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Oligomer Antiferromagnetism. I. Expediency of the Heisenberg Spin Hamiltonian in the Submolecule Model

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The use and properties of the Dirac-Heisenberg-Van Vleck electron spin exchange Hamiltonian, eq 2, in accounting for the weak interactions which give rise to antiferromagnetism within oligomeric transition metal complexes are examined in terms of the submolecule description of such complexes. The conditions under which $\mathcal{H}_{\text{DHVV}}$ may be approximated as $\mathcal{H}_{\text{ex}} = -2J_{\text{ab}}\mathbf{S}_a \cdot \mathbf{S}_b$, and the fact that J_{ab} is the average of the intersubmolecular J_{ij} , are delineated. The effect on the exchange paramagnetism when two electrons from different submolecules form a strong bond is illustrated. Rationalizations of literature observations are suggested.

Introduction

This paper is concerned with the interpretation of electron spin exchange paramagnetism which is observed for multifarious oligomeric transition metal complexes. Traditionally two types of models have been used, namely the Dirac-Heisenberg-Van Vleck¹⁻⁴ (DHVV) spin Hamiltonian and the molecular orbital (MO, usually LCAO) method. The DHVV procedure implies a Heitler-London (HL) product wave function, $\Phi = \Pi_i \phi_i$, for singly occupied weakly interacting orbitals ϕ_i of adjacent coordination units. Apart from operational differences between HL and MO approximate methods, there is a fundamental theoretical difference, namely their account of the electron correlation for the highest energy electrons in low-lying spin states. Low electron correlation is inherent in LCAO MO's, while in HL representation the electrons are strongly correlated due to their restraint within orbitals ϕ_i . Because observable spin exchange necessarily implies the presence of some very weak (~ 0.2 eV) interactions between electrons, it may be readily shown⁵ that HL product wave functions are much more valid than LCAO wave functions in describing those interactions and thermally accessible spin states.

In order to incorporate exchange paramagnetism with its HL basis into the molecular orbital theoretical framework for the remainder of the spectroscopic and structural properties of typical complexes, the concept of the submolecule within the oligomer has been proposed.⁵ This method is essentially a separation of all strongly or moderately strongly bonding interactions and their description with filled or empty molecular orbitals, from singly occupied molecular or atomic orbitals, which must necessarily be restricted to various seg-

ments of the oligomer and be very weakly interacting between such segments. (Usually these singly occupied orbitals are metal-ligand orbitals within a coordination sphere, weakly antibonding with respect to that coordination.) The submolecular region is defined by this localization of singly occupied orbitals, and therefore the submolecule prescription is based on a classification of orbitals rather than a subdivision of atoms. The submolecule is a collection of orbitals for a coordination unit around a metal, consisting of A, filled molecular orbitals representing coordination bonding within the submolecule; B, filled molecular orbitals representing the oligomer binding of the submolecule with contiguous submolecules; and C, singly occupied orbitals which may engage in direct or indirect weak exchange interactions with type C orbitals on other submolecules. Magnetically observable exchange phenomena result only from these latter intersubmolecular interactions between orbitals of type C, which may be combined in HL manner as required.

The Hamiltonian which antisymmetrizes Φ is $\mathcal{H}'_{\text{DHVV}}$ ⁶⁻¹⁰ (eq 1), where $\sigma_i = 2s/\hbar$, $s = \pm 1/2$, are spin operators for the

$$\mathcal{H}'_{\text{DHVV}} = -1/2 \sum_{i>j}^n \sum_{i>j}^n J'_{ij} (1 + \sigma_i \cdot \sigma_j) \quad (1)$$

wave functions ϕ_i written as the product, $\omega\sigma$, of orbital and spin functions. As only the spin dependence of the state energies relates to observable magnetic properties, $\mathcal{H}'_{\text{DHVV}}$ is customarily rewritten as $\mathcal{H}_{\text{DHVV}}$ (eq 2). The J_{ij} paramet-

(6) The validity of $\mathcal{H}'_{\text{DHVV}}$ has been questioned⁷ at the point of the restrictive requirements of mutual orthogonality of all ϕ_i in original derivations. Nonetheless, considerable experience and more recent theoretical investigations^{8,9} leave no doubt that $\mathcal{H}'_{\text{DHVV}}$ is correct in spite of nonorthogonality. Actual intersubmolecular interactions involve very weakly overlapping but not identically orthogonal orbitals.

(7) J. C. Slater, *Rev. Mod. Phys.*, **25**, 199 (1953).

(8) C. Herring in "Magnetism," Vol. IIB, G. T. Rado and H. Suhl, Ed., Academic Press, New York, N. Y., 1966, Chapter 1.

(9) D. F. Martin, "Magnetism in Solids," MIT Press, Boston, Mass., 1967, Chapter 5.

(10) It is to be noted that $\mathcal{H}'_{\text{DHVV}}$ describes only states arising from the Φ configuration.

(1) P. A. M. Dirac, *Proc. Roy. Soc., Ser. A*, **112**, 661 (1926); **123**, 714 (1929).

(2) W. Heisenberg, *Z. Phys.*, **38**, 411 (1926); **49**, 619 (1928).

(3) (a) J. H. Van Vleck, *Phys. Rev.*, **45**, 405 (1934); (b) J. H. Van Vleck and A. Sherman, *Rev. Mod. Phys.*, **7**, 167 (1935).

(4) J. H. Van Vleck, "The Theory of Electric and Magnetic Susceptibilities," Oxford University Press, London, 1932.

(5) I. G. Dance, unpublished work.

$$\mathcal{H}_{\text{DHVV}} = -2 \sum_{i>j}^n \sum_{i>j}^n J_{ij} s_i \cdot s_j \quad (2)$$

size the energy difference between the spin-singlet and spin-triplet states for the pair of electrons in submolecular orbitals ϕ_i and ϕ_j , according to the Lowdin¹¹ definition (eq 3).

$$J_{ij} = 1/2(E_{\text{singlet}} - E_{\text{triplet}}) \quad (3)$$

This paper explores the properties and meaning of $\mathcal{H}_{\text{DHVV}}$ as it is used with the submolecular orbital description and emphasizes the advantages of this approach to the general phenomenon of oligomer antiferromagnetism.

Description of the Illustrative Model

For the purposes of illustration the treatment will be developed for a centrosymmetric dimetallic complex with two submolecules; generalization to oligomers (or polymers) with any symmetry and any mode of metal-metal bonding or bridging coordination follows without addition to the conceptual basis. The submolecular orbitals for either submolecule are all molecular orbitals which describe the bonding within the metal coordination unit of the submolecule. The orbitals of one submolecule are denoted ϕ_i , those of the other ϕ'_i . Due to the centrosymmetry, $\phi_i \equiv \phi'_i$. Some submolecular orbitals, ϕ_k , which encompass bridging ligand atoms or are the orbitals issuing from metal-metal bonding will be common to the two submolecules, $\phi_k = \phi'_k$. These common orbitals, which account for oligomer bonding,⁵ the structural binding between submolecules, are assumed initially to be moderately bonding or antibonding and therefore not partially occupied (but see section IV where this restriction is removed).

Although submolecular orbitals ϕ_i are normally constructed as an orthogonalized set, the overlap between different submolecular orbital sets ϕ_i and ϕ'_i may be small but not identically zero. These sets are populated independently in the ground configuration (because appreciable bonding interactions *between* submolecules are incorporated in construction of submolecule orbitals). It is the singly occupied orbitals of each submolecule which determine the magnetic properties of the compound. The following calculations are performed for the case of three singly occupied orbitals at each submolecule. These orbitals are labeled ϕ_1, ϕ_2, ϕ_3 , and $\phi'_1, \phi'_2, \phi'_3$ and are shown diagrammatically in Figure 1. The HL ground configuration wave function for the oligomer is $\Phi = \phi_1 \phi_2 \phi_3 \cdot \phi'_1 \phi'_2 \phi'_3$. The 15 J_{ij} ($=J_{ji}$) reduce to nine different sets in C_i symmetry; the three intrasubmolecule interactions $J_{12} = J_{1'2'}, J_{23} = J_{2'3'}$, and $J_{13} = J_{1'3'}$ are collectively referred to as J_{intra} and the six intersubmolecular sets $J_{11'}, J_{22'}, J_{33'}, J_{12'} = J_{21'}, J_{23'} = J_{32'}, J_{13'} = J_{31'}$ are referenced as J_{inter} . Twenty molecular spin states¹² exist for the six electrons: one spin septet, $S' = 3$; five quintets, $S' = 2$; nine triplets, $S' = 1$; and five singlets, $S' = 0$. The energies of these states are obtained by application of $\mathcal{H}_{\text{DHVV}}$ to Φ .

Calculations

The matrix elements of $\mathcal{H}_{\text{DHVV}}$ between the 64 spin product functions were calculated with the aid of the rules.¹³ $\langle \phi_p | H | \phi_p \rangle = 1/2 \sum_{i>j} \sum_{i>j} J_{ij} T_{ij}$, $T_{ij} = +1$ if spins i and j are parallel, $T_{ij} = -1$ if spins i and j are antiparallel; $\langle \phi_p | H | \phi_q \rangle = -J_{ij} U$, $U = +1$ if ϕ_p and ϕ_q differ only by interchange of spins i and j , otherwise $U = 0$.

(11) P. O. Lowdin, *Rev. Mod. Phys.*, **34**, 80 (1962).

(12) Primed spin symbols refer to the oligomer, unprimed to the submolecules.

(13) H. M. McConnell, A. D. McLean, and C. A. Reilly, *J. Chem. Phys.*, **23**, 1152 (1955).

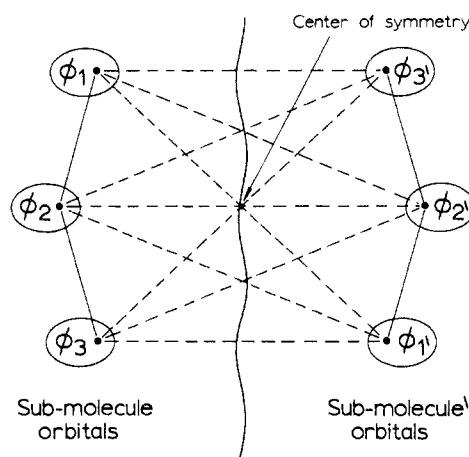


Figure 1. Symbolic representation of the spin exchange interactions between singly occupied orbitals in a centrosymmetric complex with two submolecules: intrasubmolecule interactions, J_{intra} (—); intersubmolecule interactions, J_{inter} (---). No spatial configuration is implied.

Results

I. Submolecule Spin Condition. As a consequence of the orthogonality of orbitals within each submolecule the J_{intra} are positive exchange integrals and the hypothetical isolated submolecule would be high spin, $S = 3/2$. When all intersubmolecular interactions J_{inter} are *equally* negative (antiferromagnetic coupling) the energies $E(S')$ of the oligomer spin states are dependent on the ratio $J_{\text{intra}}/J_{\text{inter}}$ as shown in Figure 2. The significant feature is that as $J_{\text{intra}}/J_{\text{inter}}$ increases beyond *ca.* 3, 16 of the excited spin states move away to high energy, leaving a manifold of four states, $S' = 0, 1, 2$, and 3, at positive energies $E(S') = -J_{\text{inter}} S'(S' + 1)$. These state energies are independent of the magnitude of J_{intra} .

This same manifold of four spin states is obtained from the exchange Hamiltonian \mathcal{H}_{ex} (eq 4 and 5) for two¹⁴ submol-

$$\mathcal{H}_{\text{ex}} = 2 \bar{J}_{\text{ab}} \mathbf{S}_a \cdot \mathbf{S}_b \quad (4)$$

$$E(S') = -\bar{J}_{\text{ab}} S'(S' + 1) \quad (5)$$

ecules of spins S_a and S_b (here $S_a = S_b = 3/2$), with $\bar{J}_{\text{ab}} = J_{\text{inter}}$. Equation 4 has previously been developed^{15,16} from eq 2 with the assumption that S_a and S_b represent good quantum numbers for the submolecules (which in most cases are conceived simply as transition metal ions). The derivation of eq 4 has been discussed by Nesbet.¹⁷ The conclusion of the present analysis is that the validity of \mathcal{H}_{ex} as an exchange Hamiltonian depends on the ratio $J_{\text{intra}}/J_{\text{inter}}$ (or the ratio of their mean values as discussed below) and indirectly on the thermal energy available: the $J_{\text{intra}}/J_{\text{inter}}$ ratio is required to be sufficiently large that the lowest set of additional $S' = 1$ states is not populated at ambient temperature.

The Hamiltonian \mathcal{H}_{ex} has been extensively applicable to coordination complexes. However, the dimeric iron dithiolene complex¹⁸ $[\text{FeS}_4\text{C}_4(\text{CF}_3)_4]_2$ manifests anomalous intramolecular antiferromagnetism which cannot be described by eq 4 and 5 but can be parametrized with eq 2, $n = 4$.¹⁹ This

(14) Equation 4 becomes $\mathcal{H}_{\text{ex}} = -2 \sum_{a>b} \bar{J}_{\text{ab}} \mathbf{S}_a \cdot \mathbf{S}_b$ when more than two submolecules are involved.

(15) Reference 9, p 324.

(16) R. L. Martin in "New Pathways in Inorganic Chemistry," E. A. V. Ebsworth, A. G. Maddock, and A. G. Sharpe, Ed., Cambridge University Press, New York, N. Y., 1968, p 180.

(17) R. K. Nesbet, *Ann. Phys. (Paris)*, **4**, 87 (1958).

(18) A. L. Balch, I. G. Dance, and R. H. Holm, *J. Amer. Chem. Soc.*, **90**, 1139 (1968).

(19) I. G. Dance, *Inorg. Chem.*, **12**, 2748 (1973).

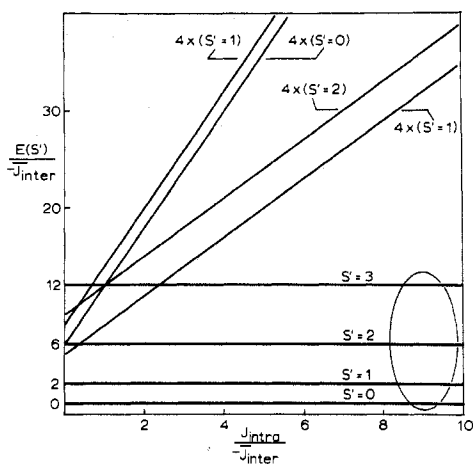


Figure 2. Energies $E(S')$ of molecular spin states S' for two interacting spin-quartet submolecules as a function of J_{intra} . $J_{11}' = J_{22}' = J_{33}' = J_{12}' = J_{21}' = J_{23}' = J_{32}' = J_{13}' = J_{31}' = J_{\text{inter}}$.

failure of \mathcal{H}_{ex} is due to an insufficiently large ratio $J_{\text{intra}} / -J_{\text{inter}}$ and is readily rationalized by an order of magnitude calculation from Figure 2. The energy E' of the lowest of the "non- \mathcal{H}_{ex} " states, the four degenerate spin triplets, is $E' = 3J_{\text{intra}} - 5J_{\text{inter}}$. For anomalous exchange paramagnetism to be observable at room temperature, $E' < \sim 1$ kK (1000 cm^{-1}). Then (in kilokaiser energy units) $J_{\text{intra}} < 1/3 + 5/3 J_{\text{inter}}$, and as J_{inter} is negative, $J_{\text{intra}} \lesssim 0.3$ kK. For a classical transition metal such as Fe^{2+} , J_{intra} is an exchange integral $K(3d_1, 3d_2)$ of magnitude 4–8 kK.²⁰ Thus, an actual submolecular J_{intra} value of *ca.* 0.3 kK corresponds to a nephelauxetic ratio β^{21} of less than 0.1. Although this analysis is approximate²² it demonstrates that only markedly delocalized (or nephelauxetic) complexes such as the dithiolenes and their analogs²³ would be expected to show "non- \mathcal{H}_{ex} " exchange paramagnetism in this manner.

II. Variable Individual J_{inter} . The above treatment assumes that the six distinct J_{inter} are equal, as are the three distinct J_{intra} . Effectively the exchange interactions have been accredited with D_{3d} symmetry, whereas in practice the dimer and hence the interactions have little more than C_i symmetry. The chemically unreasonable degeneracy of the J_{inter} is removed in Figure 3 (which is otherwise analogous to Figure 2) by setting $J_{11}' = 4\bar{J}_{\text{inter}}$, $J_{22}' = J_{33}' = \bar{J}_{\text{inter}}$, $J_{13}' = J_{31}' = J_{12}' = J_{21}' = J_{23}' = J_{32}' = 0.5\bar{J}_{\text{inter}}$, $J_{\text{inter}} = 1/9 \sum J_{\text{inter}}$. The removal of degeneracies is apparent. Nevertheless, the \mathcal{H}_{ex} manifold still emerges with the important spin states for $J_{\text{intra}} / -J_{\text{inter}} > \sim 4$, and when this ratio is > 6 their energies are given exactly by eq 6. The important result is that the

$$E(S') = -\bar{J}_{\text{inter}} S'(S' + 1) \quad (6)$$

intersubmolecule exchange parameter obtained by use of \mathcal{H}_{ex} for submolecules with more than one singly occupied orbital is in fact the canonical mean of all individual intersubmolecule interactions. The relationship between \mathcal{H}_{ex} , $\mathcal{H}_{\text{DHVV}}$, and eq 6 is expressed by eq 7 with summation over

$$\bar{J}_{\text{ab}} = \bar{J}_{\text{inter}} = \frac{\sum_k \sum_l J_{kl}}{4S_a S_b} \quad (7)$$

(20) (a) C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill, New York, N. Y., 1962, p 76; (b) J. S. Griffith, "Transition Metal Ions," Cambridge University Press, New York, N. Y., 1961, appendix 6.

(21) C. K. Jorgensen, *Progr. Inorg. Chem.*, 4, 73 (1962).

(22) The existence of the anomaly depends upon the actual combination of J_{ij} in $\mathcal{H}_{\text{DHVV}}$ and may occur for J_{intra} up to 1 kK.¹⁹

(23) J. A. McCleverty, *Progr. Inorg. Chem.*, 10, 49 (1968).

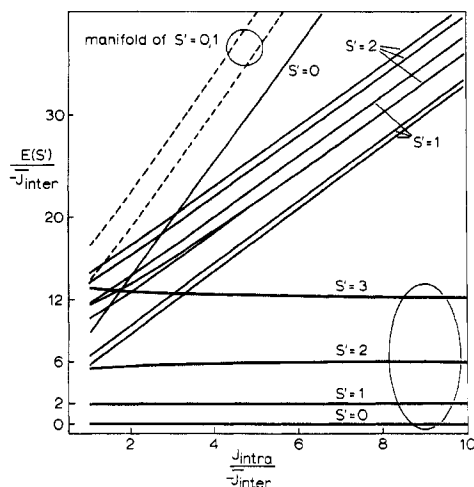


Figure 3. Energies $E(S')$ of molecular spin states S' for two interacting spin-quartet submolecules as a function of J_{intra} . $J_{11}' = 4\bar{J}_{\text{inter}}$, $J_{22}' = J_{33}' = \bar{J}_{\text{inter}}$, $J_{12}' = J_{21}' = J_{23}' = J_{32}' = J_{13}' = J_{31}' = 0.5\bar{J}_{\text{inter}}$.

the $4S_a S_b$ intersubmolecule Lowdin parameters. The effects of eq 7 were intimated in a paper of Van Vleck^{3a} and are implicit in Anderson's discussion of \bar{J}_{ab} values.²⁴ The derivation of \mathcal{H}_{ex} from $\mathcal{H}_{\text{DHVV}}$ does not depend on the equality of all J_{inter} , as has been inferred.¹⁶ Equations 6 and 7 fail only when one of the negative J_{inter} approaches J_{intra} in magnitude or when one or more J_{inter} become positive to order of magnitude $+|J_{\text{inter}}|$.

III. Variable Individual J_{intra} . In the above calculations all intrasubmolecule interactions are equal. Calculations in which the degeneracy of the individual J_{intra} is removed demonstrate the continued effectiveness of eq 6 and 7, although the energies of the "non- \mathcal{H}_{ex} " states are slightly influenced.

IV. Strong Intersubmolecule Exchange. The submolecule was defined above according to a separation of strong, spin-paired, bonding interactions, described with molecular orbitals, from weak exchange interactions, described by HL wave functions. The changeover energy is *ca.* 0.5 eV. It is now of interest to consider an intersubmolecular interaction intermediate between these classifications. This is approached by calculating the effects of a progressively more energetic interaction between two singly occupied submolecular orbitals, namely ϕ_1 and ϕ_1' of the current illustration.

In Figure 4 are plotted relative spin state energies for the (dimensionless) parameter set: all $J_{\text{intra}} = +20$; J_{11}' as independent variable, -1 to -1000 ; and all other $J_{\text{inter}} = -1.0$. All excited state energies have been normalized to the lowest spin triplet, $E(S' = 1) = 2.0$, with the divisor J_{eff} which takes the values plotted at the top of Figure 4. As $-J_{11}'$ increases from 4 through 100 to 1000, corresponding to an increased bonding stabilization for the electrons of orbitals ϕ_1 and ϕ_1' , the spin septet of the $S' = 0, 1, 2$, and 3 manifold rapidly moves to higher energies, eventually leaving just the $S' = 0, 1$, and 2 manifold well separated from any other excited states. This corresponds to conversion of \mathcal{H}_{ex} behavior for $S_a = S_b = 3/2$ to \mathcal{H}_{ex} behavior for $S_a = S_b = 1$. In conjunction with this changeover, the effective \bar{J}_{ab} of \mathcal{H}_{ex} , namely J_{eff} , changes from the average of the J_{inter} for all six submolecule orbitals to the average of J_{inter} for orbitals ϕ_2, ϕ_3, ϕ_2' , and ϕ_3' . As the magnitude of J_{11}' increases its con-

(24) P. W. Anderson, *Solid State Phys.*, 14, 99 (1963); see especially p 142.

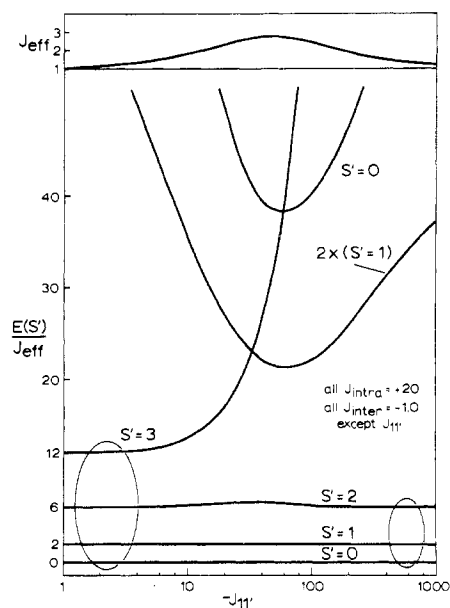


Figure 4. Energies $E(S')$ of low-lying molecular spin states S' for two interacting submolecules, each with three orbitals, as a function (decadal) of one bonding intersubmolecular interaction. The units of $E(S')$ are those of the J parameters. $E(S')$ is normalized to maintain the lowest spin triplet at $E = 2$, by the divisor J_{eff} which is plotted at the top in terms of the units of all other J . $J_{\text{intra}} = +20$; $J_{22'} = J_{33'} = J_{12'} = J_{21'} = J_{23'} = J_{32'} = J_{13'} = J_{31'} = -1$. The $\mathcal{H}_{\text{ex}} = -2J_{\text{ab}}\mathbf{S}_a \cdot \mathbf{S}_b$ manifolds for $S_a = S_b = 3/2$ and $S_a = S_b = 1$ are encircled (left and right, respectively).

tribution to the averaging of J_{inter} is diminished eventually to zero.²⁵

These calculations show that as the interaction between a pair of submolecular orbitals increases from a weak exchange interaction to strongly stabilized bonding, those orbitals are automatically factored out of the DHVV total exchange interaction and into the oligomer bonding and molecular orbital description. The corresponding change in submolecular orbital representation for the current dimer is shown in Figure 5. The remaining singly occupied orbitals at each submolecule continue to exhibit customary exchange properties, with energies $E(S') = -J_{\text{eff}}S'(S' + 1)$.

Further intersubmolecular interactions may be factored out of the exchange assemblage into the spin-paired oligomer bonding, as shown in Figure 6 for increasing $-J_{22'}$ when $J_{11'} = -500$. Eventually there remain only the singlet and triplet states for the one exchange interaction between orbitals ϕ_3 and ϕ_3' .

Thus the further expediency of $\mathcal{H}_{\text{DHVV}}$ is apparent as it correctly accommodates weak, moderate, and strong intersubmolecular interactions between electrons. It is important to note that the effect of one strongly bonding interaction is not to stabilize the diamagnetic ground state of the oligomer relative to the other excited spin states, as has been suggested,²⁶ but rather to destabilize the highest excited spin state beyond the range of thermal population. The magnetically observable consequence of the latter effect is very different from that of the former consideration.

V. Submolecule Spin State and the "Exchange Field."

There is in the literature considerable discussion, particularly

(25) J_{eff} responds to the uncoupling of $J_{11'}$ from the J_{inter} by increasing through the transition region and then reapproaching J_{inter} for $\phi_3, \phi_3', \phi_2,$ and ϕ_3' . The region of transition between weak exchange and strong bonding depends somewhat on J_{intra} magnitudes.

(26) M. Gerloch, J. Lewis, F. E. Mabbs, and A. Richards, *J. Chem. Soc. A*, 112 (1968).

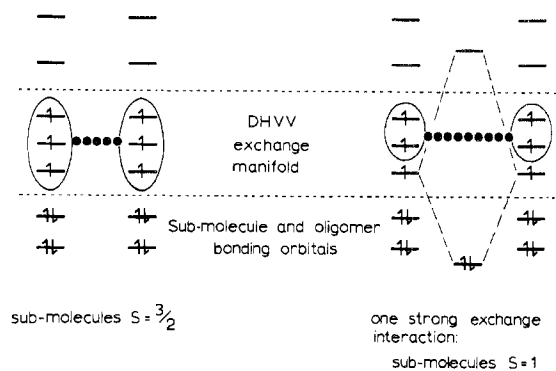


Figure 5. Submolecular orbital representations. On the left, weak exchange interactions occur between three singly occupied orbitals at each submolecule; on the right, one of these interactions is sufficiently strong to be described by formation of additional oligomer bonding molecular orbitals, leaving exchange interactions between two singly occupied orbitals at each submolecule.

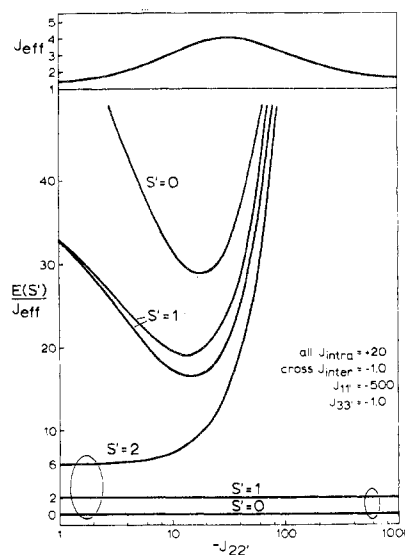


Figure 6. Energies $E(S')$ of low-lying molecular spin states S' for two interacting submolecules, each with three orbitals, as a function (decadal) of a second bonding intersubmolecular interaction, $J_{22'}$. $J_{\text{intra}} = +20$; $J_{11'} = -500$, $J_{33'} = J_{12'} = J_{21'} = J_{23'} = J_{32'} = J_{13'} = J_{31'} = -1$. Units and normalization as for Figure 4. The $\mathcal{H}_{\text{ex}} = -2J_{\text{ab}}\mathbf{S}_a \cdot \mathbf{S}_b$ manifolds for $S_a = S_b = 1$ and $S_a = S_b = 1/2$ are encircled (left and right, respectively).

for oligomeric iron(III) compounds,²⁷ of the submolecule spin states to be utilized in application of \mathcal{H}_{ex} . The hypothetical spin state of a submolecule in an oligomer is not experimentally observable. It is usually inferred from (i) the magnetic properties of the oligomer, (ii) the spin state of the isolated submolecule in the few cases where the oligomer readily dissociates, or (iii) by analogy with the properties of monomeric complexes which resemble the submolecule. Only submolecule spin states differing by one ($\Delta S = 1$) are possible with this approach [e.g., $S = 5/2, 3/2, 1/2$ for Fe(III)]. However, the results of the previous section indicate that oligomer spin state manifolds, and hence their magnetic properties, may be continuously variable between those characteristic of submolecule spin states with $\Delta S = 1/2$. In the complete $\mathcal{H}_{\text{DHVV}}$ treatment no discontinuities exist in oligomer magnetic exchange properties. If the concept of

(27) (a) J. Lewis, F. E. Mabbs, and A. Richards, *J. Chem. Soc. A*, 1014 (1967); (b) A. van den Bergen, K. S. Murray, and B. O. West, *Aust. J. Chem.*, 21, 1517 (1968); (c) W. M. Reiff, W. A. Baker, Jr., and N. E. Erickson, *J. Amer. Chem. Soc.*, 90, 4794 (1968); (d) W. M. Reiff, G. J. Long, and W. A. Baker, Jr., *ibid.*, 90, 6347 (1968).

the submolecule spin state is valuable in the description of the full electronic structure of an oligomer, and is retained to relate magnetic exchange properties with other physical properties, it is proposed here that such spin state be regarded as the result of two perturbations. The more energetic and more symmetrical of these is the primary ligand field, traditionally applied. The other is the "exchange field," which results from intersubmolecular interactions between the singly occupied orbitals. The exchange field is asymmetric at each submolecule. The influence of the exchange field is to pair *one electron per submolecule per exchange interaction*, whereas the ligand field necessarily pairs two electrons per submolecule.

VI. Applications to the Interpretation of Literature Data.

Justification for the analyses of models in the previous sections derives from their utility in the interpretation of data and elucidation of the electronic structures of oligomeric transition metal complexes. The necessity for explicit consideration of all inter- and intrasubmolecule interactions in cases where submolecule valence electrons are strongly delocalized is mentioned in section I, and this application is described in detail in the following paper.¹⁹

There is in the literature a large volume of \bar{J}_{ab} data which continues to defy unified and comprehensive quantitative interpretation, mainly because the energies involved are small. The fact that the *total* exchange interaction energy, E_{ex} , between submolecules of spin S_a and S_b is $|4\bar{J}_{ab}S_aS_b|$ may clarify some aspects of this problem. It is likely that, when S_a and/or $S_b > 1/2$, only one or two of the individual J_{inter} carry most of the intersubmolecule exchange interaction, with the remaining J_{inter} negligible. Therefore (1) in comparing complexes with very similar cluster structures but involving different metals, the total energy E_{ex} should be used rather than the average energy \bar{J}_{ab} [this principle is partially apparent in a series of trinuclear Schiff base complexes with Cu(II)-M(II) (M = Cu, Ni, Co, Fe, or Mn) interactions²⁸ and could be invoked in comparison of $[Cl_5Ru-$

(28) S. J. Gruber, C. M. Harris, and E. Sinn, *J. Chem. Phys.*, **49**, 2183 (1968).

$ORuCl_5]^{4-29}$ ($-\bar{J}_{ab} > 500 \text{ cm}^{-1}$, $S_a = S_b = 1$, $E_{ex} > 2000 \text{ cm}^{-1}$), $[(NH_3)_5CrOCr(NH_3)_5]^{4+30}$ ($-J_{ab} \approx 200 \text{ cm}^{-1}$, $S_a = S_b = 3/2$, $E_{ex} \approx 1800 \text{ cm}^{-1}$), and all $[L_nFe(III)-O-Fe(III)L_n]$ compounds ($-J_{ab} = 95 \pm 10 \text{ cm}^{-1}$, $S_a = S_b = 5/2$, $E_{ex} = 2100-2600 \text{ cm}^{-1}$) and (2) while many authors have commented on an apparent insensitivity of measured J_{ab} to ligand substituent variation within the same structural class of oligomers, such as $[ClFe(salen)]_2$ and derivatives,^{26,27a} it is also known that in other oligomers, such as $[(RpyO)CuCl_2]_2$ ³¹ and Cu(II) substituted Schiff base complexes,³² \bar{J}_{ab} is quite responsive to variation of ligand electronic structure. Although there are many interpretations which may be proffered in some of these cases, it should also be pointed out that many of the less sensitive systems are those with high S_a, S_b , and the more sensitive are often those with low S_a, S_b [often Cu(II), $S_a = S_b = 1/2$]. When total interaction energies are considered, the changes due to substituent variation are found to be more comparable.

Finally, it is recognized that the theoretical precepts presented in this paper will be subject to experimental investigation *via* magnetic susceptibility data only in complexes with no more than two submolecules. In higher oligomers, particularly where there is more than one spin per submolecule, it is often difficult to obtain an unambiguous, unprejudiced determination of the various \bar{J}_{ab} : \mathcal{H}_{ex} is already overparametrized, \mathcal{H}_{DHVV} would be more so.

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