

### Commentationes

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## Molecular Orbital Calculations on Copper Chloride Complexes

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The following paper describes a molecular orbital calculation of the Wolfsberg-Helmholz type. However, in contrast to the usual empirical determination of the  $H_{ii}$  integrals, these integrals are here computed from the wave functions of the free ions. The calculation is performed on Cu in a tetrahedral, square planar and octahedral environment of Cl, the results being subsequently compared.

Die folgende Arbeit bringt eine M. O. Berechnung vom Typ Wolfsberg-Helmholz von Kupfer-Chlorid-Komplexen mit tetraedrischer, quadratisch-ebene und oktaedrischer Anordnung der Liganden. Die Ergebnisse werden miteinander verglichen. Abweichend vom üblichen Schema wurden die  $H_{ii}$ -Integrale mittels der Wellenfunktion des freien Ions berechnet.

Un calcul O.M. du type Wolfsberg-Helmholz est effectué. Les intégrales  $H_{ii}$  y sont déterminés des fonctions d'onde des ions libres, contrairement au procédé empirique usuel. Cu est traité en coordination tétraédrique, quadratique et octaédrique de Cl; les résultats sont comparés.

### Introduction

During recent years, molecular orbital calculations have been performed in increasing numbers on complicated molecules as for instance the complexes of the transition metal ions. However, it also becomes increasingly clear that the difficulties encountered are quite considerable.

In the simple molecular orbital theory it is assumed that the orbital of an electron in a molecule can be described by a linear combination of the orbitals of the electrons in the free atoms or ions:

$$\psi_i = \sum_k C_{ik} \varphi_k . \quad (1)$$

By choosing the coefficients  $C_{ik}$  in such a way that the average energy of the system is minimised, the problem is reduced to the evaluation of the secular determinant [15]:

$$| H_{nk} - \varepsilon_i S_{nk} | = 0$$

with

$$H_{nk} = \langle \varphi_n | H | \varphi_k \rangle \quad \text{and} \quad S_{nk} = \langle \varphi_n | \varphi_k \rangle . \quad (2)$$

Generally speaking, we can distinguish between two types of calculations:

a) Calculations that are based on empirical approximations. In this type of calculations, the  $H_{ij}$ -integrals are empirically determined from the valence state

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ionisation energies. Examples of this type are the calculations of WOLFSBERG and HELMHOLZ [22]; BALLHAUSEN and GRAY [1]; VISTE and GRAY [18]; FENSKE and SWEENEY [4]; COTTON and HAAS [3].

b) Calculations in which it is tried to compute the  $H_{ij}$ -integrals from first principles. This type of calculation offers many difficulties and until now, calculations have been performed only on ionic compounds, hence on compounds for which it may be assumed that the central ion-ligand overlap-integral  $S$  and the covalency factor  $\lambda$  are so small that terms in  $S^2$  or  $\lambda^2$  can be neglected. Examples of this type are the calculations of SUGANO and SHULMAN [16]; WATSON and FREEMAN [20].

In the calculations described in this investigation, we have tried to use empirical quantities as little as possible. No restrictions have been placed on the magnitude of  $S$  and  $\lambda$ .

### Principles of the calculation

All details of the calculation described here can be found in Ref. [13]. The qualitative aspects of the molecular orbital theory and its applications to tetrahedral and octahedral complexes have been described extensively in the literature [1, 4, 13, 18, 22]. In our calculation we will use the same co-ordinate systems and combinations of ligand orbitals as given by [4, 18].

We can now limit our discussion to the computation of the  $H_{ij}$ - and  $S_{ij}$ -integrals. The Cu-functions used in this calculation are given by RICHARDSON et al. [10, 11] while the Cl-functions are from WATSON and FREEMAN [19]. Throughout the Cu-Cl distance was supposed to be  $2.22 \text{ \AA} = 4.194 \text{ a.u.}$  [7]. The calculations were performed with an IBM 1620 Data Processing System.

The  $S_{ij}$ -integrals were first expressed in terms of the  $A_n$  and  $B_n$  auxiliary functions as given by ROTHMAN [12]. With the help of these expressions, a computer program was easily written.

From the overlap-integrals  $S_{ij}$ , group overlap integrals were obtained using formulas given in Ref. [18]. It appeared that in these calculations, the ligand-ligand overlap-integrals are of considerable magnitude and cannot be neglected.

We now first turn our attention to the computation of the  $H_{ii}$ -integrals. To compute these integrals we define our one-electron Hamiltonian as follows:

$$H = -\frac{\nabla^2}{2} - \frac{Z_\alpha}{r_{1\alpha}} + \sum_{j \neq i} (1 - P_{12}) \int \frac{\varphi_j(2) \varphi_j(2)}{r_{12}} d\tau_2 - \sum_{\beta} \frac{Z_\beta}{r_{1\beta}} + \sum_k (1 - P_{12}) \int \frac{\varphi_k(2) \varphi_k(2)}{r_{12}} d\tau_2. \quad (3)$$

The first term is the kinetic energy of the electron. The second term is the potential energy of the electron in the field of the nucleus of the atom  $\alpha$  where  $\alpha$  is the atom to which the orbital  $\varphi_i$  belongs and  $Z_\alpha$  is the nuclear charge of atom  $\alpha$ . The third term of (3) represents the Coulomb and exchange interaction of the electron with the electrons in all other occupied orbitals belonging to the same atom.  $P_{12}$  is an operator which permutes the electrons 1 and 2. The fourth term is the potential energy of the electron in the field of the nuclei of the other atoms in the molecule;  $Z_\beta$  is the nuclear charge of the atom  $\beta$ . The last term is the Coulomb and exchange interaction of the electron with the electrons in all occupied orbitals belonging to the atoms  $\beta$ .

The first and second term of Eq. (3) lead to only one-centre one-electron integrals and can be calculated straight forwardly (see Roothaan [12]). The third term can be expressed in terms of the Condon and Shortley  $F^k$  and  $G^k$  integrals [2, 6]:

$$F^k = \langle R_{n_i l_i}(1) R_{n_j l_j}(2) \left| \begin{array}{c} r^k \\ r^{k+1} \\ > \end{array} \right| R_{n_i l_i}(1) R_{n_j l_j}(2) \rangle$$

$$G^k = \langle R_{n_i l_i}(1) R_{n_j l_j}(2) \left| \begin{array}{c} r^k \\ r^{k+1} \\ > \end{array} \right| R_{n_i l_i}(2) R_{n_j l_j}(1) \rangle. \quad (4)$$

Since our functions  $R_{nl}$  are linear combinations of Slater orbitals  $r^n e^{-ar}$ , all our  $F^k$  and  $G^k$  integrals are of the type:

$$I = \langle R_{m_1}(1) R_{n_1}(2) \left| \begin{array}{c} r^k \\ r^{k+1} \\ > \end{array} \right| R_{m_2}(1) R_{n_2}(2) \rangle \quad (5)$$

with

$$R_{m_i}(1) = N_{m_i} r_1^{m_i-1} e^{-a_i r_1}$$

$$R_{n_i}(2) = N_{n_i} r_2^{n_i-1} e^{-b_i r_2}.$$

Letting

$$M = m_1 + m_2; N = n_1 + n_2$$

$$A = a_1 + a_2; B = b_1 + b_2$$

and using simple mathematics, the following formula is easily derived:

$$I = \frac{N_{m_1} N_{m_2} N_{n_1} N_{n_2}}{A^M B^{N+1}} P M \cdot$$

$$\cdot \left\{ \frac{(N+k)! (M-k-1)!}{P^{M-k}} - \frac{1}{(1+P)^{M-k}} \sum_{j=0}^{N+k-1} [(N+k)! - (N-k-1)! \prod_{l=0}^{2k} (J-l)] \cdot \right.$$

$$\left. \frac{(M+J-k-1)}{J! (1+P)^J} \right\}. \quad (6)$$

Above

$$P = A/B$$

$$\prod_{l=0}^{2k} (J-l) = J(J-1) \dots (J-2k).$$

With the help of this formula FORTRAN computer programs were written for the  $F^k$  and  $G^k$  integrals.

The fourth and fifth term of Eq. (3) give the interaction of an electron of a certain atom in the molecule with all other atoms in the molecule. To compute these terms we have to calculate two- and three center integrals. This is a complicated operation and at any rate quite beyond the possibilities of our computer. There are however also other approximations in the calculation (choice of atomic orbitals, definition of the hamiltonian, etc.) and therefore an exact computation of all integrals may be superfluous. As an acceptable approximation for the fourth and fifth term of Eq. (3) we assumed in the calculation of the  $H_{ii}$  integrals that the other atoms in the molecule behave as point charges. Hence we replaced the two terms in our one-electron Hamiltonian by

$$\sum_{\beta} \frac{Z'_{\beta}}{r_{1\beta}}. \quad (7)$$

The integrals  $\langle \varphi_i^\alpha(1) | \frac{1}{r_{1\beta}} | \varphi_i^\alpha(1) \rangle$  that have to be calculated now, can be expressed in terms of  $A_n$ - and  $B_n$ -integrals and a computer program can be written.

The effective charges  $Z'_\beta$  were calculated, using shielding constants for each electron (compare Slater's method for shielding constants in one atom [14]):

Suppose orbital  $\varphi_i$  belongs to nucleus  $\alpha$  and orbital  $\varphi_j$  to nucleus  $\beta$ , then we define  $S_j(i)$  as the screening of an electron in  $\varphi_i$  from nucleus  $\beta$  by an electron in  $\varphi_j$ : With this definition we obtain for an electron in  $\varphi_i$

$$Z'_\beta = Z_\beta - \sum_j S_j(i). \quad (8)$$

The summation  $j$  extends over all occupied orbitals of atom  $\beta$ . The shielding constants  $S_j(i)$  were partly calculated and partly estimated from the form and the range of the atomic wave functions.

The procedure consists in concentrating the two electrons in "spherical shells" between  $r_{\max}$  and  $r_{\min}$ . The two spherical shells shall in general intersect each

Table 1. *Shielding constants in  $\text{CuCl}_4^{2-}$*   
The shielding constants of all lower lying orbitals were supposed to be 1,00

$\varphi_i$	$\varphi_j$	$S_j(i)$	$S_i(j)$
4s (Cu)	3s (Cl)	0,93	0,57
4s (Cu)	3p (Cl)	0,90	0,62
4p (Cu)	3s (Cl)	0,96	0,49
4p (Cu)	3p (Cl)	0,91	0,51
3d (Cu)	3s (Cl)	0,98	0,98
3d (Cu)	3p (Cl)	0,95	0,97
3s (Cl)	3s (Cl')	1,00	1,00
3s (Cl)	3p (Cl')	0,99	1,00
3p (Cl)	3p (Cl')	0,98	0,98

other. That part of the shell of electron 1 that lies outside the shell of electron 2 is considered to be completely screened (screening is 1); that part completely inside is assumed to be not screened at all while the screening in the intersection region is computed from the average densities of the electrons 1 and 2 in that region. The different contributions are then weighted for the fractional volume of electron 1 and the results added to give the total screening factor  $S_2(1)$ .

Tab. 1 gives the shielding constants used in the calculation on tetrahedral  $\text{CuCl}_4^{2-}$ . Using these data, we obtained  $H_{ii}$ -integrals for the 3d, 4s and 4p-orbitals of Cu and for the 3s and 3p-orbitals of Cl.

The  $H_{ij}$ -integrals  $\langle \varphi_i | H | \varphi_j \rangle$  were also approximated. To compute these integrals exactly we would have had to compute three- and four-centre integrals and since we were not in the position to do that, we calculated the  $H_{ij}$ -integrals with the help of the formula

$$H_{ij} = -FG_{ij} \sqrt{H_{ii}H_{jj}} \quad (9)$$

$F$  = constant;  $G_{ij}$  is a group overlap-integral.

The exactness of this formula has been studied by different authors [3,4] and in most cases the formula gives reasonable results if one takes  $F$  to lie between 1,6 and 2,0. Following WOLFSBERG and HELMHOLZ [22], we set  $F = 1,67$  for  $\sigma$ -bonding orbitals and  $F = 2,00$  for  $\pi$ -bonding orbitals.

### Iteration Process

The atomic wave functions that were used in the calculation of  $H_{ii}$  and  $H_{ij}$ -integrals are rather dependent on the configuration to which they belong. So the  $3d$ -function of copper in the  $d^9$ -configuration differs from that in the  $d^{10}$ -configuration. In our calculation we computed the  $H_{ij}$ - and  $S_{ij}$ -integrals for all intermediate configurations. Let an arbitrary configuration be given by Cu ( $d^{10-A} s^B p^C$ ) Cl $^{-D}$  which means that there are  $10 - A$  electrons in the Cu- $3d$  orbitals,  $B$  electrons in the Cu- $4s$  orbitals,  $C$  electrons in the Cu- $4p$  orbitals and  $5 + D$  electrons in the Cl- $3p$  orbitals. In our case we may suppose  $0 < A, B, C, D < 1$ . By the interpolation procedure we obtained the  $H_{ij}$  and  $S_{ij}$  integrals as functions of  $A, B, C$  and  $D$ .

For the calculation of the correct molecular orbitals and the one-electron energies we now used the following iteration process:

- a) Initial values of  $A, B, C$  and  $D$  were estimated:  $A_0, B_0, C_0$  and  $D_0$ .
- b) The  $H_{ij}$  and  $S_{ij}$ -integrals belonging to  $A_0, B_0, C_0$  and  $D_0$  were computed and the secular determinants found in this way were evaluated giving us certain molecular orbitals  $\psi_i^0$ .
- c) From the functions  $\psi_i^0$  new values of  $A, B, C$  and  $D$  were computed:  $A_1, B_1, C_1$  and  $D_1$ .
- d) The process was repeated with  $A_1, B_1, C_1$  and  $D_1$  as new initial values etc., until consistency in the values of  $A, B, C$  and  $D$  was reached.

The values of  $A, B, C$  and  $D$  for which consistency was reached were supposed to be the correct  $A, B, C$  and  $D$  and the molecular orbitals and energies belonging to it to be the correct molecular orbitals and the correct one-electron energies in our approximation. In calculating  $A, B, C$  and  $D$  from the wave functions we could not use Mulliken's method of dividing the overlap charge between the two nuclei [8] since in some cases we got negative values for  $A, B, C$  or  $D$  and this is physically impossible. Instead we defined for a molecular orbital  $\psi = C_A \varphi_A + C_B \varphi_B$  the charges on the nuclei  $A$  and  $B$  as follows:

$$Q_A = \frac{C_A^2}{C_A^2 + C_B^2}$$

and

$$Q_B = \frac{C_B^2}{C_A^2 + C_B^2}.$$

For the evaluation of the secular determinant we used a modification of an S.P.S. (Symbolic Programming System) computer program made by VELTKAMP and CLEMENT [17].

### Results of the calculation on tetrahedral $\text{CuCl}_4^{2-}$

For the ground state of tetrahedral  $\text{CuCl}_4^{2-}$  we obtained the following values of  $A, B, C$  and  $D$ :  $A = 0,541$ ;  $B = 0,116$ ;  $C = 0,506$ ;  $D = 0,730$ .

The eigenvalues and eigenfunctions belonging to the computed charge distribution are listed in Tab. 2. The results prompt us to make the following remarks:

a) The relative positions of the one-electron energies belonging to the computed charge distribution are quite different from those belonging to the ionic model

Table 2. *One-electron Energies and Molecular Orbitals in Tetrahedral CuCl<sub>4</sub><sup>2-</sup>*

$A_1$ symmetry		$\epsilon_{mo}$	4s	$\chi(\sigma)$	$\chi(s)$
$3a_1$		0,2360	1,559	- 0,950	- 0,501
$2a_1$		- 0,3958	0,038	0,983	- 0,147
$1a_1$		- 0,9075	- 0,273	0,185	1,100
$E$ symmetry		$\epsilon_{mo}$	3d	$\chi(\pi)$	
2e		- 0,3235	0,836	- 0,605	
1e		- 0,3710	0,552	0,799	

$T_1$  symmetry  $\epsilon = - 0,3227$

$T_2$ symmetry		$\epsilon_{mo}$	4p	3d	$\chi(\pi)$	$\chi(\sigma)$	$\chi(s)$
$5t_2$		0,1418	1,448	0,086	0,555	- 0,377	- 0,572
$4t_2$		- 0,3096	- 0,057	0,707	- 0,395	- 0,690	- 0,087
$3t_2$		- 0,3584	- 0,004	0,710	0,226	0,613	0,001
$2t_2$		- 0,3712	0,016	0,064	0,910	- 0,381	0,035
$1t_2$		- 0,9117	- 0,351	- 0,002	- 0,156	0,077	1,164

Table 3. *H<sub>ii</sub>-integrals in tetrahedral CuCl<sub>4</sub><sup>2-</sup>*

Symmetry	Orbital	Ionic Model	Covalent Model
$A_1$	Cu - 4s	- 0,2342	- 0,1700
	Cl - 3p $\sigma$ comb.	- 0,3894	- 0,4047
	Cl - 3s comb.	- 0,8454	- 0,8731
$E$	Cu - 3d	- 0,6104	- 0,3408
	Cl - 3p $\pi$ comb.	- 0,3291	- 0,3566
$T_1$	Cl - 3p $\pi$ comb.	- 0,2922	- 0,3227
$T_2$	Cu - 4p	- 0,0624	- 0,1364
	Cu - 3d	- 0,6091	- 0,3405
	Cl - 3p $\pi$ comb.	- 0,3406	- 0,3669
	Cl - 3p $\sigma$ comb.	- 0,3228	- 0,3429
	Cl - 3s comb.	- 0,8255	- 0,8534

( $A = 1, B = C = 0, D = 1$ ). Tab. 3 gives the  $H_{ii}$ -integrals for both cases and from this table we see that in the ionic model the energies of the ligand 3p-electrons are higher than the energies of the 3d-electrons of the central ion. So if we bring together one Cu<sup>2+</sup>-ion and four Cl<sup>-</sup>-ions, the charge of the filled ligand orbitals will flow to the partly filled central ion orbitals with lower energy. At the same time, the energy of the ligand orbitals decreases and the energy of the central ion

orbitals increases. When self consistency is obtained the energy of the ligand orbitals is just below that of the central ion orbitals. However, instead of  $\text{Cu}^{2+}$  and  $\text{Cl}^-$  we now have  $\text{Cu}^{+0,92}$  and  $\text{Cl}^{-0,73}$ .

b) The splitting of the  $d$ -orbitals is given in Fig. 1. The lefthand side of this figure gives the  $H_{ii}$ -integrals for the  $3d$ -orbitals at the computed charge distribution; the righthand side gives the energies of the molecular orbitals that are predominantly of  $3d$ -character. The splitting in the  $H_{ii}$ -integrals is only  $0,00834$  a.u. =  $74$   $\text{cm}^{-1}$ ; the splitting in the molecular orbitals is however  $0,01390$  a.u. =  $3050$   $\text{cm}^{-1}$ . In first approximation we can compare this splitting with  $\Delta = E(^2E) - E(^2T_2)$ . From optical spectra and from crystal field calculations a value of  $3500$  to  $4000$   $\text{cm}^{-1}$  for  $\Delta$  is expected [5].

c) In a number of molecular orbital calculations, the concepts of bonding and antibonding orbitals are correlated with a positive and a negative overlap population respectively [8]. This view is founded on the fact that in most cases with a positive overlap population, charge is concentrated between the nuclei, thus giving a bonding effect. However, in our calculation we must apply these considerations

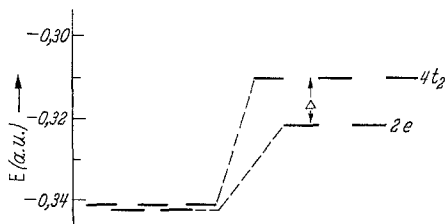


Fig. 1. Splitting of the  $d$ -orbitals in tetrahedral  $\text{CuCl}_4^{2-}$

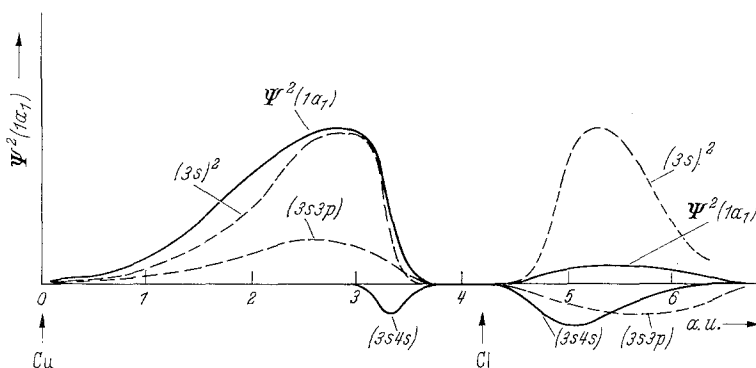


Fig. 2. Charge density in bonding  $1a_1$ -orbital

with some reserve. The  $4p$ -function of Cu has its greatest density not between the Cu- and the Cl-nuclei but on the other side of the Cl-nucleus and the same holds to a certain extent for the  $4s$ -function. This may be the reason that although we find in some bonding orbitals (for instance  $1a$  and  $1t_2$ ) a negative overlap population, these orbitals give a charge concentration between the nuclei, as can be seen by plotting  $\psi^2$  against the distance (Fig. 2).

#### Results of the calculation on square planar $\text{CuCl}_4^{2-}$

In the calculation on the ground state of square planar  $\text{CuCl}_4^{2-}$ , all overlap-integrals involving functions of two opposite ligands were neglected. With the method described above we then found for the charge distribution:  $A = 0,500$ ;  $B = 0,133$ ;  $C = 0,671$ ;  $D = 0,699$ .

So in this case we find on copper a charge of  $+0,80$  and on each of the ligands  $-0,70$ . Hence in the square planar complex there is more negative charge on the central ion compared with the tetrahedral complex.

Table 4. *One-electron Energies and Molecular Orbitals in Square Planar  $\text{CuCl}_4^{2-}$*

$A_{1g}$ symmetry		$\varepsilon_{mo}$	$4s$	$3d_{z^2}$	$\chi(\sigma)$	$\chi(s)$
	$4a_{1g}$	0,4021	1,728	0,049	-1,162	-0,644
	$3a_{1g}$	-0,3153	-0,045	0,970	-0,293	0,086
	$2a_{1g}$	-0,3780	0,072	0,257	0,904	-0,078
	$1a_{1g}$	-0,8887	-0,284	-0,006	0,184	1,119
$A_{2g}$ symmetry	$\varepsilon = -0,2955$					
$A_{2u}$ symmetry		$\varepsilon_{mo}$	$4p_z$	$\chi(\pi)$		
	$2a_{2u}$	0,0105	1,141	-0,784		
	$1a_{2u}$	-0,3593	0,231	0,862		
$B_{1g}$ symmetry		$\varepsilon_{mo}$	$3d_{x^2-y^2}$	$\chi(\pi)$		
	$2b_{1g}$	-0,2997	0,914	-0,479		
	$1b_{1g}$	-0,3631	0,411	0,881		
$B_{1u}$ symmetry	$\varepsilon = -0,3078$					
$B_{2g}$ symmetry		$\varepsilon_{mo}$	$3d_{xy}$	$\chi(\sigma)$	$\chi(s)$	
	$3b_{2g}$	-0,2730	0,771	-0,759	-0,132	
	$2b_{2g}$	-0,3393	0,659	0,670	-0,007	
	$1b_{2g}$	-0,8306	0,004	-0,004	0,999	
$E_g$ symmetry		$\varepsilon_{mo}$	$3d_{xz}, 3d_{yz}$	$\chi(\pi)$		
	$2e_g$	-0,3044	0,787	-0,663		
	$1e_g$	-0,3417	0,619	0,751		
$E_u$ symmetry		$\varepsilon_{mo}$	$4p_x, 4p_y$	$\chi(\pi)$	$\chi(\sigma)$	$\chi(s)$
	$4e_u$	0,2694	1,624	-0,546	-0,404	-0,801
	$3e_u$	-0,3180	-0,011	0,935	-0,425	-0,067
	$2e_u$	-0,3536	0,004	0,375	0,904	-0,030
	$1e_u$	-0,9262	-0,444	0,157	0,107	1,255

The molecular orbitals and the one-electron energies belonging to this charge distribution are tabulated in Tab. 4. As might be expected, the splitting of the  $3d$ -orbitals is different from that in tetrahedral  $\text{CuCl}_4^{2-}$  as can be seen from Fig. 3. The relative splitting of the  $3d$ -orbitals agrees with the literature (see for instance Ref. [9] p. 24; we used a different co-ordinate system, so  $d_{x^2-y^2}$  and  $d_{xy}$  have to



be interchanged to make a satisfactory comparison possible). The maximum splitting is equal to:  $E(d_{xy}) - E(d_{z^2}) = 0,0424$  a.u. =  $9300$  cm $^{-1}$ .

This value is a very reasonable one for square planar complexes [5]. Fig. 4 compares the  $3d$ -energies in tetrahedral and square planar  $\text{CuCl}_4^{2-}$ . The actual

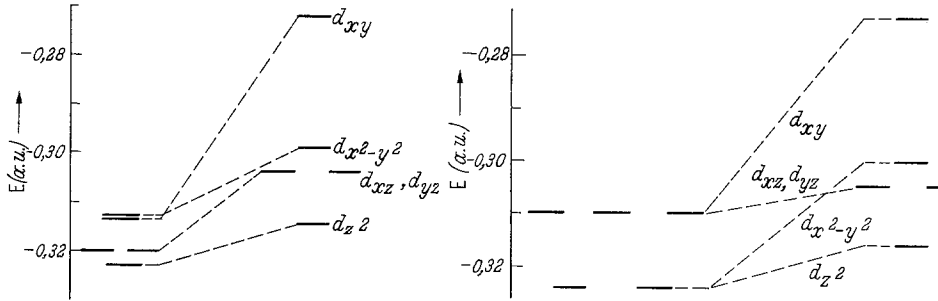


Fig. 3

Fig. 4

Fig. 3. Splitting of the  $d$ -orbitals in square planar  $\text{CuCl}_4^{2-}$ Fig. 4. Tetrahedral and square planar  $\text{CuCl}_4^{2-}$ 

structure of  $\text{CuCl}_4^{2-}$  is intermediate between the tetrahedral and the square planar structures.

### Results of the calculations on Cu in a octahedral $\text{Cl}^-$ environment

A calculation on octahedral  $\text{CuCl}_6^{4-}$  yielded the following results:  $A = 0,926$ ;  $B = 0,515$ ;  $C = 0,466$ ;  $D = 0,824$ .

Tab. 5 contains one-electron energies and the molecular orbitals of  $\text{CuCl}_6^{4-}$ . As can be seen from the table, the one-electron energies of  $\text{CuCl}_6^{4-}$  are surprisingly

Table 5. One-electron Energies and Molecular Orbitals in Octahedral  $\text{CuCl}_6^{4-}$ 

$A_{1g}$ symmetry	$\varepsilon_{mo}$	$4s$	$\chi(\sigma)$	$\chi(s)$	
$3a_{1g}$	0,5090	2,122	- 1,682	- 0,837	
$2a_{1g}$	- 0,1266	0,383	0,719	- 0,214	
$1a_{1g}$	- 0,5907	- 0,258	0,109	1,117	
$E_g$ symmetry	$\varepsilon_{mo}$	$3d$	$\chi(\sigma)$	$\chi(s)$	
$3e_g$	- 0,0548	0,997	- 0,274	- 0,051	
$2e_g$	- 0,0855	0,154	0,972	0,425	
$1e_g$	- 0,5515	- 0,043	0,038	1,004	
$T_{1g}$	$\varepsilon = - 0,0619$				
$T_{1u}$ symmetry	$\varepsilon_{mo}$	$4p$	$\chi(\pi)$	$\chi(\sigma)$	$\chi(s)$
$4t_{1u}$	0,3928	1,619	- 0,477	- 0,453	- 0,799
$3t_{1u}$	- 0,0699	- 0,137	0,984	- 0,516	0,004
$2t_{1u}$	- 0,1039	- 0,188	0,464	0,905	0,056
$1t_{1u}$	- 0,5731	- 0,194	0,037	0,076	1,104

Table 5 (Continuation)

$T_{2g}$ symmetry	$\epsilon_{mo}$	$3d$	$\chi (\pi)$
$2t_{2g}$	- 0,0582	0,975	- 0,296
$1t_{2g}$	- 0,0756	0,232	0,957

$T_{2u}$  symmetry  $\epsilon = - 0,0646$

high with respect to the one-electron energies of  $\text{CuCl}_4^{2-}$ , thus indicating that  $\text{CuCl}_6^{4-}$  is very unstable. Also the splitting of the  $3d$ -orbitals is rather small (Fig. 5). There is no possibility of experimental verification of this value, since no  $\text{CuCl}_6^{4-}$ -complex is known. There is, however, a situation in which Cu is surrounded by six Cl-ligands, namely in a  $\text{CuCl}_2$ -crystal. In this crystal Cu is found in a distorted octahedron of Cl with 4 Cl ligands at a distance of 2,30 Å and 2 Cl ligands at 2,95 Å [21]. To get an impression of the stability of Cu in this type of surrounding, we have made a very approximate calculation on Cu in a  $\text{CuCl}_2$ -crystal. As a model an idealised cubic structure of  $\text{CuCl}_2$  was used, taking 2,22 Å (as in  $\text{CuCl}_4^{2-}$ ) for the

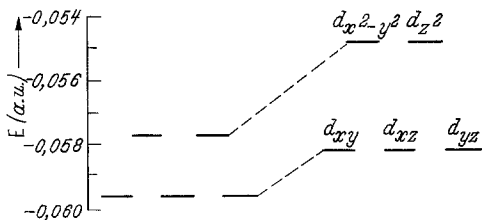


Fig. 5

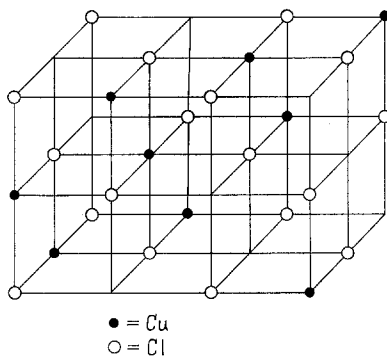
Fig. 5. Splitting of the  $d$ -orbitals in  $\text{CuCl}_6^{4-}$ 

Fig. 6

Fig. 6. Simplified model of  $\text{CuCl}_2$ -crystal

smallest Cu-Cl distance. See Fig. 6. From this  $\text{CuCl}_2$ -crystal we took a  $\text{CuCl}_6$ -unit and to this unit we applied a molecular orbital calculation. The electrons of the  $\text{CuCl}_6$ -unit are not only affected by atoms of this unit, but also by atoms situated outside the  $\text{CuCl}_6$ -unit.

This influence manifests itself in the  $H_{ii}$ -integrals and via Eq. (9) subsequently in the  $H_{ij}$ -integrals. Every atom in the  $\text{CuCl}_6$ -unit is now affected by the other atoms of the crystal owing to the potential field of these atoms. However, the combined influence of Cu- and Cl-ions is supposed to cancel when the distance to the central Cu-atom surpasses a radius  $r$  that is considered to be small enough to limit the actual computation to only a few surrounding atoms. To make the influence of the more distant atoms cancel, the group selected should be electro-neutral. For the central Cu-atom for instance it suffices to take into account the 6 Cl-atoms at  $r_0$  already considered in the  $\text{CuCl}_6$ -unit and in addition 6 Cu-atoms at  $r_0 \sqrt{2}$  and 8 Cl-atoms at  $r_0 \sqrt{3}$ . For a Cl-atom of the  $\text{CuCl}_6$ -unit we select 3 Cu-atoms at  $r_0$ , 4 Cu-atoms at  $r_0 \sqrt{3}$ , 12 Cl-atoms at  $r_0 \sqrt{2}$  and one Cl-atom at  $2r_0$ . Their "field" is calculated similarly as given by Eq. (7) and (8).

The following charge distribution was thus obtained:  $A = 0,768$ ;  $B = 0,445$ ;  $C = 1,242$ ;  $D = 0,041$ .

This results in a charge of + 0,08 on Cu and - 0,04 on Cl. The charge differences in the  $\text{CuCl}_2$ -crystal seem to be very small. However, these effective charges do not give us a good insight into the amount of charge that we can find on different sites in the complex. As stated above, the 4s- and 4p-orbitals of Cu

Table 6. Charge Distributions in the Copper-chloride Complex

Complex	Effective charge		"Spatial" Charge Distribution	
	Cu	Cl	Cu-site	Cl-site
Tetrahedral $\text{CuCl}_4^{2-}$ . . . . .	0,92	- 0,73	1,54	- 0,89
Square Planar $\text{CuCl}_4^{2-}$ . . . . .	0,80	- 0,70	1,50	- 0,88
Octahedral $\text{CuCl}_6^{4-}$ . . . . .	0,94	- 0,82	1,93	- 0,99
$\text{CuCl}_6$ -unit of $\text{CuCl}_2$ -crystal . . . . .	0,08	- 0,04	1,77	- 0,88

Table 7. One-electron Energies and Molecular Orbitals in a  $\text{CuCl}_6$ -unit of a  $\text{CuCl}_2$ -crystal

$A_{1g}$ symmetry					
	$\varepsilon_{mo}$	4s	$\chi(\sigma)$	$\chi(s)$	
$3a_{1g}$	4,603	1,911	- 1,404	- 1,056	
$2a_{1g}$	- 1,817	0,106	0,727	- 0,725	
$1a_{1g}$	- 2,261	0,348	0,346	0,564	
$E_g$ symmetry					
	$\varepsilon_{mo}$	3d	$\chi(\sigma)$	$\chi(s)$	
$3e_g$	- 1,260	0,940	- 0,471	- 0,211	
$2e_g$	- 1,626	0,363	0,886	0,072	
$1e_g$	- 1,963	0,087	- 0,107	0,980	
$T_{1g}$ symmetry	$\varepsilon = - 1,546$				
$T_{1u}$ symmetry					
	$\varepsilon_{mo}$	4p	$\chi(\pi)$	$\chi(\sigma)$	$\chi(s)$
$4t_{1u}$	1,468	1,477	- 0,672	- 0,434	- 1,019
$3t_{1u}$	- 1,548	0,008	0,758	- 0,720	- 0,181
$2t_{1u}$	- 1,795	0,081	0,522	0,653	- 0,487
$1t_{1u}$	- 2,176	0,352	0,208	0,104	0,664
$T_{2g}$ symmetry					
	$\varepsilon_{mo}$	3d	$\chi(\pi)$		
$2t_{2g}$	- 1,324	0,977	- 0,288		
$1t_{2g}$	- 1,742	0,223	0,960		
$T_{2u}$ symmetry	$\varepsilon = - 1,589$				

have their greatest density in the neighbourhood of the Cl-nucleus and so we can get a better insight into the spatial charge distribution if we associate the 4s- and 4p-electrons with the Cl-charge. Tab. 6 shows clearly that we then obtain a somewhat different impression of the charge distribution. This, however, also indicates that the 4s- and 4p-orbitals are not very suitable in describing the bonding

between Cu and Cl. The molecular orbitals and one-electron energies of a  $\text{CuCl}_6$ -unit in a  $\text{CuCl}_2$ -crystal are given in Tab. 7. Fig. 7 gives the splitting of the  $3d$ -orbitals. We now find a splitting of  $14300 \text{ cm}^{-1}$ . Experimentally, the splitting is

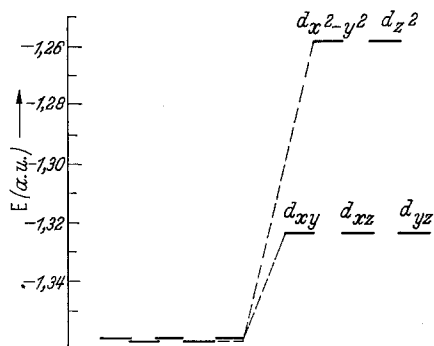


Fig. 7. Splitting of the  $d$ -orbitals in a  $\text{CuCl}_2$ -crystal

found to be  $8000 - 10000 \text{ cm}^{-1}$  but in view of the crude approximations we used in the calculation on the  $\text{CuCl}_2$ -crystal, the result is satisfactory.

Although the calculations performed here involved many approximations the results are at least qualitatively reasonably good. To discuss the results quantitatively, we must compare them with data that can be obtained from optical and magnetic spectra. This is reserved for a following paper.

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