Effect of Polar States on Superexchange Interaction. Application to Some Dimeric Copper (II) Complexes and to $CuCl_2 \cdot 2H_2O$ Linear Chain

G. Amoretti

Gruppo Nazionale di Struttura della Materia del C.N.R., Istituto di Fisica dell'Università, Parma, Italy

The effect of polar states on the superexchange interaction between two identical spin 1/2 magnetic ions is examined. The one-body potential contributions to the effective exchange constant J_{eff} are written in terms of the splitting $2\Delta_0$ between the bonding and antibonding single particle lower-states of the dimeric complex. Moreover, the energies of the basis triplet and singlet states are obtained in an approximated form as functions of Δ_0 and of two-body molecular integrals. The resulting J_{eff}, that is the splitting between the lowest singlet and the triplet, differs from that of the pure Heitler-London treatment owing to the ionic contributions to the singlet wavefunction. The theory is applied to some dimeric copper (II) complexes and to $CuCl_2 \cdot 2H_2O$ linear chain. It is shown that the polar state corrections are generally small, but that they may become important in the case of copper chlorine, where the various contributions to the Heitler-London exchange constant tend to balance each other to give a very small value. Moreover, antiferromagnetic coupling for $CuCl_2 \cdot 2H_2O$ is accounted for on the basis of a σ-ground state for the single unit, rather than a π one. The conditions to fit the experimental value of J_{eff} are also discussed.

Introduction

In a recent paper [1] the singlet-triplet splitting due to superexchange interactions in some dimeric copper(II) complexes was calculated following a generalized Heitler-London procedure [2].

In fact, the whole ground state LCAO-MO wavefunction of the single complex ion was used to build up the Heitler-London singlet and triplet states. Therefore the effective exchange integral resulted from the contribution of the following terms:

(i) two-body exchange integral

$$J_2 = \langle \psi_0^a(1)\, \psi_0^b(2)|\, r_{12}^{-1}\, |\psi_0^a(2)\, \psi_0^b(1)\rangle, \qquad (1\,a)$$

(ii) two-body coulomb integral

$$C_2 = \langle \psi_0^a(1)\, \psi_0^b(2)|\, r_{12}^{-1}\, |\psi_0^a(1)\, \psi_0^b(2)\rangle, \qquad (1\,b)$$

(iii) one-body exchange integral

$$J_1 = 2\,S\langle \psi_0^a(1)|\, [V_{Cu}^a(1) + \sum_{\{a\}}{}' V_{lig}^a(1)]\, |\psi_0^b(1)\rangle, \qquad (1\,c)$$

(iiii) one-body coulomb integral

$$C_1 = 2\langle \psi_0^b(1)|\, [V_{Cu}^a(1) + \sum_{\{a\}}{}' V_{lig}^a(1)]\, |\psi_0^b(1)\rangle, \qquad (1\,d)$$

where

$$S = \langle \psi_0^a(1)\, |\, \psi_0^b(1)\rangle . \qquad (1\,e)$$

(1), (2) is a short notation for $(\boldsymbol{r}_1)$, $(\boldsymbol{r}_2)$. The sum appearing in the one-body potential expression is extended to all the ligands of unit a, except the ligands common to the two units, to avoid counting twice their contributions to the total hamiltonian [2]. As in Ref. [1] V_{Cu}^a and V_{lig}^a will be approximated in the following as $-Z_{eff}^{Cu}/r_a$ and $-Z_{eff}^{lig}/r_{lig}$ respectively.

The expression of the exchange constant in Heitler-London approximation was:

$$J_{eff}^{H-L} = J_2 - C_2\,S^2 + J_1 - C_1\,S^2 . \qquad (2)$$

The main problems in performing the calculation were, on one side, the knowledge of the covalence parameters appearing in the ground state wavefunction and the value of the effective charge Z_{eff}^{Cu} and, on the other side, the evaluation of many multicenter one- and two-body molecular integrals contributing to J_{eff}^{H-L}. In the case of the quoted compounds the knowledge of the ground state was obtained from the comparison of the theory outlined in Ref. [2] with EPR measurements [3].

As regards Z_{eff}^{Cu}, it was pointed out [1] that the best value is the pure ionic value $Z_{eff}^{Cu} = +3$, because by considering all the contributions deriving from electron delocalization one avoids to deal with screening factors due to the presence of the ligands [4].

The computation of the molecular integrals was performed in the charge-cloud approximation

scheme for the multi-center integrals, while the most important one- and two-center integrals were directly calculated. In such a way a correct estimation of the four contributions to J_{eff}^{H-L} was possible, without entering into unnecessary more detailed calculations.

In the present work polar functions are introduced into the Heitler-London set and their effect on the evaluation of the superexchange constant is examined for the case of the compounds quoted in Ref. [1] and moreover for the case of $CuCl_2 \cdot 2H_2O$. This last compound is a dilute magnetic insulator, in which the most relevant interaction is antiferromagnetic spin coupling, with $J_{eff} = -4.71$ cm^{-1} [5], along a linear chain of spin $\frac{1}{2}$ Cu^{2+} complex ions [6]. To perform the calculation of J_{eff}, it is possible to consider a single pair of ions only [7], which has the same geometrical arrangement as in the other dimeric copper compounds. To take into account polar states is equivalent to treat the problem of spin coupling from an alternative point of view [8]. That is, one starts from the energy level scheme corresponding to the one electron (or hole) states of the whole dimeric molecule, and then one builds up all possible singlet and triplet states due to the presence of two particles in the bonding and antibonding lower states (see Figure 1). Diagonalization into this manifold shows [8] that the resulting lower energy states are similar to the Heitler-London ones, except for a mixing with polar states.
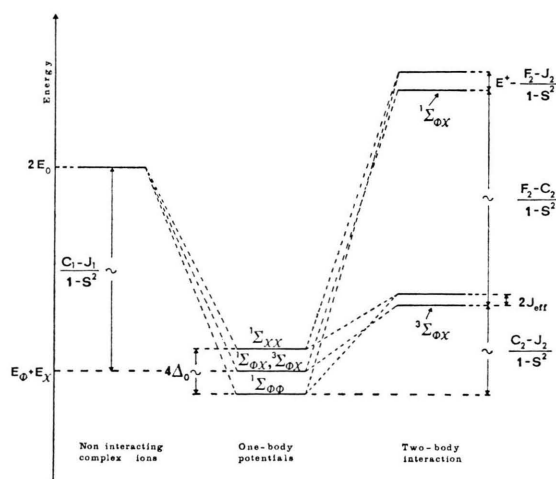
Van Dalen [9] applied such a theory to the study of superexchange in $CuCl_2 \cdot 2H_2O$, starting from a π-ground state for the single ion. He neglected in this case the one-body contributions, which are related to the splitting $2\Delta_0$ between bonding and antibonding one electron lower states [10].

The present treatment takes into account these terms also, which are very important in most cases for a correct interpretation of the exchange mechanism.

One of the aims of this work is to point out that, in the case of small overlap, as for the compounds considered here, generally ionic states give only small corrections to the Heitler-London results. Such corrections, however, may become important in particular cases, e.g. $CuCl_2 \cdot 2H_2O$, where the net exchange interaction is small.

Another purpose is to confirm that with relatively simple computation methods it is possible to account for the correct sign of J_{eff} and its numerical value also. Therefore, one may decide on the form of the single ion ground state. For example, it may be shown that for $CuCl_2 \cdot 2H_2O$, the σ-ground state deduced by Buluggiu et al. [11] from EPR measurements accounts for the correct value of the exchange constant, contrarily to the π-state calculated by Van Dalen et al. [9] following a LCAO-MO treatment.

In Section 1 of this paper the theory about the introduction of polar states is recalled and adapted to the present case. The connection between the parameter Δ_0 and the one-body integrals is shown. The expression of J_{eff}^{H-L} is thus rewritten in terms of Δ_0 and compared with an approximated analitical solution of the secular equation. Such a solution is very similar to that quoted in Ref. [9], but generalized to take into account the one-body potentials.

In Section 2 the theory is applied to the dimeric copper (II) compounds [1].

In Section 3 the case of $CuCl_2 \cdot 2H_2O$ is examined. The principal aspects of calculation in both cases of π- and σ-ground states are pointed out.

In Section 4 a comparative discussion of the results is given. The most important molecular integrals and parameters used are listed in Appendix.

1. Theory

The single complex ion one particle hamiltonian can be written, disregarding spin-orbit interaction,

Fig. 1. Energy level scheme for a system of two interacting spin 1/2 complex ions. Ferromagnetic coupling case.

unessential for isotropic exchange calculation [1, 2], as

$$\mathscr{H}_0^{a,b}(\boldsymbol{r}) = \frac{p^2}{2\,m} + V_{Cu}^{a,b}(\boldsymbol{r}) + \sum_{\{a\},\{b\}} V_{lig}^{a,b}(\boldsymbol{r})\,, \quad (3)$$

where superscripts a and b refer to the two different units in the dimer and the sums are extended to all ligands of a single unit.

The ground state of this hamiltonian is $\psi_0^{a,b}(\boldsymbol{r})$ and belongs to the eigenvalue E_0.

The hamiltonian of the two interacting particles is

$$\mathscr{H}(1,2) = \mathscr{H}(1) + \mathscr{H}(2) + r_{12}^{-1}\,, \quad (4)$$

with

$$\mathscr{H}(1) = \mathscr{H}_0^a(1) + V_{Cu}^b(1) + \sum_{\{b\}}' V_{lig}^b(1)\,,$$
$$\mathscr{H}(2) = \mathscr{H}_0^b(2) + V_{Cu}^a(2) + \sum_{\{a\}}' V_{lig}^a(2)\,. \quad (5)$$

It is clear that $\mathscr{H}(1)$ and $\mathscr{H}(2)$ have the same form and represent the hamiltonian of a single particle moving in the whole dimeric complex.

The approximated eigenstates of the hamiltonians (5), corresponding to the single unit ground state, may be written in the form of bonding and anti-bonding wavefunctions, that is

$$\Phi_0(i) = \frac{1}{\sqrt{2(1+S)}}\,[\psi_0^a(i) + \psi_0^b(i)]\,,$$
$$X_0(i) = \frac{1}{\sqrt{2(1-S)}}\,[\psi_0^a(i) - \psi_0^b(i)]\,,$$
$$i = 1,2\,. \quad (6)$$

The eigenvalues, which these states belong to, are (see also Fig. 1)

$$E_\Phi = E_0 + K_0 - \Delta_0\,,$$
$$E_X = E_0 + K_0 + \Delta_0 \quad (7)$$

where

$$K_0 = \frac{1}{2}\,\frac{C_1 - J_1}{1 - S^2}\,, \quad (8)$$

$$\Delta_0 = \frac{1}{2}\left[\frac{(C_1 - J_1)\,S}{1 - S^2} - \frac{J_1}{S}\right]\,. \quad (9)$$

The coulomb and exchange one-particle integrals are the same as in (1).

The problem of finding the lower eigenstates of the two particles hamiltonian (4) may be appro-

ached, as usual, considering the six determinantal states corresponding to all possible ways to assign two electrons (with their spins) to the states Φ_0 and X_0. As is known, they may be written as triplet and singlets wavefunctions in the following way:

$$^1\Sigma_{\Phi\Phi}: \frac{1}{2(1+S)}\,\{[\psi_0^a(1)\,\psi_0^a(2) + \psi_0^b(1)\,\psi_0^b(2)]$$
$$+ [\psi_0^a(1)\,\psi_0^b(2) + \psi_0^b(1)\,\psi_0^a(2)]\}$$
$$\cdot \frac{1}{\sqrt{2}}\,[\alpha(1)\,\beta(2) - \beta(1)\,\alpha(2)]\,, \quad (10a)$$

$$^3\Sigma_{\Phi X}^{1,0,-1}: \frac{1}{\sqrt{2(1-S^2)}}\,[\psi_0^a(1)\,\psi_0^b(2) - \psi_0^b(1)\,\psi_0^a(2)]$$
$$\cdot \begin{cases} \alpha(1)\,\alpha(2) \\ \dfrac{1}{\sqrt{2}}\,[\alpha(1)\,\beta(2) + \beta(1)\,\alpha(2)]\,, \quad (10b) \\ \beta(1)\,\beta(2) \end{cases}$$

$$^1\Sigma_{\Phi X}: \frac{1}{\sqrt{2(1-S^2)}}\,[\psi_0^a(1)\,\psi_0^a(2) - \psi_0^b(1)\,\psi_0^b(2)]$$
$$\cdot \frac{1}{\sqrt{2}}\,[\alpha(1)\,\beta(2) - \beta(1)\,\alpha(2)]\,, \quad (10c)$$

$$^1\Sigma_{XX}: \frac{1}{2(1-S)}\,\{[\psi_0^a(1)\,\psi_0^a(2) + \psi_0^b(1)\,\psi_0^b(2)]$$
$$- [\psi_0^a(1)\,\psi_0^b(2) + \psi_0^b(1)\,\psi_0^a(2)]\}$$
$$\cdot \frac{1}{\sqrt{2}}\,[\alpha(1)\,\beta(2) - \beta(1)\,\alpha(2)]\,. \quad (10d)$$

$\alpha(i)$ and $\beta(i)$ are the usual spin $1/2$ functions for particle i. It may be noted that the triplet state is identical to that of the Heitler-London scheme, while the singlet ones contain ionic contributions, as $\psi_0^a(1)\,\psi_0^a(2)$. In the following it will be clear, however, that, introducing the particle-particle interaction and diagonalizing the energy matrix in the subspace spanned by these six states, one of the resulting singlets can be written as the Heitler-London one plus a correction (very small in our cases) due to polar functions.

Such a matrix, built up taking matrix elements of hamiltonian (4) between the states (10), has the form

	$^1\Sigma_{\Phi\Phi}$	$^3\Sigma^1_{\Phi X}$	$^3\Sigma^0_{\Phi X}$	$^3\Sigma^{-1}_{\Phi X}$	$^1\Sigma_{\Phi X}$	$^1\Sigma_{XX}$
$^1\Sigma_{\Phi\Phi}$	$-2\Delta_0 + \dfrac{F_2+C_2+2J_2+4M_2}{2(1+S)^2}$	0	0	0	0	$\dfrac{F_2-C_2}{2(1-S^2)}$
$^3\Sigma^1_{\Phi X}$	0	$\dfrac{C_2-J_2}{1-S^2}$	0	0	0	0
$^3\Sigma^0_{\Phi X}$	0	0	$\dfrac{C_2-J_2}{1-S^2}$	0	0	0
$^3\Sigma^{-1}_{\Phi X}$	0	0	0	$\dfrac{C_2-J_2}{1-S^2}$	0	0
$^1\Sigma_{\Phi X}$	0	0	0	0	$\dfrac{F_2-J_2}{1-S^2}$	0
$^1\Sigma_{XX}$	$\dfrac{F_2-C_2}{2(1-S^2)}$	0	0	0	0	$2\Delta_0 + \dfrac{F_2+C_2+2J_2-4M_2}{2(1-S)^2}$

$$(11)$$

The two-body integrals F_2 and M_2 are defined as

$$F_2 = \langle \psi_0^a(1)\,\psi_0^a(2)|\, r_{12}^{-1}\, |\psi_0^a(1)\,\psi_0^a(2)\rangle\,, \qquad (12\,a)$$

$$M_2 = \langle \psi_0^a(1)\,\psi_0^a(2)|\, r_{12}^{-1}\, |\psi_0^a(1)\,\psi_0^b(2)\rangle\,. \qquad (12\,b)$$

The diagonal common term $2E_0 + 2K_0$ has been dropped because it plays no role in the calculation of J_{eff}.

Matrix (11) is very similar to that used in Ref. [9], apart from the presence of Δ_0 in the 2×2 block which must be diagonalized. Nevertheless, it may be put into the same form if one substitutes for J_2 and M_2 the renormalized parameters

$$J' = J_2 - 4\Delta_0 S\,, \qquad (13\,a)$$

$$M' = M_2 - \Delta_0(1 + S^2)\,. \qquad (13\,b)$$

In this way, the diagonalization problem is reduced to solving the equation

$$E^2 - \frac{(F_2+C_2+2J')(1+S^2)-8S\,M'}{(1-S^2)^2}$$
$$\cdot E - \frac{(F_2+J')(C_2+J')-4\,M'^2}{(1-S^2)^2} = 0\,. \quad (14)$$

In Sections 2 and 3 J_{eff} is computed solving exactly Eq. (14), but its value is practically identical to that obtained from the following approximated solution, valid for $S \ll 1$, which leads to a compact expression for J_{eff} in terms of the molecular integrals:

$$E^+ = F_2 + J' - 4\,M'\,S + 2\,F_2\,S^2 + C_2\,S^2$$
$$+ 4\,\frac{\left[M' - \dfrac{(F_2+C_2)\,S}{2}\right]^2}{F_2 - C_2}\,, \qquad (15\,a)$$

$$E^- = C_2 + J' - 4\,M'\,S + F_2\,S^2 + 2\,C_2\,S^2$$
$$- 4\,\frac{\left[M' - \dfrac{(F_2+C_2)\,S}{2}\right]^2}{F_2 - C_2}\,. \qquad (15\,b)$$

The superscripts $^+$ and $^-$ refer to the signs of the square root appearing in the solution of (14).

The resulting level scheme is shown in Fig. 1 in a typical case of ferromagnetic coupling. The lower states are a singlet, corresponding to the eigenvalue E^-, and the triplet $^3\Sigma_{\Phi X}$. They are separated by an energy splitting defined as $2J_{\text{eff}}$, while the first excited singlet is higher in energy, namely $(F_2-C_2)/(1-S^2)$ above the triplet. It may be noted that, if $(F_2 - C_2) \gg 2J_{\text{eff}}$ the situation is very similar to that of the Heitler-London theory.

From (11) and (15) one obtains, therefore, the expression for the exchange constant:

$$J_{\text{eff}} = J_2 - C_2\,S^2 - 2\Delta_0\,S$$
$$- \frac{2}{F_2-C_2}\,(C_2\,S - M')^2\,. \qquad (16)$$

It may be shown from (9) that the expression (2) for $J_{\text{eff}}^{\text{H-L}}$ is equivalent to [12]

$$J_{\text{eff}}^{\text{H-L}} = J_2 - C_2\,S^2 - 2\Delta_0\,S\,; \qquad (17)$$

so the difference ΔJ between J_{eff} and $J_{\text{eff}}^{\text{H-L}}$ is given by

$$\Delta J = - \frac{2}{F_2-C_2}\,(C_2\,S - M')^2\,. \qquad (18)$$

This formula shows that the correction to $J_{\text{eff}}^{\text{H-L}}$ due to the presence of ionic configurations is always negative, thus supporting antiferromagnetic behaviour.

As regards the eigenstates $\psi^{+,-}(1, 2)$ belonging to E^+ and E^-, they are written as a normalized linear combination of the basis singlets, with coefficients $a_{\Phi\Phi}^{+,-}$ and $a_{XX}^{+,-}$ respectively, given by

$$a_{\Phi\Phi}^{+,-} = \sqrt{\frac{(E^{+,-} - H_{66})^2}{H_{16}^2 + (E^{+,-} - H_{66})^2}}, \qquad (19\,\mathrm{a})$$

$$a_{XX}^{+,-} = \frac{H_{16}}{E^{+,-} - H_{66}} a_{\Phi\Phi}^{+,-}, \qquad (19\,\mathrm{b})$$

where H_{ij} refers to the elements of matrix (11). It is evident that these states may be written in a more suitable form, that is a normalized combination of the following wavefunctions (disregarding the spin part):

$$\psi_{\mathrm{HL}}(1, 2) = \frac{1}{\sqrt{2(1 + S^2)}} [\psi_0^{\mathrm{a}}(1)\, \psi_0^{\mathrm{b}}(2) + \psi_0^{\mathrm{b}}(1)\, \psi_0^{\mathrm{a}}(2)],$$
$$(20\,\mathrm{a})$$

$$\psi_{\mathrm{PS}}(1, 2) = \frac{1}{\sqrt{2(1 + S^2)}} [\psi_0^{\mathrm{a}}(1)\, \psi_0^{\mathrm{a}}(2) + \psi_0^{\mathrm{b}}(1)\, \psi_0^{\mathrm{b}}(2)],$$
$$(20\,\mathrm{b})$$

which are the Heitler-London singlet and a combination of polar states respectively.

Therefore

$$\psi^{+,-}(1, 2) = b_{\mathrm{HL}}^{+,-} \psi_{\mathrm{HL}}(1, 2) + b_{\mathrm{PS}}^{+,-} \psi_{\mathrm{PS}}(1, 2) \qquad (21)$$

with

$$b_{\mathrm{HL}}^{+,-} = \frac{\sqrt{2(1 + S^2)}}{2(1 - S^2)} [a_{\Phi\Phi}^{+,-} - a_{XX}^{+,-} - (a_{\Phi\Phi}^{+,-} + a_{XX}^{+,-})\, S],$$
$$(22\,\mathrm{a})$$

$$b_{\mathrm{PS}}^{+,-} = \frac{\sqrt{2(1 + S^2)}}{2(1 - S^2)} [a_{\Phi\Phi}^{+,-} + a_{XX}^{+,-} - (a_{\Phi\Phi}^{+,-} - a_{XX}^{+,-})\, S].$$
$$(22\,\mathrm{b})$$

The calculation of these coefficients (see sections 2. and 3.) confirms that the lowest singlet, corresponding to the minus sign, is practically a Heitler-London singlet with a small contribution of the ionic states. The contrary occurs for the most excited singlet.

2. Numerical Calculation for Some Dimeric Cooper (II) Complexes

The compounds under consideration are

$$[\mathrm{Cu\,(aebg)\,(C_2H_4N_4)}]\,\mathrm{SO_4 \cdot H_2O},$$

$[\mathrm{Cu\,(aebg)\,(NCS)}]\,(\mathrm{SCN})$ and $[\mathrm{Cu(NH_3)_2\,C_8H_4O_4}]$, which are shortly referred as (N_1), (N_2) and (O), respectively, to bear in mind the nature of the ligands bridging the magnetic ions. The structure of such complexes is similar to that sketched in Figure 2. In (N_1) and (N_2) the ligands are all N atoms, while in (O) the ligands 2, 3, 7, 8 are N atoms and the others are O atoms. The distances d_x, d_y and d_z are listed in the Appendix.

In Table 1a the calculated values of J_{eff} and $J_{\mathrm{eff}}^{\mathrm{H-L}}$ for the three compounds both for Slater and Clementi wavefunctions are shown toghether with the single terms of (2) and the overlap integral S. The details of calculation for S and for one- and two-body exchange and coulomb integrals were outlined in Ref. [1]. In Table 1b the parameters more strictly related to the introduction of polar states, that is M_2, M', J', b_{PS}^-, the splittings $2\Delta_0$ and $(F_2 - C_2)/(1 - S^2)$, are shown.

For F_2 the pure ionic value 0.942 a.u. of $\mathrm{Cu^+}$ has been used [9]. M_2 has been approximated as the product of S and the potential of particle 1, on side a, at the middle point of the line a—b: that is $M_2 \simeq 2\,S/R_{\mathrm{ab}}$. Such approximations are consistent with those used in calculating some other contributions the J_{eff}. In fact, to disregard the electron delocalization and to use the charge cloud approximation leads to an inaccuracy of only a few percent [1].

As regards the dependence of J_{eff} on the hybridization parameter n^2, which measures the p character of the common ligands wavefunctions for differ-

Table 1a. Values of J_{eff} and $J_{\mathrm{eff}}^{\mathrm{H-L}}$ (in cm^{-1}), of overlap S and of the various contributions to $J_{\mathrm{eff}}^{\mathrm{H-L}}$, for the three compounds (N_1), (N_2) and (O), both for Slater and Clementi wavefunctions.

|		$S \cdot 10^2$	J_1	J_2	$-C_1 S^2$	$-C_2 S^2$	$J_{\mathrm{eff}}^{\mathrm{H-L}}$	J_{eff}
N_1	Slater	0.893	−24.15	26.29	14.69	−2.38	14.45	13.87
	Clementi	0.933	−24.36	21.99	16.17	−2.63	11.17	10.98
N_2	Slater	0.886	−24.36	26.24	14.84	−2.41	14.31	13.69
	Clementi	0.886	−22.10	20.50	14.92	−2.43	10.89	10.77
O	Slater	0.686	−19.15	18.53	10.28	−1.64	8.02	6.48
	Clementi	0.748	−20.53	17.11	12.28	−1.97	6.89	6.21

Table 1b. Values of M_2, M', J', $2\Delta_0$ and $(F_2 - C_2)/(1 - S^2)$ (in cm^{-1}) and of the coefficient b_{Ps}^- in the same cases as in Table 1a.

		M_2	M'	J'	$2\Delta_0$	$\dfrac{F_2 - C_2}{1 - S^2}$	$b_{\mathrm{Ps}}^- \cdot 10^2$
N_1	Slater	570.8	41.4	7.38	1058.8	176904.1	0.2552
	Clementi	596.4	157.3	5.61	878.1	176525.4	0.1419
N_2	Slater	578.4	40.9	7.19	1074.9	176053.8	0.2631
	Clementi	579.7	174.4	6.14	810.5	175783.8	0.1143
O	Slater	522.6	-123.7	0.80	1292.5	171858.1	0.4228
	Clementi	575.2	24.0	0.62	1102.3	171528.3	0.2802

ent values of the effective charge $Z_{\mathrm{eff}}^{\mathrm{Cu}}$ of the Cu^{2+} nucleus, the behaviour is the same as discussed in Ref. [1]; the values of J_{eff} are a little smaller compared with those of $J_{\mathrm{eff}}^{\mathrm{H-L}}$, but the curve for $Z_{\mathrm{eff}}^{\mathrm{Cu}} = +3$ shows always a broad maximum roughly corresponding to $n^2 = 2/3$. Therefore, these values of $Z_{\mathrm{eff}}^{\mathrm{Cu}}$ and n^2 have been used in calculating the integrals listed in Table 1a.

3. Numerical Calculation for CuCl$_2 \cdot$ 2 H$_2$O

Figure 2 shows a segment of a polymeric chain parallel to the c axis of the unit cell in CuCl$_2 \cdot$ 2 H$_2$O [6]. Each Cu^{2+} ion is surrounded by a distorted octa-
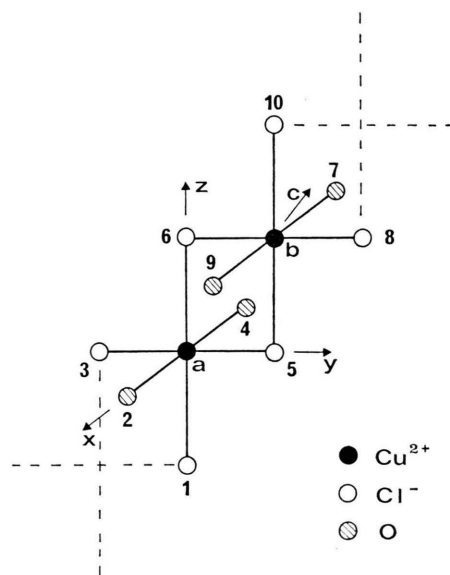
Fig. 2. A segment of a linear chain parallel to the c axis in CuCl$_2 \cdot$ 2 H$_2$O.

hedron with four Cl$^-$ ions lying in the xy plane and two O atoms along x axis.

Other authors [9] have calculated the ground state for the single unit on the basis of a LCAO-MO treatment as

$$\psi_{0\pi}^{\mathrm{a}} = 0.91\, d_{yz}^{\mathrm{a}} + \frac{0.31}{\sqrt{2}}\, (-p_z^3 + p_z^5)$$
$$+ \frac{0.18}{\sqrt{2}}\, (-p_y^1 + p_y^6). \tag{23}$$

The various contributions to the effective exchange integral calculated on the basis of this wavefunction [13] are listed in Table 2a. It appears that the greatest term is the positive two-body exchange integral J_2. Owing to the greatest extension of the $3p$ functions of Cl$^-$ ions with respect to the $2p$ functions of the ligands of the preceding complexes, in this case the value of J_2 has been calculated taking into account not only the one-center integral $\langle p_y^5(1)\, p_z^5(1)|\, r_{12}^{-1}\, |p_y^5(2)\, p_z^5(2)\rangle$, which in fact contributes only $\sim 27\%$ to the total, but also two-center integrals connecting the central ion and the common ligands, contributing $\sim 46\%$. The remaining 27% is accounted mostly by two-center integrals involving adjacent ligands.

The most important molecular integrals appearing in the expression of J_2 were evaluated by direct calculation [9, 16]. The values of the monocentric ones are listed in the Appendix. The remaining terms were evaluated in the charge cloud approximation.

The overlap integral S is very feeble [17], due to the orthogonality of the wavefunctions on the common ligands. For the same reason, the contribution to the resonance integral is small (< 1 cm^{-1}).

$S \cdot 10^2$	J_1	J_2	$-C_1 S^2$	$-C_2 S^2$	$J_{\mathrm{eff}}^{\mathrm{H-L}}$	J_{eff}
-0.211	0.23	32.94	0.48	-0.14	33.51	32.88

Table 2a. Values of J_{eff} and $J_{\mathrm{eff}}^{\mathrm{H-L}}$ (in cm^{-1}), of overlap S and of the various contributions to $J_{\mathrm{eff}}^{\mathrm{H-L}}$, for CuCl$_2 \cdot$ 2 H$_2$O, when the π-type ground state (23) is assumed.

M_2	M'	J'	$2\Delta_0$	$\dfrac{F_2 - C_2}{1 - S^2}$	$b_{\mathrm{Ps}}^{-} \cdot 10^2$
-132.8	-302.3	34.37	339.2	175330.8	0.2691

Table 2b. Values of M_2, M', J', $2\Delta_0$ and $(F_2 - C_2)/(1 - S^2)$ (in cm^{-1}) and of the coefficient b_{Ps}^{-} in the same cases as in Table 2a.

Besides one obtains a positive value for J_1 because, in this case, the terms in the ligands potential give a contribution larger than the terms involving V_a. Also the terms $-C_1 S^2$ and $-C_2 S^2$ contribute negligibly to $J_{\mathrm{eff}}^{\mathrm{H-L}}$, and therefore the approximate value $1/R_{ab}$ has been used for C_2 and $1/R_{ib}$, $i = a, 1, 3$, for the one-body coulomb integrals.

It is evident at this point that a negative value of J_{eff} can not be obtained in the case of π-ground state (23). To take into account the polar states does not modify the situation (see Tables 2a, b).

Buluggiu et al. [11] have shown that the experimental values of the **g** and **A** tensors of $CuCl_2 \cdot 2\,H_2O$ may be fitted on the basis of a σ-ground state, in which the contributions of atoms out of the xy coordination plane can be neglected, as usual for the case of an elongated octahedron.

However, these contributions may be very important for superexchange interaction. In fact, it will be shown later that a very small amount of unpaired spin on out-of-plane ligands can be essential for antiferromagnetic coupling, without affecting the fitting with EPR data.

Therefore, the ground state for the single unit may be assumed as

$$\psi_{0\sigma}^{a} = \alpha\, d_{x^2-y^2}^{a} + \xi\, d_{z^2}^{a} - \frac{\gamma}{\sqrt{2}}\left(-\sigma_x^2 + \sigma_x^4\right)$$
$$- \frac{\delta}{\sqrt{2}}\left(\sigma_y^5 - \sigma_y^3\right) - \sqrt{2}\,\varepsilon\left(-\sigma_z^6 + \sigma_z^1\right) \quad (24\,\mathrm{a})$$

where

$$\sigma^{\mathrm{i}} = n\, p^{\mathrm{i}} \mp (1 - n^2)^{1/2} s^{\mathrm{i}}. \quad (24\,\mathrm{b})$$

The upper sign refers to ligands on the positive x, y and z axes.

The value $(2/3)^{1/2}$ has been assumed for the hybridization parameter n [11]. Similarly the values $\alpha = 0.872$, $\xi = -0.064$ have been used, because they are the more critical ones for the fitting of the **g** and **A** tensor components. The calculation of the exchange constant is then made searching for the best values of δ and ε, while γ is determined from the normalization condition. Contrarily to the π-ground state case, the bridging ligands play a more important role in the evaluation of exchange-

type and overlap integrals, owing to their s character. However, one cannot calculate J_2 or S using one-center integrals only, as in Ref. [1], bearing in mind the greater overlap of 3s and 3p, with respect to 2s and 2p functions.

As regards S, the calculation is exactly performed, because the single terms are known [17]. The greatest contributions to its value are the one-center integrals on ligands 5 and 6, which, alone, would lead to an overestimation of the overlap. The correct value is obtained taking into account the negative contributions of two-centers integrals involving adiacent Cl$^-$ ligands, or connecting the central ions and the common ligands. In the case of J_2 the one-center integrals [16] contribute about 2/3 to the whole term. The remaining third is almost completely given by two-center integrals, among which the most important ones (about one half of the contribution) have the form of the coulomb self-energy of an overlap charge distribution. Of the same order, but a little smaller, is the term

$$2\,\delta^2\,\varepsilon^2\big[\langle\sigma_y^5(1)\,\sigma_z^5(1)|\,r_{12}^{-1}\,|\sigma_y^6(2)\,\sigma_z^6(2)\rangle$$
$$+ \langle\sigma_y^5(1)\,\sigma_y^6(1)|\,r_{12}^{-1}\,|\sigma_z^5(2)\,\sigma_z^6(2)\rangle\big].$$

The remaining terms contribute no more than $1 \div 2\%$ to the value of J_2. For the computation of the single terms, some two-center integrals reported in Ref. [9] have been used. In the other cases the charge cloud approximation gives suitable results. The resonance integral appearing in the expression of J_1 has been calculated as in Ref. [1], taking into account, however, that in the present case the interactions between the planar parts and between the out-of-plane parts of the ground state wavefunctions cannot be neglected.

It must be noted that, owing to the s character at the bridging ligands, in the case of the σ-ground state, the nuclear attraction integrals involving the copper ion potential are not only different from zero, but also greater, in absolute value, than those involving Cl$^-$ potential. Taking into account that the nuclear attraction integrals are the most important contributions to the resonance integral, it follows a greater absolute value of J_1 for the σ- than for the π-ground state.

Finally, the computation of C_1 and C_2 has followed essentially formulas (3) and (4) of Ref. [1], taking into account the different meaning of the coefficients. Moreover a greater number of terms has been retained in the present calculation. In particular for C_1 some other three-center terms involving adiacent ligands have been considered, while for C_2 also terms with ξ^2 or ε^2 as coefficients have been included in the charge cloud approximation. In all cases the computed values of the coulomb integrals are in good agreement (the differences are not more than 8%) with those obtained according to the approximation $1/R_{ib}$, $i = a, 1, 3$.

4. Results and Discussion

The behaviour of J_{eff} and $J_{\text{eff}}^{\text{H-L}}$ as a function of $|\varepsilon|$ for different values of δ is shown in Figs. 3a and 3b, respectively. It appears that there is a value of δ below which the experimental value of the effective exchange integral cannot be obtained. As expected, this value is greater for $J_{\text{eff}}^{\text{H-L}}$, because the presence of polar states favours antiferro-

magnetism. This situation is better pointed out in Fig. 4, where the curves in the δ, $|\varepsilon|$ plane connecting points for which J_{eff} and $J_{\text{eff}}^{\text{H-L}}$ have excatly the experimental value are reported, together with the curve for which $\gamma = \delta$.

It appears that the correct value of J_{eff} may be obtained, inside a reasonable range of values for the parameters δ and ε, only if δ is of the same order or greater than γ. This condition is obviously more restrictive for the Heitler-London case. A reasonable range of values for the parameters means that $|\varepsilon|$ must be at most of the same order as $|\xi|$. Moreover the parameters must be consistent with EPR experimental evidence.

This is the case, for example, for the values of δ, ε and γ listed in Table 3a, where J_{eff}, $J_{\text{eff}}^{\text{H-L}}$ and the various contributions to (1) are presented for some particular points of the curve (a) in Figure 4.
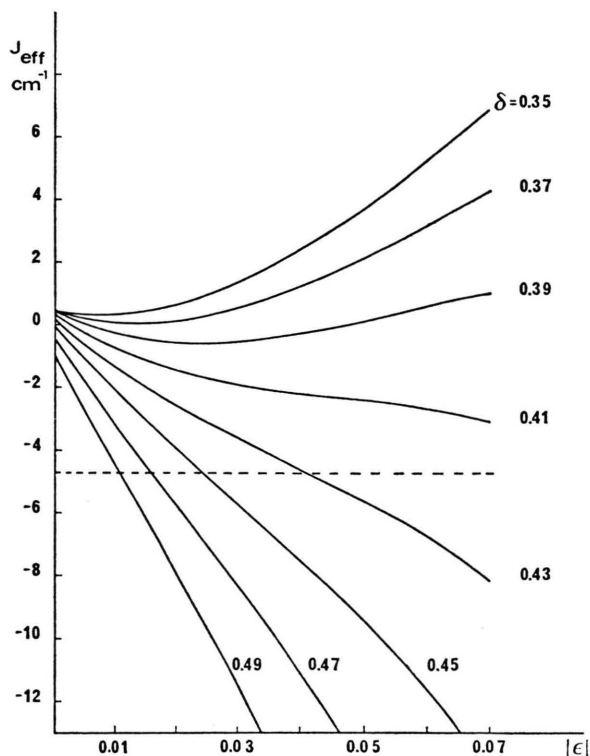

Fig. 3a. J_{eff} versus $|\varepsilon|$, for different values of δ. The dashed horizontal line represents the experimental value of the exchange constant.
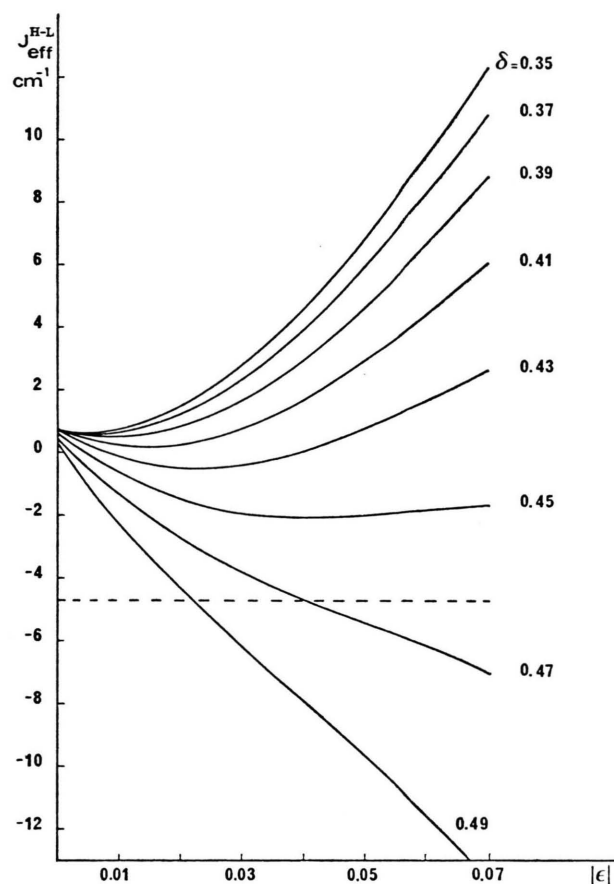
Fig. 3b. $J_{\text{eff}}^{\text{H-L}}$ versus $|\varepsilon|$, for different values of δ. The dashed horizontal line represents the experimental value of the exchange constant.

Table 3a. Values of J_{eff} and $J_{\text{eff}}^{\text{H-L}}$ (in cm^{-1}), of overlap S and of the various contributions to $J_{\text{eff}}^{\text{H-L}}$, for $CuCl_2 \cdot 2\,H_2O$. The rows correspond to the points of curve (a) in Fig. 4; the related covalence parameters are shown.

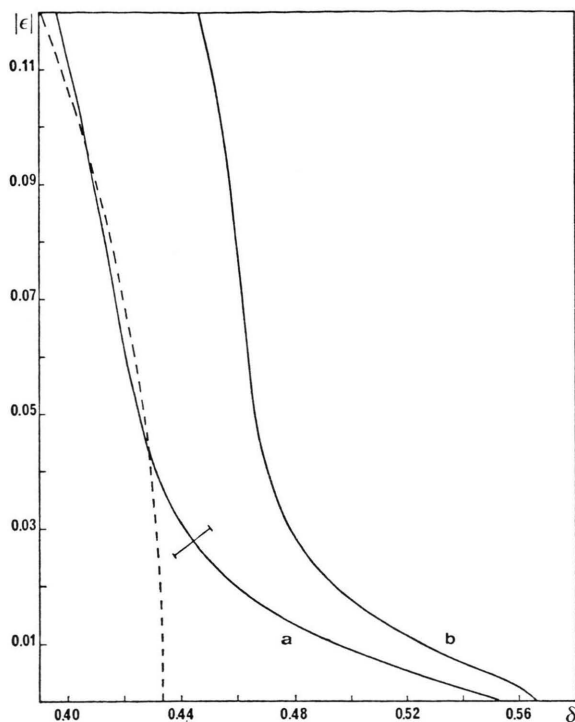| δ	ε	γ	$S \cdot 10^2$	J_1	J_2	$-C_1 S^2$	$-C_2 S^2$	$J_{\text{eff}}^{\text{H-L}}$	J_{eff}
0.430	−0.0414	0.427	0.967	−28.06	21.72	9.30	−2.83	0.13	−4.71
0.440	−0.0308	0.421	0.758	−18.01	12.94	5.70	−1.74	−1.11	−4.71
0.450	−0.0243	0.411	0.637	−13.24	8.74	4.02	−1.22	−1.70	−4.71
0.460	−0.0197	0.400	0.555	−10.46	6.30	3.05	−0.93	−2.04	−4.71
0.470	−0.0162	0.387	0.495	− 8.66	4.72	2.43	−0.74	−2.25	−4.71
0.480	−0.0133	0.373	0.450	− 7.41	3.63	2.01	−0.61	−2.38	−4.71

Fig. 4. Curves (a) and (b) connect the points in the δ, $|\varepsilon|$ plane, for which

$$J_{\text{eff}} = -4.71 \text{ cm}^{-1} \text{ and } J_{\text{eff}}^{\text{H-L}} = -4.71 \text{ cm}^{-1},$$

respectively. In the region at the left of each curve the corresponding exchange constant assumes values greater than −4.71 cm^{-1}. The maximum shift of curve (a) due to a variation of ±20% of J_{eff} is indicated by a segment. The dashed curve is the locus of points for which $\gamma = \delta$; in the region at the left of this curve $\gamma > \delta$.

It may be seen that the fitting of the exchange constant requires an inversion of role between the covalence parameters of the O and Cl ligands, with respect to the situation obtained by means of a best-fit procedure on the basis of EPR data only [11]. On the other side, such a modification does not affect substantially the fitting [18]. Moreover, it must be remembered that in Ref. [11] it has been pointed out that the value of γ was greater than usual in similar complexes, in agreement with the result of the present treatment. It is obvious that Fig. 4 must be considered bearing in mind the approximations introduced both in the theoretical expressions and in the computation procedure. That is, the exact numerical agreement requested to draw the curves of Fig. 4 is unnecessary for the aim of this work. Indeed a possible error of about ±20% and the consequent shift of the curve (a) does not affect at all the conclusions about the covalence parameters and the effect of polar states on superexchange interaction.

To examine in more detail such an effect, it can be noted that the value of ΔJ, remembering that the approximation used for M_2 means practically $M_2 \simeq 2\,C_2 S$, may be quite correctly estimated as:

$$\Delta J \simeq -\frac{2}{F_2 - C_2}(C_2 S - \Delta_0)^2 \simeq -\frac{(M_2 - 2\Delta_0)^2}{2(F_2 - C_2)}. \quad (25)$$

Using this expression, the comparison between the results for the dimeric-compounds and copper chlorine becomes easier (see Tables 1a, b and 3a, b).

Table 3b. Values of M_2, M', J', $2\Delta_0$ and $(F_2 - C_2)/(1 - S^2)$ (in cm^{-1}) and of the coefficient b_{PS}^- in the same cases as in Table 3a.

δ	ε	M_2	M'	J'	$2\Delta_0$	$\dfrac{F_2 - C_2}{1 - S^2}$	$b_{\text{PS}}^- \cdot 10^2$
0.430	−0.0414	608.8	−360.7	−15.79	1938.8	176576.5	0.7394
0.440	−0.0308	477.3	−334.8	−11.69	1623.9	176620.2	0.6380
0.450	−0.0243	400.7	−323.3	− 9.70	1448.0	176627.2	0.5835
0.460	−0.0197	349.3	−318.1	− 8.52	1334.8	176615.4	0.5498
0.470	−0.0162	311.7	−316.8	− 7.73	1257.0	176594.3	0.5281
0.480	−0.0133	283.1	−317.6	− 7.18	1201.5	176573.6	0.5137

As expected, the greater effect of ionic contributions on the superexchange interaction for $CuCl_2 \cdot 2\,H_2O$ depends on the greater value of Δ_0 with respect to the other compounds. That is, nuclear attraction favours antiferromagnetic coupling in two extents: on one side it opposes to electron repulsion and therefore lowers the value of J_{eff}^{H-L}, on the other side it favours the presence of ionic character.

This is the case of $CuCl_2 \cdot 2\,H_2O$, where the value of J_{eff}^{H-L} tends to be small and negative, because J_1 is greater than J_2, while for the other compounds these integrals are of the same order. Moreover the coefficient b_{PS}^-, although very small and decreasing with increasing δ, that is with decreasing ε and S, is greater in this case than in the others. Therefore the correction ΔJ is always relevant for the copper chlorine linear chain.

As regards the influence of effective charges on the results of Tables 3a and 3b, it is convenient to consider separately the contributions to J_1 and C_1 of the central ion and of the ligand potentials, defining the parameters

$$j_1^{Cu} = \frac{\langle \psi_0^a(1)| \, V_{Cu}^a(1) \, |\psi_0^b(1)\rangle}{Z_{eff}^{Cu}},$$

$$c_1^{Cu} = \frac{\langle \psi_0^b(1)| \, V_{Cu}^a(1) \, |\psi_0^b(1)\rangle}{Z_{eff}^{Cu}} \qquad (26a)$$

and

$$j_1^{lig} = \frac{\langle \psi_0^a(1)| \, \sum_{\{a\}}' V_{lig}^a(1) \, |\psi_0^b(1)\rangle}{Z_{eff}^{lig}},$$

$$c_1^{lig} = \frac{\langle \psi_0^b(1)| \, \sum_{\{a\}}' V_{lig}^a(1) \, |\psi_0^b(1)\rangle}{Z_{eff}^{lig}}, \qquad (26b)$$

that are listed in Table 4.

It can be easily verified that the value of J_{eff} is not very sensitive to Z_{eff}^{lig}. In fact, a variation of 50% of the assumed value of -1 leads to a variation for J_{eff} of only 2% in the third and fourth case of Table 3a, and of a maximum of 25% in the first case, which is evidently the more critical one. This is due, as one can see from Table 4, to the fact that Z_{eff}^{lig} is the multiplying factor of the less important contributions to J_{eff} and moreover to the balance mechanism between J_1 and $C_1 S^2$, which tends to reduce the effect of the variation of Z_{eff}^{lig}. It is worthwhile to note that a reduction of the ligands effective charge favours antiferromagnetic coupling if $|j_1^{lig}| > |c_1^{lig} S^2|$, as it is the case for the first three rows of Table 4.

The dependence on Z_{eff}^{Cu} is of course much stronger [1]. Therefore, the reliability of the results obtained with the assumption $Z_{eff}^{Cu} = +3$ confirms that the simple picture of a pair of complex ions as a sort of diatomic two-electron molecule, in which delocalization effects are properly taken into account, is substantially correct.

In conclusion, it has been shown that, at least in the cases considered, the effect of polar states becomes important in the calculation of the exchange constant when the Heitler-London contributions tend to balance each other to give a small value of J_{eff}^{H-L}. According to the usual theories [8, 19], this effect favours antiferromagnetism the more, the greater is the overlap S. Moreover, it has been pointed out that, for the ground state of $CuCl_2 \cdot 2\,H_2O$, a σ-type is much more suitable than a π-type wavefunction.

Acknowledgement

Table 4. The parameters defined by (26) and the values of $-c_1^{Cu} S^2$ and $-c_1^{lig} S^2$ (in cm^{-1}), for $CuCl_2 \cdot 2\,H_2O$, in the same cases as in Table 3.

δ	ε	$c_1^{Cu} \cdot 10^5$	$c_1^{lig} \cdot 10^5$	j_1^{Cu}	j_1^{lig}	$-c_1^{Cu} S^2$	$-c_1^{lig} S^2$
0.430	−0.0414	−0.5843	−0.7588	−12.17	−8.46	5.46	7.10
0.440	−0.0308	−0.5832	−0.7577	− 7.62	−4.86	3.35	4.35
0.450	−0.0243	−0.5829	−0.7576	− 5.47	−3.18	2.37	3.07
0.460	−0.0197	−0.5832	−0.7580	− 4.23	−2.23	1.80	2.33
0.470	−0.0162	−0.5837	−0.7587	− 3.43	−1.62	1.43	1.86
0.480	−0.0133	−0.5845	−0.7597	− 2.88	−1.21	1.18	1.54

Appendix

In Table A 1 the distances (in Å) d_x, d_y and d_z relating to Fig. 2 for the three dimeric compounds (N$_1$), (N$_2$), (O) and for $CuCl_2 \cdot 2H_2O$ are reported.

In Table A 2 are listed the one-center integrals which have been used in the evaluation of J_2 for copper chlorine. The nuclear attraction integrals appearing in the expression of J_1 for $CuCl_2 \cdot 2H_2O$ are listed in Table A 3. Among these, $\langle p_\sigma | r_1^{-1} | p_\sigma \rangle$ and $\langle p_\pi | r_1^{-1} | p_\pi \rangle$ are taken from Ref. [9].

Table A 1. Cu-ligands distances (in Å) for the dimeric complexes (N$_1$), (N$_2$), (O) and for $CuCl_2 \cdot 2H_2O$.

	d_x	d_y	d_z
(N$_1$)	1.96	1.96	3.06
(N$_2$)	1.99	1.99	2.95
(O)	1.99	1.99	2.31
$CuCl_2 \cdot 2H_2O$	1.93	2.27	2.92

All the integrals in Tables A 2 and A 3 are in a.u. and have been evaluated on 3s and 3p SCF wavefunctions [14] for Cl$^-$.

Table A 2. One-center two-body integrals (in a.u.) for $CuCl_2 \cdot 2H_2O$.

$\langle p_y(1)\, p_y(1) \,|\, r_{12}^{-1} \,|\, p_z(2)\, p_z(2)\rangle$	$\langle p_y(1)\, p_z(1) \,|\, r_{12}^{-1} \,|\, p_y(2)\, p_z(2)\rangle$	$\langle s(1)\, p_y(1) \,|\, r_{12}^{-1} \,|\, s(2)\, p_y(2)\rangle$	$\langle s(1)\, s(1) \,|\, r_{12}^{-1} \,|\, s(2)\, s(2)\rangle$
0.43421	0.02631	0.10698	0.56555

Table A 3. Nuclear attraction integrals (in a.u.) for $CuCl_2 \cdot 2H_2O$. (*) labels the values taken from Ref. [9].

$\langle p_\sigma^5 | r_a^{-1} | s^5 \rangle$	$\langle s^5 | r_a^{-1} | s^5 \rangle$	$\langle p_\sigma^6 | r_a^{-1} | s^6 \rangle$	$\langle s^6 | r_a^{-1} | s^6 \rangle$	$\langle p_\sigma^5 | r_1^{-1} | p_\sigma^5 \rangle$	$\langle p_\pi^5 | r_1^{-1} | p_\pi^5 \rangle$
0.05286	0.23303	0.03242	0.18183	0.14671 *	0.13770 *
$\langle p_\sigma^5 | r_1^{-1} | s^5 \rangle$	$\langle s^5 | r_1^{-1} | s^5 \rangle$	$\langle p_\sigma^6 | r_1^{-1} | s^6 \rangle$	$\langle s^6 | r_1^{-1} | s^6 \rangle$	$\langle p_\sigma^5 | r_3^{-1} | s^5 \rangle$	$\langle s^5 | r_3^{-1} | s^5 \rangle$
0.02019	0.14341	0.00812	0.09092	0.01334	0.11655

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