Effect of Polar States on Superexchange Interaction. Application to Some Dimeric Copper (II) Complexes and to CuCl$_2$·2H$_2$O Linear Chain

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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 $J_{\text{eff}}$ 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 $\Delta_0$ and of two-body molecular integrals. The resulting $J_{\text{eff}}$, 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$_2$·2H$_2$O 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$_2$·2H$_2$O is accounted for on the basis of a $\sigma$-ground state for the single unit, rather than a $\pi$ one. The conditions to fit the experimental value of $J_{\text{eff}}$ 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

$$J_2 = \langle \psi_1^0(1) \psi_1^0(2) | r_{12}^{-1} | \psi_1^0(2) \psi_1^0(1) \rangle,$$

(ii) two-body coulomb integral

$$C_2 = \langle \psi_1^0(1) \psi_1^0(2) | r_{12}^{-1} | \psi_1^0(1) \psi_1^0(2) \rangle,$$

(iii) one-body exchange integral

$$J_1 = 2S \langle \psi_1^0(1) | [V_{\text{Cu}}(1) + \sum_{a} V_{\text{lig}}(1)] | \psi_1^0(1) \rangle,$$

where

$$S = \langle \psi_1^0(1) | \psi_1^0(1) \rangle.$$

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 $Z_{\text{eff}}^\text{Cu}$ and, on the other side, the evaluation of many multicenter one- and two-body molecular integrals contributing to $J_{\text{eff}}^{\text{H-L}}$. In the case of the quoted compounds the knowledge of the ground state wavefunction was obtained from the comparison of the theory outlined in Ref. [2] with EPR measurements [3]. As regards $Z_{\text{eff}}^\text{Cu}$, it was pointed out [1] that the best value is the pure ionic value $Z_{\text{eff}}^\text{Cu} = +3$, 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 $J_{\text{H-L}}$ 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$_2$·2H$_2$O. This last compound is a dilute magnetic insulator, in which the most relevant interaction is antiferromagnetic spin coupling, with $J_{\text{eff}} = -4.71$ cm$^{-1}$ [5], along a linear chain of spin $\frac{1}{2}$ Cu$^{2+}$ complex ions [6]. To perform the calculation of $J_{\text{eff}}$, 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$_2$·2H$_2$O, starting from a $\pi$-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$_2$·2H$_2$O, 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 $J_{\text{eff}}$ 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$_2$·2H$_2$O, the $\sigma$-ground state deduced by Buluggiu et al. [11] from EPR measurements accounts for the correct value of the exchange constant, contrarily to the $\pi$-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 $\Delta_0$ and the one-body integrals is shown. The expression of $J_{\text{H-L}}$ is thus rewritten in terms of $\Delta_0$ and compared with an approximated analytical 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$_2$·2H$_2$O is examined. The principal aspects of calculation in both cases of $\pi$- and $\sigma$-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,
unessential for isotropic exchange calculation [1, 2], as

$$\mathcal{H}_{0}^{a,b}(r) = \frac{p^2}{2m} + V_{\text{Cu}}^{a,b}(r) + \sum_{(a,b)} V_{\text{lig}}^{a,b}(r), \quad (3)$$

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 $\psi_0^{a,b}(r)$ and belongs to the eigenvalue $E_0$.

The Hamiltonian of the two interacting particles is

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

with

$$\mathcal{H}(1) = \mathcal{H}_0^{a}(1) + V_{\text{Cu}}^{a}(1) + \sum_{(b)} V_{\text{lig}}^{b}(1),$$

$$\mathcal{H}(2) = \mathcal{H}_0^{b}(2) + V_{\text{Cu}}^{b}(2) + \sum_{(a)} V_{\text{lig}}^{a}(2). \quad (5)$$

It is clear that $\mathcal{H}(1)$ and $\mathcal{H}(2)$ 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 antibonding wavefunctions, that is

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

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

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

$$E_\Phi = E_0 + K_0 - A_0,$$

$$E_X = E_0 + K_0 + A_0 \quad (7)$$

where

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

$$A_0 = \frac{1}{2} \left[ \frac{(C_1 - J_1)S}{1 - S^2} - \frac{J_1}{S} \right]. \quad (9)$$

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 approached, as usual, considering the six determinantal states corresponding to all possible ways to assign two electrons (with their spins) to the states $\Phi_0$ and $X_0$. As is known, they may be written as triplet and singlets wavefunctions in the following way:

$$J_{\Phi}^{1,0} = \frac{1}{2(1 + S)} \left[ [\psi_0^a(1) \psi_0^b(2) + \psi_0^b(1) \psi_0^a(2)] + [\psi_0^a(1) \psi_0^b(2) + \psi_0^b(1) \psi_0^a(2)] \right], \quad (10a)$$

$$J_{XX}^{1,0} = \frac{1}{\sqrt{2(1 - S^2)}} \left[ [\psi_0^a(1) \psi_0^b(2) - \psi_0^b(1) \psi_0^a(2)] \right] \left[ \frac{1}{2} [\alpha(1) \beta(2) - \beta(1) \alpha(2)] \right] \quad (10b)$$

$$J_{\Phi}^{3,0} = \frac{1}{\sqrt{2(1 - S^2)}} \left[ [\psi_0^a(1) \psi_0^b(2) - \psi_0^b(1) \psi_0^a(2)] \right] \left[ \frac{1}{2} [\alpha(1) \beta(2) + \beta(1) \alpha(2)] \right] \quad (10c)$$

$$J_{XX}^{3,0} = \frac{1}{2(1 - S)} \left[ [\psi_0^a(1) \psi_0^b(2) - \psi_0^b(1) \psi_0^a(2)] \right] \left[ \frac{1}{2} [\alpha(1) \beta(2) - \beta(1) \alpha(2)] \right]. \quad (10d)$$

$\alpha(i)$ 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 $\psi_0^a(1) \psi_0^b(2)$. 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
The two-body integrals $F_2$ and $M_2$ are defined as

$$F_2 = \langle \psi_0^0(1) \psi_0^0(2) | r_{12}^{-1} | \psi_0^0(1) \psi_0^0(2) \rangle, \quad (12a)$$

$$M_2 = \langle \psi_0^0(1) \psi_0^0(2) | r_{12}^{-1} | \psi_0^0(1) \psi_0^0(2) \rangle. \quad (12b)$$

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

Matrix (11) is very similar to that used in Ref. [9], apart from the presence of $\Delta_0$ in the $2 \times 2$ 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

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

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

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

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

In Sections 2 and 3 $J_{\text{eff}}$ 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 $J_{\text{eff}}$ in terms of the molecular integrals:

$$E^+ = F_2 + J' - 4M'S + 2F_2S^2 + C_2S^2 \left[ M' - \frac{(F_2 + C_2) S^2}{2} \right] + 4 \left( \frac{M' - \frac{(F_2 + C_2) S^2}{2}}{F_2 - C_2} \right), \quad (15a)$$

$$E^- = C_2 + J' - 4M'S + 2F_2S^2 + C_2S^2 \left[ M' - \frac{(F_2 + C_2) S^2}{2} \right] - 4 \left( \frac{M' - \frac{(F_2 + C_2) S^2}{2}}{F_2 - C_2} \right). \quad (15b)$$

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 $(F_2 - C_2)$ above the triplet. It may be noted that, if $(F_2 - C_2) > 2J_{\text{eff}}$ 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:

$$J_{\text{eff}} = J_2 - 2C_2S^2 - 2\Delta_0 S$$

$$- \frac{2}{F_2 - C_2} (C_2S - M^2)^2. \quad (16)$$

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

$$J_{\text{eff-L}}^H = J_2 - 2C_2S^2 - 2\Delta_0 S; \quad (17)$$

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

$$\Delta J = - \frac{2}{F_2 - C_2} (C_2S - M^2)^2. \quad (18)$$

This formula shows that the correction to $J_{\text{eff-L}}^H$ due to the presence of ionic configurations is always negative, thus supporting antiferromagnetic behaviour.
Table 1b. Values of $M, M', J, 2A_0$ 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.

<table>
<thead>
<tr>
<th></th>
<th>$M_2$</th>
<th>$M'$</th>
<th>$J'$</th>
<th>$2A_0$</th>
<th>$(F_2 - C_2)/(1 - S^2)$</th>
<th>$b_{ps} \cdot 10^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_1$ Slater</td>
<td>570.8</td>
<td>41.4</td>
<td>7.38</td>
<td>1058.8</td>
<td>176904.1</td>
<td>0.2552</td>
</tr>
<tr>
<td>Clementi</td>
<td>598.4</td>
<td>157.3</td>
<td>5.61</td>
<td>878.1</td>
<td>176525.4</td>
<td>0.1419</td>
</tr>
<tr>
<td>$N_2$ Slater</td>
<td>578.4</td>
<td>40.9</td>
<td>7.19</td>
<td>1074.9</td>
<td>176083.8</td>
<td>0.2631</td>
</tr>
<tr>
<td>Clementi</td>
<td>579.7</td>
<td>174.4</td>
<td>6.14</td>
<td>810.5</td>
<td>175783.8</td>
<td>0.1143</td>
</tr>
<tr>
<td>$O$  Slater</td>
<td>522.6</td>
<td>-123.7</td>
<td>0.80</td>
<td>1292.5</td>
<td>171858.1</td>
<td>0.4228</td>
</tr>
<tr>
<td>Clementi</td>
<td>575.2</td>
<td>24.0</td>
<td>0.62</td>
<td>1102.3</td>
<td>171528.3</td>
<td>0.2602</td>
</tr>
</tbody>
</table>

ent values of the effective charge $Z_{eff}^{Cu}$ 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 $J_{H-L}$, but the curve for $Z_{eff}^{Cu} = +3$ shows always a broad maximum roughly corresponding to $n^2 = 2/3$. Therefore, these values of $Z_{eff}^{Cu}$ and $n^2$ have been used in calculating the integrals listed in Table 1a.

3. Numerical Calculation for CuCl$_2$·2H$_2$O

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

$$\psi_{0\pi} = 0.91 \sigma_{yz} + \frac{0.31}{\sqrt{2}} (-p_3^z + p_5^z)$$

$$+ \frac{0.18}{\sqrt{2}} (-p_y^1 + p_y^6).$$

(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 $\langle p_5^z(1) p_5^z(1) | r_{12} \rangle$ $p_5^z(2) p_5^z(2), 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$^{-1}$).

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

<table>
<thead>
<tr>
<th>$S \cdot 10^2$</th>
<th>$J_1$</th>
<th>$J_2$</th>
<th>$-C_1S^2$</th>
<th>$-C_2S^2$</th>
<th>$J_{H-L}$</th>
<th>$J_{eff}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.211</td>
<td>0.23</td>
<td>32.94</td>
<td>0.48</td>
<td>-0.14</td>
<td>33.51</td>
<td>32.88</td>
</tr>
</tbody>
</table>
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 $-C_1S^2$ and $-C_2S^2$ contribute negligibly to $J_{\text{eff}}^{\text{I-L}}$, 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 $J_{\text{eff}}$ can not be obtained in the case of $\pi$-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$_2$ · 2 H$_2$O may be fitted on the basis of a $\sigma$-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

$$
\psi_{00} = \frac{1}{2} d^2 \text{y} + \xi d^2 \text{z} - \gamma (\sigma_x^2 + \sigma_y^2) - \frac{\delta}{2} (\sigma_y^2 - \sigma_y^2) - \frac{\varepsilon}{2} (\sigma_x^2 + \sigma_y^2) \tag{24a}
$$

where

$$
\sigma = n \frac{p^1}{2} = (1 - n^2)^{1/2} s^1. \tag{24b}
$$

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 $\delta$ and $\varepsilon$, while $\gamma$ is determined from the normalization condition. Contrarily to the $\pi$-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 adjacent Cl$^-$ ligands, or connecting the central ions and the common ligands. In the case of $J_3$ 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

$$
2 \delta^2 \varepsilon^2 [\langle \sigma_y^2(1) \sigma_y^2(1) | r_{12}^2 | \sigma_y^2(2) \sigma_y^2(2) \rangle + \langle \sigma_y^2(1) \sigma_y^2(1) | r_{12}^2 | \sigma_y^2(2) \sigma_y^2(2) \rangle].
$$

The remaining terms contribute no more than $1 \div 2\%$ to the value of $J_3$. 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 $\sigma$-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 $\sigma$- than for the $\pi$-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 adjacent ligands have been considered, while for $C_2$ also terms with $\xi^2$ or $\epsilon^2$ 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 $J_{\text{eff}}$ and $J_{\text{eff-L}}^H$ as a function of $|\epsilon|$ for different values of $\delta$ is shown in Figs. 3a and 3b, respectively. It appears that there is a value of $\delta$ below which the experimental value of the effective exchange integral cannot be obtained. As expected, this value is greater for $J_{\text{eff-L}}^H$, because the presence of polar states favours antiferromagnetism. This situation is better pointed out in Fig. 4, where the curves in the $\delta, |\epsilon|$ plane connecting points for which $J_{\text{eff}}$ and $J_{\text{eff-L}}^H$ have exactly the experimental value are reported, together with the curve for which $\gamma = \delta$.

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

This is the case, for example, for the values of $\delta$, $\epsilon$ and $\gamma$ listed in Table 3a, where $J_{\text{eff}}$, $J_{\text{eff-L}}^H$ and the various contributions to (1) are presented for some particular points of the curve (a) in Figure 4.
Table 3a. Values of $J_{\text{eff}}$ and $J_{\text{eff}}^{-1}$ (in cm$^{-1}$), of overlap $S$ and of the various contributions to $J_{\text{eff}}^{-1}$, for CuCl$_2$·2H$_2$O. The rows correspond to the points of curve (a) in Fig. 4; the related covalence parameters are shown.

<table>
<thead>
<tr>
<th>$\delta$</th>
<th>$\epsilon$</th>
<th>$\gamma$</th>
<th>$S \cdot 10^2$</th>
<th>$J_1$</th>
<th>$J_2$</th>
<th>$-C_1 S^2$</th>
<th>$-C_2 S^2$</th>
<th>$J_{\text{eff}}^{-1}$</th>
<th>$J_{\text{eff}}$</th>
</tr>
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<tr>
<td>0.430</td>
<td>-0.0414</td>
<td>0.427</td>
<td>0.967</td>
<td>-28.06</td>
<td>21.72</td>
<td>9.30</td>
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<td>-4.71</td>
</tr>
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<td>0.758</td>
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<td>12.94</td>
<td>5.70</td>
<td>-1.74</td>
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<td>-0.0243</td>
<td>0.411</td>
<td>0.637</td>
<td>-13.24</td>
<td>8.74</td>
<td>4.02</td>
<td>-1.22</td>
<td>-1.70</td>
<td>-4.71</td>
</tr>
<tr>
<td>0.460</td>
<td>-0.0197</td>
<td>0.400</td>
<td>0.555</td>
<td>-10.46</td>
<td>6.30</td>
<td>3.05</td>
<td>-0.93</td>
<td>-2.04</td>
<td>-4.71</td>
</tr>
<tr>
<td>0.470</td>
<td>-0.0162</td>
<td>0.387</td>
<td>0.485</td>
<td>-8.66</td>
<td>4.72</td>
<td>2.43</td>
<td>-0.74</td>
<td>-2.25</td>
<td>-4.71</td>
</tr>
<tr>
<td>0.480</td>
<td>-0.0133</td>
<td>0.373</td>
<td>0.450</td>
<td>-7.41</td>
<td>3.60</td>
<td>2.01</td>
<td>-0.61</td>
<td>-2.38</td>
<td>-4.71</td>
</tr>
</tbody>
</table>

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

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

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

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 $\gamma$ 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 $\pm 20\%$ 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 $\Delta J$, remembering that the approximation used for $M_2$ means practically $M_2 \cong 2C_2 S$, may be quite correctly estimated as:

$$\Delta J \cong \frac{2}{F_2 - C_2} (C_2 S - A_0)^2 \cong \frac{(M_2 - 2A_0)^2}{2(F_2 - C_2)}. \quad (25)$$

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 $M_2$, $M'$, $J'$, $2A_0$ and $(F_2 - C_2)/(1 - S^2)$ (in cm$^{-1}$) and of the coefficient $b_{\gamma s}$ in the same cases as in Table 3a.

<table>
<thead>
<tr>
<th>$\delta$</th>
<th>$\epsilon$</th>
<th>$M_2$</th>
<th>$M'$</th>
<th>$J'$</th>
<th>$2A_0$</th>
<th>$(F_2 - C_2)/(1 - S^2)$</th>
<th>$b_{\gamma s} \cdot 10^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.430</td>
<td>-0.0414</td>
<td>608.8</td>
<td>-360.7</td>
<td>-15.79</td>
<td>1938.8</td>
<td>176576.5</td>
<td>0.7394</td>
</tr>
<tr>
<td>0.440</td>
<td>-0.0308</td>
<td>477.3</td>
<td>-334.8</td>
<td>-11.69</td>
<td>1623.9</td>
<td>176620.2</td>
<td>0.6380</td>
</tr>
<tr>
<td>0.450</td>
<td>-0.0243</td>
<td>400.7</td>
<td>-323.3</td>
<td>-9.70</td>
<td>1448.0</td>
<td>176627.2</td>
<td>0.5835</td>
</tr>
<tr>
<td>0.460</td>
<td>-0.0197</td>
<td>349.3</td>
<td>-318.1</td>
<td>-8.52</td>
<td>1334.8</td>
<td>176615.4</td>
<td>0.5498</td>
</tr>
<tr>
<td>0.470</td>
<td>-0.0162</td>
<td>311.7</td>
<td>-316.8</td>
<td>-7.33</td>
<td>1257.0</td>
<td>176594.3</td>
<td>0.5281</td>
</tr>
<tr>
<td>0.480</td>
<td>-0.0133</td>
<td>283.1</td>
<td>-317.6</td>
<td>-7.18</td>
<td>1201.5</td>
<td>176573.6</td>
<td>0.5137</td>
</tr>
</tbody>
</table>
As expected, the greater effect of ionic contributions on the superexchange interaction for CuCl$_2$·2H$_2$O depends on the greater value of $\Delta_0$ 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 $J^L_{\text{eff}}$, on the other side it favours the presence of ionic character.

This is the case of CuCl$_2$·2H$_2$O, where the value of $J^H_{\text{eff}}$ 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 $b_{\text{ps}}$, although very small and decreasing with increasing $\delta$, that is with decreasing $\varepsilon$ and $S$, is greater in this case than in the others. Therefore the correction $\Delta J$ 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

$$j_{1\text{Cu}} = \frac{\langle \psi^a_0(1) \mid V^a_{\text{Cu}}(1) \mid \psi^a_0(1) \rangle}{Z^{\text{Cu}}_{\text{eff}}},$$

$$e_{1\text{Cu}} = \frac{\langle \psi^a_0(1) \mid V^a_{\text{Cu}}(1) \mid \psi^b_0(1) \rangle}{Z^{\text{Cu}}_{\text{eff}}},$$

and

$$j_{1\text{lig}} = \frac{\langle \psi^b_0(1) \mid \sum_{[s]} V^b_{\text{lig}}(1) \mid \psi^b_0(1) \rangle}{Z^{\text{lig}}_{\text{eff}}},$$

$$e_{1\text{lig}} = \frac{\langle \psi^b_0(1) \mid \sum_{[s]} V^b_{\text{lig}}(1) \mid \psi^0_0(1) \rangle}{Z^{\text{lig}}_{\text{eff}}},$$

that are listed in Table 4.

It can be easily verified that the value of $J_{\text{eff}}$ is not very sensitive to $Z^{\text{lig}}_{\text{eff}}$. In fact, a variation of 50% of the assumed value of $-1$ leads to a variation for $J_{\text{eff}}$ 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 $Z^{\text{lig}}_{\text{eff}}$ is the multiplying factor of the less important contributions to $J_{\text{eff}}$ and moreover to the balance mechanism between $J_1$ and $C_1S^2$, which tends to reduce the effect of the variation of $Z^{\text{lig}}_{\text{eff}}$. It is worthwhile to note that a reduction of the ligands effective charge favours antiferromagnetic coupling if $|j_{1\text{lig}}| > |e_{1\text{lig}} S^2|$, as it is the case for the first three rows of Table 4.

The dependence on $Z^{\text{Cu}}_{\text{eff}}$ is of course much stronger [1]. Therefore, the reliability of the results obtained with the assumption $Z^{\text{Cu}}_{\text{eff}} = +3$ 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 $J^H_{\text{eff}}$. 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$_2$·2H$_2$O, a $\sigma$-type is much more suitable than a $\pi$-type wavefunction.

Acknowledgement

The Author wish to thank Prof. V. Varacca, Prof. E. Buluggiu and Dr. A. Vera for many helpful discussions and Prof. G. Dascola for his encouragement during the development of this work.

Table 4. The parameters defined by (26) and the values of $-c_{1\text{Cu}} S^2$ and $-c_{1\text{lig}} S^2$ (in cm$^{-1}$), for CuCl$_2$·2H$_2$O, in the same cases as in Table 3.

<table>
<thead>
<tr>
<th>$\delta$</th>
<th>$\varepsilon$</th>
<th>$c_{1\text{Cu}} \cdot 10^5$</th>
<th>$c_{1\text{lig}} \cdot 10^5$</th>
<th>$j_{1\text{Cu}}$</th>
<th>$j_{1\text{lig}}$</th>
<th>$-c_{1\text{Cu}} S^2$</th>
<th>$-c_{1\text{lig}} S^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.430</td>
<td>-0.0414</td>
<td>-0.5845</td>
<td>-0.7588</td>
<td>-12.17</td>
<td>-8.46</td>
<td>5.46</td>
<td>7.10</td>
</tr>
<tr>
<td>0.440</td>
<td>-0.0308</td>
<td>-0.5832</td>
<td>-0.7577</td>
<td>-7.62</td>
<td>-4.86</td>
<td>3.35</td>
<td>4.35</td>
</tr>
<tr>
<td>0.450</td>
<td>-0.0243</td>
<td>-0.5829</td>
<td>-0.7576</td>
<td>-5.47</td>
<td>-3.18</td>
<td>2.37</td>
<td>3.07</td>
</tr>
<tr>
<td>0.460</td>
<td>-0.0197</td>
<td>-0.5832</td>
<td>-0.7580</td>
<td>-4.23</td>
<td>-2.23</td>
<td>1.80</td>
<td>2.33</td>
</tr>
<tr>
<td>0.470</td>
<td>-0.0162</td>
<td>-0.5837</td>
<td>-0.7587</td>
<td>-3.43</td>
<td>-1.62</td>
<td>1.43</td>
<td>1.86</td>
</tr>
<tr>
<td>0.480</td>
<td>-0.0133</td>
<td>-0.5845</td>
<td>-0.7597</td>
<td>-2.88</td>
<td>-1.21</td>
<td>1.18</td>
<td>1.54</td>
</tr>
</tbody>
</table>
Appendix

In Table A1 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$_2$·2H$_2$O are reported.

In Table A2 are listed the one-center integrals which have been used in the evaluation of $J_2$ for copper chloride. The nuclear attraction integrals appearing in the expression of $J_1$ for CuCl$_2$·2H$_2$O are listed in Table A3. 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 A1. Cu-ligands distances (in Å) for the dimeric complexes $(N_1)$, $(N_2)$, (O) and for CuCl$_2$·2H$_2$O.

<table>
<thead>
<tr>
<th></th>
<th>$d_x$</th>
<th>$d_y$</th>
<th>$d_z$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(N_1)$</td>
<td>1.96</td>
<td>1.96</td>
<td>3.06</td>
</tr>
<tr>
<td>$(N_2)$</td>
<td>1.99</td>
<td>1.99</td>
<td>2.95</td>
</tr>
<tr>
<td>(O)</td>
<td>1.99</td>
<td>1.99</td>
<td>2.31</td>
</tr>
<tr>
<td>CuCl$_2$·2H$_2$O</td>
<td>1.93</td>
<td>2.27</td>
<td>2.92</td>
</tr>
</tbody>
</table>

All the integrals in Tables A2 and A3 are in a.u. and have been evaluated on 3s and 3p SCF wavefunctions [14] for Cl$^-$.  

### Table A2. One-center two-body integrals (in a.u.) for CuCl$_2$·2H$_2$O.

| $\langle p_\gamma(1) p_\gamma(1) | r_1 | p_\gamma(2) p_\gamma(2) \rangle$ | $\langle s(1) p_\gamma(1) | r_1 | s(2) p_\gamma(2) \rangle$ | $\langle s(1) s(1) | r_1^{-1} | s(2) s(2) \rangle$ |
|---------------------------------|---------------------------------|---------------------------------|
| 0.43421                         | 0.02631                         | 0.10698                         |

### Table A3. Nuclear attraction integrals (in a.u.) for CuCl$_2$·2H$_2$O. (*) labels the values taken from Ref. [9].

| $\langle p_\sigma^5 | r_1^{-1} | s^5 \rangle$ | $\langle s^5 | r_1^{-1} | p_\sigma^5 \rangle$ | $\langle p_\sigma^5 | r_1^{-1} | p_\sigma^5 \rangle$ | $\langle p_\sigma^5 | r_1^{-1} | p_\sigma^5 \rangle$ | $\langle p_\sigma^5 | r_1^{-1} | p_\sigma^5 \rangle$ |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| 0.05286         | 0.23303         | 0.03242         | 0.18183         | 0.14671*        |
| 0.13770*        |                 |                 |                 |                 |

[12] This is exactly true in the usual limit $S^2 \ll 1$.
[13] Here and in the following the SCF wavefunctions of Watson et al. [14] for Cu$^{2+}$ and Cl$^-$ and of Clementi et al. [15] for O have been used.
[16] The one-center integrals were calculated by means of a computer program, kindly supplied by Prof. L. Oleari of the Institute of Physical Chemistry of the University of Parma.
[17] The overlap integrals and two-center integrals of the type $\langle \psi | r_1^{-1} | \psi \rangle$ were calculated by numerical integration in elliptic coordinates. The computer program has been supplied by Prof. L. Oleari [16].