Cornell University. The hospitality of the Cornell Department of Chemistry is gratefully acknowledged as the support of National Science Foundation through the special program for joint

U.S.–Russian research (supplement to CHE-8912070). The author is grateful to the referee for instructive comments. The author is also grateful to Professor R. Hoffmann and Dr. J. S. Miller and Dr. I. A. Misurkin for helpful discussions. Professor R. Hoffmann and Dr. P. Kazmaier carefully read the manuscript and made valuable remarks concerning the style. Their kind help is gratefully acknowledged. The author also would like to thank Professor O. Kahn and Dr. C. Kollmar for valuable remarks concerning the nickelocenium derivative and for preprints of their papers. I thank Jane Jorgensen for the perfect drawings.

- ¹ J. S. Miller, A. J. Epstein, and W. M. Reiff, *Chem. Rev.* **88**, 201 (1988).
- ² J. S. Miller, A. J. Epstein, and W. M. Reiff, *Acc. Chem. Res.* **23**, 114 (1988).
- ³ Proceedings of the Symposium on Ferromagnetic and High Spin Molecular Based Materials, edited by J. S. M. Miller and D. A. Dougherty, *Mol. Cryst. Liq. Cryst.* **176** (1989).
- ⁴ *NATO ASI Series*, edited by D. Gatteschi, O. Kahn, J. S. Miller, and F. Palacio (Kluwer Academic, Dordrecht, 1991).
- ⁵ Z. G. Soos and P. C. M. McWilliams, *Mol. Cryst. Liq. Cryst.* **176**, 369 (1989).
- ⁶ A. L. Tchougreeff and I. A. Misurkin, in *Electron–Electron Correlation Effects in Low-Dimension Conductors and Superconductors*, Research Reports in Physics, edited by A. A. Ovchinnikov and I. I. Ukrainskii (Springer, Berlin, 1991), p. 152.
- ⁷ A. L. Tchougreeff and I. A. Misurkin, *Chem. Phys.* **153**, 371 (1991).
- ⁸ A. L. Tchougreeff and I. A. Misurkin, *Phys. Rev. B* (to be published).
- ⁹ D. C. Mattis, *The Theory of Magnetism* (Harper & Row, New York, 1965).
- ¹⁰ R. McWeeny and B. T. Sutcliffe, *Methods of Molecular Quantum Mechanics* (Academic, London, 1969).
- ¹¹ E. M. Shustorovich and M. E. Dyatkina, *Zh. Strukt. Khim.* **1**, 109 (1960) (in Russian); *J. Struct. Chem. (USSR)* **1**, 98 (1960) (in English).
- ¹² D. A. Dixon, A. Suna, J. S. Miller, and A. J. Epstein in Ref. 4.
- ¹³ O. Kahn in Ref. 4; C. Kollmar, M. Couty, and O. Kahn, *J. Am. Chem. Soc.* **113**, 7994 (1991); C. Kollmar and O. Kahn, *ibid.* **113**, 7987 (1991); *J. Chem. Phys.* (to be published).
- ¹⁴ T. E. Peacock, *Electronic Properties of Aromatic and Heterocyclic Molecules* (Academic, London, 1965).
- ¹⁵ R. J. Boyd and M. A. Whitehead, *J. Chem. Soc. Dalton Trans.* **73**, 78 (1972).
- ¹⁶ A. D. Bacon and M. C. Zerner, *Theor. Chim. Acta* **53**, 21 (1979).
- ¹⁷ G. Blyholder, J. Head, and F. Ruetter, *Theor. Chim. Acta* **60**, 429 (1982).
- ¹⁸ J. L. Robbins, N. Edelstein, B. Spencer, and J. C. Smart, *J. Am. Chem. Soc.* **104**, 1882 (1982).
- ¹⁹ Y. S. Sohn, D. N. Hendrickson, and H. B. Gray, *J. Am. Chem. Soc.* **93**, 3603 (1971).
- ²⁰ J. S. Miller and A. J. Epstein, *J. Am. Chem. Soc.* **109**, 3850 (1987).
- ²¹ H. M. McConnell, *Proc. Robert A. Welch Found. Conf. Chem. Res.* **11**, 144 (1967).
- ²² W. E. Broderick and B. M. Hoffman, *J. Am. Chem. Soc.* **113**, 6334 (1991).
- ²³ W. E. Broderick, J. A. Thompson, E. P. Day, and B. M. Hoffman, *Science* **249**, 401 (1990).
- ²⁴ O. Kahn and C. Kollmar (private communication).
- ²⁵ R. Georges in Ref. 4.
- ²⁶ J. B. Goodenough, *Magnetism and the Chemical Bond* (Interscience, New York, 1963), Eq. (162), p. 167.
- ²⁷ M. E. Fisher, *J. Math. Phys.* **4**, 278 (1963).
- ²⁸ S. H. Liu, *J. Magn. Magn. Mater.* **82**, 294 (1989).
- ²⁹ H. M. McConnell, *J. Chem. Phys.* **39**, 1910 (1963).
- ³⁰ A. L. Buchachenko, *Mol. Cryst. Liq. Cryst.* **176**, 307 (1989).

The Journal of Chemical Physics is copyrighted by the American Institute of Physics (AIP). Redistribution of journal material is subject to the AIP online journal license and/or AIP copyright. For more information, see <http://ojps.aip.org/jcpo/jcpcr/jsp>
Copyright of Journal of Chemical Physics is the property of American Institute of Physics and its content may not be copied or emailed to multiple sites or posted to a listserv without the copyright holder's express written permission. However, users may print, download, or email articles for individual use.