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Prescription for Stabilization of Ferromagnetic Exchange in Molecular Solids via Admixing of the Ground State with a Virtual Charge-Transfer Excited State

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Abstract: A McConnell model for stabilization of ferromagnetic coupling in linear chains comprised of alternating radical cation donors, D, and radical anion acceptors, A, requires the admixture of an triplet excited state with the ground state. Such stabilization was proposed for forward, but not retro, charge transfer between an e^3 D (or A) and an A (or D) with one electron in a nondegenerate orbital. The electron configurations, via either forward or retro charge transfer, that stabilize ferromagnetic coupling are identified and tabulated for systems possessing singly, doubly, or triply degenerate partially occupied molecular orbitals, POMOs. The extended McConnell model and its mathematical embodiment as the generalized Hubbard model offer a convenient guide to explore ferro-, antiferro-, and ferrimagnetic phenomena in molecular (organic, organometallic, main group, polymeric, and/or inorganic coordination complex) systems. Assuming virtual charge transfer involves only the POMO, to achieve ferromagnetic coupling a stable radical (neutral, radical cations/radical anions, or radical ions with small diamagnetic counter ions) must possess a degenerate non-half-filled POMO. Additionally the lowest excited state formed via virtual charge transfer (retro or forward) must possess the same spin multiplicity as the ground state and admixes with the ground state to stabilize the ferromagnetically coupled ground state. Since ferromagnetism is a bulk phenomenon, to be achieved ferromagnetic coupling must be present and dominate throughout the solid. Demanding, novel chemical syntheses as well as physical, experimental, and theoretical insight are necessary to test these concepts and establish a deeper understanding of cooperative phenomena in molecular solids. The requirement for a radical to possess a non-half-filled degenerate POMO limits the structure of a radical to D_{2d}, C_3, or higher symmetry. Intrinsic doubly, triply, or greater degenerate orbitals are not necessary, and accidental degeneracies suffice. The report of ferromagnetism in $[\mathrm{Fe^{III}(C_5Me_5)_2}]^{\bullet+}[\mathrm{TCNE}]^{\bullet-}$ affords the opportunity to test these concepts in real systems.

Ferromagnetism in a molecular solid requires spin alignment throughout the bulk and although rare is the subject of avid interest.[1] Three mechanisms have been postulated for the stabilization of ferromagnetic coupling in a molecular solid: (1) Heitler–London spin exchange between positive spin density on one radical and negative spin density on another,[2] (2) admixing of a virtual triplet excited state with the ground state for a chain of alternating radical cation donors and radical anion acceptors,[3] and (3) very high spin multiplicity molecules which have ferromagnetic domains.[4] Experimental evidence for ferromagnetic behavior[5] in a molecular compound has been limited to the charge-transfer salts of decamethylferrocene with tetracyanoethylene,[1a,6] TCNE, and to a lesser extent the 1:1 complex with hexacyanobutadiene.[1a,7] The fundamental physical phenomena that govern the stabilization of ferromagnetism in this class of molecular charge-transfer complexes are unknown; however, it is appealing to apply[1a,6b] the admixing of a virtual triplet excited state with the ground-state model originally proposed by McConnell[3,8] as these complexes possess both the crystal and electronic structures described by him. The specific structure for which McConnell's model is applicable is a chain structure comprised of alternating radical cation donors, D, and radical anion acceptors, A, i.e., $\cdots D^{\bullet+}A^{\bullet-}D^{\bullet+}A^{\bullet-}D^{\bullet+}A^{\bullet-}\cdots$.

Admixture of a $m_s = 1$ Excited State to Stabilize Ferromagnetic Coupling. The essence of this McConnell model is that if an excited state, ES, with $m_s = 1$ arising from either a $m_s = 1$ donor, D[9], or $m_s = 1$ acceptor, A[9], but not both, formed by either virtual retro ($D^0 + A^0 \leftarrow D^{\bullet+} + A^{\bullet-}$) or virtual forward ($D^{2+} + A^{2-} \leftarrow D^{\bullet+} + A^{\bullet-}$) charge transfer admixes with the ground state, GS, then ferromagnetic coupling will be stabilized.[3,5,8] By using Hund's rule[10,11a] the lowest energy excited state that can virtually admix with the ground state can be identified enabling the prediction of the magnetic coupling. This model can be illustrated for a $D^{\bullet+}$ with a double degenerate, d,[12] partially occupied molecular orbital, POMO, containing three electrons, i.e., d^3, and an $A^{\bullet-}$ with a nondgenerate, s,[12] POMO, containing one electron, i.e., s^1.[13] For this $D^{\bullet+}/A^{\bullet-}$ pair in the absence of spin interactions two ground states, GS_{FO} and GS_{AF}, Figure 1, exist at equal energy and lead to simple paramagnetic behavior.

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(5) Ferromagnetic coupling in a molecular solid is essentially equivalent to stabilization of a triplet state. A mechanism leading to bulk ferromagnetism based on ferromagnetic coupling in a molecular solid has been previously discussed.[1a,6b]

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(9) Throughout the paper the arguments hold for either D/A or the reverse A/D.[8] For convenience D and A are assumed to be neutral; however, they may be ionic.

(10) Hund's rule was originally proposed for atoms (e.g., McWeeny, R. *Coulson's Valence*; Oxford University Press: 1979; pp 102–103); however, it was later successfully applied to molecules and biradicals (e.g., Lahti, P. M.; Rossi, A.; Berson, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 4362–4363. Seeger, D. E.; Lahti, P. M.; Rossi, A.; Berson, J. A. *J. Am. Chem. Soc.* **1986**, *108*, 1251–1265 and ref 11a).

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(12) Throughout the paper the orbital degeneracies of a singly, doubly, triply, quadruply, or quintuply (intrinsic or accidental) are denoted as s (a or b symmetry), d (e symmetry), t (t symmetry), q, and p, respectively.

(13) The ferromagnetic charge-transfer complex $[\mathrm{Fe^{III}(C_5Me_5)_2}]^{\bullet+}$-$[\mathrm{TCNE}]^{\bullet-}$[1a,6] possesses the d^3/s^1 electron configuration.

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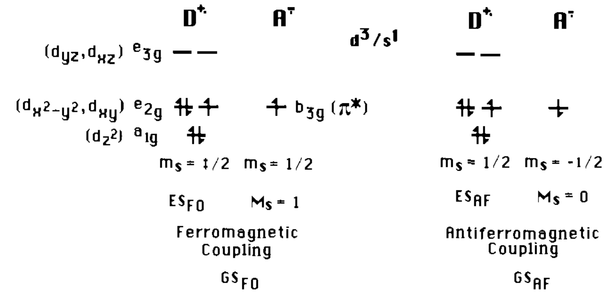

Figure 1. Paramagnetic ground states assuming no spin interactions between radical ions.

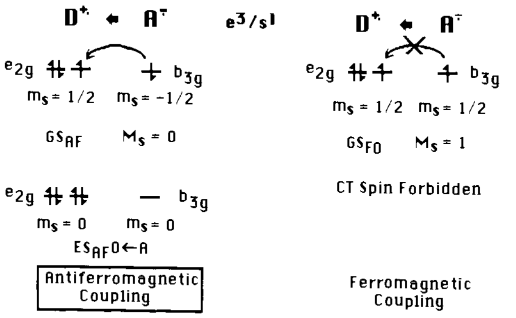

Figure 2. Schematic illustration of stabilization of antiferromagnetic coupling via retro charge transfer from a s^1 $A^{\bullet-}$ to d^3 $D^{\bullet+}$

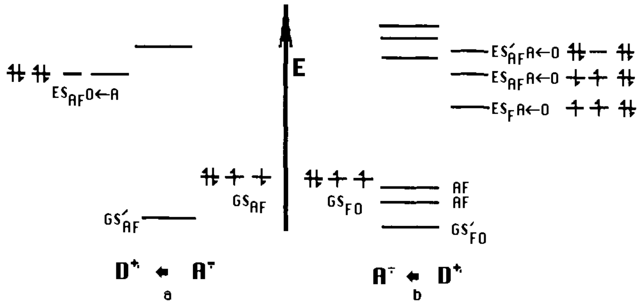

Figure 3. Schematic state diagram depicting the relative energy of the ground and excited states before and after admixing to stabilize antiferromagnetic coupling for virtual $D^{\bullet+} \leftarrow A^{\bullet-}$ charge transfer (a) and ferromagnetic coupling for virtual $A^{\bullet-} \leftarrow D^{\bullet+}$ charge transfer (b) via the McConnell mechanism. The energy scale is arbitrary.

Spin interactions between the ions can lead to lowering of either GS_{FO} or GS_{AF} and ferro- or antiferromagnetic coupling.[5] GS_{FO} with $M_s \equiv m_s^A + m_s^D = 1$ is ferromagnetically coupled; whereas GS_{AF} with $M_S = 0$ is antiferromagnetically coupled, Figure 1. The GS lowered in energy is the one that has the greatest probability of admixing with the lowest energy virtual charge-transfer excited state. For each direction of charge transfer Hund's rule can be used to predict the lowest charge-transfer excited state. Magnetic coupling (ferro-, ferri-, or antiferromagnetic) thus can be predicted for a specific direction of charge transfer. An example is the retro charge transfer for the above case, Figure 2. Since the $D^{\bullet+}$ can only accept a $m_s = -{}^1/_2$ electron via virtual charge transfer from $A^{\bullet-}$ and GS_{AF}, not GS_{FO}, has a $m_s = -{}^1/_2$ electron, then the admixture of the $ES_{AF}{}^{D\leftarrow A}$ excited state will lower the energy of GS_{AF} (to GS'_{AF}) with respect to GS_{FO} and should lead to antiferromagnetic coupling, Figure 3a.

For virtual forward charge-transfer excited state $ES_{FO}{}^{A\leftarrow D}$, $ES_{AF}{}^{A\leftarrow D}$, and $ES'_{AF}{}^{A\leftarrow D}$ are possible, Figure 4. From Hund's rule the easiest lost $D^{\bullet+}$ electron has $m_s^D = -{}^1/_2$ and can only be virtually transferred to the ferromagnetically coupled $A^{\bullet-}$, i.e., $ES_{FO}{}^{A\leftarrow D}$. Transfer of a $m_s^D = {}^1/_2$ electron to an antiferromagnetically coupled $A^{\bullet-}$ requires admixture of higher excited states, i.e., $ES_{AF}{}^{A\leftarrow D}$ or $ES'_{AF}{}^{A\leftarrow D}$. Thus, for forward charge transfer the ferromagnetically coupled ground state, GS_{FO}, may lead to bulk ferromagnetic behavior as observed for $[Fe^{III}(C_5Me_5)_2]^{\bullet+}[TCNE]^{\bullet-}$,[1a,6] Figure 3b.

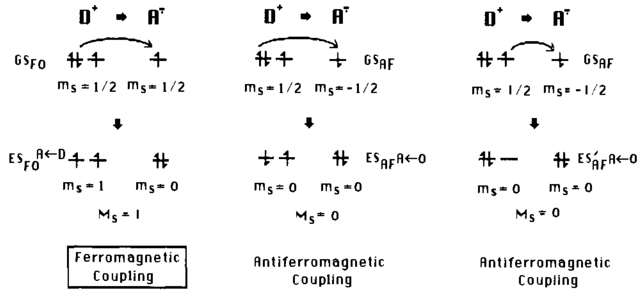

Figure 4. Schematic illustration of stabilization of ferromagnetic coupling via forward charge transfer from a d^3 $D^{\bullet+}$ to a s^1 $A^{\bullet-}$.

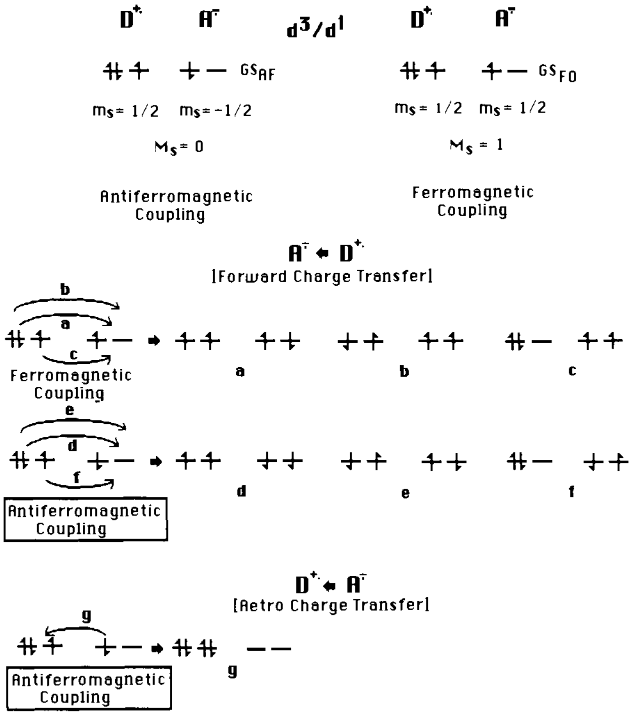

Figure 5. Antiferromagnetic (GS_{AF}) and ferromagnetic (GS_{FO}) coupled ground states for the d^3/s^1 electronic configuration (top) and stabilization of antiferromagnetic coupling via either forward charge transfer from a d^3 $D^{\bullet+}$ to a $d^1 A^{\bullet-}$ (middle) or retro charge transfer from an d^1 $A^{\bullet-}$ to d^3 $D^{\bullet+}$ (bottom).

The pair of preceding examples for a d^3/s^1 electron configuration leads to contrasting magnetic coupling depending on the direction of virtual charge transfer; however, at our present level of understanding an a priori prediction of the direction of charge transfer cannot be made.[14] Nevertheless, if McConnell's model is appropriate and the direction of charge transfer is known, then the magnetic coupling can be predicted.

If $A^{\bullet-}$'s valence electron is in a degenerate orbital (e.g., d not s), then in the absence of spin interactions two ground states, GS_{FO} and GS_{AF}, akin to those discussed above for the d^3/s^1 electron configuration case exist, Figure 5 (top). Admixing the lowest excited state formed from virtual retro charge transfer by the above argument leads to the stabilization of GS_{AF} and to antiferromagnetic coupling, Figure 5 (bottom). Forward charge transfer

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(14) Intuition based on solution data suggests that for $[Fe^{III}(C_5Me_5)_2]^{\bullet+}[TCNE]^{\bullet-}$ retro charge transfer should dominate as (1) $[Fe(C_5Me_5)_2]^n$ (n = 0, 1+) and planar $[TCNE]^n$ (n = 0, 1-) are known compounds that undergo reversible redox processes whereas $[Fe(C_5Me_5)_2]^{2+}$ has never been characterized and in solution can only be irreversibly formed via the oxidation of $[Fe(C_5Me_5)_2]^{\bullet+}$ and (2) although $[TCNE]^{2-}$ can be reversibly formed via reduction of $[TCNE]^{\bullet-}$ it is constrained to be in an excited state geometry (Dixon, D. A.; Miller, J. A. *J. Am. Chem. Soc.* **1987**, *109*, 3656). The applicability of the McConnell mechanism requires that the relative energy of the doubly charged excited state as compared to that of the neutral (retro charge transfer) excited state is determined in part by solid state (e.g., long range coulombic interactions) effects.

Table I. Magnetic Coupling for Homospin Systems[9,12,a,b]

D (or A)	A (or D)	D → A	A → D	example
		Spin $^1/_2$ Systems		
s^1	s^1	AF	AF	[TMPD][TCNQ],[c] $[\mathrm{TTF}][\mathrm{Pt(S_2C_4F_6)_2}]$,[d] $\mathrm{V(C_6H_6)_2}$,[e] $[\mathrm{Cr(C_6H_6)_2}]\mathrm{I}$[f]
d^1	s^1	AF	FO	$[\mathrm{Ni^{III}(C_5Me_5)_2}]^{\bullet+}[\mathrm{TCNE}]^{\bullet-}$[24]
d^3	s^1	FO	AF	$[\mathrm{Fe^{III}(C_5Me_5)_2}]^{\bullet+}[\mathrm{TCNE}]^{\bullet-}$[1a,6]
t^1	s^1	AF	FO	
t^5	s^1	FO	AF	
d^1	d^1	FO	FO	$\mathrm{Co^{II}(C_5H_5)^{\bullet}}$,[19] $\mathrm{NO^{\bullet}}$[18]
d^3	d^1	AF	AF	
t^1	d^1	FO	FO	
t^5	d^1	AF	AF	
d^3	d^3	FO	FO	$[\mathrm{Fe^{III}(C_5Me_5)_2}]^{\bullet+}[\mathrm{BF_4}]^{-}$[24]
t^1	d^3	AF	AF	
t^5	d^3	FO	FO	
t^1	t^1	FO	FO	
t^5	t^1	AF	AF	
t^5	t^5	FO	FO	
		Spin 1 Systems		
d^2	d^2	AF	AF	$\mathrm{O_2}$,[21] $[\mathrm{Ru(OEP)}]_2$[22a]
d^2	t^2	FO	AF	
d^2	t^4	AF	FO	
t^2	t^2	FO	FO	
t^2	t^4	AF	AF	
t^4	t^4	FO	FO	
		Spin $^3/_2$ Systems		
t^3	t^3	AF	AF	$\mathrm{V(C_5H_5)_2}^{\bullet}$[23b]
		Spin 2 Systems		
q^4	q^4	AF	AF	
		Spin $^5/_2$ Systems		
p^5	p^5	AF	AF	$\mathrm{Mn^{II}(C_5H_5)_2}$[23a]

[a] AF refers to antiferromagnetic coupling and FO to ferromagnetic coupling. [b] POMO orbital degeneracy (intrinsic or accidental): s = singly (a or b), d = doubly (e), t = triply (t), q = quadruply, or p = quintuply. [c] Ohmasa, M.; Kinoshita, M.; Sano, M.; Akamatu, H. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 1998. [d] Bray, J. W.; Interrante, L. V.; Jacobs, I. S.; Bonner, J. C. *Extended Linear Chain Compounds*; Miller, J. S., Ed.; Plenum Publishing Corporation: **1983**; Vol. 3, pp 353–415. [e] Fischer, E. O.; Joos, G.; Meer, W. *Z. Naturforsch., B: Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.* **1958**, *13B*, 456–457. [f] Karimov, Yu. S.; Chibrikin, V. M.; Shchegolev, I. F. *J. Chem. Phys. Sol.* **1963**, *24*, 1683–1685.

also leads to stabilization of $\mathrm{GS_{AF}}$ and to antiferromagnetic coupling as the easiest lost $\mathrm{D^{\bullet+}}$ electron has $m_s = -^1/_2$. Although $\mathrm{A^{\bullet-}}$ possesses a vacant orbital which can accept an electron with $m_s = \pm^1/_2$, the lowest excited state to maximize spin multiplicity requires an electron with $m_s = +^1/_2$, Figure 5 (middle). Thus, unlike the d^3/s^1 case antiferromagnetic coupling is stabilized regardless of the direction of virtual charge transfer. This is the basis for the aforementioned "but not both" statement.[8]

Generalized Hubbard Model. The competition among the various excited states in the lowering of the total ground-state energy in principle can be evaluated by a generalized Hubbard model.[15a] This model is useful in examining the competition between delocalization, as indicated by the nearest-neighbor charge-transfer integral, β, and the energy of transferring an electron between the neighboring sites, ΔE. For $\Delta E \gg \beta$, the energy difference between singlet (antiferromagnetic) and triplet (ferromagnetic) alignments is $\sum J_{\mathrm{ij}}\mathbf{S}_{\mathrm{i}}\cdot\mathbf{S}_{\mathrm{j}}$ where $\mathrm{S_i}$ and $\mathrm{S_j}$ are the spins on adjacent sites i and j, and J_{ij} is an effective exchange interaction. From perturbation analysis it can be shown that the effective exchange interaction resulting from each $J_{\mathrm{ij}} \sim \beta^2/\Delta E$. The sum of all the possible exchange interactions between a pair of neighboring sites is $J_{\mathrm{ij}} \sim \Sigma\beta_n^{\,2}/\Delta E_n$ where n refers to each allowed virtual excitation (e.g., as shown in Figure 5 for d^3 $\mathrm{D^{\bullet+}}$ and d^1 $\mathrm{A^{\bullet-}}$). Thus, the resulting J_{ij} is the sum of the contributions from each possible excitation weighted by the square of the overlap integral (which varies with excitation and is inversely proportional to the excitation energy) and in principle can be evaluated.

Table II. Magnetic Coupling for Heterospin Systems[9,12,a,b]

D (or A)	A (or D)	D → A	A → D	example
		Spin $^1/_2$–1 Systems		
s^1	d^2	FI	FI	
s^1	t^2	FO	FI	
s^1	t^4	FI	FO	
d^1	d^2	FI	FO	
d^1	t^2	FO	FO	
d^1	t^4	FI	FI	
d^3	d^2	FO	FI	
d^3	t^2	FI	FI	
d^3	t^4	FO	FO	
t^1	d^2	FI	FO	
t^1	t^2	FO	FO	
t^1	t^4	FI	FI	
t^5	d^2	FO	FI	
t^5	t^2	FI	FI	
t^5	t^4	FO	FO	
		Spin $^1/_2$–$^3/_2$ Systems		
s^1	t^3	FI	FI	$[\mathrm{Cr^{III}(C_5Me_5)_2}]^{\bullet+}[\mathrm{TCNE}]^{\bullet-}$[24]
d^1	t^3	FI	FO	
d^3	t^3	FO	FI	
t^1	t^3	FI	FO	
t^5	t^3	FO	FI	
		Spin 1–$^3/_2$ Systems		
d^2	t^3	FI	FI	
t^2	t^3	FI	FO	
t^4	t^3	FO	FI	

[a] Since $\mathrm{S_D} \neq \mathrm{S_A}$, FI refers to ferrimagnetic coupling and FO to ferromagnetic coupling. [b] POMO orbital degeneracy (intrinsic or accidental): s = singly (a or b), d = doubly (e), t = triply (t), q = quadruply, or p = quintuply.

The magnetic coupling of the solid is dependent upon the total sum of pairwise interactions among the spins, $\Sigma J_{\mathrm{ij}}\mathbf{S}_{\mathrm{i}}\cdot\mathbf{S}_{\mathrm{j}}$. Hence, the generalized Hubbard model can be used as a guide to the chemical and physical modifications of the solid to enhance the ferromagnetic coupling. For example, chemical modifications (e.g., design features) of the molecular units to decrease ΔE_n and/or increase β_n should increase the ferromagnetic exchange interaction and lead to the stabilization of ferromagnetic coupling. The application of the pressure should increase the overlap and consequently the relative and absolute magnitude of the β_n, again improving the magnetic properties. Application of this generalized Hubbard model to the permethylmetallocenium radical anion salts[1a] in in progress.[15b]

Generalization to Systems with Other Than d^3(s^1 or d^1) Electron Configurations. We wish to point out that $\mathrm{D^{\bullet+}}$'s and $\mathrm{A^{\bullet-}}$'s or more generally D's and A's with different electron configurations can be anticipated to support ferromagnetic coupling via the McConnell mechanism and treated with a generalized Hubbard model. These combinations of electron configurations are necessary but not sufficient for bulk ferromagnetic behavior[5] via the McConnell mechanism. Opposing effects (e.g., retro vs. forward virtual charge transfer) or magnitude of the stabilization (e.g., inversely proportional to distance and energy difference between the mixing states) may obscure the effect and lead to other phenomena, e.g., para-, meta-, or ferrimagnetism.[16] Additionally, other mechanisms[1c,d,2,4] for molecular-based ferromagnetic behavior may be operative.

The results of the evaluation of stabilization (antiferromagnetic, AF, or ferromagnetic, FO) are summarized in Table I for homospin (m_s = $^1/_2$, 1, $^3/_2$, 2, and $^5/_2$) systems ($m_s^{\mathrm{D}} = m_s^{\mathrm{A}}$). For

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Table III. Electron Configuration of Representative Radicals

electron configuration	S	radical	acronym	symmetry	ref
s^1	$^1/_2$	p-$[(NC)_2CC_6H_4C(CN)_2]^{\bullet-}$	$[TCNQ]^{\bullet-}$	D_{2h}	*a*
		$[C_4(CN)_6]^{\bullet-}$		C_{2v}	7, *b*
		p-$[Cl_2C_6(CN)_2O_2]^{\bullet-}$	$[DDQ]^{\bullet-}$	C_{2h}	*c*
		$[CC(CN)_2]_3^{\bullet-}$		D_{3h}	36
		$[H_2C_2S_2C]_2^{\bullet+}$	$[TTF]^{\bullet+}$	D_{2h}	35, *d*
		$[F_2CCF_2]^{\bullet-}$		C_{2h}	*e*
		$[V(C_6H_6)_2]^{\bullet}$		D_6	*f*
		p-$[Me_2NC_6H_4NMe_2]^{\bullet+}$	$[TMPD]^{\bullet+}$	D_{2h}	*g*
		$[M(S_2C_2R_2)_2]^{z-}$		D_{2h}	*h*
		$R_2NO^{\bullet}$		C_{2v}	*i*
		$[M(phthalocyanine)]^{\bullet+}$	$[MPc]^{\bullet+}$	D_{4h}	*j*
		$[C(NMe_2)]_3^{\bullet}$		D_{3h}	*k*
		$[Tc_2Cl_8]^{3-}$		D_{4h}	*l*
		$[Re_2Cl_4(PR_3)_4]^{\bullet+}$		D_{4h}	*m*
		$[(NC)_2CC(CN)_2]^{\bullet-}$	$[TCNE]^{\bullet-}$	D_{2h}	6b, *n*
		$[Cr(C_6H_6)_2]^+$		D_6	26a
d^1	$^1/_2$	$NO^{\bullet}$		$C_{\infty v}$	18, *o*
		$Co(C_5R_5)_2^{\bullet}$		D_5	19
		$[Ni(C_5R_5)_2]^{\bullet+}$		D_5	19
		$[Ru(octaethylporphyrin)]^{\bullet+}$	$[Ru(OEP)]_2^{\bullet+}$	D_{4d}	22a
		$[O_2]^{\bullet+}$		$D_{\infty h}$	*p*
		$[M(octacyanophthalocyanine)]^{\bullet-}$		D_{4h}	*q*
		$[Fe(C_6R_6)_2]^{\bullet+}$		D_6	26a
		$[Co(S_2C_4R_4)_2]^{2-}$		D_{3h}	*h*
d^2	1	$[Ru(octaethylporphyrin)]$	$[Ru(OEP)]_2$	D_{4h}	22a
		O_2		$D_{\infty h}$	21, *p*
		$[C_6(NEt(CH_2))_6]^{2+}$		C_{3h}	1b, 8
		$[C_6(NC_2H_4)_6]^{2+}$		C_{3h}	1b, 8, 32
		$[C_5R_5]^+$		D_{5h}	*r*
		$[Co(C_6R_6)_2]^+$		D_6	26a
		$Ni(C_5H_5)_2$	$NiCp_2$	D_5	19
		$[Co(S_2C_4R_4)_2]^-$		D_{2h}	*h*
		$[Fe(S_2C_2(CN)_2)_2]^{2-}$		D_{2h}	*h*
d^3	$^1/_2$	$[Fe(C_5R_5)_2]^{\bullet+}$		D_5	19
		$[C_6(NEt(CH_2))_6]^{\bullet+}$		C_{3h}	1b, 8
		$[C_6(NC_2H_4)_6]^{\bullet+}$		C_{3h}	1b, 8, 32
		$[Ru(octaethylporphyrin)]^{\bullet-}$	$[Ru(OEP)]_2^{\bullet-}$	D_{4h}	22a
		$[C(NMe_2)]_3^{2+}$		C_{3h}	*k*
		$[C_6H_2(OMe)_2]_3^{\bullet+}$		C_{3h}	1b, 8, *s*
		$[(Me_2N)_2CC(NMe_2)_2]^{\bullet+}$			34
		$[(RS)_2CC(SR)_2]^{\bullet+}$			34, 35
t^3	$^3/_2$	$[Cr(C_5R_5)_2]^+$		D_5	19
		$[Ru(O_2CO)_2]_2^+$		D_{4h}	*t*
		$[Ru(O_2CMe)_2]_2^+$		D_{4h}	*u*
		$V(C_5H_5)_2$	VCp_2	C_5	19
t^4	1	$[V(C_6R_6)_2]^+$		D_6	26a
		$[Mn(C_5H_5)_2]^+$		D_5	19
		$Cr(C_5H_5)_2$	$CrCp_2$	C_5	19
t^5	$^1/_2$	$[Ti(C_6H_6)_2]^+$		C_6	26b
q^5	$^5/_2$	$[Mn(C_5H_5)_2]$		D_5	19

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heterospin ($m_s = {}^1/_2 - 1, {}^1/_2 - {}^3/_2$, and $1 - {}^3/_2$) systems ($m_s^D \neq m_s^A$) due to incomplete spin cancellation antiferromagnetic coupling should lead to ferrimagnetic behavior, Fl, and the predicted FO and Fl interactions are summarized in Table II. It is assumed that the ground-state D and A each possess one or more unpaired electrons (i.e., m_s^D, $m_s^A \geq 1/2$) and they form a chain composed of alternating D and A, i.e., ···DADA···. Representative radicals as a function of electron configuration (intrinsic or accidental) which may serve as components for the preparation of a molecular/organic ferromagnet are listed in Table III.

In contrast to the McConnell model[3,8] ions may not be necessary, but stable radicals are required. Homomolecular species (D ≡ A) in principle are sufficient as long as virtual disproportionation ($D^{2+} + D^0 \leftarrow 2D^{\bullet+}$)[6b] dominates and one of the species formed via disproportionation has $m_s > {}^1/_2$, vide infra. Since the key point is mixing of an excited state ($m_s^{ES} \geq {}^1/_2$) with a ground

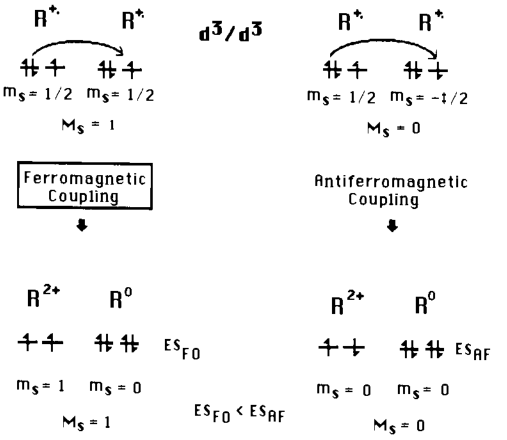

Figure 6. Schematic illustration of stabilization of ferromagnetic coupling via disproportionation between d^3 radicals, R$^{\bullet+}$. ES$_{FO}$ is stabilized as ES$_{AF}$ is a higher excited state than ES$_{FO}$, i.e., ES$_{FO}$ < ES$_{AF}$.

state with spin conservation, a chain structure as proposed by McConnell[3] may not be requisite, but designing materials with strong state mixing is important. Organic or inorganic based polymer chain and network structures[1d] (albeit not molecular solids[17]) as well as nonchain structures with the proper admixture of excited and ground states should suffice.

Homospin Systems—$m_s = {}^1/_2$. For an A with the ground-state spin residing in a s orbital, ferromagnetic coupling can be stabilized by forward charge transfer from a D with a d^3 or t^5 electron configuration.[13] For retro charge transfer although antiferromagnetic coupling is predicted for the d^3/s^1 electron configuration, ferromagnetic coupling can result if the D possesses a d^1 [18] or t^1 electron configuration. The complex $[\mathrm{Ni^{III}(C_5Me_5)_2}]^{\bullet+}[\mathrm{TCNE}]^{\bullet-}$ which is isomorphous to the orthorhombic phase of $[\mathrm{Fe^{III}(C_5Me_5)_2}]^{\bullet+}[\mathrm{TCNE}]^{\bullet-}$ possesses the d^1/s^1 electronic configuration, and preliminary analysis of the suscepbility data is consistent with antiferromagnetic behavior.

Several homomolecular $m_s = {}^1/_2$ electron configurations (i.e., d^1/d^1, d^3/d^3, t^1/t^1, and t^5/t^5) stabilize ferromagnetic coupling via virtual disproportionation, Figure 6. For virtual disproportionation an electron on one site is transferred to an adjacent site. For ferromagnetically coupled GS$_{FO}$ the electron with $m_s = -{}^1/_2$ can be virtually transferred to the adjacent site which can only accept an electron with $m_s = -{}^1/_2$. For the antiferromagnetically coupled GS$_{AF}$ the site can only accept a $m_s = +{}^1/_2$ electron; however, loss of such an electron from the donor would result in the formation of a higher excited state. Thus, ES$_{FO}$ is lower energy than ES$_{AF}$, and ferromagnetic coupling is stabilized. Virtual disproportionation between $[\mathrm{Fe(C_5Me_5)_2}]^{\bullet+}$'s is invoked as an additional mechanism for stabilizing ferromagnetic coupling between chains by ferromagnetically coupling in-registry chains and thus providing a mechanism for establishing bulk ferromagnetic behavior as observed for $[\mathrm{Fe(C_5Me_5)_2}]^{\bullet+}[\mathrm{TCNE}]^{\bullet+}$.[6b] Cobaltocene and its analogues[19] (d^1) might be a model system to investigate this point as ferromagnetic coupling is predicted for this homomolecular compound.[20] The t^1/d^1 and t^5/d^3 configurations should stabilize ferromagnetic coupling regardless of the direction of virtual charge transfer. Examples of such systems, however, have yet to be identified.

$m_s = 1$. Ferromagnetic coupling via the McConnell mechanism is anticipated for several electron configurations involving t orbitals. Homomolecular compounds or ions with a t^4 electron configuration via virtual disproportionation should also stabilize ferromagnetic coupling by the McConnell model. The d^2/d^2 configuration is expected to exhibit antiferromagnetic coupling.[21] The complex $[\mathrm{Ru^{II}(OEP)}]_2$ (OEP = octaethylporphyrin) possesses parallel chains of ground-state $m_s = 1$ (d^2) dimers[22a] in the solid. Preliminary susceptibility data are consistent with the presence of antiferromagnetic behavior.[22b]

Examples of a higher spin multiplicity homomolecular system are $\mathrm{V^{II}(C_5H_5)_2}$ and $\mathrm{Mn^{II}(C_5H_5)_2}$ with a $m_s = {}^3/_2$ $(a_{1g})^1(e_{2g})^2$, t^3, and $m_s = {}^5/_2$ $(a_{1g})^1(e_{2g})^2(e_{3g})^2$, q^5, ground states, respectively.[19b] Antiferromagnetic behavior is observed for these complexes as predicted by this model,[23] Table I.

Heterospin Systems. Heterospin systems, i.e., systems with different spin magnitudes on the donors and acceptors, provide an opportunity to obtain ferrimagnetic as well as ferromagnetic solids. Within this simple nearest-neighbor model antiferromagnetic coupling of adjacent spins of the D and A sublattices could only produce incomplete cancellation of the total spin and thus lead to ferrimagnetic behavior.

$m_s^D = {}^1/_2$; $m_s^A = 1$. For the lower symmetry s and d electron configurations two combinations support ferromagnetic coupling, i.e., d^3/d^2 with forward charge transfer and d^1/d^2 with retro charge transfer. Several combinations (d^1/t^2, d^3/t^4, t^1/t^2, and t^5/t^4) are ferromagnetic invariant of direction of electron transfer. Illustrative systems have yet to be identified for these electron configurations.

$m_s^D = {}^1/_2$; $m_s^A = {}^3/_2$. Several electron configurations, depending on the direction of virtual charge transfer, can stabilize ferromagnetic coupling. The t^3/s^1 configuration expected for $[\mathrm{Cr(C_5Me_5)_2}]^{+}[\mathrm{TCNE}]^{\bullet-}$ due to an accidental degeneracy of the cations e_{2g} and a_{1g} orbitals[19] is predicted to exhibit ferrimagnetic coupling for either retro or forward charge transfer. Preliminary magnetic susceptibility data show high susceptibility that is characteristic of either ferri- or ferro- but not paramagnetic, behavior.[24] Detailed analysis is required to distinguish between these two magnetic states.

General Considerations. Assuming the virtual charge transfer involves only the POMO, in order to stabilize ferromangetic coupling via the McConnell mechanism *stable radicals must possess a nonhalf-filled degenerate POMO*. Thus, for homonuclear systems ferromagnetic stabilization requires radicals with a d^1, d^3, t^1, t^2, t^4, or t^5 POMO. These radicals must avoid structural/electronic distortions that lower the symmetry and break the degeneracies, e.g., the Jahn–Teller effect; however, accidentally degenerate systems (e.g., high spin transition, lanthanide, and actinide metal coordination complexes) are sufficient. The chains need not be comprised of charged radical donors and acceptors as originally suggested by McConnell[3] but may be homomolecular radicals or radical ions. For example, chains of radicals [or radical ions with small diamagnetic counterions (e.g., Na$^+$ or Cl$^-$)] possessing a nonhalf-filled degenerate POMO could via virtual disproportionation exhibit ferromagnetic behavior via the McConnell mechanism.

Complex Systems. By using the above arguments the magnetic coupling of materials with complex electronic configurations can be predicted. For example, $[\mathrm{Fe^{III}(C_5Me_5)_2}]^{\bullet+}[\mathrm{Fe^{III}Cl_4}]^{-}$ possesses a $m_s = {}^1/_2$ $(e_{2g})^3$, d^3, and $m_s = {}^5/_2$ e^{2}t^3, q^5, electron configurations

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(17) We define a molecular solid as a solid comprised of low molecular weight molecules or ions that do not possess extended covalent bonding in the solid state. However, shorter than van der Waal separations may be present in the solid. Dissolution into conventional aqueous of organic solvents leads to solvation of the noninteracting ions or molecules that were used to prepare the molecular solid.

(18) $S = {}^1/_2$ NO$^\bullet$ is an example of a d^1 homomolecular system; however, due to dimerization at low temperature antiferromagnetic behavior is observed. Skaarup, S.; Skanke, P. N.; Boggs, J. E. *J. Am. Chem. Soc.* **1976**, *98*, 6106.

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(20) Gouy solution magnetic measurements for $\mathrm{Co(C_5H_5)_2}^\bullet$ show a substantial deviation from Curie–Weiss behavior.[19b]

(21) Triplet oxygen, O$_2$, and triplet carbenes have this d^2/d^2 electronic structure (intrinsic and accidental, respectively) and are antiferromagnetic at lower temperature. This is due to dimerization to $(\mathrm{O_2})_2$. *Comprehensive Inorganic Chemistry*; Pergamon Press: 1973; Vol. *2*, pp 705–709.

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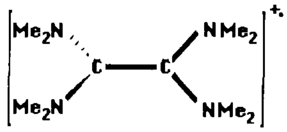
for the cation and anion, respectively. The lowest excited state via virtual forward charge transfer would conserve spin and stabilize ferromagnetic coupling, whereas retro charge transfer would stabilize antiferromagnetic coupling. This complex does not have a chain structure[25] but should be investigated. Additionally, $[V(C_6R_6)_2]^+$ as the hypothetical $[TCNE]^{\bullet-}$ salt would have the $(e_{2g})^3(a_{1g})^1$,[26a] t^4, and $(b_{3g})^1$, s^1, electron configurations for the cation and anion, respectively. Virtual retro charge transfer and forward charge transfer would stabilize ferromagnetic and ferrimagnetic coupling, respectively, which may lead to ferro- or ferrimagnetic behavior in this compound should 3-D coupling and the generalized McConnell mechanism dominate.

Symmetry of the Radicals. For radicals with intrinsic POMO degeneracies the relatively high symmetry required by either the radical D or A, if not both, restricts the choice of compounds to those which belong to specific point groups. For doubly degenerate orbitals the molecule or ion must belong to the D_{2d}, C_3, or higher point groups. For triply degenerate systems the point groups are further restricted to the cubic (T and O) and I_h groups.[27] As noted above the effective orbital symmetry need not be rigorous and can be accidental. However, unpaired electrons residing in orbitals of different local symmetry may lead to partial or full cancellation of the net magnetic moment and lead to ferri- and antiferro- if not more complex magnetic behavior.

Organic Ferromagnets. Many of the electron configurations that support ferromagnetic coupling via the McConnell mechanism require partial occupancy of triply degenerate orbitals which requires a cubic space group or an accidental orbital degeneracy. Both situations are well-characterized for transition-metal-based, coordination-based compounds but are very rare for organic compounds.[27,28] An a prior prediction of accidentally degenerate orbitals is difficult to make except for large low-symmetry radicals with several pseudo equivalent radical sites.[29] Except, for example, complex poly($R_2NO^\bullet$) radicals[30] these radicals are neither thermally nor chemically stable. Consequently, we limit our scope to prepare an organic ferromagnet based on the McConnell model by identification of stable D_{2d}, C_3, or higher symmetry $m_s = {}^1/_2$ radicals with a degenerate POMO.[31] Breslow[1b,8] previously pointed out the necessity of a triplet state[31] and has focused research toward the synthesis of stable organic triplets.[1b,8,32] He has limited his search to organic radicals with C_3 or higher symmetry; presumably because the planarity should support the $\cdots D^{\bullet+}A^{\bullet-}D^{\bullet+}A^{\bullet-}\cdots$ chain described by McConnell.[3] Radicals possessing D_{2d} symmetry, albeit rare, in principle may possess a POMO of d (e) symmetry. For example, twisted ethylene (D_{2d}) is a triplet[33] (d^2), and a stable radical cation derivative such as d^1 $[(Me_2N)_2CC(NMe_2)_2]^{\bullet+}$,[34,35a] **1**, or $[(RS)_2CC(SR)_2]^{\bullet+}$,[35,36] **2**, if they possess the D_{2d} structure, should be suitable candidates for preparing an organic ferromagnet. Hexacyanotrimethylenecyclopropane, **3**, is predicted to have an e^4 HOMO, and oxidation should lead to an e^3, d^3 radical cation.[37] Since neutral **3** has never been isolated, other derivatives with electron-donating groups, e.g., NR_2, to stabilize the radical cation, e.g., **4**, would have to prepared and studied.



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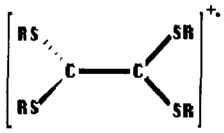

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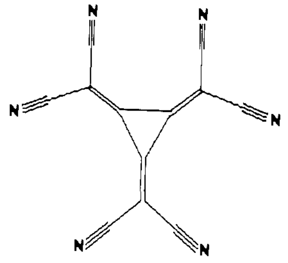

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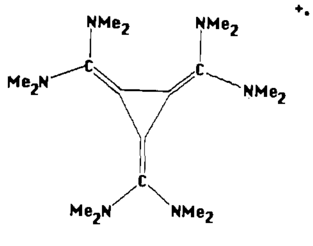

4

Summary. The extended McConnell model and its mathematical embodiment as the generalized Hubbard model offer a convenient guide for the synthetic chemist to prepare new materials for exploration of ferro-, antiferro-, and ferrimagnetic phenomena in molecular systems. For a compound to exhibit bulk ferromagnetism via the McConnell mechanism ferromagnetic coupling is necessary. Assuming the virtual charge transfer excitation involves only the POMO, to achieve ferromagnetic coupling in a molecular material (organic, organometallic, main group, polymer, and/or inorganic coordination complex) via the McConnell mechanism at least one type of radical (neutral, radical cations/radical anions, or radical ions with small diamagnetic counterions) must possess a degenerate POMO that is not half-filled, and the lowest excited state formed via virtual charge transfer (retro or forward) possesses the same spin multiplicity and mixes with the ground state to stabilize the ferromagnetically coupled ground state. The requirement for a radical to possess an intrinsically degenerate POMO limits the structure of a radical to D_{2d}, C_3, or higher symmetry where symmetry lowering distortions do not occur. Intrinsic doubly and triply degenerate orbitals are not necessary, and accidental degeneracies suffice. Since ferromagnetism is a bulk phenomenon, to be achieved the aforementioned ferromagnetic coupling must be established throughout the solid.[5] Extensive chemical syntheses of cleverly designed radicals as well as physical, experimental, and theoretical insight are necessary to test these concepts and establish a deeper understanding of cooperative phenomena in molecular solids.

Acknowledgment. We gratefully acknowledge partial support by the Department of Energy Division of Materials Science (Grant No. DE-FG02-86ER45271.A000).

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(27) The postulated so-called Buckminsterfullerene, C_{60}, with I_h symmetry (Kroto, H. W.; Heath, J. R.; O'Brian, S. C.; Curl, R. F.; Smalley, R. E. *Nature (London)* **1985**, *318*, 162–163) when oxidized or reduced should possess a q^9 or t^5 electron configuration, respectively (Hale, P. D. *J. Am. Chem. Soc.* **1986**, *108*, 6087–6088). Since the center cavity of the C_{60} species can accept a small cation or anion, the reduced or oxidized C_{60} may exhibit cooperative magnetic properties in the solid state.

(28) Accidentally degenerate POMO's for organic compounds are rare and limited to triplet carbenes (e.g., Hoffmann, R.; Zeiss, G. D.; van Dine, G. W. *J. Am. Chem. Soc.* **1968**, *90*, 1485–1499. Humphreys, R. W. R.; Arnold, D. R. *Can. J. Chem.* **1977**, *55*, 2286–2291. McMahon, R. J.; Chapman, O. C. *J. Am. Chem. Soc.* **1986**, *108*, 1713–1714.) and higher spin multiplicity polycarbenes[1b,1c] with less than D_{2d} symmery (e.g., Seeger, D. E.; Berson, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 5146–5147. Rule, M.; Matlin, A. R.; Seger, D. E.; Hilinski, E. F.; Dougherty, D. A.; Berson, J. A. *Tetrahedron* **1982**, *38*, 787–798) and ref 29.

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