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End-On Azido-Bridged Copper Dimers: Spin Population Analysis and Spin Polarization Effect as Exhibited by Valence-Bond/Broken Symmetry, Density Functional Methods

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Abstract: Within the general context of homometallic spin-coupled copper(II) dimers, we define the quantity ΔP^2(Cu), the difference of copper squared spin populations as calculated for the high-spin (i.e., triplet) and broken symmetry spin states. In the specific case of an azido-bridged copper(II) dimer, the antiferromagnetic part of the exchange coupling constant is then shown, using density functional (DF), valence bond−broken symmetry (VB−BS) techniques, to be proportional to this quantity. This provides a quantifier of the exchange phenomenon alternative to that usually used, that is, Δ^2, squared of the singly occupied molecular orbital splitting in the triplet state. Moreover, spin polarization, through the spin population being delocalized from one copper ion onto the other one, offers the possibility of changing the sign of ΔP^2(Cu), thus resulting in a *ferromagnetic* contribution, for weak magnetic orbital overlap, here found at the VB ground-state level. Phenomenologically, this last effect can be formulated in terms of McConnell's mechanism I for ferromagnetic interaction in solid free radicals (McConnell, H. M. *J. Chem. Phys.* **1963**, *39*, 1910). We finally show that the standard copper basis sets commonly used for inorganic chemistry computations may be deficient. This leads to exaggerated spin delocalization and to bad agreement between DF computed (Mulliken) spin populations and those recently measured by polarized neutron experiments (Aebersold, M. A. et al.: *J. Am. Chem. Soc.* **1998**, *120,* 5238).

1. Introduction

Quite a few μ-azido (N_3^-) copper(II) complexes have been known for about three decades now. As it turns out, the azide ion can bridge two copper(II) ions either in an "end-on" (μ_2-1,1-N_3) fashion[1−3] (cf. Figure 1a), in which case ferromagnetism is favored, or in an "end-to-end" (i.e., μ_2-1,3-N_3) fashion,[4,5] allowing for a strong antiferromagnetic coupling between the two metal ions (cf Figure 1b). Other azido copper complexes are known beside the first two cited, characterized either by an asymmetric end-to-end bridging mode[1,6,7] or by the coexistence, between the same two copper ions, of one azido bridge with another bridging unit,[8−10] such as hydroxide ions for example. There exist moreover mixed (N_3 and other bridging unit) chains.[11−13] In this case, both ferromagnetism and antiferromagnetism may be observed. One can finally find end-on chains[14,15] and alternating "end-end"/"end-on" chains.[3,16,17] As can be seen, the azide ion thus exhibits a remarkable variety of bonding motifs in its different bridging modes and constitutes therefore a very interesting magnetic coupler.

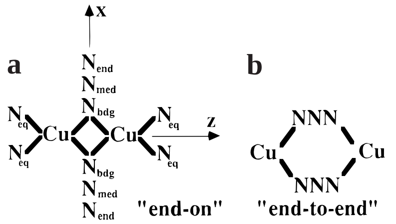

Figure 1. Schematic representation of the end-on (a) and end-end (b) bridging modes of azido anions. In (a) is also given the axis system used throughout: *z* along the copper−copper direction, and *x* defining the magnetic plane.

The most striking fact concerning the azide ion is that it leads to ferromagnetism or antiferromagnetism depending on its mode

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of bridging: end-on or end-to-end, respectively. Models[18−22] have been developed in the last thirty years to understand the magnetic properties of binuclear metal complexes in general and copper dimers in particular. Among these, two simple approaches emerge because of their conceptual simplicity. The first one relies on the use of localized (mutually nonorthogonal) fragments (the natural magnetic orbitals, or NMOs) built from metal and bridge orbitals,[23,24] and the second one builds orthogonal (but not strictly localized) magnetic orbitals (the OMOs) from the two singly occupied molecular orbitals.[18] In both cases, the singlet−triplet energy gap is expressed as the sum of a ferromagnetic contribution (proportional to the self-repulsion of the overlap density between the magnetic orbital) and of an antiferromagnetic contribution, usually dominant as the magnetic orbital overlap (or, alternatively, as the energetic gap between the two singly occupied magnetic orbitals, SOMOs), increases. Orthogonality, or accidental degeneracy, of the two magnetic orbitals would be therefore the common way to get ferromagnetism, for example, by varying the Cu−N−Cu bridging angle (a task more easily achieved computationally than by way of synthesis, however). The crossover of the magnetic orbitals would occur around 108° for the end-on azide species,[25,26] against 98° for μ_2-hydroxo species,[27] for example.

As these theories are applied to the case of the azido-bridged complexes, either end-to-end or end-on, strong antiferromagnetic interaction is expected to occur,[22] in agreement with experiment as far as the end-to-end case is concerned, but at odds with the ferromagnetic interaction observed for end-on complexes. This analysis is however performed within the so-called "active electron approximation", involving spin delocalization mechanisms; that is, the HOMO of the bridges is implicitly assumed to be much lower in energy than the d metal orbitals,[22] a condition that might be fulfilled for very electronegative bridges such as halogeno or hydroxo, but not for azido anions.

One could think that quantum chemistry would help, through the use of ab initio (density functional) codes. From this computational point of view, we calculated exchange coupling constants in the case of (isolated) end-on bridged dimers, with or without counteranions, using at first standard (nonhybrid) exchange-correlation potentials, and found systematically the singlet state to be the most stable (the methodology we used will be discussed in section 2). Others,[28,29] however, obtained the expected ferromagnetism, but using the B3-LYP (hybrid) method within the broken symmetry approach (see section 2.2). We emphasize in this study the use of spin populations as an "empirical" tool for quantifying the exchange interaction and the appearance of a related possible spin polarization effect.

In effect, and to remedy this clear contradiction between naive theoretical prediction and experiment, spin polarization has been invoked,[22,30] an effect based on the (so far) neglected role of doubly occupied molecular orbitals. This mechanism has been recently corroborated by Tuczek et al. by means of an optical spectroscopic investigation of μ-1,1-azido copper(II) dimers.[31] It turns out that Kahn's phenomenological spin polarization model is there found to be a spin Hamiltonian description of the charge-transfer−ligand excitation interaction via π* orbitals. This last valence bond−configuration interaction (VB−CI) mechanism involves excitations from the bridge orbitals (i.e., it goes beyond the "active electron" approximation[32]), whereas our results are obtained at the valence bond−ground-state (VB−GS or Heitler−London) level[23] by taking into account metal (d) and bridge (p) orbitals.

This paper is organized in the following way. After a brief introduction on how we came to the definition of the quantity ΔP^2(Cu) (section 3), we present an analytical expression of ΔP^2(Cu) for two bridged (end-on azido and linear oxo) Cu(II) dimers reflecting two topological situations (section 4). We then perform a detailed spin population and exchange coupling analysis of end-on azido-bridged copper dimers (section 5), before commenting on spin polarization mechanisms (section 6) and concluding (section 7).

2. Computational Details

2.1. Model Complexes. We performed our calculations in C_{2v} symmetry, with the following axis system: the *z* axis is set along the metal−metal direction, the *x* axis along the azido−azido direction, and the *y* axis perpendicular to the $Cu_2(N_3)_2$ plane (see Figure 1a). In all cases, the equatorial nitrogens (N_{eq}) of the peripheral ligands (pyridine or ammonia) are located in the *xz* plane.

Our model complex is the $[Cu_2(N_3)_2L_4]^{2+}$ cation (L = NH_3 or pyridine) with a square planar local environment for the copper ions, corresponding to the experimental geometry[2]: $d(\mathrm{Cu{-}Cu}) = 3.042$ Å, $\Theta = \mathrm{Cu{-}N_{bdg}{-}Cu} = 100.5°$, $d(\mathrm{Cu{-}N_{bdg}}) = 1.977$ Å and $d(\mathrm{Cu{-}N_{eq}}) = 2.019$ Å. We finally removed/added the counterions $(ClO_4^-)_2$ to the experimental compound geometry in order to check its effect on the magnetism of the copper dimer.

2.2. Quantum Chemistry Codes. Most of the calculations make use of the Amsterdam LCAO density-functional programs (ADF 2.3) developed by Baerends and co-workers.[33−38] We considered there only the potential referred to as "VBP" (Vosko, Wilk, and Nusair's exchange and correlation energy[39,40] completed by nonlocal gradient corrections to the exchange by Becke[41] as well as to the correlation by Perdew[42]). We used triple-ζ (plus polarization) basis sets for all atoms.

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We used also the Gaussian-94 package,[43] first to reproduce Alvarez et al.'s results[28] (as we knew them by the time we completed our investigations) on the planar copper dimer and then to compare them with ours. They succeeded[28,29] in effect in reproducing the ferromagnetism of the dimer by using the hybrid B3-LYP method,[44] which mixes exact Hartree–Fock exchange with Becke's[41] and uses besides the Lee–Yang–Parr correlation functional.[45]

3. Exchange Coupling within Cu Dimers

3.1. Definition of the Quantity ΔP^2(Cu). The exchange phenomenon is essentially related to the degree of overlap between the magnetic orbitals. There is a pretty way to visualize the spatial extension of the atomic basis functions. It consists of applying to our problem Bertrand's analysis[46] of the spin populations. This analysis requires as a preliminary the convergence of two spin states, "HS" (high-spin state of maximum spin) and "BS" (broken symmetry state, with Ms = 0), whose full use for magnetic coupling computation purposes had been initiated by Noodleman.[47−49]

For homonuclear copper(II) dimers, one can write the following relations between the dimer HS (triplet) or BS copper spin populations (i.e., $P_{HS/BS}$(Cu)) and those relative to the monomers "A" or "B" (i.e., $P_{A/B}$(Cu)),[46] say for Cu_A of monomer A:

$$\left\{\begin{aligned} P_A(\mathrm{Cu_A}) &= (P_{HS}(\mathrm{Cu_A}) + P_{BS}(\mathrm{Cu_A}))/2 \\ P_B(\mathrm{Cu_A}) &= (P_{HS}(\mathrm{Cu_A}) - P_{BS}(\mathrm{Cu_A}))/2 \end{aligned}\right\} \qquad (1)$$

($\Sigma_{q\in A} P_A(q) = 1$, i.e., the scattered spin population among the atoms "q" of monomer A—metal, bridge, and peripheral ligands—is normalized to unity). Following then Malrieu et al.,[50] if the semilocalized magnetic orbitals are expressed as

$$\left\{\begin{aligned} \Phi_A &= \lambda d_A + \mu d_B \\ \Phi_B &= \mu d_A + \lambda d_B \end{aligned}\right\} \qquad (2)$$

($d_{A/B}$ are copper d orbitals) one can see easily that

$$\left\{\begin{aligned} P_{HS}(\mathrm{Cu_A}) &= \lambda^2 + \mu^2 \\ P_{BS}(\mathrm{Cu_A}) &= \lambda^2 - \mu^2 \end{aligned}\right\} \Rightarrow \left\{\begin{aligned} \lambda^2 &= P_A(\mathrm{Cu_A}) \\ \mu^2 &= P_A(\mathrm{Cu_B}) \end{aligned}\right\} \qquad (3)$$

$P_A(\mathrm{Cu_A})$ (respectively $P_B(\mathrm{Cu_B})$) thus stands for the local spin population on monomer A (respectively B) whereas $P_A(\mathrm{Cu_B})$ (respectively $P_B(\mathrm{Cu_A})$) stands for the spin population delocalized from A to B (respectively from B to A). Therefore, for the overlap S_{AB} between the two monomers A and B

$$S_{AB}^2 = 4\lambda^2\mu^2 = 4P_A(\mathrm{Cu_A})P_A(\mathrm{Cu_B}) = P_{HS}^2(\mathrm{Cu_A}) - P_{BS}^2(\mathrm{Cu_A}) \qquad (4)$$

We defined the quantity (used extensively in the following sections)

$$\Delta P^2(\mathrm{Cu_A}) \equiv P_{HS}^2(\mathrm{Cu_A}) - P_{BS}^2(\mathrm{Cu_A}) \qquad (5)$$

which turns out to be equal to S_{AB}^2 in this simple example (i.e., neglecting metal−bridge overlap). Equation 5 being valid for both Cu_A and Cu_B (by symmetry), we will speak of ΔP^2(Cu) from now on.

Equation 5 generalizes somewhat Malrieu et al.'s eq 14, where they set (in our notations) $P_{HS}(\mathrm{Cu}) = 1$ (in the valence bond limit): $\lambda^2 + \mu^2$ equals 1 in the absence of ligand contribution in the above Φ_A and Φ_B (cf. eq 2). Stated otherwise, and for weak overlap ($S_{AB} \approx 0$), $\mu \approx 0$, $P_{HS/BS}(\mathrm{Cu}) \approx 1$, and $\Delta P^2(\mathrm{Cu}) \approx 0$, whereas for strong overlap ($S_{AB} \approx 1$), $\lambda^2 = \mu^2 = {}^1/_2$, $P_{HS}(\mathrm{Cu}) \approx 1$, $P_{BS}(\mathrm{Cu}) \approx 0$, and $\Delta P^2(\mathrm{Cu}) \approx 1$.

3.2. Our Proposal. Within the valence bond−broken symmetry (VB−BS) approximation, the antiferromagnetic coupling is proportional to the squared magnetic orbital overlap:[47,51,52]

$$J_{AF}^{BS} \approx -US_{AB}^2 \qquad (6)$$

where U is the charge-transfer energy, the difference between the covalent A−B and the ionic $A^-{-}B^+/A^+{-}B^-$ configurations (with $H = -JS_A{\cdot}S_B$). Let us recall here that, originally,[47] eq 6 was derived as a metal−metal super-exchange term, that is, without explicitly taking into account the bridging orbitals (a task done later on[48]). Such a dependency of J_{AF} on the squared overlap of the magnetic orbitals has then been demonstrated computationally[51,52] for two different systems, [H−He−H] and $[\mathrm{H{-}F{-}H}]^-$ by varying the H-bdg distance (bdg = He, F^-). There, the fourth power of the $\langle \mathrm{H}|\mathrm{bdg}\rangle$ overlap was used, but $S_{AB} \approx \langle \mathrm{H}|\mathrm{bdg}\rangle^2$.

Computationally, the total exchange coupling constant J_S (= $J_F + J_{AF}$) can be determined from the difference of the high-spin and broken symmetry spin-state energies E_{HS} and E_{BS} according to[49]

$$J_S = \frac{2(E_{BS} - E_{HS})}{1 + S_{AB}^2} \equiv \frac{J_{DFT}}{1 + S_{AB}^2} \qquad (7)$$

where J_{DFT} is defined as $J_S(S_{AB}{=}0)$. Therefore, when $J_F \ll |J_{AF}|$, one can expect a good correlation between J_{DFT} and ΔP^2(Cu) for weak overlap S_{AB}:

$$J_{DFT} \approx J_{AF}^{BS} \approx -U\Delta P^2(\mathrm{Cu}) \qquad (8)$$

From its definition in section 3.1, ΔP^2(Cu) is always positive and J_{AF} negative. Moreover, the fact that the quantity ΔP^2(Cu) is not zero originates from the transferred spin population from one copper atom to the other one (factor $\mu \neq 0$ in eqs 2 and 3). Therefore, it has been argued,[46] based on previous work on the broken symmetry method,[47,48,52] that the different spin populations calculated for the metallic atoms in the HS and BS states are presumably due to the superexchange contribution (but see section 6, where this point is more fully discussed).

3.3. Link with McConnell's Mechanism. It is instructive to realize that our proposal presents a close formal analogy to McConnell's approach of *intermolecular* ferromagnetism in solid free radicals:[53−56]

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$$H_J = -\sum_{\substack{i\in A\\ j\in B}} J_{ij}^{AB}\, S_A^i \cdot S_B^j \approx -S_A\cdot S_B \sum_{\substack{i\in A\\ j\in B}} J_{ij}^{AB}\, \rho_A^i\, \rho_B^j \qquad (9)$$

in a kind of local spin description[57,58] (i.e., $S_A = \Sigma_i S_A^i = \Sigma_i \rho_A^i S_A$) of the exchange interaction where the A and B regions (i.e., monomers), spatially separated, bear spin populations $\{\rho_A^i\}$ and $\{\rho_B^j\}$ on atoms $i \in$ A and $j \in$ B, respectively. This model predicts the presence of ferromagnetic interactions when atoms i and j, at short contact, bear spin population ρ_A^i and ρ_B^j of opposite sign. Implicit in writing H_J as McConnell did, is the assumption that the *intra*monomer terms are identical for each state (triplet and singlet) on which the Hamiltonian acts.[56]

Adapting phenomenologically this proposal to the case of *intramolecular* exchange coupling, and considering the HS and BS spin states of copper(II) dimers, we have the following: $\langle S_A\cdot S_B\rangle = +S_AS_B$ for HS and $\langle S_A\cdot S_B\rangle = -S_AS_B$ for BS. Moreover, calling $P_A(\mathrm{Cu_A}) = P_B(\mathrm{Cu_B}) = P_L$ ("L" for local) and $P_A(\mathrm{Cu_B}) = P_B(\mathrm{Cu_A}) = P_T$ ("T" for transmitted), the spin populations on sites A and B are given by $(P_L + P_T)$ in HS and $\pm(P_L - P_T)$ in BS. We thus obtain from eq 9 the following energies for HS and BS:

$$\begin{Bmatrix} E_{HS} = -S_AS_B\cdot J_{dd}^{AB}[+(P_L + P_T)^2] = -S_AS_B\cdot J_{dd}^{AB}(+P_L^2 + 2P_LP_T + P_T^2) \\ E_{BS} = -S_AS_B\cdot J_{dd}^{AB}[-(P_L - P_T)^2] = +S_AS_B\cdot J_{dd}^{AB}(-P_L^2 + 2P_LP_T - P_T^2) \end{Bmatrix} \qquad (10)$$

and the following exchange coupling constant

$$J_{DFT} \approx \frac{E_{BS} - E_{HS}}{2S_AS_B} = 8J_{dd}^{AB}P_LP_T = 2J_{dd}^{AB}\Delta P^2(\mathrm{Cu}) \qquad (11)$$

where[56] J_{dd}^{AB} are two-center exchange integrals (assumed negative in McConnell's approximation). We thus recover formally eq 8, although it does not mean that $-2J_{dd}^{AB} = U$. This last formal identity only occurs as one expresses the results of one theory of molecular magnetism into another one, let us say, from Kahn's VB[23] into Hoffmann's MO[18] theories, as done for example in ref 24.[59]

It will be shown analytically in section 4, and computationally in section 5, that, for certain bridge orbital topologies (including the azido one), ΔP^2(Cu) (or, alternatively, the transmitted spin population of eqs 10 and 11) can become negative, in contrast to the simple treatment presented in section 3.1 (there as a result of not taking into account the bridge orbitals).

4. Analytical Expressions for ΔP^2(Cu)

The exchange interaction stands as the extreme case of a very weak bond. To study it, it seems therefore more appropriate to use Heitler−London (HL) wave functions than MO wave functions.[23,24,60] The exchange interaction can be then interpreted by considering only the VB *ground-state configuration* (VB−GS) without at first taking into account interactions between ground− and metal−metal charge-transfer configurations.

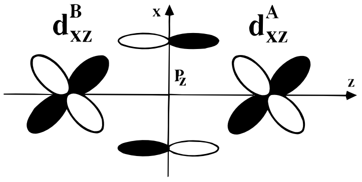

Figure 2. d and p atomic orbitals for the metal and bridge, respectively, for the end-on azido bridged Cu(II) dimer.

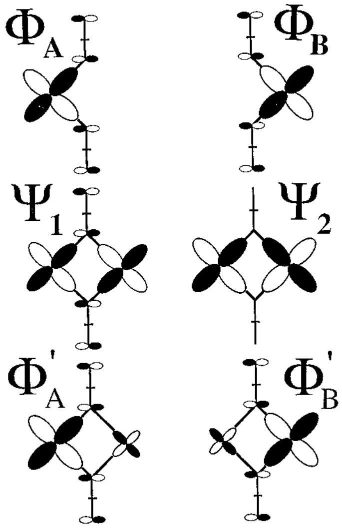

Figure 3. Schematic representation for an end-on azido-bridged copper dimer: (top) the two localized NMOs Φ_A and Φ_B; (middle) the two SOMOs Ψ_1 and Ψ_2 in the triplet state; (bottom) the two partially delocalized OMOs Φ_A' and Φ_B'.

Therefore, we will consider in what follows two identical Cu(II) ions (spin doublet, $S_A = S_B = 1/2$; orbital singlet, L = 0) located at sites A and B, following Kahn and Briat.[23,24,61] We will call Φ_A and Φ_B the two (not necessarily orthogonal) NMOs for A and B, delocalized toward the surrounding ligands (bridging and peripheral), and solution, each, of the VB spin Hamiltonian for the fragments A−X and X−B, respectively (X = azido bridge).

Two topologies are considered, corresponding to end-on azido and linear oxo bridges, respectively. But our discussion applies as well to any type of bridge, as long as it involves only one (s or p) orbital, as its topology ranges it into one of the two classes treated below in sections 4.1 and 4.2.

4.1. First Topological Situation (Azido Bridge). In the case of the azido-bridged complex, we have (see Figure 2 for a representation of the individual orbitals involved, and Figure 3 (top) for that of $\Phi_{A,B}$)

$$\begin{Bmatrix} \Phi_A = a\mathrm{p} + b\mathrm{d}_A \\ \Phi_B = a\mathrm{p} + b\mathrm{d}_B \end{Bmatrix} \qquad (12)$$

with a and $b > 0$ due to the symmetry of the p orbital, here a normalized antisymmetric linear combination of the bridging $\mathrm{N_{bdg}}$ and ending $\mathrm{N_{end}}$ nitrogen $\mathrm{p_z}$ orbitals. Of course, the interaction of the azide ion with Cu(II) involves not only the HOMO of the azide anion but also lower-lying ligand orbitals. But, as far as the magnetic properties of the azido-bridged copper dimer are concerned, we will restrict ourselves to these two magnetic orbitals as defined in eq 12.

Calling $s = \langle \mathrm{d_A}|\mathrm{p}\rangle = \langle \mathrm{d_B}|\mathrm{p}\rangle < 0$ (and $|s| < 0.1$), we have

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(56) Deumal, M.; Novoa, J. J.; Bearpark, M. J.; Celani, P.; Olivucci, M.; Robb, M. A. *J. Phys. Chem. A* **1998**, *102*, 8404.

(57) Bertrand, P.; More, C.; Guigliarelli, B.; Fournel, A.; Bennett, B.; Howes, B. *J. Am. Chem. Soc.* **1994**, *116*, 3078−3086.

(58) Bertrand, P.; Camensuli, P.; More, C.; Guigliarelli, B. *J. Am. Chem. Soc.* **1996**, *118*, 1426−1434.

(59) Kahn's antiferromagnetic term ($-2\Delta S_{AB}$, where Δ is the singly occupied molecular orbital gap in the triplet state) is there transformed into a Hoffmann's like term (the "true" one varying as $-\Delta^2/U$) through recourse to NMO one-electron energies and to the Wolfsberg−Helmholz approximation).

(60) Dance, I. G. *Inorg. Chim. Acta* **1974**, *9*, 77.

(61) Kahn, O.; Briat, B.; Galy, J. *J. Chem. Soc., Dalton Trans.* **1977**, 1453−1457.

$$\left\{\begin{matrix}\langle\Phi_A|\Phi_A\rangle = 1 = a^2 + b^2 + 2abs \\ S_{AB} = a^2 + 2abs = 1 - b^2\end{matrix}\right\} \qquad (13)$$

Notice that S_{AB} is usually positive (because of the sign convention adopted in writing Φ_A and Φ_B). But $S_{AB} = 0$ (or $b^2 = 1$) actually admits two positive roots for the parameter a: 0 and $2|s|$; that is, $S_{AB} < 0$ within the range $[0,2|s|]$. Notice finally that, to take into account peripheral ligands in this explicit derivation, one would just have to redefine d_A and d_B as Cu−ligand (d_{Cu-L}) orbitals.

One can now construct two MOs from the localized fragment orbitals Φ_A and Φ_B, thus recovering the symmetric and antisymmetric SOMOs $\Psi_{1,2} = (2(1 \pm S_{AB}))^{-1/2}(\Phi_A \pm \Phi_B)$ of the HS (triplet) state (see Figure 3 middle). These molecular orbitals are then recombined in order to obtain monomer orbitals $\Phi'_{A,B} = (2^{-1/2})(\Psi_+ \pm \Psi_-)$, mutually orthogonal but partly delocalized onto the other metal (Figure 3 bottom). Mulliken atomic spin populations are then calculated for the HS and BS spin states. The mathematical details are given in Appendix. Finally,

$$\Delta P^2(\mathrm{Cu}) = \frac{S_{AB}a^2(1 - 2s^2)}{(1 + S_{AB})^2} = \frac{S_{AB}(S_{AB} - 2abs)(1 - 2s^2)}{(1 + S_{AB})^2} \qquad (14)$$

Notice that, in the first line of eq 14, ΔP^2(Cu) is of the sign of S_{AB} and can thus become negative (i.e., J_{AF} in eq 8 can turn ferromagnetic!). In the second line of eq 14, the leading contribution to ΔP^2(Cu) is proportional to S_{AB}^2, corrected by a term which cancels for $s = 0$.

4.2. Second Topological Situation (Linear Oxo Bridge). By way of contrast, we illustrate our method by considering alternatively such a topology[19] as encountered in linear M−O-M dimers for example (see Figure 4 for a representation of the individual orbitals involved and Figure 5 for schemes of the NMOs (top), SOMOs (middle), and OMOs (bottom)):

$$\left\{\begin{matrix}\Phi_A = -ap + bd_A \\ \Phi_B = +ap + bd_B\end{matrix}\right\} \qquad (15)$$

(a and $b > 0$) with

$$\left\{\begin{matrix}\langle\Phi_A|\Phi_A\rangle = 1 = a^2 + b^2 + 2abs \\ S_{AB} = -a^2 - 2abs = b^2 - 1 < 0\end{matrix}\right\} \qquad (16)$$

and $s = -\langle d_A|p\rangle = \langle d_B|p\rangle > 0$. Notice that, here, S_{AB} turns out to be *negative* because of our chosen description of the magnetic orbitals (the sign differences between Φ_A and Φ_B are confined to the bridging p orbital). Along the same line as that presented in section 4.1, it could be easily shown that

$$\Delta P^2(\mathrm{Cu}) = \frac{-S_{AB}a^2(1 - 2s^2)}{(1 - S_{AB})^2} = \frac{S_{AB}(S_{AB} + 2abs)(1 - 2s^2)}{(1 - S_{AB})^2} > 0 \qquad (17)$$

As S_{AB} is strictly negative here, ΔP^2(Cu) will be always positive, and J_{AF} negative (as it should).

4.3. Illustration from the Literature. We can briefly compare our results with those obtained by Hart et al.,[51,52] analyzed within the MO formalism. In their paper, two three center-, four-electron systems are considered: $H-X_s-H$ (s−s−s) and $H-X_p-H$ (s−p−s), where X_s = He and $X_p = F^-$. Had we apply the developments of section 4.1, we would obtain for $H-X_s-H$ (for small overlap S_{AB}): $J_{AF} \sim -4a^2S_{AB}$. S_{AB}, formally equal to that expression given in eq 13, can change its sign (and so does J_{AF}). This behavior is clearly illustrated by Figure 7 of Hart et al.'s paper,[51] where a transition from antiferromagnetism to ferromagnetism is observed for large H−H distances (i.e., for small mixing a coefficients, called "λ_s" in ref 51: compare their Figure 6). For $H-X_p-H$ however, all quantities can be expressed as done in section 4.2; i.e., $S_{AB} < 0$ cannot change its sign, and J_{AF} remains truely antiferromagnetic (compare their Figure 8) for all mixing coefficients (shown in their Figure 9). The authors concluded that "the ordering of the symmetric and antisymmetric orbital energies is reversed for the two cases" and that "while H−Xp−H contains interactions of the same type, H−Xs−H contains two competing interactions".

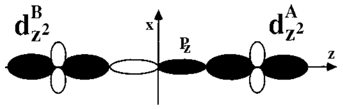

Figure 4. d and p atomic orbitals for the metal and bridge, respectively, for the linear oxo-bridged Cu(II) dimer.

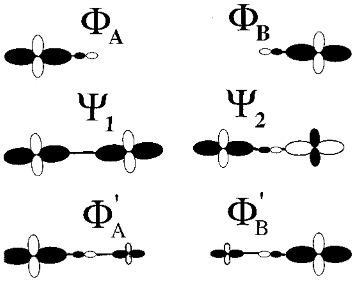

Figure 5. Schematic representation for a linear oxo-bridged copper dimer: (top) the two localized NMOs Φ_A and Φ_B; (middle) the two SOMOs Ψ_1 and Ψ_2 in the triplet state; (bottom) the two partially delocalized OMOs Φ_A' and Φ_B'.

5. Calculations on $[Cu_2(N_3)_2L_4]^{2+}$

5.1. Preliminary Remarks. We start our discussion by presenting our results for copper dimers, with two ligands (L = NH_3 or Pyr), with or without counteranions $(ClO_4^-)_2$, and with two copper basis sets (see below). The shapes and energies of the occupied MOs for a single azide anion have already been presented and discussed elsewhere.[22] Let us here simply restate that the Π_g HOMOs of N_3^- (mixture of both bridging−N_{bdg}− and terminal−N_{end}−nitrogen's p_z orbitals: see Figure 6a) are located high in energy, well separated from the next occupied MO, an equal mixture of both N_{end} s−p_x orbitals, lower by ∼6.7 eV according to Charlot et al.).[22]

We present in Table 1 the computed Mulliken spin populations for a series of copper dimers, ordering them according to the increasing copper spin population for the sake of clarity. We started our investigations by calculating the spin density map for the experimental complex with pyridine ligands and then replaced these peripheral ligands by ammoniac molecules, only to verify that this replacement yields sufficiently close results (spin populations, exchange coupling constants) to be extended to the rest of our calculations (see the first two columns of Table 1). In both cases, J_{DFT} is found to be antiferromagnetic and of the same order of magnitude (∼−1400 and ∼−1000 cm^{-1}, respectively). The change of peripheral ligand is still a significant one, as stated by others,[62,63] and both results will be exploited below.

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(62) Román, P.; Guzmán-Miralles, C.; Luque, A.; Beitia, J. I.; Cano, J.; Lloret, F.; Julve, M.; Alvarez, S. *Inorg. Chem.* **1996**, *35*, 3741−3751.

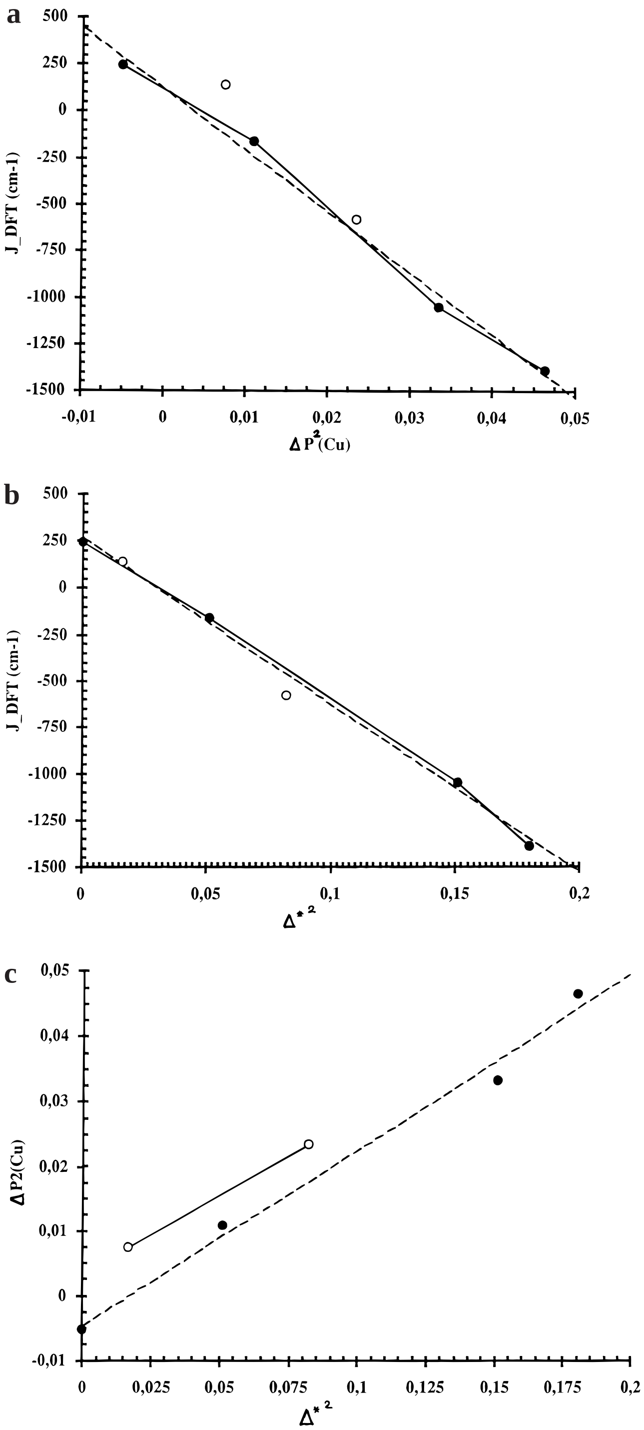

Figure 6. (a) Linear plot of J_{DFT} as a function of ΔP^2(Cu) for various $[Cu_2(N_3)_2L_4]^{2+}$ cations (broken line given by eq 19d). The two open circles stand for cation−counteranion complexes (not included in the fit). (b) Linear plot of J_{DFT} as a function of Δ^{*2} for various $[Cu_2(N_3)_2L_4]^{2+}$ cations (broken line given by eq 19c). The two open circles stand for cation−counteranion complexes (not included in the fit). (c) Linear plot of ΔP^2(Cu) as a function of Δ^{*2} for various $[Cu_2(N_3)_2L_4]^{2+}$ cations (broken line given by eq 19a). The two open circles stand for cation−counteranion complexes (not included in the fit).

Upon adding the counteranions ClO_4^- (two of them, disposed symmetrically with respect to the *yz* plane, thus keeping an overall C_{2v} nuclear symmetry), the exchange coupling improves quite substantially (becoming more ferromagnetic by ∼470 cm^{-1}: compare the second and third columns of Table 1). This illustrates once again the need of introducing explicitly the counterions for quantitative purposes as their contribution to the exchange coupling is far from being negligible.[63]

We systematically found antiferromagnetism between two coupled copper atoms bridged by end-on azido ions with exchange potentials and copper basis set IV provided by ADF (later called "Cu_ADF"). That is the primary reason we decided to calculate the exchange coupling constants for other dimers $[M_2(N_3)_2L_8]$ bridged by the same azide ions (where M stands for Mn, Fe, Co, Ni, and Cu). For these dimers, however, we found ferromagnetism to be the rule, as measured experimentally for M = Mn → Ni (to be published).

We can already notice the correlation between the copper spin population and the J_{DFT} values: the local (respectively transmitted) spin population keeps increasing (respectively decreasing) while the latter decreases in magnitude. It is known that LDA generally tends to produce larger overlaps than UHF.[50] Therefore, hybrid potentials (such as B3-LYP[45]) tend to decrease the overlap between magnetic orbitals (when compared to those obtained from LDA), thus increasing (respectively decreasing) the local (respectively transmitted) metal spin population. As it then turns out, this yields the expected ferromagnetism (last column of Table 1, a result already announced by Alvarez et al.[28] and recently published[29]).

We wondered therefore whether spatially contracting the copper valence orbitals would not also increase the ferromagnetic contribution to the exchange coupling, thus leading to a withdrawal of the spin population from the other metallic site. In effect, the copper spin populations experimentally measured for azido compounds (∼0.78) by polarized neutron diffraction techniques are much larger than the calculated ones[30] (<0.55). We therefore created copper atoms with the set of exponents of zinc, of ground electronic configuration $[Ar]3d^{10}4s^2$, to check the effect on the calculated *J* constants, aside from the choice of exchange correlation potentials (as with B3-LYP[28,29]). We will call these new copper atoms "Cu_Zn".

We did not aim here at optimizing the copper basis set (a specialty by itself). However, it is still intriguing to notice that there is a systematic gain in bonding energy upon passing from the standard ADF copper basis set (Cu_ADF) to the Cu_Zn one (see Table 1, comparing columns 2 and 4 on one hand, columns 3 and 5 on the other hand). By remembering that the spin population on the copper is experimentally found to be ∼0.78, it seems urgent to optimize the copper basis set anew for such (bio)inorganic complexes, especially by taking into account the degree of delocalization of the valence orbitals, to predict (or retropredict) the correct ferromagnetic exchange coupling.

The use of the Cu_Zn basis set notably ameliorates the calculated *J* value ($J_{DFT} \approx -162$ cm^{-1} without counteranions, $J_{DFT} \approx +143$ cm^{-1} with them). One can verify therefore that the choice of the basis set has a dramatic effect on the calculated spin coupling! Looking now at the copper spin populations, they further increase upon going from Cu_ADF (0.455) to Cu_Zn (0.506) without counteranions, and from Cu_ADF (0.476) to Cu_Zn (0.531) with them, thus getting closer to those obtained for B3-LYP (0.554) with the Gaussian package (last column of Table 1).

The spin populations found on the azido anions do not exhibit any remarkable trend, either on N_{bdg} (between 0.13 and 0.16) or on N_{end} (between 0.11 and 0.13) atoms. The median nitrogen N_{med} bears almost no spin population in all cases. These spin populations (apart may be from the small negative spin

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[63] Ruiz, E.; Alemany, P.; Alvarez, S.; Cano, J. *Inorg. Chem.* **1997**, *36*, 3683−3688.

Table 1. Results Obtained for $[Cu_2(N_3)_2L_4]^{2+}$ Cations, Varying the Copper Basis Set (Cu_ADF or Cu_Zn), the Presence or Absence of Counteranions, and the Peripheral Ligation (Pyridine or Ammonia)[a]

	L = Pyr	L = NH_3				
	Cu_ADF	Cu_ADF	Cu_ADF and $(ClO_4)_2$	Cu_Zn	Cu_Zn and $(ClO_4)_2$	Gaussian B3-LYP
$P_{HS}(Cu)$	*0.417*	*0.441*	*0.476*	*0.506*	*0.531*	*0.554*
$P_{HS}(N_{bdg})$	+0.159	+0.150	+0.159	+0.134	+0.140	+0.136
$P_{HS}(N_{med})$	−0.004	−0.010	−0.001	−0.007	+0.002	−0.028
$P_{HS}(N_{end})$	+0.121	+0.130	+0.125	+0.121	+0.117	+0.116
$P_{BS}(Cu)$	*0.357*	*0.401*	*0.451*	*0.495*	*0.525*	*0.559*
$P_A(L)$	0.115	0.135	0.110	0.120	0.103	0.111
$P_A(Cu_A)$	0.387	0.421	0.464	0.501	0.528	0.556
$P_{A/B}(N_{bdg})$	$b = 0.080$	$b = 0.077$	$b = 0.080$	$b = 0.067$	$b = 0.070$	$b = 0.068$
$P_{A/B}(N_{med})$	$m = -0.004$	$m = 0.001$	$m = 0.000$	$m = 0.003$	$m = 0.001$	$m = 0.014$
$P_{A/B}(N_{end})$	$e = 0.061$	$e = 0.061$	$e = 0.063$	$e = 0.061$	$e = 0.058$	$e = 0.058$
$P_B(Cu_A)$	0.0300	0.0198	0.0126	0.0054	0.0035	−0.0023
$P_B(L)$	0.012	0.009	0.004	0.003	0.001	0.000
$\Delta P^2(Cu)$	*0.0464*	*0.0333*	*0.0234*	*0.0108*	*0.0074*	*−0.0051*
E_{HS} (eV)	−315.033	−109.796	−163.266	−111.937	−165.263	(−104361.521[b])
E_{BS} (eV)	−315.119	−109.861	−163.302	−111.947	−165.254	(−104361.506[b])
J_{DFT} (cm^{-1})	−1388	−1048	−581	−162	+143	+246
Δ (eV)	0.571	0.642	0.504	0.521	0.321	0.042
Δ^* (eV)	*0.424*	*0.388*	*0.286*	*0.226*	*0.128*	*0.003*

[a] Given in each case is a spin population and an energetic analysis. Note that Δ corresponds to occupied (majority spin) magnetic orbital splittings whereas Δ^* corresponds to empty (minority spin) magnetic orbital splittings. [b] Total energies in Hartrees.

population on N_{med}) are in keeping with a dominant spin delocalization mechanism.[30]

5.2. Fitting Models for J_{DFT}. We applied Bertrand's analysis of the spin populations calculated for the different Cu dimer species. The local and transferred spin populations for the $[Cu_2(N_3)_2L_4]$ copper dimers are reported in Table 1. We can see there that the local copper spin populations $P_A(Cu_A)$ ($= P_B(Cu_B)$) follow the calculated spin populations P_{Cu}, but more interestingly, the transmitted spin populations $P_B(Cu_A)$ ($= P_A(Cu_B)$) keep decreasing steadily until becoming, for the Gaussian calculation, actually negative! Moreover, there is a very good correlation between the calculated J_{DFT} spin coupling constant (assuming the weak overlap regime to hold) and $\Delta P^2(Cu)$, as can be seen on Figure 6a (even by including the *negative* transmitted quantity!).

For the sake of clarity, we will below give fit results that do not include the data with counteranions (but this does not change much the values of the optimized parameters). Moreover, we want to compare synoptically three approaches: VB−GS (Kahn: $J_{AF} \approx -2\Delta S_{AB}$),[23] VB−BS (Noodleman: $J_{AF} \approx -US^2_{AB}$),[47] and MO (Hoffmann: $-\Delta^2/U$).[18] To estimate S_{AB}, and in the case of relatively large overlap S_{AB} (or small ligand−metal overlap s), we can write (from eq 14)

$$\Delta P^2(Cu) \approx \frac{S^2_{AB}}{(1 + S_{AB})^2} \Rightarrow S_{AB} \approx \frac{\sqrt{\Delta P^2(Cu)}}{1 - \sqrt{\Delta P^2(Cu)}}$$

rather than $S_{AB} \sim \Delta P^2(Cu)^{1/2}$ (this estimation of the overlap will be useful for Kahn's and Noodleman's models). We thus obtain from the data in Table 1

$$J_{DFT}\,(cm^{-1}) \approx \begin{cases} -16320\Delta^* S_{AB} + 270 & (rms = 57)\ \ (a) \\ -29000S^2_{AB} + 269 & (rms = 56)\ \ (b) \\ -\Delta^{*2}/7210 + 271 & (rms = 33)\ \ (c) \\ -32900\Delta P^2(Cu) + 115 & (rms = 56)\ \ (d) \end{cases} \qquad (19)$$

Several points can be noticed:

(i) The first remark deals with the intercept values, 270 cm^{-1} for the first three modes, and 115 cm^{-1} for ours. The difference (i.e., ~155 cm^{-1}) can be ascribed to a negative $\Delta P^2(Cu)$ contribution ($-155/32900 \approx -0.005$), that is, to the ferromagnetic contribution to the exchange coupling resulting from spin polarization (cf. section 3.3).

(ii) The VB prefactor (~2 eV) of the first equation is as expected (cf. eq 19a).

(iii) The VB−BS prefactor is $U \sim 3.6$ eV (eq 19b), close to that of $\Delta P^2(Cu)$ ($\sim S^2_{AB}$), 4.1 eV (eq 19d). These values are to be compared with 6.5 eV obtained from photoelectron spectroscopy for copper chlorides[64] and to 5.9 eV (Anderson's estimate[65]).

(iv) It would be hard, for the data listed in Table 1, to find any correlation between J_{DFT} and Δ, the SOMO gap (as for Hoffmann's model[18]). Using, however, the *empty* (β spin) copper orbitals (called the SOMO*s in Table 1), as done by others,[66] one obtains good fits (the dashed line on Figure 6b). The reason for that choice lies in the fact that the bridge and copper α spin−orbitals mix too much to yield suitable SOMO gaps.[66] Such is not the case however with the β spin−orbitals.

(v) Both fits of J_{DFT} as a function of $\Delta P^2(Cu)$ and Δ^{*2} imply that there is a linear relationship between these two last parameters (black circles in Figure 6c):

$$\Delta P^2(Cu) \approx 0.272\ \Delta^{*2} - 4.5 \times 10^{-3} \qquad (rms = 2.0 \times 10^{-3}) \quad (20a)$$

or

$$\Delta^{*2} \approx 3.645\Delta P^2(Cu) - 17.5 \times 10^{-3} \qquad (rms = 7.4 \times 10^{-3}) \quad (20b)$$

The effect of adding the counteranions appears very clearly in Figure 6c in the form of a shift from the open circles: either Δ^* is systematically reduced or $\Delta P^2(Cu)$ is systematically increased (as the result of opening some new exchange, pathway), or both.

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(64) Didziulis, S. V.; Cohen, S. L.; Gewirth, A. A.; Solomon, E. I. *J. Am. Chem. Soc.* **1988**, *110*, 250.

(65) Anderson, P. W. *Phys. Rev.* **1959**, *115*, 2−13.

(66) Brown, C. A.; Remar, G. J.; Musselman, R. L.; Solomon, E. I. *Inorg. Chem.* **1995**, *34*, 688.

6. Spin Polarization Mechanisms

The expression "spin polarization" (as we use it in this paper) now has to be explicated (in response to a reviewer). A recent polarized neutron diffraction experiment realized on an end-on azido-bridged Cu(II) dimer (triplet state) showed the following features: large spin populations on the metals (0.78), relatively small ones on the bridging nitrogen (0.07), and a *negative* small spin population (-0.02) on the middle nitrogen of the azido ion.[30] No such negative spin population can be found at the active-electron approximation, through spin delocalization only, as both NMOs bear an α spin.

Therefore, Kahn first proposed[22,30] that the two electron spins of the azido ion orbital might be polarized; i.e., the spin populations borne on both ends of the anion would be of opposite sign. This is then supposed to force ferromagnetic alignment of the two metallic spins as a consequence of locally applying Hund's rule. This would predict, however, negative spin populations on the *bridging* nitrogens of the azido ions, not on the *central* ones.

To go beyond these concepts (limited by the "active electron" approximation) requires some configuration interaction to occur within the doubly occupied molecular orbitals of the azido groups. This has been shown experimentally by Von Seggern et al. by means of the VB−CI model[31] implicating ligand excitations (LE). From an ab initio MO−CI point of view, calculations have been performed for various copper dimers[67−72] as a way to remedy the lack in neglecting these doubly occupied bridge orbitals, especially through double spin polarization (DSP) terms.

It is interesting at this point to add that both the (VB−CI) LE[30,31] and the (MO−CI) DSP[68] terms present a (ligand orbital) topology dependency. Such a property is already known to occur in biradicals, where the two concerted single polarizations can be *additive* or *competitive*, depending on the bridging atom topologies, thus favoring either the singlet or the triplet state.[73]

Having now set the framework within which spin polarization mechanisms are usually explicited and discussed, let us come back to our own findings. We speak *analogically* of a spin polarization mechanism, when the transmitted spin population P_T from one copper site onto the other one becomes *negative* (cf. section 3.3). Obviously, the total spin population on Cu (i.e., $P_L + P_T$) is, however, always positive. Only Bertrand's procedure[46] (cf. section 3.1) allows us to distinguish, through comparison of the HS and BS copper spin populations, between P_L and P_T. Therefore, it is important to state that our analytical expressions for $\Delta P^2(\mathrm{Cu})$ are obtained (i) within the context of the broken symmetry method and (ii) within the atomic Mulliken partitioning scheme of the spin population.

As to the first point (i), let us recall here that the broken symmetry state for a Cu(II) dimer is an artificial state of mixed-spin symmetry and lowered space symmetry, constructed as a linear combination of the singlet and triplet states.[49] The use of this BS state, of no physical reality, turns out to be very useful for computational purposes, though, as it includes in its fabrics direct exchange (ferromagnetic), superexchange (antiferromagnetic), and ligand−metal spin polarization (LSP). Let us emphasize, however, that no DSP term is included in the broken symmetry method[48] (the most serious omission of this method).

The LSP effect, rather than superexchange involving only metallic orbitals,[46] is the real "physical" agent transferring copper spin population from one metallic site onto the other one (via the bridge orbitals, where the NMOs overlap). Not taking it into account (as first done in section 3.1) amounts to set $a = 0$ (through $s = \langle \mathrm{p}|\mathrm{d}\rangle = 0$) in eq 14. Without direct metal−metal overlap, $S_{AB} = 0$ and $\Delta P^2(\mathrm{Cu}) = 0$. More generally, $\Delta P^2(\mathrm{Cu}) \sim S_{AB}^2$ (second halves in eq 14) if metal−metal overlap exists, in which case one recovers eq 4. Within this context, it can be easily shown from eq 1 that $P_{HS}(\mathrm{Cu}) = P_{BS}(\mathrm{Cu}) + 2P_T$, where, to first order in S_{AB}, $P_T \approx a^2 S_{AB}/4$ (azido case). A key feature of our model lies therefore in the bridge orbital topology, allowing for negative P_T in some cases (as for the azido topology class), whose effect is here artificially exhibited through comparison of the HS and BS states, as we transform NMOs into OMOs (as implemented in the Appendix).

As to the second point (ii), and in order to illustrate as simply as possible the importance of the atomic partitioning scheme in the final expression adopted by the quantity $\Delta P^2(\mathrm{Cu_A})$, we now give some hints as to how to calculate $\Delta P^2(\Phi_A)$ for example, that is, without internal distinction in the NMOs between copper and azido atomic orbitals (the LSP effect is now masked, rather than explicited as in eq 12). Writing eq A-2 explicitly in terms of the NMOs $\{\Phi_{A,B}\}$, and along the same path as that followed in the Appendix, it can be shown that $P_A(\Phi_A) = [1 + (1 - S_{AB}^2)^{-1/2}]/2 > 1$ and $P_B(\Phi_A) = [1 - (1 - S_{AB}^2)^{-1/2}]/2 < 0$. Therefore, $P_{HS}(\Phi_A) = 1$ and $P_{BS}(\Phi_A) = (1 - S_{AB}^2)^{-1/2} > 1$, yielding finally, $\Delta P^2(\Phi_A) = -S_{AB}^2/(1 - S_{AB}^2)$. In that case, $\Delta P^2(\Phi_A)$ is *always* negative for a NMO-based Mulliken partitioning scheme, and Noodleman's antiferromagnetic term $-US_{AB}^2$ would have to be approximated by $+U\Delta P^2(\Phi_A)$ (rather than $-U\Delta P^2(\mathrm{Cu_A})$)!

Let us finally emphasize that we present our proposal (explained in eq 8), and thus the quantity $\Delta P^2(\mathrm{Cu})$, at a *phenomenological* level only, although a rigorous link can be established between eq 8 and Kahn's valence bond model[23] (to be published). At the present level, the rationalization of our model is thus based on the following: (i) its formal analogy to Mc Connell's own proposal (also approximate; cf. eq 9); (ii) the fact that, depending on the bridging orbital topology, ΔP^2(Cu) can effectively turn out negative (as it does for the azido bridge; cf. section 4); and (iii) the fact that we effectively obtain a good linear correlation between computed J_{DFT} exchange coupling constants and $\Delta P^2(\mathrm{Cu})$, as derived from a Mulliken spin population analysis, even when $\Delta P^2(\mathrm{Cu}) < 0$ (cf. section 5).

7. Conclusions

As a result of our investigations on Cu dimers, we can now draw the following conclusions: (1) We showed that the quantity $\Delta P^2(\mathrm{Cu}) \equiv P_{HS}^2(\mathrm{Cu}) - P_{BS}^2(\mathrm{Cu})$ provides a simple means of quantifying the antiferromagnetic contribution to the exchange coupling between two copper(II) monomers. In the case of end-on azido-bridged copper(II) dimers, $\Delta P^2(\mathrm{Cu})$ can become negative. This has been phenomenologically interpreted as the manifestation of a spin polarization effect, reminiscent of McConnell's model[53] of ferromagnetism for interacting radicals (cf. sections 3.3 and 6).

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No such inversion of sign is possible within Noodleman's broken symmetry approach,[47] in which $J_{\mathrm{AF}} \sim S_{\mathrm{AB}}^2$, or within Hoffmann et al.'s molecular orbital approach,[18] in which $J_{\mathrm{AF}} \sim \Delta^2$. However, it can be shown that, within the context of Kahn's VB model,[23] this effect can be physically related to the fact that Δ and S_{AB} do not cancel for exactly the same set of structural parameters[74] (to be published).

(2) For $[\mathrm{Cu_2(N_3)_2L_4}]^{2+}$ dimers for which $S_{\mathrm{AB}}^2 \ll 1$, using two different Cu basis sets (Cu_ADF and Cu_Zn), different ligands (Pyr and NH_3), quantum chemistry codes (ADF and Gaussian), and exchange correlation functionals (VBP or B3-LYP), all our computational results could be harmonized by correlating the exchange coupling $J_{\mathrm{DFT}} \equiv -2(E_{\mathrm{BS}} - E_{\mathrm{HS}})$ with $\Delta P^2(\mathrm{Cu})$.

(3) We conclude further that the disagreement between theory and experiment in the calculation of the exchange coupling for azido-bridged Cu dimers most probably originates (at least using ADF) from a defficiency of the Cu basis set. By relocalizing the magnetic orbitals (through the replacement of Cu_ADF by Cu_Zn, as here checked, or by using an appropriate exchange correlation functional as done by others[28,29]), one restitutes the expected ferromagnetism, although the computed copper spin populations are still too small compared to the experimental ones.

(4) Finally, the quantity $\Delta P^2(\mathrm{Cu})$ thus offers the possibility of an alternative tool for magnetostructural studies to that based on Hoffmann's MO approach,[18] currently used at a qualitative level only, although at the price of two computed states (HS = triplet and BS) instead of one (the triplet).

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Appendix

Within the framework of the azido topology, as defined in section 4.1, and from the two localized fragment orbitals Φ_{A} and Φ_{B}, one constructs two (symmetric and antisymmetric) SOMOs, typical for a HS-type calculation:

$$\begin{cases} \Psi_1 = \dfrac{1}{\sqrt{2(1+S_{\mathrm{AB}})}}[\Phi_{\mathrm{A}} + \Phi_{\mathrm{B}}] = \dfrac{1}{\sqrt{(1+S_{\mathrm{AB}})}}\left[2a\dfrac{\mathrm{p}}{\sqrt{2}} + b\dfrac{\mathrm{d_A} + \mathrm{d_B}}{\sqrt{2}}\right] \\ \Psi_2 = \dfrac{1}{\sqrt{2(1-S_{\mathrm{AB}})}}\left[\Phi_{\mathrm{A}} - \Phi_{\mathrm{B}}\right] = \dfrac{\mathrm{d_A} - \mathrm{d_B}}{\sqrt{2}} \end{cases} \tag{A-1}$$

To apply Bertrand's approach[46] to our problem (cf. section 3.1), using both HS and BS state spin population analysis, we now want to recombine these two MOs in order to obtain (mutually orthogonal) monomer orbitals partly delocalized onto the other metal:

$$\begin{cases} \Phi'_{\mathrm{A}} = \dfrac{1}{\sqrt{2}}[\Psi_1 + \Psi_2] \\ = {}^1\!/_2\left[\left(\dfrac{\mathrm{b}}{\sqrt{(1+S_{\mathrm{AB}})}} + 1\right)\mathrm{d_A} + \left(\dfrac{b}{\sqrt{(1+S_{\mathrm{AB}})}} - 1\right)\mathrm{d_B} + \dfrac{2a}{\sqrt{(1+S_{\mathrm{AB}})}}\mathrm{p}\right] \\ \Phi'_{\mathrm{B}} = \dfrac{1}{\sqrt{2}}[\Psi_1 - \Psi_2] \\ = {}^1\!/_2\left[\left(\dfrac{b}{\sqrt{(1+S_{\mathrm{AB}})}} - 1\right)\mathrm{d_A} + \left(\dfrac{b}{\sqrt{(1+S_{\mathrm{AB}})}} + 1\right)\mathrm{d_B} + \dfrac{2a}{\sqrt{(1+S_{\mathrm{AB}})}}\mathrm{p}\right] \end{cases} \tag{A-2}$$

This new set of orbitals are suited for Bertrand's analysis as they correspond to the two monomer (partially delocalized) functions after mutual interaction as suited within the broken symmetry method. We then calculate the Mulliken atomic spin populations (for $\mathrm{Cu_A}$ in Φ'_{A}, i.e., $P_{\mathrm{A}}(\mathrm{Cu_A})$, in Φ'_{B}, i.e., $P_{\mathrm{B}}(\mathrm{Cu_A})$, etc):

$$\begin{cases} P_{\mathrm{A}}(\mathrm{Cu_A}) = P_{\mathrm{B}}(\mathrm{Cu_B}) = {}^1\!/_4\left(\dfrac{b}{\sqrt{(1+S_{\mathrm{AB}})}} + 1\right)\left(\dfrac{b}{\sqrt{(1+S_{\mathrm{AB}})}} + 1 + \dfrac{2as}{\sqrt{(1+S_{\mathrm{AB}})}}\right) \\ P_{\mathrm{A}}(\mathrm{Cu_B}) = P_{\mathrm{B}}(\mathrm{Cu_A}) = {}^1\!/_4\left(\dfrac{b}{\sqrt{(1+S_{\mathrm{AB}})}} - 1\right)\left(\dfrac{b}{\sqrt{(1+S_{\mathrm{AB}})}} - 1 + \dfrac{2as}{\sqrt{(1+S_{\mathrm{AB}})}}\right) \\ P_{\mathrm{A}}(\mathrm{N}) = P_{\mathrm{B}}(\mathrm{N}) = \dfrac{a^2 + abs}{1 + S_{\mathrm{AB}}} \end{cases} \tag{A-3}$$

Consequently, in terms of the HS (i.e., P_{HS}) and the BS (i.e., P_{BS}) spin populations

$$\begin{cases} P_{\mathrm{HS}}(\mathrm{Cu_A}) = P_{\mathrm{A}}(\mathrm{Cu_A}) + P_{\mathrm{B}}(\mathrm{Cu_A}) = \dfrac{1 + abs}{1 + S_{\mathrm{AB}}} \\ P_{\mathrm{HS}}(\mathrm{Cu_B}) = P_{\mathrm{A}}(\mathrm{Cu_B}) + P_{\mathrm{B}}(\mathrm{Cu_B}) = \dfrac{1 + abs}{1 + S_{\mathrm{AB}}} \\ P_{\mathrm{HS}}(\mathrm{N}) = P_{\mathrm{A}}(\mathrm{N}) + P_{\mathrm{B}}(\mathrm{N}) = 2\dfrac{a^2 + abs}{1 + S_{\mathrm{AB}}} \end{cases} \tag{A-4}$$

and

$$\begin{cases} P_{\mathrm{BS}}(\mathrm{Cu_A}) = P_{\mathrm{A}}(\mathrm{Cu_A}) - P_{\mathrm{B}}(\mathrm{Cu_A}) = +\dfrac{b + as}{\sqrt{1 + S_{\mathrm{AB}}}} \\ P_{\mathrm{BS}}(\mathrm{Cu_B}) = P_{\mathrm{B}}(\mathrm{Cu_B}) - P_{\mathrm{A}}(\mathrm{Cu_B}) = -\dfrac{b + as}{\sqrt{1 + S_{\mathrm{AB}}}} \\ P_{\mathrm{BS}}(\mathrm{N}) = P_{\mathrm{A}}(\mathrm{N}) - P_{\mathrm{B}}(\mathrm{N}) = 0 \end{cases} \tag{A-5}$$

An analytical expression for $\Delta P^2(\mathrm{Cu})$ is then straightforwardly derived. The same procedure can be applied to the linear oxo-bridged Cu(II) dimer.

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