

# Ab Initio Direct Calculation of the Singlet-Triplet Separation in Cupric Acetate Hydrate Dimer

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**Abstract:** The singlet-triplet (ST) splitting of cupric acetate hydrate dimer has been calculated in an ab initio scheme. The method, based on a perturbative development of the CI problem, directly gives the ST splitting. The  $2K_{ab}$  ferromagnetic zeroth order contribution is far from being negligible ( $\sim 230 \text{ cm}^{-1}$ ). The direct super-exchange mechanism (coupling with ionic states) only cancels the direct exchange. The double-spin polarization of the acetate ligands gives a  $\approx -50 \text{ cm}^{-1}$  antiferromagnetic contribution. Other second-order effects appear to be negligible. Higher order contributions involving super-exchange and polarization of the ligands and 3d closed shells have been summed up to all orders. Their antiferromagnetic numerical effect depends on the choice of the perturbation treatment and lies between  $-90$  and  $-214 \text{ cm}^{-1}$ , which gives a final result consistent with that of the experiment.

Magnetic exchange interactions in metal dimer complexes have been observed for many years and widely studied.<sup>2-18</sup> Cupric acetate hydrate dimer is the most famous example (Figure 1), and since 1951 more than one paper each year has been published on this sole complex. We shall also concentrate on this "reference" complex for, through the many experimental results and the various theoretical treatments, one can obtain an enlightening overall view of the evolution of the sometimes conflicting ideas and concepts held on antiferromagnetism.

In 1952, Bleaney and Bowers<sup>2</sup> were the first to explain the anomalous magnetic susceptibility data experimentally observed by Guha<sup>3</sup> and their own ESR data, by the antiferromagnetic coupling of the  $\text{Cu}^{2+}$  ions: in this now classical scheme the ground state is a diamagnetic singlet state and a low-lying paramagnetic triplet state may be thermally populated, the energy gap between those states being referred to as the coupling constant  $J$ .

In 1956 Figgis and Martin<sup>4</sup> reinvestigated the temperature dependence of the susceptibility ( $2J = -286 \text{ cm}^{-1}$ ) and correlated the antiferromagnetic behavior to the existence of a  $\delta$  bond between

the copper atoms. This " $\delta$ -bond" hypothesis has been taken up by Ross<sup>5a</sup> to interpret the previously published ESR data. Ross and Yates<sup>5b</sup> using the valence bond theory calculated a  $2J$  value of  $-4 \text{ cm}^{-1}$  for a  $\delta$ -bond model and a  $2J$  value of  $1600 \text{ cm}^{-1}$  for a  $\sigma$ -bond model.

The discrepancy of the first value with the experimental value could be alleviated by a reduction of 25% in the effective nuclear charge from the value predicted by Slater's rule! The  $\delta$ -bond model was again invoked by Kato et al.<sup>6</sup> in their review on Cu(II) complexes with subnormal magnetic moments and by Tonnet et al.<sup>7</sup> for the interpretation of the electronic spectrum.

However a MO treatment by Ballhausen et al.<sup>8</sup> suggested a level scheme based upon a copper-copper  $\sigma$  bond. Later, Ballhausen et al.,<sup>9</sup> using a coupled chromophore model, proposed a new interpretation of the electronic spectra of the cupric acetate which was not based on a direct copper-copper bond. These calculations predicted that the effect of configuration interaction would be a depression of the energy of the triplet ground state but an evaluation of the singlet-triplet splitting was not possible, due to computational difficulties.

Jotham and Kettle,<sup>10</sup> using a model which incorporates spin exchange and metal-metal bonding, were able to fit very precisely the temperature dependence of the magnetic moment. However, the spin exchange strikingly appeared to be ferromagnetic and direct in origin, although the overall pattern of energy levels leads to antiferromagnetism. In subsequent calculations,<sup>11</sup> these authors however stated that the metal-metal bonding energies contribute very little to the stability of the complex. This opinion was shared by Goodgame et al.,<sup>12</sup> who suggested that metal-metal bonding is not important in explaining the antiferromagnetism and that the spin coupling proceeds by super exchange via the carboxylate bridge.

This interpretation was solely based upon comparison of bond lengths on a pair of analogous copper(II) acetate and formate dimers but had been already proposed a long time ago in the first paper of Bleaney and Bowers.<sup>2</sup>

This "Super-exchange" idea then became increasingly favored. Gregson, Martin, and Mitra<sup>13</sup> reinvestigated the magnetic anisotropy but could not provide any evidence for either models. The first real semiquantitative approach to this problem was made by Hoffmann et al.<sup>14</sup> their MO analysis attempted to establish a link between the antiferromagnetic exchange interaction and the difference in energies between predominantly  $d_{x^2-y^2}$  MO's, this difference reflecting the extent of super exchange via the bridging groups. A quite similar approach was proposed by Kahn et al.<sup>15</sup> which leads to a slightly different expression of the singlet-triplet splitting. Although these energies were obtained from simple

(1) (a) Laboratoire de Chimie de Coordination. (b) Laboratoire de Physique Quantique.

(2) Bleaney, B.; Bowers, K. D. *Proc. R. Soc. London, Ser. A* **1952**, *214*, 451-465.

(3) Guha, B. C. *Proc. R. Soc. London, Ser. A* **1951**, *206*, 353-373.

(4) Figgis, B. N.; Martin, R. L. *J. Chem. Soc.* **1956**, 3837-3846.

(5) (a) Ross, I. G. *Trans. Faraday Soc.* **1959**, *55*, 1057-1063. (b) Ross, I. G.; Yates, J. *Ibid.* **1959**, *55*, 1064-1069.

(6) Kato, M.; Jonassen, H. B.; Fanning, J. C. *Chem. Rev.* **1964**, *64*, 99-128.

(7) Tonnet, M. L.; Yamada, S.; Ross, I. G. *Trans. Faraday Soc.* **1964**, *60*, 840-849.

(8) Forster, L. S.; Ballhausen, C. J. *Acta Chem. Scand.* **1962**, *16*, 1385-1392.

(9) Hansen, A. E.; Ballhausen, C. J. *Trans. Faraday Soc.* **1965**, *61*, 631-639.

(10) Jotham, R. W.; Kettle, S. F. A. *J. Chem. Soc. A* **1969**, 2821-2825.

(11) Jotham, R. W.; Kettle, S. F. A. *Inorg. Chem.* **1970**, *9*, 1390-1395.

(12) Goodgame, D. M. L.; Hill, N. J.; Marsham, D. F.; Scapoki, A. C.; Smart, M. L.; Troughton, P. G. H. *J. Chem. Soc., Chem. Commun.* **1969**, 629-630.

(13) Gregson, A. K.; Martin, R. L.; Mitra, S. *Proc. R. Soc. London, Ser. A* **1971**, *320*, 473-486.

(14) Hay, P. J.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1975**, *97*, 4884-4899.

(15) Kahn, O.; Briat, B. *J. Chem. Soc., Faraday Trans. 2* **1976**, *72*, 268-281.

(16) Gerloch, M.; Harding, J. H. *Proc. R. Soc. London, Ser. A* **1978**, *360*, 211-227.

(17) Kawamori, A. *J. magn. Reson.* **1978**, *31*, 423-430.

(18) (a) Doedens, R. J. *Prog. Inorg. Chem.* **1976**, *21*, 209-230. (b) Moreland, J. A.; Doedens, R. J. *Inorg. Chem.* **1978**, *17*, 674-679.

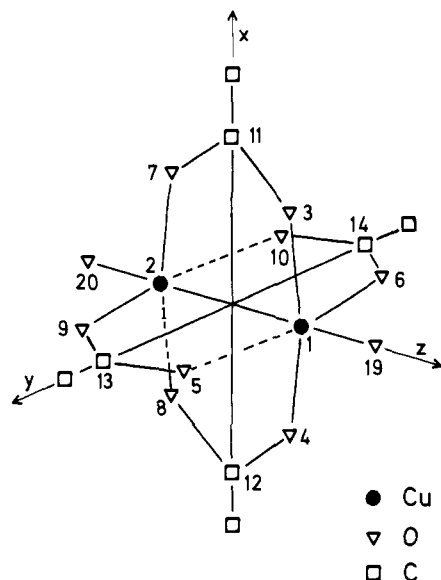


Figure 1. Schematic representation of the cupric acetate hydrate dimer, with axes location and atom numbering.

extended Hückel calculations, Hoffmann's (or Kahn's) scheme seems sufficiently heuristic as it predicts the trends observed in a series of dimers and the effect of geometrical distortions, electronegativity, and variations of substituents. It should be noted that these calculations suggest an antibonding  $\delta$  interaction between the copper ions. Gerloch and Harding,<sup>16</sup> using a classical valence bond formalism, proposed a super-exchange mechanism which could not be based on spin-orbit mixing of  $xy$  and  $x^2 - y^2$  states but could be based on a configuration mixing of such functions: the  $g$  values and zero field splitting were also reproduced within this super-exchange model as within the  $\delta$ -bond model.

An interesting, although very approximate, evaluation of the exchange processes on the acetate bridge has been recently attempted by Kawamori<sup>17</sup> in order to interpret NQR data. His approach is somewhat similar in nature to the double-spin polarization mechanism which will be discussed later in this paper.

Empirical correlations<sup>18</sup> have been also proposed to relate the effects of variations of the carboxylate substituent on the acetate bridge and of the axial donor ligand upon the magnitude of the Cu-Cu interaction. It is unfortunately clear that the existing body of such data cannot be satisfactorily rationalized.

The straightforward conclusion of this short review is that there is to date no clear understanding of the real origin of the antiferromagnetic coupling in cupric acetate,  $\delta$  bond,  $\sigma$  bond, and super exchange and what kind of super exchange.

Therefore it seemed important to calculate the singlet-triplet splitting with a nonempirical method coupled with configurational interaction in order to determine the factors which play a major role in the determination of the magnitude of this splitting.

We report in this paper the results of such ab initio direct calculations performed on the cupric acetate dimer.

## Method

**1. Computational Details and SCF Results.** All electron ab initio SCF-MO calculations were carried out by using the IBMOL-6 computational scheme.<sup>19</sup> The calculations were performed by using the geometry determined by a neutron diffraction structural study<sup>20</sup> of  $\text{Cu}_2(\text{O}_2\text{CCH}_3)_4 \cdot 2\text{H}_2\text{O}$ . The planes of the two water molecules have been arbitrarily rotated in order to ensure  $D_{2h}$  symmetry.

The basis set for the oxygen, carbon, and hydrogen atoms consists of Gaussian type orbitals, with optimized exponents obtained from ref 21 and contracted in a single- $\zeta$  form (7/3 to 2/1) for the O and C atoms and (3 to 1) for the H atom. The basis set for the copper atom [ $2D(3d)(4s)^2$ ], which originally consists

Table I. Magnetic Orbital a Obtained through a  $\pi/4$  Rotation of the  $\sigma_u, \sigma_g$  Symmetry MO's<sup>a</sup>

AO	atom				
	Cu <sub>1</sub>	Cu <sub>2</sub>	O <sub>3</sub>	C <sub>11</sub>	O <sub>7</sub>
$3d_{x^2-y^2}$	0.97014	0.01884			
	0.65823	0.00139			
1s			0.03377	-0.01319	-0.00616
2s			-0.12313	0.05052	0.02764
2p <sub>x</sub>			0.23499	-0.01387	0.03022
2p <sub>y</sub>			0	0	0
2p <sub>z</sub>			0.02908	0.06407	0.02872

<sup>a</sup> The larger coefficients are given for one of the four nearly equivalent acetate bridges only.

Table II. Total Populations

AO	atom				
	Cu <sub>1</sub>	O <sub>3</sub>	O <sub>5</sub>	C <sub>11</sub>	C <sub>13</sub>
s	6.3854	3.7484	3.7472	3.0165	3.0161
x	4.2333	1.6321	1.5672	1.1106	0.8418
y	4.2221	1.5660	1.6328	0.8434	1.1063
z	4.1350	1.5021	1.5034	0.8094	0.8092
$x^2 - y^2$	1.2635				
xy	1.9985				
xz	1.9990				
yz	1.9985				
$z^2$	1.9609				
atomic charge	28.1965	8.4487	8.4508	5.7676	5.7653
net charge	+0.8035	-0.4487	-0.4508	+0.2324	+0.2347

of 10/5/4 GTO's,<sup>22</sup> is then extended by addition of one more s diffuse function with a 0.0555 exponent and one "polarization" p function with a 0.106 exponent; these modifications provide a better description of the valence region of the molecule. The Cu atom GTO's are finally contracted in a double- $\zeta$  form for the valence electrons (11/6/4  $\rightarrow$  5/3/2).

The SCF calculation of the singlet ground state, represented by a monodeterminantal function, leads to a slightly negative value for the lowest unoccupied MO (LUMO) which is built on the antisymmetric combination  $\sigma_u$  of the  $d_{x^2-y^2}$  copper atomic orbitals. The highest occupied MO (HOMO) is the corresponding symmetric combination  $\sigma_g$  of the  $d_{x^2-y^2}$  copper AO's. The  $\sigma_u$  and  $\sigma_g$  symmetry MO's have been localized through a  $\pi/4$  rotation in order to obtain the so-called "magnetic orbitals" a and b, which are similar to those frequently used in the literature.<sup>14,15</sup>

The most significant AO's coefficients of the a (or b) magnetic orbital are shown in Table I.

It is evident at this point, as expected, that the singlet ground state (and perhaps the triplet state also) cannot be represented by just one Slater determinant.

The computed total populations (for each orbital and each atom), using Mulliken's definitions,<sup>23</sup> are shown in Table II and indicate a  $d^9s^1$  configuration for the copper atom. Finally, a strong antibonding total overlap population is observed between the two copper atoms which rules out the  $\delta$ -bond hypothesis.

The (IJ,KL) molecular bielectronic integrals, which will be used

(19) Clementi, E.; Lie, G.; Pavanl, R.; Gianolio, L. "IBMOL-6" Program, Technical Report DDC-771, Montedison, S.P.A., 1977.

(20) Brown, G. M.; Chidambaram, R. *Acta Crystallogr., Sect. B*, 1973, B29, 2393-2403. The structure of the cupric acetate hydrate dimer has also been redetermined by X-ray studies: Meester de, P.; Fletcher, S. R.; Skapski, A. C. *J. Chem. Soc., Dalton Trans.* 1973, 2575-2578. The results of both determinations are in excellent agreement.

(21) Whitman, D. R.; Hornback, C. J. *J. Chem. Phys.* 1969, 51, 398-402.

(22) The basis set has been optimized by A. Serafini. As it will appear later on, the most relevant Cu configuration for the complex should be ( $d^9s^1$ )  $\text{Cu}^+$ . We believe however that our double- $\zeta$  3d basis set is flexible enough to give reliable results.

for the direct calculation of the different contributions to the singlet-triplet splitting, have been calculated by using a program written at our laboratory.<sup>24</sup>

**2. The Direct Calculation of the Singlet-Triplet Energy Difference: Formalism. Zeroth-Order ST Splitting.** In both states, the  $d_{x^2-y^2}$  atomic orbitals on each Cu atom are single occupied.

Let us call  $a$  and  $b$  (eq 1) the two localized SCF MO's, where

$$a \simeq d^A_{x^2-y^2} + t \quad b \simeq d^B_{x^2-y^2} + t' \quad (1)$$

$t$  and  $t'$  are tails on the acetate ligands. The two  $a$  and  $b$  MO's are linear combinations of the nearly degenerate symmetry MO's (eq 2). The zeroth order singlet and triplet states may be represented by eq 3a,b for the  $S_z = 0$  component.

$$\sigma_u \simeq (a - b)/\sqrt{2} \quad \sigma_g \simeq (a + b)/\sqrt{2} \quad (2)$$

represented by eq 3a,b for the  $S_z = 0$  component.

$${}^1\Psi_0 = A[(\prod_{i=1}^n \bar{ii})(a\bar{b} + b\bar{a})]/\sqrt{2} = (\phi_1 + \phi_2)/\sqrt{2} \quad (3a)$$

$${}^3\Psi_0 = A[(\prod_{i=1}^n \bar{ii})(a\bar{b} - b\bar{a})]/\sqrt{2} = (\phi_1 - \phi_2)/\sqrt{2} \quad (3b)$$

The degenerate  $S_z = \pm 1$  components of the triplet state are obtained by replacing the  $(a\bar{b} - b\bar{a})/2^{1/2}$  factor by the direct products  $ab$  or  $\bar{a}\bar{b}$ , respectively. When symmetry MO's are used, both states do not have the same expression (eq 4a,b) and it is more convenient to keep localized MO's.

$${}^1\Psi_0 = A[(\prod_{i=1}^n \bar{ii})(\sigma_g\bar{\sigma}_g - \sigma_u\bar{\sigma}_u)]/\sqrt{2} \quad (4a)$$

$${}^3\Psi_0 = A[(\prod_{i=1}^n \bar{ii})(\sigma_g\bar{\sigma}_u - \sigma_u\bar{\sigma}_g)]/\sqrt{2} \quad (4b)$$

The zeroth-order singlet-triplet energy splitting is given by the well-known exchange integral  $K_{ab}$ .

$$\Delta E^{\circ}_{ST} = +2K_{ab} \quad (5)$$

**Second-Order ST Splitting.** Excited states' energies are frequently calculated through direct CI, but the calculation of such a small energy difference through brute force techniques would be rather unreliable, since approximations (such as MO set truncations) are compulsory for such a many-electron problem. As noticed a long time ago<sup>25-27</sup> perturbation theory allows direct calculations of energy differences. The calculation of the transition energy is much shorter than the calculation of the total energy of a given state.

Moreover, J.P.M.<sup>25</sup> noticed that the singlet-triplet splitting for a given zeroth-order configuration is even easier to calculate as it will appear sooner. Actually the second-order CI corrections on the singlet and triplet states are

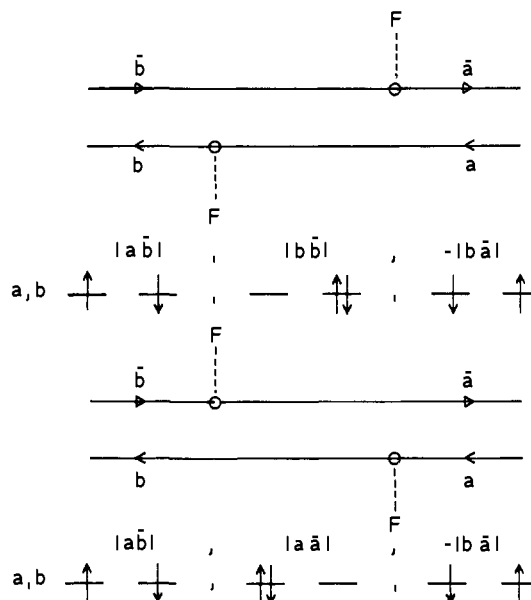
$$\epsilon^2_{ST} = \sum_{1 \neq \Psi_0} \left| \frac{\langle {}^{1,3}\Psi_0 | H | 1 \rangle}{E_0 - E_1} \right|^2 \quad (6)$$

Turning back to eq 3, one sees immediately that

$$\Delta E^2_{ST} = \epsilon^2_S - \epsilon^2_T = 2 \sum_1 \frac{\langle \phi_1 | H | 1 \rangle \langle 1 | H | \phi_2 \rangle}{E_0 - E_1} \quad (7)$$

The second-order singlet-triplet energy difference is given by a summation over the excited determinants which interact with

Diagram I



both  $\phi_1 = |a\bar{b}|$  and  $\phi_2 = |b\bar{a}|$ ; these determinants are much less numerous than those involved in eq 6. The most direct way to generate the various contributions of eq 7 takes advantage of the diagrammatic technique.<sup>28</sup> The choice of the vacuum state is arbitrary; one might choose for instance  $\phi_1 = |a\bar{b}|$  but in that case  $\phi_2$  appears as a doubly excited determinant and the diagrams are not symmetrical. A more convenient choice is the ( $S_z = 1$ )  $|ab|$  determinant,  $a$  and  $b$  being holes as are the doubly occupied MO's  $i$ , while  $\bar{a}$  and  $\bar{b}$  and the virtual MO's will appear as particles with  $\phi_1$  and  $\phi_2$  becoming singly excited determinants. The singlet-triplet energy difference appears as the sum of the diagrams which start from  $\phi_1$  and lead to  $\phi_2$  through two successive interaction lines (eq 8).

$$\left[ \begin{array}{c} \bar{b} \\ \rightarrow \\ \leftarrow \\ b \end{array} \right] \begin{array}{c} \circ \\ \vdots \\ \circ \end{array} \begin{array}{c} \bar{a} \\ \rightarrow \\ \leftarrow \\ a \end{array} \right] \times (-2) = \Delta E^2_{ST} \quad (8)$$

$\phi_1 = |a\bar{b}| \quad |1\rangle \quad -\phi_2 = -|b\bar{a}|$

Among all these processes, previous authors suspected the ionic structures  $a\bar{a}$  or  $b\bar{b}$  (i.e.,  $A^-B^+$  or  $A^+B^-$ ) to play the dominant role, since they are pure singlet orbitals and therefore can only act on the singlet component. The resulting diagrams (Diagram I) give

$$\epsilon^2_{SE} = \frac{4F_{ab}^2}{E_0 - E_{|a\bar{a}|}} = \frac{4F_{ab}^2}{\Delta E_{a \rightarrow b}}$$

where  $F$  is the Fock operator of the system.

This contribution is the so-called super-exchange contribution first invoked by Anderson<sup>29</sup> and extensively discussed by Hoffmann et al.<sup>14</sup> It should be noticed that the numerator may be expressed as the energy splitting between the symmetrical and antisymmetrical MO's

$$2F_{ab} = \langle \sigma_g | F | \sigma_g \rangle - \langle \sigma_u | F | \sigma_u \rangle$$

(23) Mulliken, R. S. *J. Chem. Phys.* **1955**, *23*, 1833-1840.  
 (24) Serafini, A., private communication.  
 (25) Malrieu, J.-P.; Claverie, P.; Diner, S. *Theor. Chim. Acta* **1968**, *8*, 404-423.  
 (26) Malrieu, J.-P.; *J. Chem. Phys.* **1967**, *47*, 4555-4558.  
 (27) Tolmachev, Y. V. "Advances in Chemical Physics"; Prigogine, I. Ed.; Interscience: London, 1969; Vol. XIV, pp 421-71.

(28) Hellmann-Feynman diagrams were used throughout this discussion. However, the nature of the relevant interactions has been explicitated for each diagram. The corresponding formula can be derived from Slater's classical rules. The most compact notation has been used for the determinants, omitting the closed shells which play no role in the process.

Diagram II

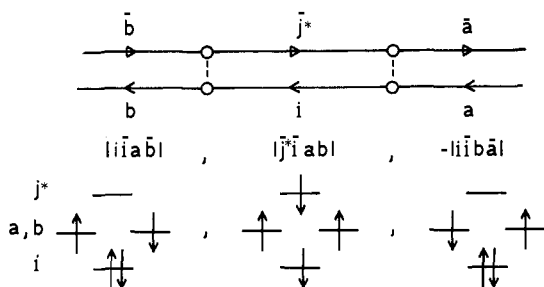
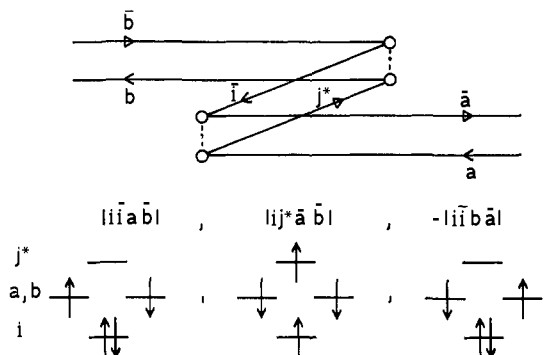


Diagram III



The denominator may be expressed as

$$\Delta E_{a \rightarrow b} \approx -(J_{aa} - J_{ab})$$

where  $J_{aa}$  and  $J_{ab}$  are the electrostatic monocentric and bicentric integrals, respectively.

If the orbitals  $a$  and  $b$  were strictly localized on the Cu atoms, the  $F_{ab}$  integral would be a through-space interaction which would be rather small because of the concentrated character of the  $d$  orbitals. The delocalization tails of the open shells on the ligands may help to enlarge this contribution. One may however notice at this stage that the delocalization on the ligands, which also increases the differential overlap between  $a$  and  $b$ , should increase the magnitude of the  $K_{ab} = (ab, ab)$  exchange integral, which is of the opposite sign.<sup>30</sup>

A more general contribution will arise from all singly excited determinants  $i \rightarrow j^*$ , which, due to spin conditions, must be  $i \rightarrow \bar{j}^*$  excitations from the  $|i i a b|$  reference state; the corresponding determinants are then  $|j^* i a b|$ , with parallel spins ( $S_z = 1$ ) on the Cu atoms and parallel spins ( $S_z = -1$ ) on the ligands (Diagram II).

The contribution from these determinants is

$$-2 \frac{(i b, j^* b)(i a, j^* a)}{\Delta E^3_{ij^*}} = -2 \frac{\langle i | K_b | j^* \rangle \langle j^* | K_a | i \rangle}{\Delta E^3_{ij^*}}$$

where  $K_b$  and  $K_a$  are the exchange operators and  $\Delta E^3_{ij^*}$  is the triplet  $i \rightarrow j^*$  excitation energy in the ligand, with changed signs. (All transition energies will be negative in the forthcoming discussion.)

Of course, one may invoke the opposite coupling between spins ( $S_z = -1$  on the Cu atom pair and  $S_z = +1$  in the previously closed shells), i.e., the  $|j^* i \bar{a} \bar{b}|$  determinants. These determinants, which are obviously degenerate compared with the preceding ones, formally appear as triply excited with respect to the  $|a b|$  ( $S_z = 1$ ) reference state since one has to reverse the two spins on the

Diagram IV

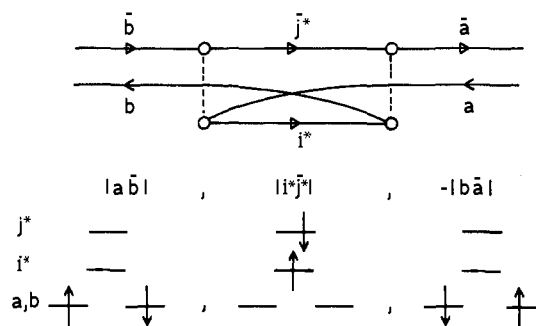
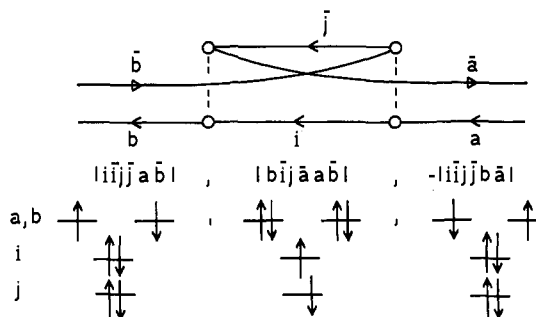


Diagram V



Cu atoms. The corresponding diagram (Diagram III) is obtained by a simple modification of the previous one.

$$\frac{-2 \langle i | K_a | j^* \rangle \langle j^* | K_b | i \rangle}{\Delta E^3_{ij^*}}$$

These processes represent a *double-spin polarization* effect, i.e., a simultaneous flip of the spins on the Cu centers and the spins (with opposite directions) on the ligands (or closed shells of the Cu atoms). In a qualitative mode, this contribution may be understood from the symmetry considerations; the singlet state is antisymmetrical, while the triplet is symmetrical, with respect to spin permutation, and the UHF operator should involve the  $(K_a - K_b)$  operator in the singlet and the  $(K_a + K_b)$  operator in the triplet. The difference in the spin polarization should lead to the above-mentioned differential effect (plus higher order corrections).<sup>31</sup>

The double-spin polarization (DSP) correction is therefore given by eq 9.

$$\epsilon^2_{\text{DSP}} = -4 \sum_i \sum_{j^*} \frac{\langle i | K_a | j^* \rangle \langle j^* | K_b | i \rangle}{\Delta E^3_{ij^*}} \quad (9)$$

We will discuss later on the order of magnitude and symmetry dependence of this DSP contribution.

The doubly excited determinants involve one hole or particle from both states. The following three cases should be distinguished.

(i) |I| involves  $a$  and  $b$  (Diagram IV and eq 10). This contribution represents a simultaneous charge transfer from the Cu atoms to the ligand virtual MO's. It is a correlation effect.

$$\epsilon^2_{(\text{Cu} \rightarrow \text{L})^2} = 2 \sum_{i^*} \sum_{j^*} \frac{(a i^*, b j^*)(a j^*, b i^*)}{\Delta E_{a \rightarrow i^*} + \Delta E_{b \rightarrow j^*}} \quad (10)$$

(29) Anderson, P. W. *Solid State Phys.* **1963**, *14*, 99-214.

(30) Charlot, M. F.; Kahn, O, personal communication. *Proc. Int. Conf. Coord. Chem.* **21th 1980**, 389.

(31) Ginsberg, A. P. *J. Am. Chem. Soc.* **1980**, *102*, 111-117. Ginsberg suggested to calculate UHF wave functions for analogous bimetallic bridged molecules which would allow us to take into account the spin polarization at the SCF level, but the process for the singlet is not clear.

Diagram VI

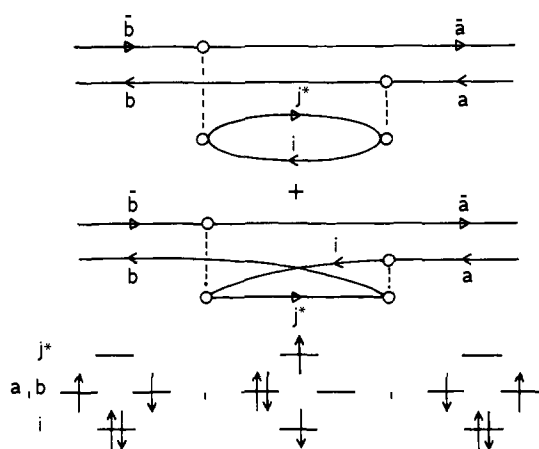
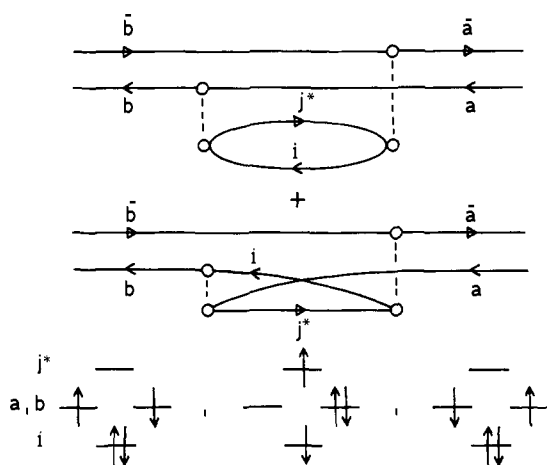


Diagram VII



(ii) |I) involves  $\bar{a}$  and  $\bar{b}$  (Diagram V and eq 11). This contribution represents a simultaneous charge transfer from the ligands (or other closed shells) to the Cu atoms.

$$\epsilon^2_{(L \rightarrow Cu)^2} = 2 \sum_i \sum_j \frac{(ai, bj)(aj, bi)}{\Delta E_{i \rightarrow a} + \Delta E_{j \rightarrow b}} \quad (11)$$

(iii) |I) involves  $a$  and  $\bar{b}$  or  $\bar{a}$  and  $b$  (Diagram VI). In all these diagrams, the intermediate state  $|j^*ia\bar{a}|$  represents a left-right charge transfer between the Cu atoms plus an excitation of the ligand closed-shell subspace (ligands and d orbitals).

One may also consider a  $\beta$ -spin excitation of the closed-shell subspace, i.e., the  $|ij^*a\bar{a}|$  determinant which gives the same contribution and the  $|j^*ibb|$  intermediate determinants, and their  $\beta$ -spin associates (see Diagram VII).

The second-order final contribution of the whole [(Cu  $\rightarrow$  Cu)SE + polarization] process is given by eq 12. The only triply ex-

$$\epsilon^2_{SE+P} = \sum_i \sum_{j^*} \frac{8(ab, ij^*)^2 - 4(ab, ij^*)[(ai, bj^*) + (aj^*, bi)]}{\Delta E_{a \rightarrow b} + \Delta E_{i \rightarrow j^*}} \quad (12)$$

cited-state contribution involved in the energy difference is part of the spin polarization effect already considered when eq 9 was established.

There are not other second-order differential corrections. However, as will be seen later on, the same procedure may be applied to higher orders, at which these excited states play an important role through their interaction with the ionic states  $|a\bar{a}|$  or  $|b\bar{b}|$ . Some important contributions from fourth and higher orders will be presented in the Results.

### 3. Construction of a Convenient Semilocalized MO Basis Set.

The preceding formalism is valid whatever the MO basis set. These MO's may be the canonical symmetry MO's; they may also be localized MO's obtained through the Boys criterion<sup>32</sup> for in-

stance. In this work, an intermediate set has been built which localizes the orbitals on the Cu atoms and keeps delocalized MO's on the ligands, avoiding however the delocalization between the acetate bridges in order to separate the processes inside a given bridge from the processes involving different bridges.

From intuitive grounds, one may divide the molecular orbitals of the system into different sets:  $\alpha$ , the inner-shell localized MO's, which cannot play any role in the problem for reasons of both energetic depth and spatial localization;  $\beta$ , the doubly occupied 3d MO's of the Cu atoms, which were taken to be localized on each atom;  $\gamma$ , the ligand occupied MO's of the acetate bridges, which essentially differ from those of an isolated acetate ligand by the polarization due to the positive Cu centers and by delocalization tails;  $\delta$ , the open-shell 3d<sub>x<sup>2</sup>-y<sup>2</sup></sub>, a and b MO's on each Cu atom.

These four sets represent the occupied MO's. The valence virtual MO's (obtained in a minimal basis set) may be viewed as the following:  $\epsilon$ , the (repolarized) ligand valence virtual MO's;  $\zeta$ , two 4s type atomic orbitals on the Cu atoms.

The same partition could be used for large basis sets which would introduce other virtual MO's; among them the most important ones are those which would allow repolarization and correlation of the electrons in the 3d<sup>8</sup> doubly occupied MO's.

In practice, such a semilocalized MO basis set is obtained through the following procedure.

As already mentioned, the a and b singly occupied d<sub>x<sup>2</sup>-y<sup>2</sup></sub> SCF MO's are obtained through a  $\pi/4$  rotation of the (HOMO-LUMO)  $\sigma_u$  and  $\sigma_g$  symmetry orbitals. This is the  $\delta$  subspace.

The symmetry-adapted (canonical) SCF MO's of an acetate molecule are projected in the space of the doubly occupied SCF MO's of the supermolecule (eq 13).

$$|i'\rangle = \sum_k \langle k|i\rangle |k\rangle \text{ doubly occupied} \quad (13)$$

The same process is possible for each acetate bridge, and these projected MO's are then properly orthogonalized through a  $S^{-1/2}$  procedure; the  $\gamma$  space of SCF MO's is thus obtained and closely resembles the MO's of the isolated ligands. This enables us to analyze the role of various excitation processes within the ligands ( $\sigma$  or  $\pi$  excitations, intra- or interligand processes, ...).

The  $\epsilon$  set of virtual MO's of the ligand is obtained through the same procedure (projection of the virtual SCF MO's of an acetate molecule into the space of an empty SCF MO in the complex).

Localized doubly occupied 3d MO's for the Cu atoms are obtained according to the same (projection + orthogonalization) procedure.

This equivalent MO set is well suited to discuss the order of magnitude of the various contributions and follows the intuitive description of the complex. The use of fully localized MO's would in turn lead to fully localized excitations, and the delocalized character of the excitations in the acetate bridges would be lost; the effect of this delocalization would be shifted to higher orders of perturbation.

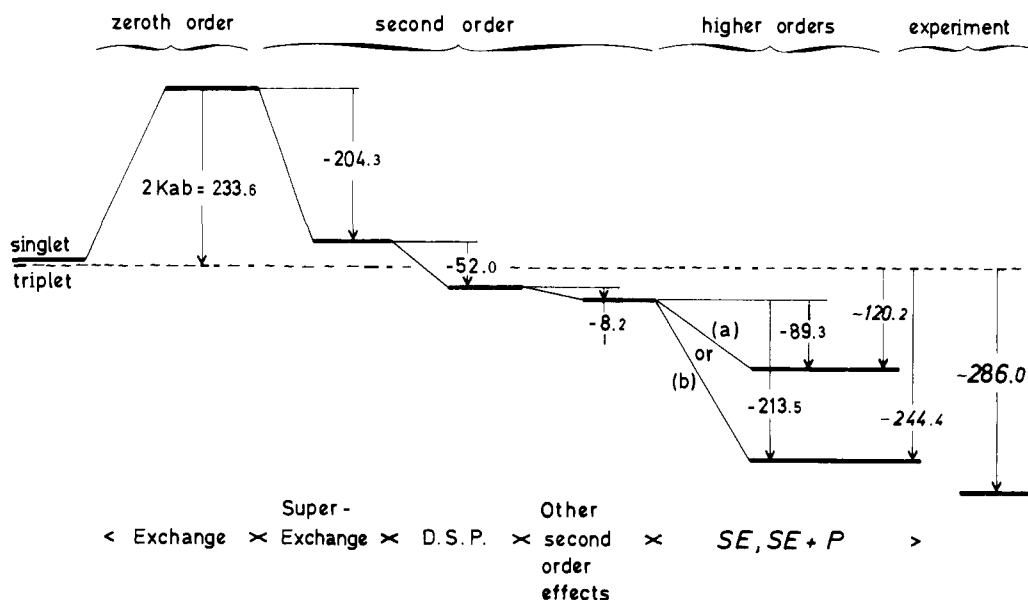
## Results

**1. Exchange and Super-Exchange Contributions.** As already mentioned, the triplet favoring  $2K_{ab}$  exchange integral and the super-exchange singlet favoring mechanism involve the ab differential overlap distribution, i.e., the through-space overlap of the 3d AOs, but the delocalization tails on the ligands (see Table I) enlarge these opposite contributions.

Table III and Figure 2 summarize the various contributions. The exchange integral is far from being negligible, leading to a 233.6-cm<sup>-1</sup> stabilization of the triplet state. This value should be compared with the pure 3d, 3d bicentric exchange integral<sup>33</sup> in order to estimate the role of the tails in the ligand with respect to the through-space exchange. The large value of this exchange integral is in strong contrast with the usual assumption of a

(32) Boys, S. E. "Quantum Theory of Atoms, Molecules and the Solid State"; Lowdin, P. O., Ed.; Academic Press: New York, 1966; p 253.

(33) The bicentric exchange integral between 3d orbitals, neglecting orthogonalization effects, would be 0.52 cm<sup>-1</sup>.



**Figure 2.** Schematic representation of the various contributions to the singlet-triplet energy splitting (in  $\text{cm}^{-1}$ ; the triplet energy is taken at zero at each stage). (a) and (b) are SE, SE + P perturbation methods as described in Table III and in text.

**Table III.** Numerical Values of the Various Contributions to the Singlet-Triplet Energy Splitting (in  $\text{cm}^{-1}$ )

order	contribution	value	total
zeroth order	exchange ( $2K_{ab}$ )	+233.6	
second order	super exchange	-204.3	+29.3 <sup>c</sup>
	DSP	-52.0	-22.7 <sup>c</sup>
	other second-order effects	-8.2	-30.9 <sup>c</sup>
higher order	SE, SE + P	a or b	-89.3 or -120.2 or -213.5 or -244.4 <sup>c</sup>

<sup>a</sup> Infinite summation of diagrams perturbing the neutral state ( $\epsilon_{SE, SE+P}^{\infty}$ ). <sup>b</sup> Diagonalization of an effective second-order perturbed Hamiltonian involving the neutral and ionic states, according to Brandow's QDMPT. <sup>c</sup> Totals.

negligible value ( $\approx 1-50 \text{ cm}^{-1}$ ).<sup>14</sup>

The super-exchange mechanism only compensates the direct exchange and brings almost to zero the singlet-triplet energy splitting: this 204.3- $\text{cm}^{-1}$  effect is also far from being negligible, but the triplet state still remains lower by 29.3  $\text{cm}^{-1}$ . This result is rather disappointing since the most convincing explanations are based on this very mechanism. The near cancellation of exchange and super-exchange contributions is however totally surprising in view of our previous remarks concerning the role of the tails, but it is difficult to ascertain that this is a general feature. One should now notice that the energy denominator of the super-exchange crucial contribution has been calculated exactly, according to the Epstein-Nesbet definition, i.e., as the difference between mean values of the exact hamiltonian

$$\Delta E = 1/2 \langle |a\bar{b} + b\bar{a}| H | |a\bar{b} + b\bar{a} \rangle - \langle |a\bar{a}| H | |a\bar{a} \rangle \quad (14)$$

which appears to be 15.4 eV, in reasonable agreement with the approximate expression proposed by Hoffmann et al.<sup>14</sup>

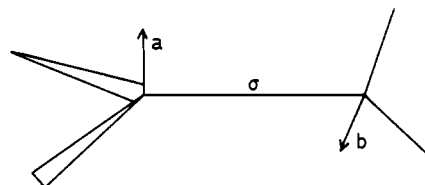
**2. Double-Spin Polarization (DSP) Contributions.** The spin polarization correction involves the  $\langle i|K_a|j^* \rangle \langle j^*|K_b|i \rangle$  product of integrals. The exchange operators are very local, and the  $ij^*$  transition distribution should be important on *both* centers. This means that the doubly occupied 3d MO's of the Cu atoms, which are well localized, cannot contribute to both Cu atoms, which are well localized, cannot contribute to both integrals. The spin polarization of the 3d closed shells may be important but should

not contribute to the S-T energy difference in a significant manner.

On the contrary, the  $ij^*$  transition distributions of the acetate bridges may have important amplitudes in both Cu atoms. They may be divided into intraligand excitations  $i_L \rightarrow j^*_L$  and interligand excitations  $i_L \rightarrow j^*_{L'}$ ,  $L' (\neq L)$  being perpendicular or coplanar to L. Since  $K_a$  is a symmetrical operator with respect to the plane of the acetate bridges, the  $\sigma\pi^*$  or  $\pi\sigma^*$  excitation contributions will be negligible. The  $\pi\pi^*$  excitations have low transition energies, and, therefore, the energy denominators in eq 9 should be small. However, the differential overlap between the  $\pi$  AO's of the oxygen atoms of the ligands and the Cu atoms also are rather small. On the other hand, the  $\sigma$  lone pair of the oxygen atoms strongly overlaps the 3d AO's, but the  $\sigma^*$  antibonding MO's are more remote in space and quite high in energy. It is therefore difficult to predict the relative order of magnitude of the  $\sigma$ - and  $\pi$ -spin polarization contributions.

The main question concerns the sign of this effect. The  $i \rightarrow j^*$  spin polarization contribution will be ferromagnetic if the  $ij^*$  distribution is antisymmetrical (i.e., if  $i$  is symmetrical and  $j^*$  antisymmetrical with respect to the  $(X,Y)$  plane of symmetry perpendicular to the Cu-Cu bond or the reciprocal) and ferromagnetic otherwise. In most cases, the lowest transition energies concern allowed antisymmetric ( $S \rightarrow A$ ) or ( $A \rightarrow S$ ) transitions, and, provided the numerators are equivalent, *the double-spin polarization corrections should in general act in favor of the singlet state*. However, because of the spatial dependence of the numerator integrals, the total DSP effect is a balance of opposite contributions.

One should mention here that the DSP effect is invoked (and dubbed Dynamic spin polarization) for a completely different problem, namely, the singlet-triplet inversion of cyclobutadiene and of the 90° twisted ethylene;<sup>34</sup> in the last case a and b are the perpendicular  $2p_z$  AO's of the carbon atoms.



(34) Borden, W. T. *J. Am. Chem. Soc.* **1975**, *97*, 5968-5970. Kollmar, H.; Staemmler, V. *Ibid.* **1977**, *99*, 3583-3587. Borden, W. T.; Davidson, E. R.; Hart, P. *Ibid.* **1978**, *100*, 388-392. Kollmar, H.; Staemmler, V. *Theor. Chim. Acta* **1978**, *48*, 223-229.

In such a case,  $F_{ab}$  is zero and the super-exchange mechanism cannot explain the lower energy of the singlet. The DSP effect reduces to the antisymmetrical  $\sigma\sigma^*$  valence excitation of the C-C bond, the other excitations being negligible on one center at least.

In our case, there is no such physical concentration of the DSP effect on a single excitation process. This mechanism has been invoked for the cupric acetate hydrate dimer by Kawamori,<sup>17</sup> who tried to estimate the spin density on the oxygen atoms and the  $\pi$ -induced DSP contribution through approximate evaluation of exchange processes on the oxygen atoms. In order to obtain the experimental result, an incredibly low  ${}^3\pi\pi^*$  transition energy (1000  $\text{cm}^{-1}$ ) had to be considered.

When being calculated with relevant  ${}^3\pi\pi^*$  transition energies and without assumptions on the numerator integrals, the lowest  $\pi\pi^*$  process, repeated on the four acetate bridges, gives  $-30.2 \text{ cm}^{-1}$  in favor of the singlet. However, the second symmetrical  $\pi\pi^*$  transition partly compensates ( $5.6 \text{ cm}^{-1}$ ) for this antiferromagnetic contribution.

Other contributions appear from  $\sigma\sigma^*$  excitation processes, involving the  $\sigma$  lone pairs of the oxygen atoms, and the final  $\sigma + \pi$  intraligand DSP contribution is calculated to be  $-41.1 \text{ cm}^{-1}$  in favor of the singlet state. It should be noted at this point that the preceding effects now bring the S-T balance of the right-hand side ( $-11.8 \text{ cm}^{-1}$ ), but one still remains far from the experimental value ( $-286 \text{ cm}^{-1}$ ).

We suspect the interligand DSP excitations  $i_L \rightarrow j^*_L$  ( $L' \neq L$ ) to be negligible. However,  $i_L$  and  $j^*_L$  may both have important components in the Cu centers if they are  $\sigma$ -ligand MO's. Since the  $\pi$  MO's have no tails in the Cu  $d_{x^2-y^2}$  AO's, the  $\pi$  interligand contributions should be negligible. The calculation finally yields a  $-10.9\text{-cm}^{-1}$  value for the overall interligand DSP contribution, which divides into  $-7.8 \text{ cm}^{-1}$  for the perpendicular pairs of ligands ( $\rightarrow$  DSP) and  $-3.1 \text{ cm}^{-1}$  for the opposite pairs of ligands ( $\leftarrow$  DSP, see Table III).<sup>35</sup>

The total DSP contribution is  $-52 \text{ cm}^{-1}$ .

**3. Other Second-Order Contributions.** The other second-order contributions should be much weaker because they involve bicentric integrals, i.e., the interactions between overlap distributions on both Cu centers. This is the case for the  $(a_i, b_j)$  integrals of  $\epsilon^2_{(L \rightarrow \text{Cu})^2}$  or  $(a_i^*, b_j^*)$  integrals appearing in  $\epsilon^2_{(\text{Cu} \rightarrow L)^2}$  (eq 10 and 11). As a matter of fact, the calculated  $\epsilon^2_{(\text{Cu} \rightarrow L)^2}$  is negligible whereas the  $(L \rightarrow \text{Cu})^2$  double transfers from the ligands to the Cu atoms yield a  $-5.9\text{-cm}^{-1}$  value ( $-3.5 \text{ cm}^{-1}$  for the excitations from the same ligand and  $-2.4 \text{ cm}^{-1}$  for the excitations from perpendicular or opposite ligands).

In the same way, the second-order super-exchange and polarization effect, which involves  $(a_i, b_j^*)$  integrals (eq 12) proportional to the  $ab$  overlap, cannot therefore be large,  $-2.2 \text{ cm}^{-1}$ .

One should also try to calculate the  $\text{Cu} \rightarrow \text{Cu}^*$ ,  $\text{Cu} \rightarrow L^*$ , and  $L \rightarrow \text{Cu}^*$  excitations which involve the 3d doubly occupied orbitals in the virtual MO's. The first and third contributions are required to have an appropriate set of 3d atomic orbitals which are not available in our basis set, so these contributions are not calculated.

At this stage, the result is rather disappointing: the second-order corrected singlet-triplet separation is  $-30.9 \text{ cm}^{-1}$ , i.e., approximately 10% of the  $-286\text{-cm}^{-1}$  experimental value. It should however be noted that the  $+233.6\text{-cm}^{-1}$  ferromagnetic direct exchange contribution actually compels the antiferromagnetic contributions to be  $233.6 + 286 = 519.6 \text{ cm}^{-1}$ . The calculated second-order contributions ( $-264.5 \text{ cm}^{-1}$ ) represent half the desired antiferromagnetic correction. The remaining discrepancy may be due to one of the three following defects: the neglect of processes involving closed-shell 3d MO's in the second-order contributions (however, due to their local character, they should not give important bicentric terms); the use of a minimal basis set, especially for the ligands (it is not clear how this would significantly change the above-mentioned contributions and in what direction); the lack of convergence of the perturbation series (this factor is

(35) These values have been calculated by using an approximate Epstein-Nesbet perturbation, where the  $J_{ij}$  integrals are roughly evaluated in order to save computation time; the Moller-Plesset corresponding contribution has been rigorously calculated, giving a  $-9.8 \text{ cm}^{-1}$ , which is comparable.

Diagram VIII

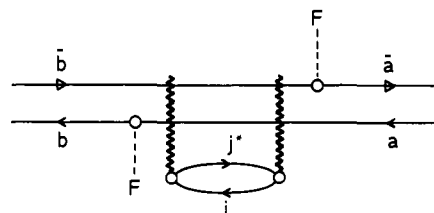


Diagram IX

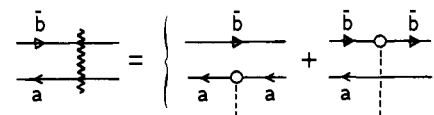
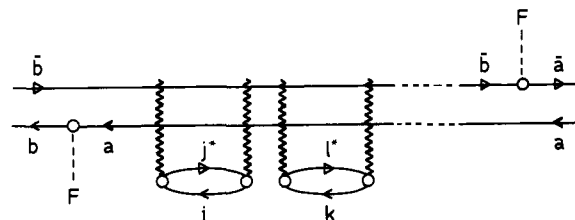


Diagram X



the most likely).

**4. Higher Order Contributions.** Higher order contributions are so numerous that they cannot be calculated in a complete way. Since all high order diagrams are obtained from the second-order ones by inserting additional interactions lines, they necessarily involve  $\langle \phi_1 | H | I \rangle \dots \langle K | H | \phi_2 \rangle$  products and the selected processes are those which involve the determinants having the largest coupling with  $\phi_1$  and  $\phi_2$ . In our case, these are undoubtedly the ionic  $|a\bar{a}\rangle$  and  $|b\bar{b}\rangle$  states leading to super-exchange contributions.

It was already noticed that, with a somewhat smaller transition energy, the super-exchange effect would be larger. The calculated excitation energy  $|a\bar{b}\rangle \rightarrow |a\bar{a}\rangle$  may be overestimated because of the use of doubly occupied MO's of the diradical neutral state for the representation of an ionic state. Nevertheless, the reorganization of these MO's in the ionic states cannot appear as a second-order effect acting on the diradical state; it goes through the interaction between the polarized ionic states such as  $|ij^*a\bar{a}\rangle$  with the ionic determinants  $|i\bar{i}a\bar{a}\rangle$  in a fourth-order contribution

$$\epsilon^4_{SE,SE+P} = \sum \frac{|\langle \text{neutral} | H | \text{ionic} \rangle \langle \text{ionic} | H | \text{ionic polarized} \rangle|^2}{(\Delta E_{\text{neutral} \rightarrow \text{ionic}})^2 (\Delta E_{\text{neutral} \rightarrow \text{ionic polarized}})}$$

This contribution might enter in a second-order correction if (i) the zeroth-order wave function was built as a linear combination of the neutral and ionic determinants or (ii) the problem was treated according to Brandow's quasi-degenerate many-body perturbation theory<sup>36</sup> (see below).

The  $\langle \text{ionic} | H | \text{ionic polarized} \rangle$  matrix elements between the  $|i\bar{i}a\bar{a}\rangle$  and  $|a\bar{a}ij^*\rangle$  determinants is dominated by the strong dipolar field created by the  $A^-B^+$  pair

$$\begin{aligned} \langle i\bar{i}a\bar{a} | H | i\bar{i}j^*a\bar{a} \rangle &= \langle i | F + J_a - J_b + \sigma(K) | j^* \rangle \\ &\simeq \langle i | J_a - J_b | j^* \rangle \end{aligned}$$

where  $\langle i | F | j^* \rangle = 0$  (Brillouin's theorem for the SCF calculation) and  $\sigma(K)$  is a linear combination of exchange operators: each of them giving negligible contributions in comparison with the Coulombic operators  $J_a$  and  $J_b$ .

The fourth-order corresponding diagrams are Diagrams VIII and IX, where the zigzag line represents two matrix elements given in eq 15.

(36) Brandow, B. H. *Rev. Mod. Phys.* **1967**, *39*, 771-828; *Lect. Theor. Phys.* **1968**, *b11*, 55-64.

$$\epsilon_{SE,SE+P}^4 = \sum_i \sum_{j^*} 4 \frac{|(i|J_a - J_b|j^*)F_{ab}|^2}{(\Delta E_{a \rightarrow b})^2 (\Delta E_{a \rightarrow b} + \Delta E_{i \rightarrow j^*})} \quad (15)$$

The factor 4 includes the  $\phi_1/\phi_2$  interchange and the spin interchange.

According to a well-known procedure, one may sum up analogous even-order diagrams which are obtained by inserting several (SE + P) doubly excited states into the basic order diagram of the super-exchange process (Diagram X), and one finds the series

$$4 \frac{F_{ab}^2}{\Delta E_{a \rightarrow b}} [1 + x + x^2 + \dots] = 4 \frac{F_{ab}^2}{\Delta E_{a \rightarrow b} (1 - x)}$$

where  $x = \sum_i \sum_{j^*} 2(i|J_a - J_b|j^*)^2 / \Delta E_{a \rightarrow b} (\Delta E_{a \rightarrow b} + \Delta E_{i \rightarrow j^*})$ .

The final (SE, SE + P) contribution, including the polarization effects of the ionic states at all orders on the super-exchange mechanism, is thus obtained as eq 16.

$$\epsilon_{SE,SE+P}^\infty = 4 \frac{F_{ab}^2}{\Delta E_{a \rightarrow b} - \sum_i \sum_{j^*} \frac{2(i|J_a - J_b|j^*)^2}{\Delta E_{a \rightarrow b} + \Delta E_{i \rightarrow j^*}}} - 4 \frac{F_{ab}^2}{\Delta E_{a \rightarrow b}} \quad (16)$$

The  $i \rightarrow j^*$  polarization excitations essentially belong to two types: polarization of the ligands, which should be excitations in the same ligand  $i_L \rightarrow j^*_L$  in order to have a significant amplitude; polarization of the 3d closed shells on each reionized Cu atom. The polarization of the 3d shell when its occupation number changes is known to be very important (cf. the  $\Delta$ SCF polarization energies for the ionization of the d AO's of a transition metal element,<sup>37,38</sup> which decreases the 3d ionization potential by ca. 7 eV with respect to the ground-state Koopman's values).

The polarization of the ligands may be calculated easily. One may notice that the Coulombic field operator  $J_a - J_b$  is antisymmetrical and the  $ij^*$  transition distribution must be antisymmetrical (optically allowed) to avoid cancellation. In such a case, the following identity holds true.

$$\langle i|J_a - J_b|j^* \rangle = 2 \langle i|J_a|j^* \rangle$$

The corresponding terms have been completely calculated. The double summation resulting from the ligands polarization and appearing in the energy denominator of eq 16 is equal to 2.26 eV, 60% of which is derived from the allowed  $\pi\pi^*$  excitation (i.e., the  $\pi$  polarization). The ligand polarization actually diminishes the transition energy relative to the  $a \rightarrow b$  super-exchange (or charge-transfer) effect from 15.5 to 13.1 eV; this significantly increases the super-exchange effect.

The 3d polarization effect is quite different. The doubly occupied 3d orbitals will contract or expand according to the charge decrease or increase in the  $3d_{x^2-y^2}$  level. In order to evaluate this effect correctly, we should use a more appropriate set of 3d atomic orbitals; our basis set is not chosen accordingly. Moreover, when going from  $3d^9$  to  $3d^8$  or  $3d^{10}$ , the correlation energies of the 3d shells significantly change, which require f orbitals for their calculation to be taken into account. As it was impossible to calculate these 3d shell energy changes through ab initio techniques, we decided to estimate them from experimental spectroscopic values. Remembering that the SCF population resembles a  $d^9s^1$  population (Table II), we tried to compare the two ( $3d^9s^1$ )  $Cu^+$  atoms with a [( $3d^8s^1$ )  $Cu^{2+}$ , ( $3d^{10}s^1$ )  $Cu^0$ ] pair. Figure 3 summarizes the main data taken from atomic tables.<sup>39</sup> (Since, in our problem, the  $d^8$  electrons are in closed shells, the  $^1D$  state has been considered.)

Experiment therefore suggests that when 3d repolarization changes are taken into account, the ( $Cu^{2+}$ ,  $Cu^0$ ) pair is 16.1 eV above the  $2(Cu^+)$  pair. Taking into account the change of the electrostatic interaction for a 2.61-Å interatomic Cu-Cu distance,

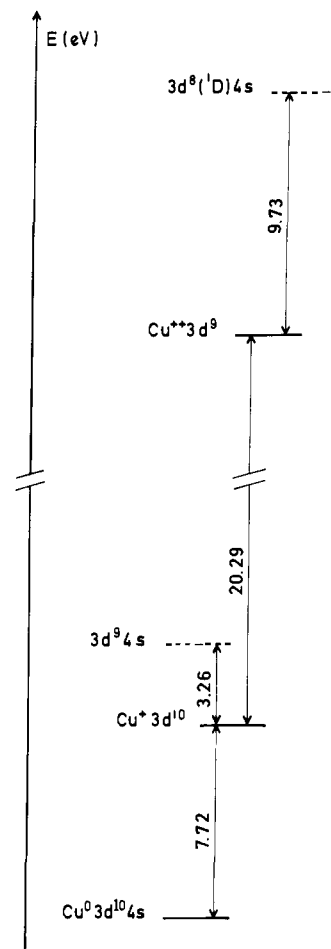


Figure 3. 3d shell energy changes estimated from experimental spectroscopic values.<sup>39</sup>

one obtains a 10.6-eV value for the  $Cu^+ \dots Cu^+ \rightarrow Cu^{2+} \dots Cu^0$  transition energy, instead of the 15.5-eV value which was calculated without 3d repolarization and correlation changes. This means that the 3d shell repolarization and correlation changes decrease the ionic state energy by 4.9 eV.

$$\sum_{ij^*} \frac{|(i|J_a - J_b|j^*)|^2}{\Delta E_{i \rightarrow j^*}} \simeq -4.9 \text{ eV}$$

Moreover, one should notice that in eq 16 the energy denominator is now different, for it consists of  $(\Delta E_{a \rightarrow b} + \Delta E_{i \rightarrow j^*})$ , i.e.,  $15.5 + \Delta E_{i \rightarrow j^*}$ . Since the individual  $\Delta E_{i \rightarrow j^*}$  transition energies are not available, it is impossible to calculate the double summation and we are compelled to give an estimate of the tempered polarization energy of the 3d shells, appearing in eq 16. If we assume that

$$\Delta E_{a \rightarrow b} + \Delta E_{i \rightarrow j^*} \simeq 2\Delta_{ij^*} \text{ (i.e., } \Delta E_{i \rightarrow j^*} \simeq 16.3 \text{ eV)}$$

one then obtains

$$\sum_{ij^* \in d} \frac{|(i|J_a - J_b|j^*)|^2}{\Delta E_{a \rightarrow b} + \Delta E_{i \rightarrow j^*}} \simeq 2.4 \text{ eV}$$

which certainly underestimates this effect.

The final value of the (SE, SE + P) effect, summed to all orders, then becomes

$$\epsilon_{SE,SE+P}^\infty = -89.3 \text{ cm}^{-1}$$

The overall calculated value of the singlet-triplet energy splitting is then (Table III and Figure 2)

$$2K_{ab} + \epsilon_{ST}^2 + \epsilon_{SE,SE+P}^\infty = -120.2 \text{ cm}^{-1}$$

and shows the right sign and the right order of magnitude com-

(37) Hillier, I. H.; Guest, M. F.; Higginson, B. R.; Lloyd, D. R. *Mol. Phys.* **1974**, *27*, 215-223.

(38) Coutière, M. M.; Demuyck, J.; Vellard, A. *Theor. Chim. Acta* **1972**, *27*, 281-287. Demuyck, J.; Vellard, A. *Ibid.* **1973**, *28*, 241-265. Demuyck, J.; Vellard, A.; Wahlgren, U. *J. Am. Chem. Soc.* **1973**, *95*, 5563-5574.

(39) Moore, C. E. *Natl. Bur. Stand. (U.S.) Circ.* **1949**, No. 467.



Diagram XI

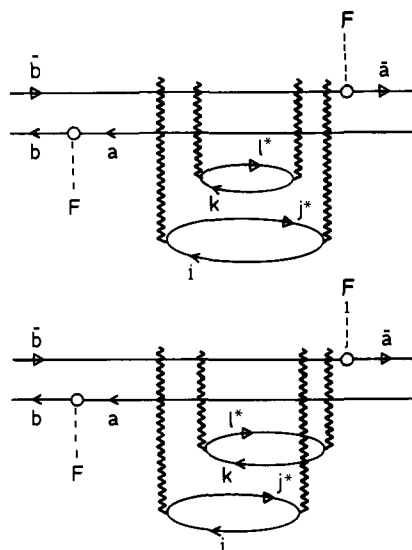
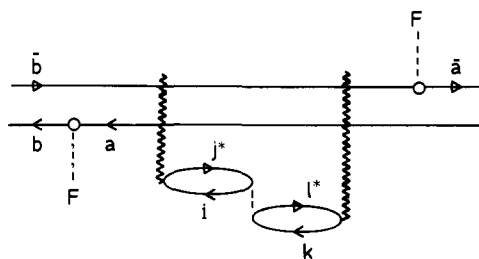


Diagram XII



pared to the  $-286\text{-cm}^{-1}$  experimental value. If one remembers the large value of the ferromagnetic  $2K_{ab}$  contribution ( $+233.6\text{ cm}^{-1}$ ), one sees that we now reach 70% of the total desired antiferromagnetic correction ( $-353.8\text{ cm}^{-1}$  calculated vs.  $-519.6\text{ cm}^{-1}$  experimental).

### Final Discussion

What may be the origin of the still remaining discrepancy with experiment? One may invoke (i) the limitation of the basis set for the various contributions that we explicitly calculated such as the ferromagnetic  $2K_{ab}$  contribution, the double-spin polarization, or the super-exchange + polarization of the ligands and (ii) other higher order effects and/or lack of convergence of our perturbation treatment, although we cannot see any other important specific contribution. Of course, other diagrams may contribute to the antiferromagnetic energy such as those involving simultaneous polarization (Diagram XI).

However, the simultaneous polarizations of said ligands  $L_1$  and  $L_2$  also introduce repulsive effects such as interactions between parallel transition dipoles (see Diagram XII).

The main difficulty certainly concerns the convergence of the perturbation process. The definition of the perturbation expansion of the CI problem is not unique, and different choices of the nonperturbed  $\mathcal{H}_0$  hamiltonian are possible.<sup>40</sup> In the most usual scheme, i.e., the Moller-Plesset one,<sup>41</sup> the energy denominators are differences between the mono-electronic energies of the holes and the energies of the particles. Then, the neutral  $|ab\rangle$  and ionic  $|a\bar{a}\rangle$  determinants are degenerate and should be treated in a multireference state procedure. This can be done in the so-called quasi-degenerate many-body perturbation theory proposed by Brandow,<sup>36</sup> which consists in diagonalizing an effective hamiltonian  $\mathcal{H}^{\text{eff}}$  reduced to the nearly degenerate subspace S, the  $\mathcal{H}^{\text{eff}}_K$  matrix

elements of which are perturbed by the determinants of the complementary subspace.

$$\mathcal{H}^{\text{eff}}_{KL} = \langle K|H|L\rangle + \sum_{I \in S} \frac{\langle K|H|I\rangle \langle I|H|L\rangle}{E^0_K - E^0_I}$$

$$K, L \in S$$

In our problem, the degenerate subspace has to be built from the neutral and ionic determinants  $|ab\rangle$ ,  $|b\bar{a}\rangle$ ,  $|a\bar{a}\rangle$ , and  $|b\bar{b}\rangle$ , or  $(|ab\rangle - |b\bar{a}\rangle)/2^{1/2}$ ,  $(|a\bar{a}\rangle - |b\bar{b}\rangle)/2^{1/2}$ ,  $(|ab\rangle + |b\bar{a}\rangle)/2^{1/2}$ , and  $(|a\bar{a}\rangle + |b\bar{b}\rangle)/2^{1/2}$ , the two last combinations being the only states with the same spin and space symmetry. The  $|a\bar{a}i^*j^*\rangle$  excited states, which are only weakly coupled to the neutral state (cf.  $\epsilon^2_{SE+P}$ ), essentially contribute to the ionic diagonal state

$$\begin{array}{cccc} (|ab\rangle + |b\bar{a}\rangle)/2^{1/2} & (|a\bar{a}\rangle + |b\bar{b}\rangle)/2^{1/2} & |a\bar{a}(i^*j^* + j^*i^*)\rangle/2^{1/2} & \dots \text{ and} \\ E_0 & 2F_{ab} & \delta_{ij^*} & \dots \text{ others} \\ & E_0 + \Delta E_{a \rightarrow b} & h_{ij^*} & \dots \\ & & E_0 + \Delta E_{a \rightarrow b} + & \dots \\ & & \Delta E_{i \rightarrow j^*} & \dots \end{array}$$

where  $\delta_{ij^*} = (ab, ij^*)[2(ab, ij^*) - (ai, bj^*) - (aj^*, bi)]$  and  $h_{ij^*} = \langle i|J_a - J_b|j^*\rangle$ .

This interaction matrix transforms into

$$\begin{array}{c} \Delta E_0 + \frac{\delta^2_{ij^*}}{\epsilon_i - \epsilon_{j^*}} \quad 2F_{ab} - \frac{\delta_{ij^*} h_{ij^*}}{\epsilon_i - \epsilon_{j^*}} \\ \Delta E_0 + \Delta E_{a \rightarrow b} + \frac{h^2_{ij^*}}{\epsilon_i - \epsilon_{j^*}} \end{array}$$

in the second-order MP development of the QDMBPT.

One may neglect  $\delta_{ij^*}$ , and by treating the diagonalization to the second order, one obtains the effect of the SE + P determinants as

$$\epsilon^B_{SE,SE+P} = 4 \frac{F_{ab}^2}{\Delta E_{a \rightarrow b} + \sum_{ij^*} \frac{h^2_{ij^*}}{\epsilon_i - \epsilon_{j^*}}} - \frac{4 F_{ab}^2}{\Delta E_{a \rightarrow b}} \quad (17)$$

which differs significantly from eq 16 by the smaller subdenominator ( $\epsilon_i - \epsilon_{j^*}$  instead of  $\Delta E_{a \rightarrow b} + \Delta E_{i \rightarrow j^*}$ ). The energy of the ionic state is diminished by the whole polarization energy instead of being diminished by a tempered polarization energy.

An attempt to evaluate the ligand polarization energy in the Moller-Plesset perturbation yields a 2.75-eV value. By adding the experimental 5.16-eV value for the 3d polarization energy, one obtains

$$\epsilon^B_{SE,SE+P} = -213.5\text{ cm}^{-1}$$

for the whole (SE,SE + P) Brandow's correction.

The difference between the previously used Rayleigh-Schrödinger perturbation expansion from the neutral states ( $\epsilon^{\infty}_{SE,SE+P}$ ) and the Brandow's QDMBPT expansion ( $\epsilon^B_{SE,SE+P}$ ) illustrates the uncertainties of the convergence of the CI process. We believe that the later process overestimates the super-exchange effect: as a matter of fact, the energy of the ionized state is that of a polarized ionic determinant which no longer interacts with the neutral state through the  $F_{ab}$  integral

$$\langle i|\bar{y}a\bar{a}|H|i\bar{i}(a\bar{b} + b\bar{a})/2^{1/2}\rangle < F_{ab}/2^{1/2}$$

the polarized closed shell MOs being no longer identical.

$$\langle i|i\rangle < 1$$

Nevertheless, we believe that the lack of convergence in the CI process is the main factor for the persisting discrepancy between our calculated value and the experimental value. We would like to insist on the fact that the effect of the polarization of the ionic state does not appear as a polarization effect but as a correlation effect when symmetry representations are used. For instance, if symmetry MO's are used, the two basic closed-shell determinants

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$\sigma_u^2$  and  $\sigma_g^2$  both interact with the  $|ij^*\sigma_u\bar{\sigma}_g|$  determinants

$$\begin{array}{l}
 \bar{i}\bar{i}\sigma_u\sigma_u \quad \bar{i}\bar{i}\sigma_g\sigma_g \quad ij^*\sigma_g\sigma_u \dots \\
 E \quad \quad K\sigma_g\sigma_u \quad (ij^*,\sigma_g\sigma_u) \\
 \quad \quad \quad E' (\approx E) \quad (ij^*,\sigma_g\sigma_u) + \text{exchange} \\
 \quad \quad \quad \quad \quad \quad E + \Delta E_{ij^*}
 \end{array}$$

where  $(ij^*,\sigma_g\sigma_u) = (i|J_a - J_b|j^*)/2$ , since  $\sigma_g\sigma_u \approx (a\bar{a} - b\bar{b})/2$  and exchange is negligible. One finds the same corrections as previously described but now through double-excitation processes; this clearly reflects the correlation nature of this effect. This subtle interchange of the same physical effect from singly to doubly excited determinants, when going from a localized to delocalized scheme, is well-known for other problems such as the ESCA ionization processes in symmetrical molecules.<sup>42,43</sup>

### Conclusion

The singlet-triplet splitting in cupric acetate hydrate dimer has been calculated at the ab initio level, allowing one to reach firmer conclusions in an area which has only received qualitative or semiempirical treatments.

The difficulty lies in the smallness of the calculated quantity ( $10^{-7}$  times the total electronic energy).

To reach the desired accuracy, we used a differential many-body perturbation expansion which gives the energy difference directly. The S-T separation appears to result from four essential contributions.

(1) The ferromagnetic contribution  $2K_{ab}$  is far from being negligible ( $\sim 200 \text{ cm}^{-1}$ ); certainly it is not a direct through-space exchange between the 3d AO's, but it goes through the tails on the ligands.

(2) The direct Anderson-Hoffmann super-exchange mechanism, i.e., the mixture of the diradical singlet state with ionic states, only cancels this ferromagnetic contribution. It certainly also goes through the delocalization on the ligands.

(3) The double-spin polarization is far from being negligible ( $\sim 50 \text{ cm}^{-1}$ ); it is obtained through the product of the effect of two local exchange operators  $K_a$  and  $K_b$  on the  $ij^*$  transition distribution of the ligands and is therefore essentially independent on the Cu...Cu distance; it mainly depends on the electronic structure of the ligand and will strongly stabilize the singlet if the ligands possess dipole-allowed low-energy  $ij^*$  transition with

high amplitudes near the metal atoms.

(4) The direct super-exchange effect is in practice doubled by the correlated motion of the electrons in the ligands and in the d shells. The  $3d_{x^2-y^2} (a) \rightarrow 3d_{x^2-y^2} (b)$  electron jump is partly followed by a reverse left-right motion of electrons in the ligands, a contraction of the 3d closed shell of the donor atom, and an expansion of the 3d closed shell of the acceptor atom. The 3d closed-shell repolarization simply depends on the nature of the metal atom and may be mimicked through a simple diminution of the energy of the ionic state in the SE neutral-ionic interaction. The polarization of the ligand accompanying the Cu-Cu charge transfer essentially depends on the electronic properties of the ligands, especially their longitudinal polarizability.

This approximate repartition of the S-T splitting among the above-mentioned contributions may be questioned from several grounds.

(i) The basis set is minimal and larger basis sets might provide for instance a somewhat smaller value of  $2K_{ab}$ .

(ii) There is some arbitrariness in the choice of our semilocalized SCF MO's; the use of different equivalent sets (for instance, canonical MO's) would be worthwhile to assess the stability of the various contributions.

(iii) Some efforts remain to be made to study the convergence behavior of the perturbation expansion, the role of higher excited states to include simultaneous polarization effects. It is clear that we may have chosen a definition of our perturbation process which would have given an apparent good numerical agreement with experiment; we preferred to show the remaining uncertainties of the CI expansion.

Nevertheless, we think that the present analysis may help experimentalists to understand, even through qualitative schemes, the magnetic properties of such complexes. The major conclusions, which will be of interest to chemists even though they might look distressing, are that among the different mechanisms previously suggested as exclusive explanations for the S-T separation, several of them are in fact of qualitative significance. We hardly think that the above-mentioned sources of error could change the distribution of the various contributions to such an extent that this fundamental conclusion would be reversed.

**Acknowledgment.** This work was supported by the CNRS and the calculations were performed at the CIRCE Computing Center (Orsay, France). We wish to thank O. Kahn who originally directed our attention to this problem. We are also indebted to A. Serafini for his help at the SCF calculation level and for writing the (IJ,KL) program and to M. Pelissier for discussion on various aspects of this work.

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