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Azido-, hydroxo-, and oxo-bridged copper(II) dimers: spin population analysis within broken-symmetry, density functional methods

Catherine Blanchet-Boiteux, Jean-Marie Mousseca

Laboratoire de Métalloprotéines, Magnétisme et Modèles Chimiques, Service de Chimie Inorganique et Biologique, UMR 5046, Département de Recherche Fondamentale sur la Matière Condensée, CEA-Grenoble, 17 rue des Martyrs, 38054 Grenoble Cedex 9, France

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Abstract. Within the general context of homometalic spin-coupled Cu(II) dimers, we propose to relate the antiferromagnetic part of the exchange coupling constant, \( J_{AF} \), to the quantity \( \Delta P^2(Cu) \). the difference of copper squared spin populations as calculated for the high-spin (i.e. triplet) and broken-symmetry spin states, through \( J_{AF} \approx -U\Delta P^2(Cu) \), where \( U \) is interpreted as the covalent–ionic term. This proportionality is illustrated for three “bare” Cu(II) dimers (i.e. without peripheral ligation, so as to enhance the antiferromagnetic contribution) bridged by azido, hydroxo, or oxo groups. This provides an alternative quantifier of the exchange phenomenon to that usually used, i.e. \( \Delta^2 \), the square of the singly occupied molecular orbital splitting in the triplet state. Moreover, and quite interestingly, the quantity \( \Delta P^2(Cu) \) can become negative (i.e. induce ferromagnetism) without apparently affecting the proportionality relation.

Key words: Exchange coupling – Antiferromagnetism – Valence-bond – Broken-symmetry – Spin populations

1 Introduction

In the search for efficient ferromagnetic couplers, the end-on azido [1–6] and the hydroxo [7, 8] units count among the best ones currently available, whereas the oxo bridge has been presented recently as such on computational grounds [9] (although still without firm theoretical justification).

Models [10–15] have been developed in the last 30 years to understand the magnetic properties of binuclear metal complexes, in general, and copper dimers, in particular. The singlet–triplet energy gap is then expressed as the sum of ferromagnetic, \( J_F \), and antiferromagnetic, \( J_{AF} \), contributions, the latter usually being dominant as the magnetic orbital overlap increases (this is presented in more detail in Sect. 2). Orthogonality, or accidental degeneracy, of the two magnetic orbitals would therefore be the common way to get ferromagnetism, for example, by varying the Cu-bridge-Cu bridging angle. The crossover of the magnetic orbitals would thus occur around 108° for the end-on azide species [16, 17], against 98° for \( \mu_2 \)-hydroxo species [7], for example.

More generally, it is therefore crucial to be able to identify and understand the main ferromagnetic mechanisms in these complexes (accidental degeneracy of the magnetic orbitals, spin polarization, etc., see later) and to be able to quantify properly both ferromagnetic and antiferromagnetic contributions (for the latter ones, this is usually done within the context of the molecular orbital (MO) formalism, see Sect. 2).

The point of this contribution is not to discuss the intricacies rationalizing the observed (or computed) ferromagnetism exhibited by these species, especially by the azido-bridged species [4, 5, 15]: this issue has been addressed elsewhere by the same authors [18, 19]. Rather, and from a computational point of view, we attempt to calculate the \( J \) coupling constants for the three title compounds, as already done by others by density functional theory [6, 9, 20–22] or ab initio techniques [23, 24], stressing how copper spin populations can be used as quantifiers of the (antiferromagnetic part of the) exchange phenomenon (via magneto-structural correlations). In that sense, our spin-population-based contribution will be presented as “computational” evidence (rather than theoretical justification) in favor of our proposal, which exhibits a new twist related to the previously-mentioned race toward better ferromagnetic couplers.

2 Exchange coupling models

At the heart of the valence bond (VB) and MO approaches is the concept of magnetic orbitals, comprising metallic and bridge orbitals mediating the exchange interaction between the two magnetic monomers having unpaired spins. They also implicitly rest on the “active electron approximation”, i.e. on the assump-
tion that the bridge orbitals lie much lower in energy than the metallic (and magnetic) d orbitals. If this condition is generally verified for electronegative halogeno or oxo/hydroxo bridges, this is not the case for the azido ion, as soon recognized [15]. Equivalently, only the two unpaired electrons (i.e., for copper dimers) are explicitly taken into account in the exchange interaction phenomenon (i.e., the role of the doubly occupied MOs is usually neglected). We briefly present and then quantitatively test three alternative molecular magnetism models, as they appeared in the literature in the 1970s and early 1980s (Sects. 2.1–2.3). We will thus consider a symmetric A-X-B dimer made of metallic ions, surrounded by bridging and terminal ligands and containing only one unpaired electron each as is the case of a Cu(II) dimer.

2.1 MO model

In this approach, the magnetic orbitals (in the absence of interaction) can be derived from the two singly occupied MOs (SOMO), \( \Psi_{1,2} \), of the low-lying triplet state. One thus constructs \( \Phi_{A,B} = (1/2^{1/2}) (\Psi_1 \pm \Psi_2) \), orthogonal MOs (OMO) which are orthogonal but not strictly localized. Hay et al. [11] derived the following approximate expressions

\[
J_{\text{MO}}^{\text{AF}} \approx -\frac{\Delta^2}{U} \\
J_{\text{F}}^{\text{MO}} = 2j',
\]

where \( U \) is the charge-transfer energy (difference between the covalent A-B and the ionic A\(^{-}\)-B\(^{+}\)/A\(^{+}\)-B\(^{-}\) configurations), both quantities \( \Delta \) and \( U/\Delta \ll U \) leading to the “kinetic” (antiferomagnetic) part of the exchange. The ferromagnetic term, \( j' \), is the two-electron exchange integral on the basis of \( \Phi_A \) and \( \Phi_B \) (the “potential” part of the exchange). In the following, in order to distinguish the \( U \) values deduced from magnetostuctural correlations based on the MO or VB approaches, we write \( J_{\text{AF}}^{\text{MO}} \approx -\Delta^2/K \) and consider \( K \) as a fitting parameter (more on this point in Sect. 3.4).

2.2 VB model

An alternative interpretation of these phenomena goes back to Heitler and London the view of the chemical bond as they expressed the exchange term using localized (VB) orbitals. Following them, Kahn and Briat [25, 26] derived the magnetic orbitals as the highest occupied MOs (HOMO) for the localized A-X and X-B nonorthogonal fragments \( \Phi_A \) and \( \Phi_B \) (\( S_{AB} = \langle \Phi_A | \Phi_B \rangle \)), therefore called natural MOs (NMO). They obtained the following expressions:

\[
J_{\text{AF}}^{\text{NMO}} = -2 \frac{\Delta S_{AB}}{1 + S_{AB}^2} \\
J_{\text{F}}^{\text{NMO}} = 2(j - kS_{AB}^2)
\]

\( \Delta \) is, again, the energy gap between the two molecular orbitals in A – X – B, now built from the interacting \( \Phi_A \) and \( \Phi_B \) in the triplet state. The ferromagnetic \( j \) contribution is described as the self-repulsion of the overlap density \( \rho_{AB} = \Phi_A \Phi_B \) and \( k \) is a Coulombic integral related to \( \rho_{AA} = \Phi_A^2 \). For \( S_{AB}^2 \ll 1 \), one utilizes the following approximate expressions: \( J_{\text{F}}^\text{NMO} \approx 2j \) and \( J_{\text{AF}}^\text{NMO} \approx -2\Delta S_{AB} \).

2.3 VB–broken-symmetry model

Finally, a ( spatially) broken-symmetry (BS) state, \( \Psi_{\text{BS}}(r_1, r_2) \) can be constructed [27, 28] as an “outer product” of monomer spin functions (i.e., of the two NMOs) as \( \Phi_A(r_1)\Phi_B(r_2) \). \( \Psi_{\text{BS}} \) is thus not an eigenstate of spin but a (artificial) state of mixed spin, which turns out to be computationally very useful. In effect, and from its use, Noodleman [29] derived the following expression for \( J_{\text{AF}}(S_{AB}^2 \ll 1) \)

\[
J_{\text{AF}}^\text{VB–BS} \approx -U S_{AB}^2 \\
J_{\text{F}}^\text{VB–BS} = 2j',
\]

which was verified quantitatively [30, 31] and where \( U \) is, again, the charge-transfer energy.

2.4 Definition of the quantity \( \Delta P^2(Cu) \)

Both (MO and VB) approaches [13] stand as two rigorously alternative and equivalent ways of describing the exchange interactions if one properly takes into account covalent–ionic mixing, whereas Noodleman’s approach allows the unification of both nonorthogonal VB and (limited) configuration interaction viewpoints [29] in the weak overlap regime, though. Notice also that, as \( \Delta \) is usually proportional to \( S_{AB} \), \( J_{\text{AF}} \sim \Delta \sim S_{AB} \).

Both NMOs and OMOs can be related in the following general manner:

\[
\Phi_A = \lambda \Phi_A' + \mu \Phi_B' \\
\Phi_B = \mu \Phi_A' + \lambda \Phi_B',
\]

with \( S_{AB} = 2\lambda \mu \) and \( \lambda^2 + \mu^2 = 1 \). To second order in \( S_{AB} \), \( \lambda \approx 1 - S_{AB}^2/8 \) and \( \mu \approx S_{AB}/2 \). As the VB–BS method makes use of these NMOs, [29] one easily derives:

\[
P_{\text{HS}}(\Phi_A') = \lambda^2 + \mu^2 \Rightarrow \lambda^2 = \frac{P_{\text{HS}}(\Phi_A')}{2} \\
P_{\text{BS}}(\Phi_A') = \lambda^2 - \mu^2 \Rightarrow \mu^2 = \frac{P_{\text{HS}}(\Phi_A') - P_{\text{BS}}(\Phi_A')}{2},
\]

i.e.,

\[
S_{AB}^2 = 4\lambda^2 \mu^2 = P_{\text{HS}}(\Phi_A')^2 - P_{\text{BS}}(\Phi_A')^2.
\]

Equation (6) is actually equivalent to Malrieu’s Eq. (14) with \( P_{\text{HS}} = 1 \) where the OMOs are taken to be the copper \( d_{2s} \) atomic orbitals [32].

In practice, one does not calculate the Mulliken spin population of delocalized MOs, but atomic spin populations (here copper ones). As such, this restriction implies that \( \Delta P^2 \) becomes strictly equal to \( S_{AB}^2 \) only for a negligible weight of the bridging and ligand orbitals.