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Oligomer Antiferromagnetism.
III. The Validity of Heitler–London Approximate Wavefunctions, and the Sub-Molecule Model

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The molecular orbital model and the Dirac–Heisenberg–Van Vleck (DHVV) exchange hamiltonian model for observable magnetic exchange interactions in oligometallic complexes are critically examined in terms of the validity of the implied LCAO or Heitler–London · (HL) wavefunctions for weak interactions between electrons. It is concluded that in all cases the DHVV–HL method is preferable, and that LCAO descriptions are theoretically invalid due to their incorrect account of electron correlation. The one identifiable exception to this conclusion is where fortuitous high-spin/low-spin crossover exists in the oligomer. In order to accommodate the DHVV–HL method within the full electronic structure model for the oligomer the concept of sub-molecular classification of orbitals is proposed.

Introduction

In transition metal complexes containing more than one coordination moiety the observed magnetic properties often differ from the predicted sum of the properties of the component units. These phenomena are due to a coupling of electron spins and are termed intramolecular* antiferromagnetism or ferromagnetism, depending upon whether antiparallel or parallel spin coupling is stabilized, respectively. The number of types of transition metal compounds which manifest such cooperative magnetic phenomena is increasing:[1–4] additional interest derives from the antiferromagnetism of metalloproteins[5] and other biological iron compounds.[6] This paper discusses theoretical devices by which such phenomena are accounted and interpreted, with suggestions for expansion to a valid and expedient sub-molecule model.

A necessary but insufficient indication of spin-coupling is a non-Curie temperature dependence of paramagnetic susceptibility. Molecular states with different susceptibility contributions are sufficiently low-lying ($\leq$ *ca.* 1000 cm^{-1}) above the ground state to be subject to variable thermal population throughout accessible temperature ranges. One consequence of the facts that energy observables are necessarily less than *ca.* 0.2 ev and open shell states are involved, is that the phenomenon is not amenable to *a priori* theoretical calculation at present.[7,8] Interpretational treatments are therefore essentially empirical. However, the interpretation, particularly as it relates to interpretations of other molecular properties, must be made within a valid and conceptually simple theoretical framework.

Discussion

Two theoretical schemes for observable spin states in oligometallic compounds are customarily considered,[5b,9] namely the Dirac–Heisenberg–Van Vleck (DHVV) spin hamiltonian and the molecular orbital (MO) method.

The conceptual form of the MO method is illustrated in Fig. 1. Linear combinations of monomer orbitals $\emptyset_i$ produce oligomer (dimer) molecular orbitals ψ_m,

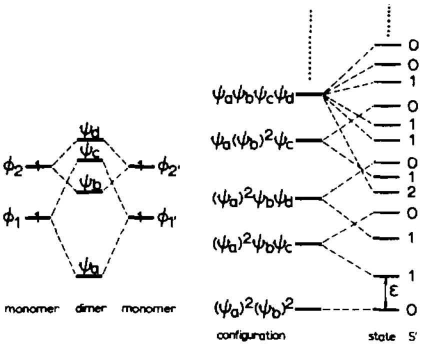

Figure 1. The derivation of molecular spin states, S′, from configurations supported by molecular orbitals ψ formed from sub-molecular orbitals $\emptyset$.

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* Cooperative magnetic interactions in non-molecular compounds are not discussed here.

which support a ground configuration and a series of excited configurations. The energies of these configurations are described in terms of one-electron orbital energies $E(\psi_m)$, and two-electron coulomb energies of types $C(\psi_m,\psi_m)$ and $C(\psi_m,\psi_n)$.* The energies of observable spin states derived from these configurations are determined by energies $K(\psi_m,\psi_n)$**(always positive), with allowance for symmetry permitted configurational interaction. The array of total spin states above the ground state and the complexity of contributions to their energies is clearly apparent.

The DHVV method is conceptually very different. For the Heitler–London (HL) product wavefunction, $\Phi = \prod_{i=1}^{n} \varnothing_i$, antisymmetrization and determination of the spin-dependent state energies is effected by the two-electron hamiltonian H'_{DHVV} (equation (1)) first introduced by Dirac and Heisenberg and expounded in chemical contexts by Van Vleck.[10] In the example of Fig. 1 the total HL wavefunction is

$$H'_{DHVV} = -1/2 \sum_{i>j}^{n} \sum^{n} J_{ij}' \, (1 + \sigma_i \cdot \sigma_j) \tag{1}$$

$\varnothing_1\varnothing_2\varnothing_{1'}\varnothing_{2'}$, with each of the four electrons able to take positive or negative spin. The σ are spin operators ($2s/\hbar$) for the singly-occupied orbitals $\varnothing$ which are simply written as the product of orbital and spin functions. For magnetic phenomena only the spin dependence of the exchange energies is important, and equation (1) can be rewritten as equation (2). Between each pair of electrons

$$H_{DHVV} = -2 \sum_{i>j}^{n} \sum^{n} J_{ij} \mathbf{s}_i \cdot \mathbf{s}_j \tag{2}$$

there is an exchange interaction which is parametrized in the Löwdin[11] manner as the energy difference between the spin-singlet and spin-triplet states (equation (3)). This energy difference may be related also to the $\varnothing_i,\varnothing_j$ orbital

$$E_{singlet} - E_{triplet} = 2J_{ij} = \frac{2K'(\varnothing_i,\varnothing_j) - 2S^2C'(\varnothing_i,\varnothing_j)}{1 - S^4} \tag{3}$$

overlap (S) and C′ and K′ integrals.[1,11–13] The oligomer spin states are considered to arise from one HL configuration.

More important than the operational difference between these two methods of representing low-lying spin states is the fundamental theoretical difference, namely their account of electron correlation for the highest energy electrons. Low electron correlation is inherent in MO's formed by LCAO, whereas in HL representations the electrons are strongly correlated due to their constraint within sub-oligomer orbitals $\varnothing_i$. In conventional, moderately strongly bonding situations MO methods no doubt provide the better first approximation to electronic structure, but HL methods become more appropriate as overlap decreases,[14] as, for example, in diatomic molecules at large internuclear distance. Therefore, if the close-lying spin states responsible for observable exchange paramagnetism are due to some weak electronic interactions, it follows that *those* interactions are better described in HL terms, being misleadingly represented by LCAO molecular orbitals.

This point is readily illustrated with the case of a dimer of two units each with one singly occupied orbital $\varnothing$. Molecular orbitals ψ_a and ψ_b may be formed (S is the $\varnothing_1/\varnothing_2$ overlap):

$$\psi_b = (2 + 2S)^{-1/2}(\varnothing_1 + \varnothing_2)$$
$$\psi_a = (2 - 2S)^{-1/2}(\varnothing_1 - \varnothing_2)$$

with one-electron energies E_b and E_a respectively. This system supports four states, three spin singlets and one spin triplet, derived from the MO configurations $(\psi_b)^2$, $(\psi_b)(\psi_a)$, $(\psi_a)^2$, or the HL configurations $\varnothing_1\varnothing_2$, $(\varnothing_1)^2$, $(\varnothing_2)^2$. These states are represented diagrammatically in Fig. 2, which emphasizes the correlation between pure MO representation and pure HL representation, in terms of variable MO energy parameters* on the left, and variable HL energy parameters on the right. The two totally symmetric singlets, ^1Z and ^1W, undergo configuration interaction which increases as $(E_a - E_b)$ decreases (*i.e.*, $S(\varnothing_1,\varnothing_2)$ decreases) and $K(\psi_a,\psi_b)$ increases, resulting in mixing of the $(\psi_b)^2$ and $(\psi_a)^2$ configurations. In the limit of complete configurational interaction the wavefunction of the lowest singlet ^1W is reverted to $(\varnothing_1)(\varnothing_2)$ HL form. Similarly the upper singlet ^1Z changes from $(\psi_a)^2$ pure MO form to $[(\varnothing_1)^2 + (\varnothing_2)^2]$ pure HL form with increasing configuration interaction, and the other two states correlate as shown in Fig. 2. The transition between LCAO and HL wavefunctions may be described continuously in terms of the "unsymmetrical molecular orbitals" of Coulson and Fischer.[14]

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* Coulomb integrals are symbolized C instead of the conventional J to avoid confusion with the empirical or Löwdin J parameter.

** The two-electron integrals referenced in this paper are defined as follows (nuclei a,b; electrons 1,2):

$$\text{Hamiltonian} = H_0 + H_1 + H_2$$
$$H_0 = -\frac{h^2}{8\pi^2 m}(\nabla_1^2 + \nabla_2^2) - Ze^2\left(\frac{1}{r_{a1}} + \frac{1}{r_{b2}}\right)$$
$$H_1 = \frac{Z^2e^2}{r_{ab}} - Ze^2\left(\frac{1}{r_{b1}} + \frac{1}{r_{a2}}\right)$$
$$H_2 = \frac{e^2}{r_{12}}$$
$$C(\psi_m,\psi_n) = \iint \psi_m^*(1)\psi_n^*(2) \,|\, H_2 \,|\, \psi_m(1)\psi_n(2) d\tau_1 d\tau_2$$
$$K(\psi_m,\psi_n) = \iint \psi_m^*(1)\psi_n^*(2) \,|\, H_2 \,|\, \psi_m(2)\psi_n(1) d\tau_1 d\tau_2$$
$$C'(\varnothing_m,\varnothing_n) = \iint \varnothing_m^*(1)\varnothing_n^*(2) \,|\, H_1 + H_2 \,|\, \varnothing_m(1)\varnothing_n(2) d\tau_1 d\tau_2$$
$$K'(\varnothing_m,\varnothing_n) = \iint \varnothing_m^*(1)\varnothing_n^*(2) \,|\, H_1 + H_2 \,|\, \varnothing_m(2)\varnothing_n(1) d\tau_1 d\tau_2$$

* See footnote ** in preceding column.

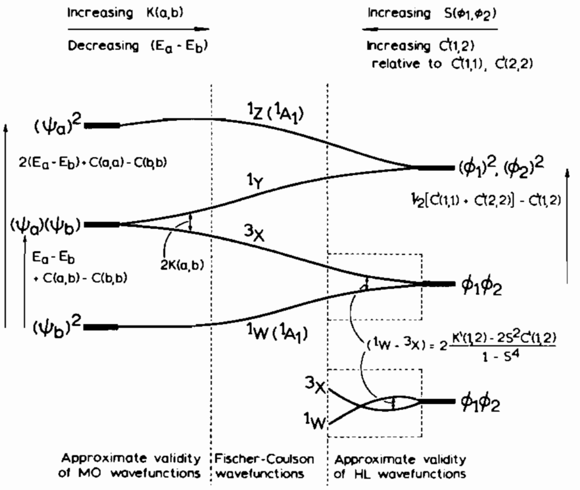

Figure 2. Correlation diagram for the molecular orbital (MO) and Heitler–London (HL) representations of the molecular spin states of a dimer with one singly-occupied orbital per monomer. The orbital descriptions and definitions of integrals are given in the text.

Observable molecular ferro- or antiferro-magnetism for such a system requires that the first excited spin state lie within *ca.* 0.1 ev of the ground state. The only conditions under which this can occur are those of the boxed sections in Fig. 2, where the wavefunctions are far better approximated by the HL product form $\varnothing_1\varnothing_2$. This conclusion is confirmed by analysis of either the HL or MO representations. In the HL approximation the proximity of the ^1W and ^3X states arises directly (equation (3)) as the difference between energies K′ and C′ which may themselves be small when $\varnothing_1$ and $\varnothing_2$ have limited spatial interaction. (Equation (3) shows that either state may be the ground state, corresponding to "ferromagnetic" or "antiferromagnetic" coupling (alternative boxed regions of Fig. 2)). If LCAO wavefunctions are premised their invalidity is readily demonstrated by examination* of the configurational composition of the lower spin singlet as a function of $[E(^3X)–E(^1W)]$. This difference cannot be less than $C(\psi_a,\psi_b)$, which is unlikely to fall below 0.1 ev except for extensively delocalized orbitals. Further, for minimum $[E(^3X)–E(^1W)]$ the ground singlet state wavefunction contains a large proportion of $(\psi_a)^2$ configuration mixed with the $(\psi_b)^2$ configuration, effectively reverting to $\varnothing_1\varnothing_2$ HL wavefunctions** and refuting the LCAO approximation.

Thus the MO model for copper(II) acetate and homologs, proposed[9c] but not prosecuted,[9d] is theoretically self-contradictory and invalid: implicit in that treatment is assignment of full weight to charge-transfer configurations Cu(I) and Cu(III) in *thermally* populated states, which is clearly inappropriate.

The previous arguments assert the greater validity of HL configurations over LCAO configurations as first approximation to the description of weak, magnetically observable interactions between singly occupied orbitals. Stronger interactions, namely chemical bonding, produce excited states which may be described with MO functions; however, being thermally inaccessable they have no influence on the magnetism and may be factored out of the exchange treatment.[15] Consequently the general treatment of magnetic exchange between sub-molecular moieties in oligomeric transition metal complexes need consider only the singly occupied orbitals at each sub-molecule which engage in zero or weak exchange with related orbitals of adjacent sub-molecules. In order to fully justify the use of the complete HL product wavefunction incorporating *all* such orbitals in the oligomer, the legitimacy of product wavefunctions for the singly-occupied orbitals *within* each sub-molecular moiety must be considered.

The sub-molecule, defined below, is in effect a transition metal coordination complex (although possibly incapable of independent existence) which will exist in one of two different spin-state conditions. (i) In the normal circumstance, when the ground (paramagnetic) spin state is widely separated from all excited states, the singly-occupied orbitals necessary to generate this ground state are othogonalized and a product wavefunction is appropriate. (ii) Alternatively, a second sub-molecule spin state may lie close to the ground spin state. The two ways in which this can occur are illustrated in Fig. 3 for the case of two sub-molecule orbitals $\varnothing_1$ and $\varnothing_2$ with one-electron energies E_1 and E_2 respectively. In the left boxed region the high (^3L) and low (^1M) spin states are closelying as a result of a very small value of $K(\varnothing_1,\varnothing_2)$, and the HL product function $\varnothing_1\varnothing_2$ approximately represents

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* In MO terms the $^1W–^3X$ energy separation is: (See also footnote ** on page 78)

$$^3X - {}^1W = C(a,b) - 1/2[C(a,a) + C(b,b)] - K(a,b) + \{[1/2(C(a,a) + C(b,b))]^2 + [K(a,b)]^2 + [(E_a–E_b) + C(a,a)][(E_a–E_b)–C(b,b)]\}^{1/2}$$

and the relative proportion of $(\psi_a)^2$ MO function mixed into the $(\psi_b)^2$ function for the ^1W ground state is

$$1 - \frac{(E_a–E_b) - C(b,b) + C(a,b) - (^3X–^1W)}{K(a,b)}$$

$(^3X - {}^1W)$ cannot be less than C(a,b) or greater than C(a,b) $+ \sqrt{[(E_a–E_b) + C(a,a)][(E_a–E_b) - C(b,b)]}$. This separation is minimized for minimized $(E_a–E_b)$, C(a,b), C(a,a) and C(b,b): the minimum occurs when $(E_a–E_b) \sim C(b,b)$, i.e., when $(^3X - {}^1W) \sim C(a,b)$, under which conditions the ground state wavefunction consists of almost equal weight of $(\psi_a)^2$ function intermixed with $(\psi_b)^2$ function.

** When $\psi_b = (2 + 2S)^{-1/2}(\varnothing_1 + \varnothing_2)$ and $\psi_a = (2 - 2S)^{-1/2}(\varnothing_1 - \varnothing_2)$, admixture of (S–1)/(S+1) of the excited $(\psi_a)^2$ configuration into the $(\psi_b)^2$ ground configuration reverts the ground state wavefunctions to $(2 + 2S^2)^{-1/2}[\varnothing_1(1)\varnothing_2(2) + \varnothing_2(1)\varnothing_1(2)]$, the pure HL singlet wavefunction.

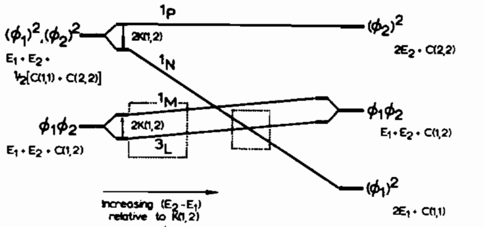

Figure 3. Correlation diagram for the energies of molecular spin states arising from two electrons and two available (orthogonal) orbitals, as a function of the relative values of the one-electron and two-electron energies. Integrals are defined in the text.

both states. This situation is not generally encountered for orthodox complexes: the one known example[16] is a dithiolene complex where extensive electron delocalization over the ligands leads to a very small value of $K(\emptyset_1,\emptyset_2)$. In the center boxed region of Fig. 3 the proximity of two different spin states is the well-studied fortuitous crossing of high and low spin states which occurs in some types of complexes.[17] Purely product wavefunctions may not be valid for the low-spin state (^1N in the example of Fig. 3) at the cross-over, and the effect of this sub-molecule state on the inter-sub-molecule exchange interactions is not simply incorporated in the HL–DHVV scheme.

The occurrence of the spin crossover should be detectable in practice through study of structural analogs with electronic differences sufficient to upset the fortuitous balance (*ca.* 200 cm^{-1}) of larger energies which cause the effect. Persistence of similar observable exchange paramagnetism through such a series of complexes would argue against a spin-crossover, and vindicate the use of HL product functions in description of the spin interactions.

The conclusion from the above arguments is that in all cases of magnetically observable spin exchange interactions, with the detectable exception of the case where high-spin/low-spin crossover occurs in a sub-molecular moiety, the implied use of Heitler–London product wavefunctions as the basis of the theoretical model is a valid simplifying assumption.* The DHVV spin hamiltonian model, which is derived from an HL description, is therefore recommended. Further general properties of this model and interpretations of the J parameters it yields are expounded in a separate paper.[15] It is first necessary to accommodate the HL basis of magnetic exchange phenomena within the *complete* electronic structure model for the oligomer.

The Sub-Molecule Concept

An electronic structure model for an oligometallic complex should incorporate the diverse observables usually available. In addition to the magnetic properties two other important types of information are (i) "oligomer bonding", namely the structural and thermodynamic aspects of the binding of the component metal coordination units, and (ii) the electron and nuclear spectroscopic properties. Oligomer bonding may vary widely in energy, from electrostatic association with a free energy decrease of only a few kcal mole^{-1} (in which case the dissociated units may have independent existence) to direct and bridged multiply-bonded linkages (then the separated units are hypothetical), even though magnetic exchange interactions with energies less than 2 kcal mole^{-1} are present in both cases. Many of the spectroscopic properties (ii) are closely similar to those of the separated components or analogous monometallic systems, and are normally interpreted in the framework of ligand field theory or MO theory for metal complexes.

Proposed here is a general theoretical prescription, which (i) supplies a conventional molecular orbital scheme for monometallic coordination segments, (ii) accommodates a wide range of oligomer bonding strengths by MO methods as appropriate, and (iii) permits the implicit use of HL product functions in the interpretation of exchange paramagnetism. The essential strategy of the concept is to separate all strong or moderately strong (> 0.5 ev) electronic interactions and their attendant molecular orbitals before describing the remaining singly-occupied orbitals, which can therefore engage only in weak interactions.

Although the sub-molecule may be loosely regarded as a coordination segment within the oligomer the value of the method is a classification of orbitals rather than a sub-division of atoms. After arbitrary assignments of coordination segments the bonding within each of them is described in conventional MO fashion, and fully-occupied, singly-occupied and empty orbitals distinguished. Then all interactions except those $<$ *ca.* 0.2 ev between these coordination segments, possibly involving bridging atoms, possibly metal–metal bonds, are described with appropriate molecular orbitals and electron populations. The bonding stabilization which results is the "oligomer bonding". At this stage the total molecular orbital scheme and electron population is independent of the initial arbitrary assignment of coordination segments.

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* Conversely, pure LCAO functions are in most cases theoretically invalid. Nevertheless, note that two closelying spin states in an *oligomer* may have parentage in two different configurations which arise from strongly bonding interactions between sub-molecules, and therefore are correctly represented in MO terms. This spin state proximity is, however, the result of a fortuitous balance of very much larger energies. The salient, fundamental observation of intramolecular antiferromagnetism in multifarious oligomeric copper complexes, together with the fact that similar exchange energies occur in hundreds of copper complexes of the dimeric copper acetate class, are *ipso facto* arguments against the accidental degeneracy of MO states. Furthermore, it is highly improbable that the *manifolds* of excited spin states necessary to account for the cooperative magnetic properties of numerous oligomeric iron, cobalt and nickel complexes are all accidental near degeneracies.

The remaining *singly-occupied* orbitals, which may of course be molecular orbitals within coordination moieties, are necessarily non-interacting or very weakly interacting and restricted to separate coordination units. It is the locality of these orbitals which defines the sub-molecule within the oligomer. The remaining filled or empty molecular orbitals of the total scheme which are associated with the same set of atoms as each localized set of singly-occupied orbitals are collected with them and termed the set of sub-molecule orbitals.

Thus the sub-molecule is defined as a collection of orbitals for a coordination unit, consisting of (A) filled molecular orbitals representing coordination bonding within the sub-molecule, (B) some filled orbitals which represent the oligomer bonding of the sub-molecule with adjacent sub-molecules, and (C) some singly-occupied orbitals, essentially non-bonding with respect to the sub-molecule, which may engage in direct or indirect weak exchange interactions with similar orbitals on other sub-molecules. Magnetically observable exchange phenomena are considered only in terms of interactions between sub-molecular orbitals of type C, which may be combined in HL form as required. Intra-sub-molecule bonding and related spectroscopic properties derive from orbitals A, and may be treated by conventional means. Spectroscopic properties unique to the oligomer are interpreted in terms of the oligomer bonding molecular orbitals. Considerations of sub-molecule coordination number and sub-molecular orbital symmetry need not be explicitly incorporated in this general treatment, which is based only on the populations of interacting orbitals.

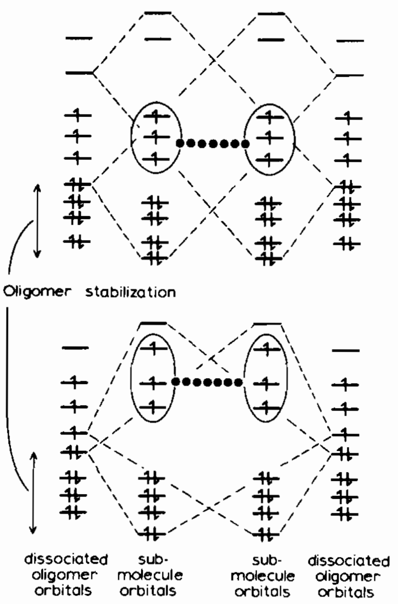

Figure 4. Representation of sub-molecule orbitals, oligomer bonding stabilization and inter-sub-molecule weak exchange interactions for a centrosymmetrical dimer. The orbitals and configurations at the left and right extremes correspond to the hypothetical dissociated dimer: molecular orbital bonding (broken lines) between these, utilizing empty (upper diagram) or singly-occupied (lower diagram) acceptor orbitals leads to the oligomer stabilization marked. In both cases there are three singly-occupied sub-molecular orbitals (encircled) between which the weak inter-sub-molecular exchange interactions (.....) occur, with Heitler–London rather than molecular orbital representation.

Possibilities for metal–metal bonding are handled with the same approach, according to the strength of interaction and population of orbitals.

This representation is demonstrated in the generalized orbital diagrams of Fig. 4 and 5. These diagrams illustrate centrosymmetric dimers, but the same principles may be used to develop similar diagrams for other cluster types. Fig. 4 applies to the case, amongst others, where the sub-molecule is chemically plausible as a monomer resulting from oligomer dissociation, such as $[Fe(salen)Cl]_n$, n = 1,2[18] and $[MS_4C_4R_4]_n^{-n}$.[19] Fig. 5 illustrates construction of sub-molecular orbitals where bridging groups X contribute to oligomer bonding, and possibly the spin exchange, as for example in the many systems with $L_nFeOFeL_n$ or $(L_nM–X–)_2$ coordination.

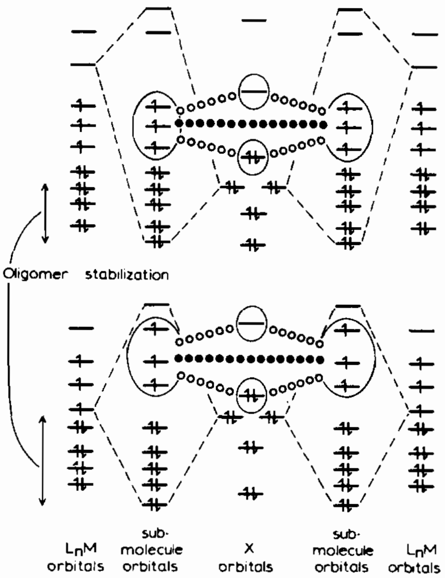

Figure 5. Representation of sub-molecular orbitals, oligomer bonding stabilization, and inter-sub-molecule weak exchange interactions for a dimetallic complex with a bridging group, $L_nM–X–ML_n$. The oligomer stabilization results from the population of bonding molecular orbitals formed from X orbitals and L_nM orbitals. The upper illustration shows the use of empty L_nM orbitals, the lower utilizes singly-occupied L_nM orbitals. In both cases there remain three singly-occupied sub-molecule orbitals available for inter-sub-molecule weak exchange interactions, which may be direct (.....) or indirect (ooooo) *via* filled or empty X orbitals as marked.

Marked on the figures are orbitals of type A, and the formation of population of molecular orbitals, B, leading to oligomer stabilization. At each sub-molecule the singly-occupied, non-bonding or weakly antibonding orbitals available for spin exchange interactions are shown, three in each of the examples. The weak, non-LCAO, interactions between these orbitals, leading to the manifold of oligomer spin states, are portrayed symbolically. In Fig. 5 are shown indirect exchange routes through filled or empty X orbitals, as well as direct exchange. No fundamental difference between these exchange mechanisms is recognized, indirect exchange (superexchange) being regarded as direct exchange using HL product functions of sub-molecule orbitals expanded into bridging group orbitals.[20,21] The symmetry, degeneracy and occupancy of X orbitals may determine the details of the exchange sign and magnitude.[1,2]

The electronic structure model proposed by Gray *et al.*[22] in rationalization of the interesting properties of $[(\mathrm{HEDTA})\mathrm{FeOFe}(\mathrm{HEDTA})]^{-2}$ and $[(\mathrm{EDTA})\mathrm{FeOFe}(\mathrm{EDTA})]^{-4}$ is in effect equivalent to the 'sub-molecule within the dimer' proposal, in that the spin exchange orbitals (all five iron 3d orbitals) are distinguished from the dimer bonding orbitals (Fe–O–Fe, with some π component). Molecular orbital representation of the thermally accessible spin-dependent states is rejected, and the electronic spectra are interpreted within the set of sub-molecule orbitals, in this case by conventional ligand field methods.* The sub-molecule model also bears some resemblance to the 'coupled chromophore' model[23] for copper(II) acetate.

The converse of the separation of exchange interactions and oligomer stabilization bonding is that magnetic arguments in support of appreciable metal–metal bonding are necessary but not sufficient.[24]

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* The observed[22] intensity enhancement for the ligand field transitions is also readily explained by exchange mixing of the sub-molecule spin states.

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