Molecular orbital calculations on copper-chloride complexes

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MOLECULAR ORBITAL CALCULATIONS
ON
COPPER-CHLORIDE COMPLEXES

P. ROS

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PROEFSCHRIFT

TER VERKRIJGING VAN DE GRAAD VAN
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AAN DE TECHNISCHE HOGESCHOOL TE EINDHOVEN
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PROF. DR. G.C.A. SCHUIT

Aan mijn Ouders
Aan Dina en Marianne

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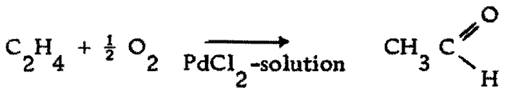
CHAPTER I

INTRODUCTION

Chemists have for a long time been interested to know what determines the stability of the chemical compounds. The last few years, however, this question has not only been a matter of curiosity, but an answer to the question has become a necessity because in several branches of chemistry problems have arisen that are closely connected with the stability of compounds. As an instance, we may refer to the theory of catalysis.

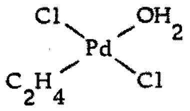
Until a few years ago, research on catalysis had been almost entirely empirical. Only in a few cases had it been possible to explain the working of a catalyst. It was then tried to change the empirical character of catalysis research, some of the methods being attempts to relate this research to the theories of the solid state, of the surfaces of the solid state, of the structure of the solid state, etc.
It turned out that in order to understand the fundamental problems of catalysis, knowledge of the theories on chemical bonding was indispensable.

To explain the working of a catalyst in a certain reaction, it is often necessary to assume the existence of an "intermediate complex". A good example of this is given by the catalysis reaction known as the "Wacker reaction" (1, 2):



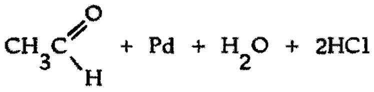
$$C_2H_4 + \tfrac{1}{2} O_2 \xrightarrow[\text{PdCl}_2\text{-solution}]{} CH_3C\begin{matrix}\diagup\!\!\diagup O\\ \diagdown H\end{matrix}$$

A transition complex in this reaction is the palladium complex formed from $PdCl_2(H_2O)_2$ and C_2H_4



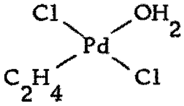
(1, 3)

This complex decomposes immediately with water into



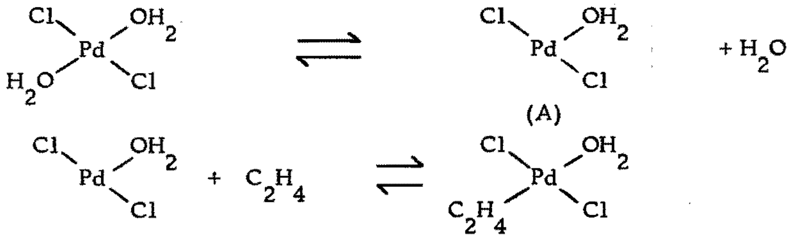
$$CH_3C\begin{matrix}\diagup\!\!\diagup O\\ \diagdown H\end{matrix} + Pd + H_2O + 2HCl$$

The palladium metal, which is precipitated by the decomposition, produces, together with oxygen and HCl, the complex $PdCl_2(H_2O)_2$ and so the cycle is closed. The formation of the intermediate complex

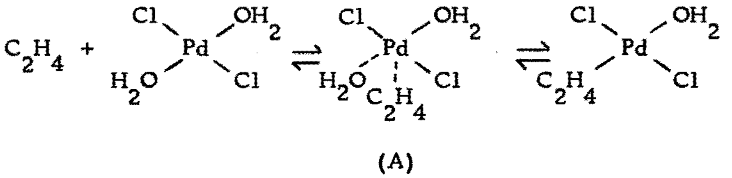


can proceed along two paths

(a)



(b)



In both cases there exists an unstable complex (A) that fulfils the following conditions:

(a) it must be formed rapidly from the reactants;

(b) it must be unstable, i.e., it must decompose rapidly into the reaction products.

From these considerations we see that catalysis provides two problems to the theoretical chemists -

(a) Given a catalysis reaction, what types of intermediate complexes may be formed?

(b) What is the stability of the complexes under (a)?

Considering the current theories on inorganic complexes, namely the crystal field theory and the molecular orbital theory (See Chapter II), we notice that the crystal field theory, even in its most perfect form, gives us little information about the stability of the complexes. For, as has been shown by Van Eck (4) and worked out by Schuit (5) in several papers, the crystal field theory gives us only some information about the destabilisation of complexes in which the central ion contains d-electrons, but the theory does not tell us anything about the stabilisation necessary for these complexes.

On the contrary, the molecular orbital theory accounts for both the stabilisation (bonding) and the destabilisation (anti-bonding) effects in complexes.

Therefore it is obviously necessary to use a molecular orbital description when dealing with the stability of complexes.

A further study of the literature shows us that the molecular orbital theory has mostly been applied qualitatively; only in a few cases have quantitative results been obtained. It will be shown in the following Chapter that this fact must be ascribed to the vast amount of computational work that an exact molecular orbital calculation requires.

Therefore quantitative molecular orbital calculations have only been performed on small molecules such as H_2, CO, etc. But since quantitative molecular orbital calculations of more complicated systems are becoming important nowadays, ever more attempts are being made to perform such calculations. Sometimes this is done by using empirical parameters (6), in other cases the calculation is only carried out on a limited part of the total problem (7).

In the investigation described here, it is attempted to perform a molecular orbital calculation from first principles. It is tried to carry out the calculation in as simple a manner as possible so that the calculation may be executed on a fairly small computer. However, this causes that the calculation cannot be performed exactly; on several points approximations have to be introduced. Our calculation possesses the same character as the calculations of Gray (6), but differs in that less use is made of empirical parameters.

The subject of this calculation is the tetrachlorocuprate(II) ion. This complex was chosen for the following reasons:

(a) The Cu^{2+} ion possesses nine 3d-electrons, so there is only one hole in the 3d shell. This fact simplifies a number of calculations and allows of some approximations.

(b) The structure of the $CuCl_4^{2-}$ ion has been investigated thoroughly by X-ray analyses.

(c) The $CuCl_4^{2-}$ ion presents a large amount of experimental information, for instance, position and intensity of the optical transitions, magnetic susceptibility and E.P.R. data.

These properties of the $CuCl_4^{2-}$ ion have caused several investigations and calculations. The following survey summarises a number of these investigations.

(a) Ballhausen (8) was one of the first to pay attention to the $CuCl_4^{2-}$ ion. He used a purely qualitative crystal field description.

(b) Felsenfeld (9) successfully accounted for the distortions in the $CuCl_4^{2-}$ ion by using an ionic model in which the energy of the system is represented by a compromise between the crystal field stabilisation energy of the cupric ion and the mutual Coulombic repulsion of the four chloride ligands.

(c) The complete qualitative theory of energy levels of Cu^{2+} (including spin orbit coupling effects) has been given by Liehr (10) for various crystal symmetries.

(d) In a paper on the absorption spectra of Cu^{2+} in oxide systems, Pappalardo (11) gave an explanation of the spectrum of Cu^{2+}. Using parameters obtained from the spectra of octahedrally coordinated Cu^{2+}, he obtained satisfactory values of the transition energies in tetrahedrally coordinated Cu^{2+}.

(e) Furlani (12) calculated the term systems of the configuration $(3d)^9$ according to the point charge model for an increasingly flattened tetrahedral structure and could then explain the near-infrared spectrum of $CuCl_4^{2-}$. However, he did not publish many details about his calculation.

(f) Lohr and Lipscomb (13) made an empirical molecular orbital calculation on $CuCl_4^{2-}$ by using Slater wave functions and Coulomb integrals that were estimated from ionisation potentials. They varied the bond angles in the complex and found a minimum of the total orbital energy for a distorted tetrahedral structure.

(g) Morosin and Lawson (14), to account for the configurations and spectra of $CuCl_4^{2-}$ and $CuBr_4^{2-}$, used a modification of the ionic model employed by Felsenfeld.

Most of these calculations are based on the crystal field theory and agree reasonably well with the experiments. This is supposed to be caused by the fact that $CuCl_4^{2-}$ may be described satisfactorily by an ionic model and that covalency effects are not important. For complexes that have a more covalent character it is expected that the crystal field approximation will give less good results. On the other hand, there are data that cannot be explained by the crystal field theory at all (charge transfer spectra, for instance).

The following molecular orbital calculation is not meant to improve the crystal field calculations; on the contrary, at best we can hope that our results will be of the same quality. It would not be the first time for a refinement of a model to cause a worsening of the results of a calculation. However, this may not be a reason to reject the refined model, because in principle it may offer us more possibilities and improve our knowledge of the chemical bond.

The purpose of the following work is to go a step further in the direction of a complete molecular orbital calculation from first principles, and at the same time to construct a method that can be carried out comparatively easily.

The following calculation is applied not only to Cu^{2+} in a tetrahedral Cl^- environment (Chapter III), but also to Cu^{2+} in a square planar Cl^- environment (Chapter IV) and to Cu^{2+} in an octahedral Cl^- environment (Chapter V). This is done because it allows of

(a) the studying of the splitting of the d-orbitals in different environments,

(b) the comparison of the stability of the different environments.

REFERENCES

1. J. Schmidt: Chem. and Ind. (1962), 54.
2. J. Schmidt: Angew. Chem. 74, (1962), 93.
3. P. Ros: Unpublished Work (Internal report of Inorg. Chem. Dep., (June 1962), Technological University, Eindhoven).
4. C.L. van Panthaleon van Eck: Thesis, Leiden (1958).
5. G.C.A. Schuit: Rec. Trav. Chim. 81, (1962), 19; 81, (1962), 481; 83, (1964), 5.
6. H.B. Gray, C.J. Ballhausen: Inorg. Chem. 1, (1962), 111.

7. S. Sugano, R.G. Shulman: Phys. Rev. 130, (1963), 517.
8. C.J. Ballhausen: Dan. Mat. Fys. Medd. 29, (1954), no 4.
9. G. Felsenfeld: Proc. Roy. Soc. London A 236, (1956), 506.
10. A.D. Liehr: J. Phys. Chem. 64, (1960), 43.
11. R. Pappalardo: Mol. Spectr. 6, (1961), 554.
12. C. Furlani, G. Morpurgo: Theor. Chim. Acta 1, (1963), 102.
13. L.L. Lohr, W.N. Lipscomp: Inorg. Chem. 2, (1963), 911.
14. B. Morosin, K. Lawson: Mol. Spectr. 12, (1964), 98.

CHAPTER II

MOLECULAR ORBITAL THEORY

II-1 GENERAL INTRODUCTION

The problems encountered in the preceding pages can be summarised as follows: How to find the description of an inorganic complex that offers a satisfactory explanation of the stability, the optical spectra and the magnetic properties of this complex. Several theories have been proposed in the course of time, the most important being

(a) valence bond theory;
(b) crystal field theory;
(c) molecular orbital theory.

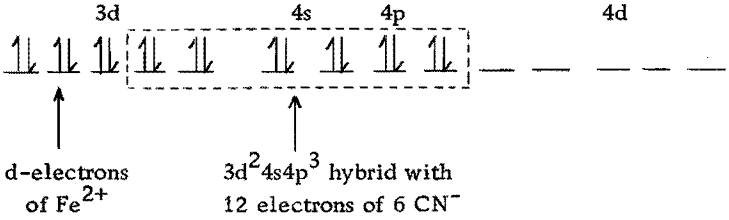
(a) Valence Bond Theory

This theory is the oldest of the three and was given by L. Pauling (1). He proposes for octahedral complexes MX_6 a d^2sp^3 hybridisation for the orbitals of the central ion. Two d-orbitals, one s-orbital and three p-orbitals are mixed to a lineair combination that points to the corners of an octahedron. Two cases may be distinguished:

(1) Inner hybridisation: $3d^24s4p^3$

This type of hybridisation occurs for ligands that form strong covalent bonds, such as for instance CN^-.

Example: $Fe(CN)_6^{4-}$

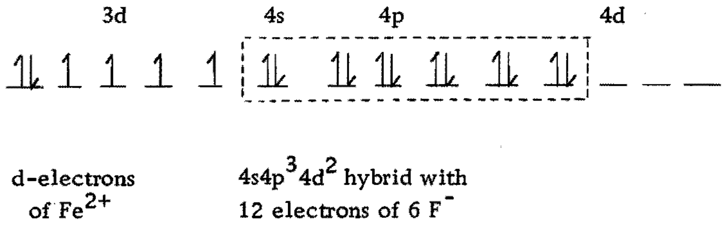


The total spinmoment is zero, the compound is diamagnetic.

(2) External hybridisation: $4s4p^34d^2$

This type is demonstrated by ligands that form principally ionic compounds (e.g. F^-).

Example: FeF_6^{4-}



According to this theory FeF_6^{4-} possesses four unpaired electrons in good agreement with susceptibility measurements.

The magnetic behaviour of complexes is thus satisfactorily explained by the theory. However, the optical spectra and the stability remain largely unexplained. In this respect the theory is unsatisfactory.

(b) Crystal Field Theory

Between 1950 and 1960 the crystal field theory was resuscitated by Hartmann (2), Orgel (3), Griffith (4) and others and was then applied to the particular case of transition metal ions (for a full treatment see Ref.(4)).

The theory starts from the model of a compound MX_6 in which the ligands X cause an electrostatic field on the site of the central ion. In this electrostatic field the degeneracy of the d-orbitals of the central ion is partly removed.

Comparing $Fe(CN)_6^{4-}$ with FeF_6^{4-}

we see that the crystal field theory gives an equally good explanation of the magnetic behaviour of inorganic complexes but is also capable of giving qualitative information on the optical spectra of the complexes of transition metal ions; these spectra are chiefly caused by the electron transfer of $t_{2g} \rightarrow e_g$.

Quantitatively the theory is less satisfactory. Attempts to calculate Δ from first principles have dismally failed. The essential cause of this failure lay in the approximation of considering the ligands as point charges or point dipoles, thus ignoring covalent interactions between central ion and ligands. Neither is the crystal field theory capable of predicting the positions of the charge transfer bands which are observed in the optical spectra. In actual practice the theory is still often used in a parametric form.

(c) Molecular Orbital Theory

The molecular orbital approximation dates from the early thirties and was introduced at that time by Van Vleck (5), Mulliken and others, especially for diatomic molecules.

The important assumption in this theory is that the orbital of a single electron is not localised on one of the atoms but is spread over the whole molecule or complex. This assumption is sustained by experimental data. For instance, the hyperfine structure in the E.P.R. spectrum of $IrCl_6^{2-}$ can only be explained by the supposition that the electron of which information is obtained in the spectrum of the Ir-ion, occurs for a considerable time in the neighbourhood of the Cl-nuclei (6). We shall discuss the molecular orbital theory more in detail.

II-2 FREE ATOMS

The theory of free atoms and ions has been dealt with in great detail by Condon and Shortley (7), Racah (8), and a fairly complete description has been given by Griffith in his book: "The Theory of Transition Metal Ions" (4), to which we will refer later.

From the theory it is concluded that the electrons are distributed over certain orbitals, characterised by the quantum numbers n, l, m_l, s and m_s, in "ket notation":

$$|n, l, m_l, s, m_s\rangle$$

For instance, $|2, 1, 0, \frac{1}{2}, \frac{1}{2}\rangle$ is an orbital with $n = 2$, $l = 1$, $m_l = 0$, $s = \frac{1}{2}$ and $m_s = \frac{1}{2}$.

As a first approximation the orbitals of the separate electrons are assumed to be given by

$$\phi = R_{nl} Y_{lm_l} \tau_{sm_s} \qquad (2.1)$$

R_{nl} is the radial part of the wave function ϕ, Y_{lm_l} being the angle-dependent part. τ_{sm_s} is a spinfunction.

For the quantum numbers the following holds:

$l \leqslant n-1$ with n and l integers

$l = 0, 1, 2, 3, \ldots$ s-, p-, d-, f-, ... functions

$-l \leqslant m_l \leqslant l$

$s = \frac{1}{2}$ for a single electron

$-s \leqslant m_s \leqslant s$

The functions Y_{lm_l} can be written as:

$$Y_{lm_l} = \Theta_{lm_l}(\theta)\ \Phi m_l(\varphi) \qquad (2.2)$$

The Θ_{lm_l} are associated Legendre polynominals in $\cos\theta$ and

$$\Phi_{m_l} = \frac{1}{\sqrt{2\pi}} e^{im_l\varphi}$$

The functions Y_{lm_l} are therefore complex. It is more convenient to use real functions that are defined as follows ($|lm_l\rangle = Y_{lm_l}$):

$$
\begin{array}{ll}
l = 1 & \left\{ \begin{array}{ll}
\frac{1}{\sqrt{2}}\left(|11\rangle + |1\,{-1}\rangle\right) & \sim \sin\theta\cos\varphi \\
\frac{-i}{\sqrt{2}}\left(|11\rangle - |1\,{-1}\rangle\right) & \sim \sin\theta\sin\varphi \\
|10\rangle & \sim \cos\theta
\end{array} \right. \\
l = 2 & \left\{ \begin{array}{ll}
\frac{-1}{\sqrt{2}}\left(|21\rangle - |2\,{-1}\rangle\right) & \sim \sin\theta\cos\theta\cos\varphi \\
\frac{i}{\sqrt{2}}\left(|21\rangle + |2\,{-1}\rangle\right) & \sim \sin\theta\cos\theta\sin\varphi \\
\frac{1}{i\sqrt{2}}\left(|22\rangle - |2\,{-2}\rangle\right) & \sim \sin^2\theta\sin 2\varphi \\
\frac{1}{\sqrt{2}}\left(|22\rangle + |2\,{-2}\rangle\right) & \sim \sin^2\theta\cos 2\varphi \\
|20\rangle & \sim (3\cos^2\theta - 1)
\end{array} \right.
\end{array}
\qquad (2.3)
$$

The one-electron wave functions can now be written as:

$$
\begin{aligned}
ns &= \left(\frac{1}{4\pi}\right)^{\frac{1}{2}} R_{ns} \\
np_x &= \left(\frac{3}{4\pi}\right)^{\frac{1}{2}} R_{np} \sin\theta\cos\varphi \\
np_y &= \left(\frac{3}{4\pi}\right)^{\frac{1}{2}} R_{np} \sin\theta\sin\varphi \\
np_z &= \left(\frac{3}{4\pi}\right)^{\frac{1}{2}} R_{np} \cos\theta \\
nd_{xz} &= \left(\frac{15}{4\pi}\right)^{\frac{1}{2}} R_{nd} \sin\theta\cos\theta\cos\varphi \\
nd_{yz} &= \left(\frac{15}{4\pi}\right)^{\frac{1}{2}} R_{nd} \sin\theta\cos\theta\sin\varphi \\
nd_{xy} &= \left(\frac{15}{16\pi}\right)^{\frac{1}{2}} R_{nd} \sin^2\theta\sin 2\varphi \\
nd_{x^2-y^2} &= \left(\frac{15}{16\pi}\right)^{\frac{1}{2}} R_{nd} \sin^2\theta\cos 2\varphi \\
nd_{z^2} &= \left(\frac{5}{16\pi}\right)^{\frac{1}{2}} R_{nd} (3\cos^2\theta - 1)
\end{aligned}
\qquad (2.4)
$$

In the following we shall, where necessary, indicate which functions are going to be used.

II-3 MOLECULES

This treatment of molecules starts from the assumption that the atoms in a molecule are located in a fixed position and do not vibrate. For an electron 1 in an orbital ψ_i in this molecule we then obtain:

$$H_i \psi_i(1) = E_i \psi_i(1) \tag{2.5}$$

in which

$$H_i = -\frac{\nabla_1^2}{2} - \sum_{\alpha} \frac{Z_\alpha}{r_{\alpha 1}} + \sum_{j \neq i} \frac{\psi_j(2)\,\psi_j(2)}{r_{12}} - \sum_{j \neq i} \delta(s_i, s_j) \frac{\psi_j(2)\,\psi_j(1)}{r_{12}} P_{12} \tag{2.6}$$

Equation (2.6) is written in atomic units.
The summation α is over all nuclei in the molecule, the summation j over all occupied orbitals in the molecule. Z_α is the electrical charge of nucleus α. P_{12} is a permutation that changes the electrons 1 and 2.

The wave equation (2.6) cannot be solved exactly, so we have to find an approximate solution for ψ_i.
We suppose therefore that the electron 1 is not localised on a certain atom but has been spread over the whole molecule. Let us assume that the wave functions $\phi_1, \ldots\ldots, \phi_n$ have been found for the free atoms of the molecule. Some of these $\phi_1, \ldots\ldots\ldots, \phi_n$ belong to a certain nucleus, for instance, $\phi_1, \ldots\ldots, \phi_j$ belong to nucleus α, others to another nucleus, etc.
We now approximate ψ_i with a linear combination of atomic orbitals (LCAO-approximation), i.e.:

$$\psi_i = \sum_{k=1}^{n} C_{ik}\, \phi_k \tag{2.7}$$

The coefficients C_{ik} are chosen in such a way that the energy E_i of ψ_i is minimal; hence:

$$\frac{\partial E}{\partial C_{ik}} = 0 \tag{2.8}$$

Starting from n independent atomic orbitals we thus find n equations with n variables. Defining

$$\begin{aligned} H_{kl} &= \langle \phi_k \,|\, H \,|\, \phi_l \rangle \\ S_{kl} &= \langle \phi_k \,|\, \phi_l \rangle \end{aligned} \tag{2.9}$$

the equations may be written as:

$$\begin{aligned} (H_{11} - E_i S_{11})\, C_1 + (H_{12} - E_i S_{12})\, C_2 + \ldots\ldots + (H_{1n} - E_i S_{1n})\, C_n &= 0 \\ (H_{n1} - E_i S_{n1})\, C_1 + (H_{n2} - E_i S_{n2})\, C_2 + \ldots\ldots + (H_{nn} - E_i S_{nn})\, C_n &= 0 \end{aligned} \tag{2.10}$$

They can only have a non-trivial solution if the determinant of the coefficients (the secular determinant) is zero, hence:

$$\begin{vmatrix} H_{11} - E_iS_{11} & \cdots\cdots\cdots\cdots & H_{1n} - E_iS_{1n} \\ \vdots & & \vdots \\ H_{n1} - E_iS_{n1} & \cdots\cdots\cdots\cdots & H_{nn} - E_iS_{nn} \end{vmatrix} = 0 \qquad (2.11)$$

This gives rise to an n^{th}-degree equation with n solutions for E_i : $E_1, \ldots\ldots, E_n$. With the help of this E_i we find from (2.10) the coefficients c_{ik}.

This is the most elementary form of the molecular orbital theory. Different variations have been proposed and if used later on they will be discussed then.

Since the number of atomic orbitals can, under certain circumstances, be quite considerable, the actual computation of the determinant may be difficult. One of the most powerful tools of the molecular orbital method is then given by the group theory. It shows the way to the construction of the correct linear combinations of the atomic orbitals which leads to a drastic reduction in the number of integrals H_{kl} and S_{kl} that have to be computed. This of course facilitates the solution considerably.

II-4 GROUP THEORY

Inorganic complexes posses a number of symmetry elements. The complex NiF_6^{4-} for instance, remains invariant under rotations over an angle of 90, 180 and 270 degrees around the z-axis, also under rotations over 120 and 240 degrees around the (1, 1, 1)-axis etc. All symmetry operations that leave the overall aspect of the complex unchanged form a group known as the symmetry group. Every complex is thus characterised by its own symmetry group.
The most important to us are:

octahedral complexes with the octahedral group O_h;
tetrahedral complexes with the tetrahedral group T_d;
square planar complexes with the square planar group D_{4h}.

A complete discussion of the group theory can be found in the References (4), (9), (10) and (27).

The essentials of the group theory that are important to us will now be summarised.

A group G is considered to be a collection of elements that have the following properties:

(a) The product of two elements of the group is again an element of the group.
(b) The multiplication is associative:

$$(g*h)*k = g* (h*k) .$$

(c) There is a unit element E such that $E*g = g*E = g$ for all g in G.
(d) Every element g of G has an inverse g^{-1} that also belongs to G, such that $g*g^{-1} = g^{-1}*g = E$.

The groups G and H are said to be isomorphic if there exists a 1 : 1 correspondence between their elements: $g \rightleftharpoons h$.
Each element g of G corresponds with only one element h of H such that if $g_i * g_j = g_k$ then also $h_i * h_j = h_k$.

The groups G and H are said to be homomorphic if one element g_i of G corresponds with m elements $h_{i1}, \ldots\ldots, h_{im}$ of H such that, if $g_i * g_j = g_k$, then also also (one of the h_{il})*(one of the h_{jl}) = (one of the h_{kl}).

A matrix representation of a group G is a group of matrices that is homomorphic with the group G. The matrix representation is irreducible if it cannot be subdivided into matrix representations of a lower dimension (with smaller matrices). The character of a matrix representation is the trace of the matrices of that representation. If the number of elements of a group is finite (finite group) there is only a limited number of irreducible representations. The characters of these representations are "orthogonal", that is:

$$\sum_g \chi_i^*(g)\, \chi_j(g) = h\, \delta_{ij} \tag{2.12}$$

where χ_i and χ_j are the characters of two representations of a group,
h is the number of elements of that group,
$\delta_{ij} = 0$ if χ_i and χ_j belong to different irreducible representations,
$\delta_{ij} = 1$ if χ_i and χ_j belong to identical irreducible representations, hence if $\chi_i(g) = \chi_j(g)$.

Since a finite group has only a limited number of independent characters, these can be collected conveniently in a character table. The character of any reducible representation can always be written as the sum of a number of characters from the character table. Let $\chi(g)$ be the character of a reducible representation, then the number of times that a character $\chi_i(g)$ from the character table occurs in $\chi(g)$ is given by

$$n_i = \frac{1}{h} \sum_g \chi(g)\, \chi_i(g^{-1}) \tag{2.13}$$

For the relevant groups O_h, T_d and D_{4h} the characters are given (Ref. (4)). Table II-1 gives the characters of the group T_d.

Table II-1 Character Table for T_d

T_d	E	$8C_3$	$3C_2$	$6\sigma_d$	$6S_4$
A_1	1	1	1	1	1
A_2	1	1	1	-1	-1
E	2	-1	2	0	0
T_1	3	0	-1	-1	1
T_2	3	0	-1	1	-1

We shall also make use of the direct product of representations. Suppose Γ_i and Γ_j are representations of G and

then
$$\Gamma_i(g) \times \Gamma_j(g) = \Gamma_k(g)$$

also holds.
$$\chi_i(g) \cdot \chi_j(g) = \chi_k(g) \qquad (2.14)$$

So the character of the direct product is the product of the characters of the representations Γ_i and Γ_j.
The character χ_k can now be reduced to a sum of characters from the character table. All the representations of a group can thus be multiplied and the results are gathered in a multiplication table. Multiplication tables for O_h, T_d and D_{4h} are given in Ref. (4). Table II-2 is a multiplication table for T_d.

Table II-2 Multiplication Table for the representations of T_d

T_d	A_1	A_2	E	T_1	T_2
A_1	A_1	A_2	E	T_1	T_2
A_2	A_2	A_1	E	T_2	T_1
E	E	E	$A_1 + A_2 + E$	$T_1 + T_2$	$T_1 + T_2$
T_1	T_1	T_2	$T_1 + T_2$	$A_1 + E + T_1 + T_2$	$A_2 + E + T_1 + T_2$
T_2	T_2	T_1	$T_1 + T_2$	$A_2 + E + T_1 + T_2$	$A_1 + E + T_1 + T_2$

The different irreducible representations of a group describe in point of fact a certain symmetry pattern. To find out the symmetry of a certain function we shall have to investigate in which irreducible representation this function fits. Sometimes we need a combination of functions to give a type of symmetry fitting in the irreducible representation. To find this combination we apply projection operators.

The projection operator $\varepsilon(\Gamma)$ belonging to an irreducible representation Γ of G is defined by:

$$\varepsilon(\Gamma) = \frac{n_\Gamma}{h} \sum_g \chi_\Gamma(g^{-1})\, g \qquad (2.15)$$

where n_Γ is the dimension of the representation Γ.
Operation with $\varepsilon(\Gamma)$ on a function f (x, y, z) produces a function of similar symmetry behaviour as the representation Γ. In this manner we can classify the functions according to the different irreducible representations of G and this possibility of classification is of major importance.

Consider, for instance, the integral

$$I = \langle f(x,y,z) \mid g(x,y,z) \rangle$$

where f(x, y, z) belongs to Γ_i and g(x, y, z) belongs to Γ_j.

Now if $\Gamma_i \neq \Gamma_j$ the integral I vanishes. Hence if functions belong to different irreducible representations it is possible to predict on symmetry arguments that the integral is zero. We can go even further. An n-dimensional representation Γ possesses n basis components $\gamma_1, \ldots\ldots, \gamma_n$.
The integral I is also zero if the two functions f(x, y, z) and g(x, y, z) belong to the same representation Γ but differ in that they belong to different basis components of Γ.
The integral

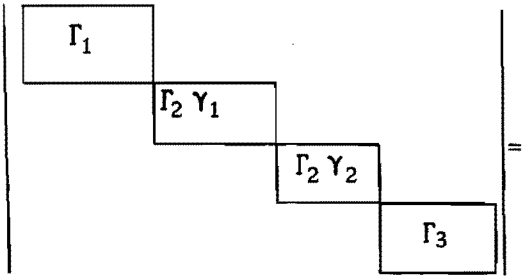
$$I = \langle f(x,y,z) \mid \underline{Op.} \mid g(x,y,z) \rangle$$

can only be different from zero if the product $\Gamma_i \times \Gamma_{op} \times \Gamma_j$ contains the totally symmetrical representation.

Frequent use will be made of these fundamental principles. It has been shown above that the molecular orbital theory gives rise to integrals of the type

$$H_{ij} = \langle \Phi_i \mid H \mid \Phi_j \rangle$$
$$S_{ij} = \langle \Phi_i \mid \Phi_j \rangle$$

It now becomes possible to classify the Φ's according to the irreducible representations of the symmetry group of the molecule. If Φ_i and Φ_j now belong to different irreducible representations or to the same representation but to different basis components of this representation, then H_{ij} and S_{ij} are identically equal to zero (H is a totally symmetrical operator and belongs to A_1).
In the secular determinant large parts simply vanish and the determinant acquires the blockform:



(2.16)

Each block in this determinant belongs to only one basis component of an irreducible representation of the group.

There are other applications of the group theory, for instance in the determination of selection rules for spectral transitions and in the treatment of the spin-orbit coupling. Some of these will be dealt with later.

II-5 TETRAHEDRAL COMPLEXES

In tetrahedral complexes the central ion is surrounded by four ligands that occupy positions on the vertices of a tetrahedron. The central ion is supposed to be in the origin of the coordinate system; the ligands are then found at equal distances in the following directions:

$L_1 \rightarrow (1,1,1)$ $L_2 \rightarrow (1,-1,-1)$ $L_3 \rightarrow (-1,1,-1)$ $L_4 \rightarrow (-1,-1,1)$

The axes of the central ion and of the ligands in relation to the main coordinate system are chosen as illustrated in Fig. 2.1. They have the following directions:

$x_M = (1,0,0)$ $x_1 = (1,-1,0)$ $x_2 = (1,1,0)$ $x_3 = (1,1,0)$ $x_4 = (1,-1,0)$
$y_M = (0,1,0)$ $y_1 = (1,1,-2)$ $y_2 = (1,-1,2)$ $y_3 = (1,-1,-2)$ $y_4 = (1,1,2)$
$z_M = (0,0,1)$ $z_1 = (-1,-1,-1)$ $z_2 = (-1,1,1)$ $z_3 = (1,-1,1)$ $z_4 = (1,1,-1)$

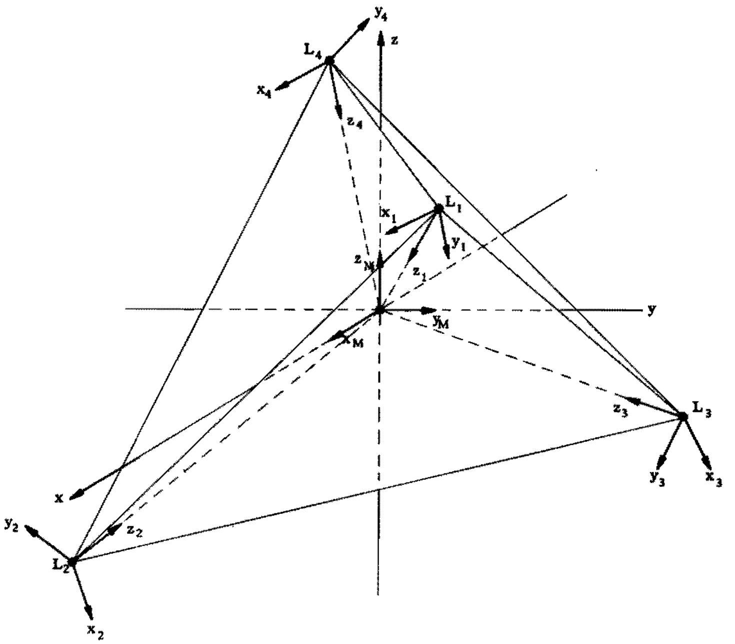


Fig. 2.1 Coordinate systems used for a tetrahedral complex

The central ion is supposed to be a transition metal ion from the third row of the periodical system, hence only 3d, 4s, and 4p-orbitals are of importance in determining the chemical bonds. The ligands are supposed to have s and p-orbitals available for bonding.

These orbitals now have to be classified according to the irreducible representations of the tetrahedral group. The operations of T_d are:

(a) unit operation E,
(b) 8 rotations through 120°, i.e. $\pm 120^\circ$ around (1, 1, 1), (1, -1, -1), (-1, 1, -1), and (-1, -1, 1),
(c) 3 rotations through 180°, i.e. around (1, 0, 0), (0, 1, 0) and (0, 0, 1),
(d) 6 reflections σ_d, i.e. in a plane through (0, 0, 1) and (1, 1, 0); (0, 0, 1) and (1, -1, 0); (1, 0, 0) and (0, 1, 1); (1, 0, 0) and (0, -1, 1); (0, 1, 0) and (1, 0, 1); (0, 1, 0) and (1, 0, -1),
(e) 6 improper rotations S_4, i.e. $\pm 90^\circ$ around (1, 0, 0), (0, 1, 0) and (0, 0, 1).

To apply the projection operators of T_d to the orbitals of the central ion we must first determine how the elements of T_d operate on these orbitals.
We can then apply the projection operators (2.15) to the orbitals of the central ion and then find, for instance:

$$\begin{array}{lll} \varepsilon(A_1)\, s = s & \varepsilon(A_1)\, p_x = 0 & \varepsilon(A_1)\, d = 0 \\ & \varepsilon(A_1)\, p_y = 0 & \text{for all d-orbitals} \\ & \varepsilon(A_1)\, p_z = 0 & \end{array}$$

and similar expressions for the other representations.
Hence:

s belongs to A_1

and, analogously:

$d_{x^2-y^2}$ and d_{z^2} belong to E

$$\left.\begin{array}{c} p_x,\ p_y \text{ and } p_z \\ d_{yz},\ d_{xz} \text{ and } d_{xy} \end{array}\right\} \text{belong to } T_2$$

We can improve on this classification by distinguishing according to the different basis components of the representations. This is facilitated by the application of some tables given by Griffith (Ref.(4), Table A16).
Consider, for instance, the E representation. The basis components are $E\theta$ and $E\varepsilon$ and from the table we see:

$$C_4^z\, E\theta = E\theta$$
$$C_4^z\, E\varepsilon = -E\varepsilon$$

We must now construct linear combinations of $d_{x^2-y^2}$ and d_{z^2}:

$$\psi_1 = a_1\, d_{x^2-y^2} + b_1\, d_{z^2}$$

$$\psi_2 = a_2\, d_{x^2-y^2} + b_2\, d_{z^2}$$

in such a way that

$$C_4^z\, \psi_1 = \psi_1$$
$$C_4^z\, \psi_2 = -\psi_2 \qquad (2.17)$$

Now ψ_1 belongs to the $E\theta$-component and ψ_2 to the $E\varepsilon$-component of the representation E.
From equation (2.17) follows

$$C_4^z\, (a_1 d_{x^2-y^2} + b_1 d_{z^2}) = -a_1 d_{x^2-y^2} + b_1 d_{z^2} = a_1 d_{x^2-y^2} + b_1 d_{z^2}$$

hence

$$a_1 = 0$$

and

$$C_4^z(a_2 d_{x^2-y^2} + b_2 d_{z^2}) = -a_2 d_{x^2-y^2} + b_2 d_{z^2} = -a_2 d_{x^2-y^2} - b_2 d_{z^2}$$

hence

$$b_2 = 0.$$

According to this

d_{z^2} belongs to $E\theta$
$d_{x^2-y^2}$ belongs to $E\varepsilon$

Acting in a similar manner for all metal orbitals we obtain the results given in the second column of Table II-3.

Table II-3 Classification of the atomic orbitals of tetrahedral complexes according to the irreducible representations of T_d

Representation of T_d	Metal orbitals	Ligand orbitals	Type of bonding
$A_1 a_1$	s	$s_1+s_2+s_3+s_4$ $z_1+z_2+z_3+z_4$	σ-bonding σ-bonding
$A_2 a_2$	-	-	
$E\varepsilon$	$d_{x^2-y^2}$	$(x_1+x_2-x_3-x_4)$	π-bonding
$E\theta$	d_{z^2}	$-(y_1+y_2-y_3-y_4)$	π-bonding
T_{1x}	-	$x_1+x_2+x_3+x_4-\sqrt{3}(y_1+y_2+y_3+y_4)$	no-bonding
T_{1y}	-	$x_1-x_2-x_3+x_4+\sqrt{3}(y_1-y_2-y_3+y_4)$	no-bonding
T_{1z}	-	$-2(x_1-x_2+x_3-x_4)$	no-bonding
$T_{2\xi}$	$\left.\begin{matrix}p_x\\ d_{yz}\end{matrix}\right\}$	$s_1+s_2-s_3-s_4$ $z_1+z_2-z_3-z_4$ $-\sqrt{3}(x_1+x_2+x_3+x_4)-(y_1+y_2+y_3+y_4)$	σ-bonding σ-bonding π-bonding
$T_{2\eta}$	$\left.\begin{matrix}p_y\\ d_{xz}\end{matrix}\right\}$	$s_1-s_2+s_3-s_4$ $z_1-z_2+z_3-z_4$ $\sqrt{3}(x_1-x_2-x_3+x_4)-(y_1-y_2-y_3+y_4)$	σ-bonding σ-bonding π-bonding
$T_{2\zeta}$	$\left.\begin{matrix}p_z\\ d_{xy}\end{matrix}\right\}$	$s_1-s_2-s_3+s_4$ $z_1-z_2-z_3+z_4$ $2(y_1-y_2+y_3-y_4)$	σ-bonding σ-bonding π-bonding

The metal orbitals have now been classified according to the irreducible representations of the tetrahedral group. The manner in which this has been done is, indeed, not the quickest but it can be applied generally. The ligand orbitals, for instance, can be classified in the same way. Application of the projection operators of T_d followed by classification according to the different basis components of the irreducible representations gives the results presented in the third column of Table II-3. The fourth column of Table II-3 indicates in addition the type of bonding, viz.

σ - bonding (no nodal planes),
π - bonding (one nodal plane), or
no - bonding.

Fig. 2.2 illustrates some combinations of ligand orbitals.

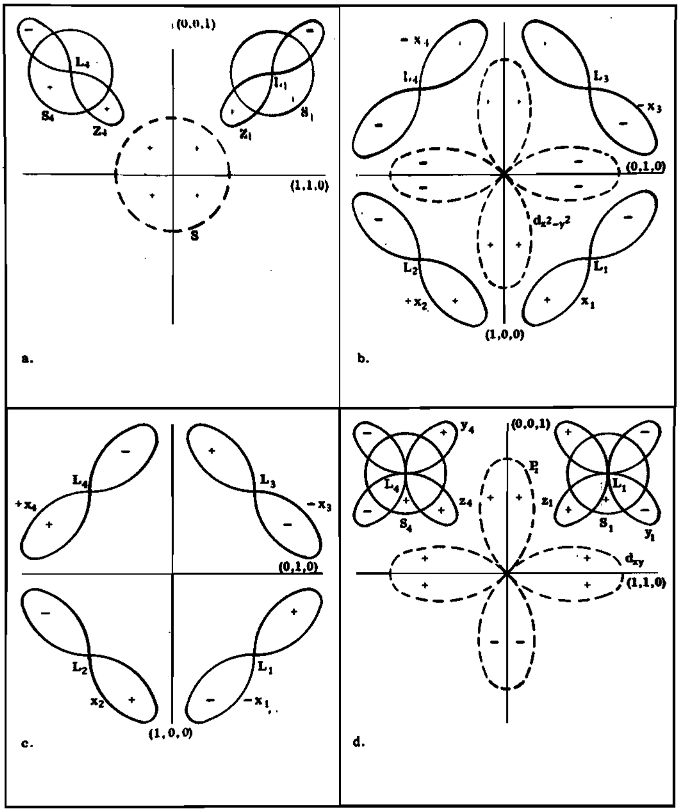


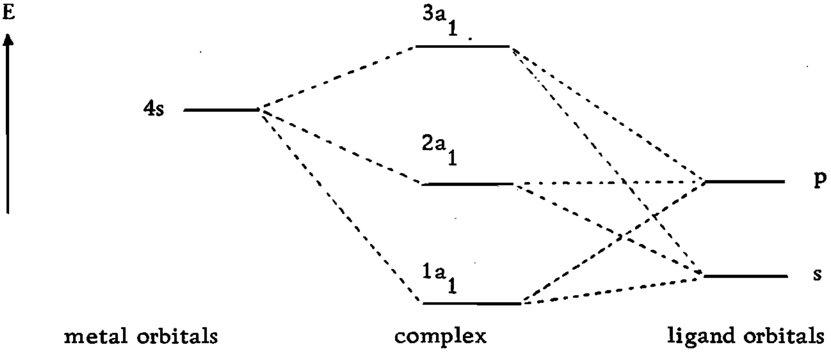
Fig. 2.2 Combinations of ligand-orbitals of a tetrahedral complex that belong to an irreducible representation of T_d.

a. A_1a_1-orbitals in a plane determined by (0,0,1) and (1,1,0)
b. Projection of the $E\ell$-orbitals on the xy-plane
c. Projection of the T_{1z}-orbitals on the xy-plane
d. $T_2\zeta$-orbitals in a plane determined by (0.0.1) and (1.1.0).

Without this classification according to the irreducible representations of T_d we have to deal with a 25 x 25 determinant. This determinant is now seen to decompose into the following blocks:

one 3 x 3 determinant for A_1
two identical 2 x 2 determinants for E
three identical 1 x 1 determinants for T_1
three identical 5 x 5 determinants for T_2.

By solving these determinants we find a number of one-electron energies, i.e.: three for the A_1, two for the E, one for the T_1 and five for the T_2-symmetry. For the A_1-symmetry we expect for instance:



A similar energy level scheme can also be made up for all symmetry-types and the complete system of energy levels for the electrons in the complex can then be assembled. A qualitative scheme for tetrahedral complexes is to be found in Fig. 2.3.

Substituting the energies found in the equations (2.10) we can find the correct one-electron orbitals of the complex as linear combinations of metal and ligand orbitals. These orbitals are now to be filled up with the relevant electrons of the metal ion and the ligands.

In the complex $CuCl_4^{2-}$ there are 41 "valence electrons", viz.

10 d-electrons of Cu
1 s-electron of Cu
8 s-electrons of 4 Cl
20 p-electrons of 4 Cl
2 extra electrons.

Assume the complex to be perfectly tetrahedral.

This gives us for $CuCl_4^{2-}$ the configuration

$$\text{Inner Core } (1t_2)^6 (1a_1)^2 (2t_2)^6 (2a_1)^2 (1e)^4 (3t_2)^6 (t_1)^6 (2e)^4 (4t_2)^5 \quad (2.17a)$$

The only partly occupied shell is $4t_2$ with one electron missing. The $CuCl_4^{2-}$ thus has a $^2T_2$-ground state (Ref.(4), page 226). For the first excited state of $CuCl_4^{2-}$ we expect

$$\text{IC } (1t_2)^6 (1a_1)^2 (2t_2)^6 (2a_1)^2 (1e)^4 (3t_2)^6 (t_1)^6 (2e)^3 (4t_2)^6 \quad (2.17b)$$

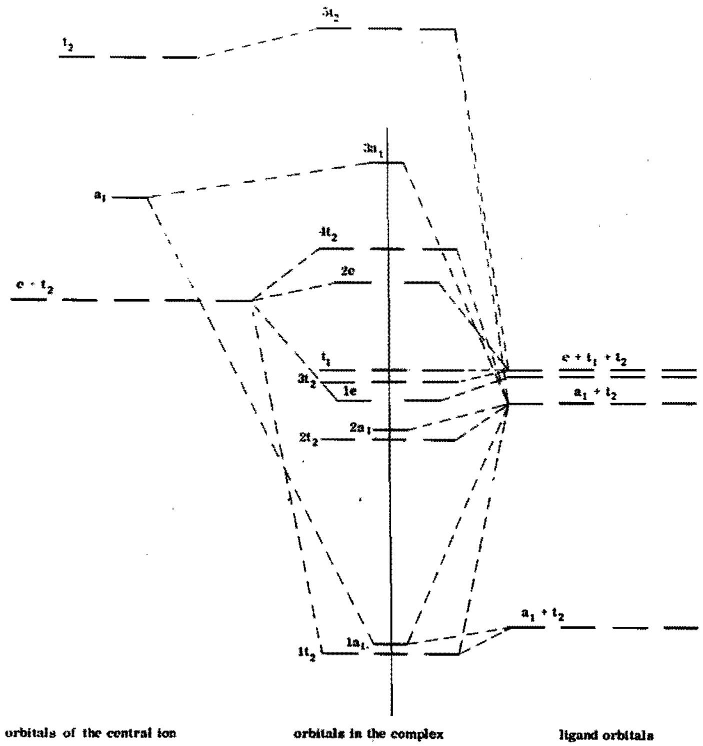


Fig. 2.3 Qualitative scheme of the one-electron energies in tetrahedral complexes

The electron hole is present here in the 2e-orbital, hence this excited state is a ^2E-term. The symmetry of other excited states can be determined in a similar manner, for instance,

$$IC\ (1t_2)^6\ (1a_1)^2\ (2t_2)^6\ (2a_1)^2\ (1e)^4\ (3t_2)^6\ (t_1)^5\ (2e)^4\ (4t_2)^6$$

is a $^2T_1$-term.

II-6 OCTAHEDRAL COMPLEXES

After the discussion of the tetrahedral complexes, the octahedral complexes can be dealt with summarily. The systems of axes for the central ion and for the ligands of an octahedral complex are chosen according to Fig. 2.4.
The orbitals of the central ion and ligands are now classified according to the irreducible representations of the group O_h giving the results of Table II-4. Solution of the remaining secular determinant then produces a number of eigenvalues for the one-electron energies.

Table II-4 Classification of the atomic orbitals of octahedral complexes according to the irreducible representations of O_h

Representation of O_h	Metal orbitals	Ligand orbitals	Type of bonding
$A_{1g}a_{1g}$	s	$s_1 + s_2 + s_3 + s_4 + s_5 + s_6$ $z_1 + z_2 + z_3 + z_4 + z_5 + z_6$	σ-bonding σ-bonding
$A_{1u}a_{1u}$	-	-	
$A_{2g}a_{2g}$	-	-	
$A_{2u}a_{2u}$	-	-	
$E_g\varepsilon$	$d_{x^2-y^2}$	$\sqrt{3}\,(s_1 - s_2 + s_4 - s_5)$ $\sqrt{3}\,(z_1 - z_2 + z_4 - z_5)$	σ-bonding σ-bonding
$E_g\theta$	d_{z^2}	$2s_3 + 2s_6 - s_1 - s_2 - s_4 - s_5$ $2z_3 + 2z_6 - z_1 - z_2 - z_4 - z_5$	σ-bonding σ-bonding
$E_u\varepsilon$	-	-	
$E_u\theta$	-	-	
$T_{1g}x$	-	$x_3 - y_1 - x_4 + y_6$	no-bonding
$T_{1g}y$	-	$x_2 - y_3 - x_6 + y_5$	no-bonding
$T_{1g}z$	-	$x_1 - y_2 - x_5 + y_4$	no-bonding
$T_{1u}x$	p_x	$s_1 - s_4$ $z_1 - z_4$ $x_3 + y_2 - x_5 - y_6$	σ-bonding σ-bonding π-bonding
$T_{1u}y$	p_y	$s_2 - s_5$ $z_2 - z_5$ $x_1 + y_3 - x_6 - y_4$	σ-bonding σ-bonding π-bonding
$T_{1u}z$	p_z	$s_3 - s_6$ $z_3 - z_6$ $x_2 + y_1 - x_4 - y_5$	σ-bonding σ-bonding π-bonding
$T_{2g}\xi$	d_{xz}	$x_3 + y_1 + x_4 + y_6$	π-bonding
$T_{2g}\eta$	d_{yz}	$x_2 + y_3 + x_6 + y_5$	π-bonding
$T_{2g}\zeta$	d_{xy}	$x_1 + y_2 + x_5 + y_4$	π-bonding
$T_{2u}\xi$	-	$x_1 - y_3 + x_6 - y_4$	no-bonding
$T_{2u}\eta$	-	$x_3 - y_2 + x_5 - y_6$	no-bonding
$T_{2u}\zeta$	-	$x_2 - y_1 + x_4 - y_5$	no-bonding

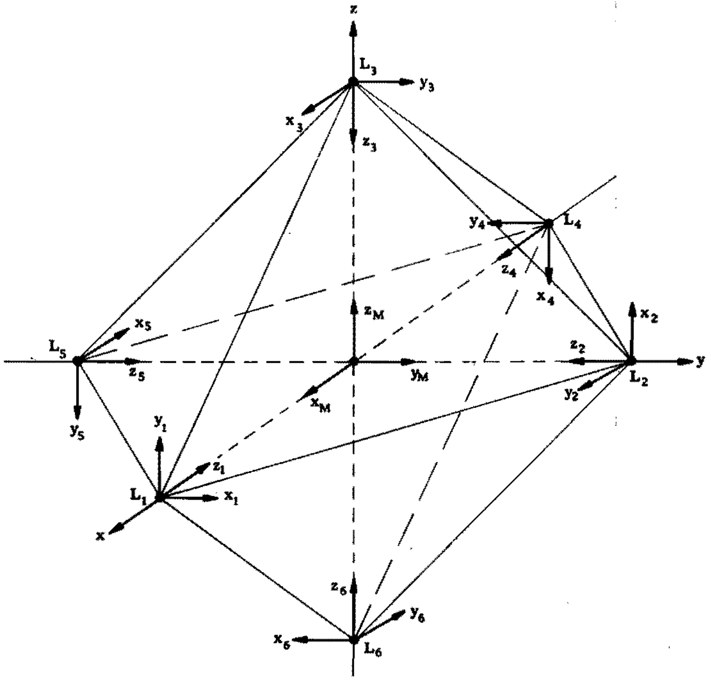


Fig. 2.4 Coordinate systems used for an octahedral complex

For the complex $CuCl_6^{4-}$ the ground state would be

$$IC\,(1e_g)^4\,(1a_{1g})^2\,(1t_{1u})^6\,(2e_g)^4\,(2a_{1g})^2\,(2t_{1u})^6\,(1t_{2g})^6\,(3t_{1u})^6\,(t_{2u})^6\,(t_{1g})^6\,(2t_{2g})^6\,(3e_g)^3$$

The ground state is now ^2E_g and it can easily be seen that the first excited state is $^2T_{2g}$.

II-7 SQUARE PLANAR COMPLEXES

The choice of axes for these complexes is shown in Fig. 2.5. Table II-5 presents the classification of the one-electron functions according to the irreducible representations of D_{4h}.

The ground state of $CuCl_4^{2-}$ in a square planar surrounding is $^2B_{2g}$. Some excited states are $^2A_{1g}$, $^2B_{1g}$, ^2E_g etc.

II-8 LOWER SYMMETRIES

The cases discussed so far concern a perfect tetrahedral, octahedral or square planar structure. In actual practice it often occurs that these tetrahedral, octahedral or square planar structures are more or less distorted.

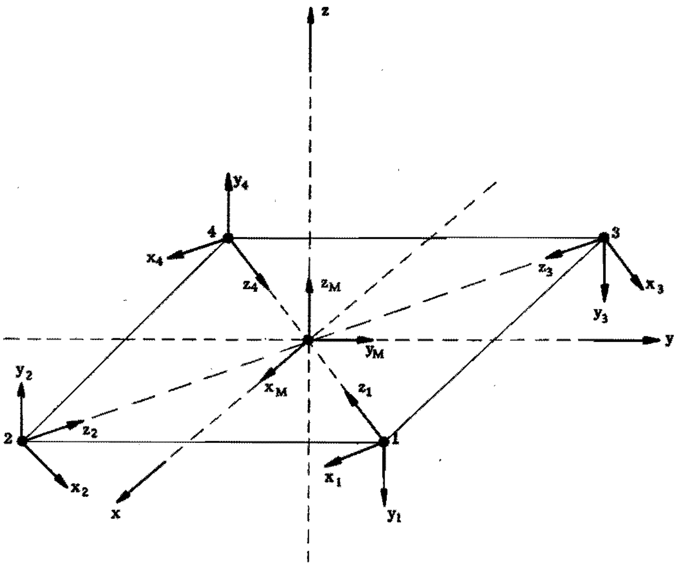


Fig. 2.5 Coordinate systems used for a square planar complex

Here we shall only be concerned with a single type of distortion of the tetrahedron, viz. that in which the ligands are displaced parallel to the z-axis in the direction of the xy-plane (See Fig. 2.6).

In the extreme case this distortion leads to a square planar structure. In intermediate situations the complex possesses the D_{2d}-symmetry. The coordinate systems are chosen analogously to those in the tetrahedral complex, i.e.

$$\begin{array}{lllll} x_M = (1,0,0) & x_1 = (1,-1,0) & x_2 = (1,1,0) & x_3 = (1,1,0) & x_4 = (1,-1,0) \\ y_M = (0,1,0) & y_1 = (a,a,-2) & y_2 = (a,-a,2) & y_3 = (a,-a,-2) & y_4 = (a,a,2) \\ z_M = (0,0,1) & z_1 = (-1,-1,-a) & z_2 = (-1,1,a) & z_3 = (1,-1,a) & z_4 = (1,1,-a) \end{array}$$

$(a = z/z_o)$.

The characters of D_{2d} are given in Table II-6.

Table II-7 shows the classification of the one-electron wave functions according to the irreducible representations of D_{2d}.

Fig. 2.7 shows how the transfer from tetrahedral symmetry to square planar symmetry via the D_{2d}-symmetry affects the energy levels in the complex.

II-9 QUANTITATIVE ASPECTS

In Section II-3 we saw that the application of the molecular orbital theory to a complex leads to a secular determinant. This determinant can be split up into a blockform with the help of the group theory. In order to solve these blocks we must calculate the remaining integrals H_{ij} and S_{ij}.

Table II-5 Classification of the atomic orbitals of a square planar complex according to the irreducible representations of D_{4h}

Representation of D_{4h}	Metal orbitals	Ligand orbitals	Type of bonding
$A_{1g}a_{1g}$	s d_{z^2}	$s_1 + s_2 + s_3 + s_4$ $z_1 + z_2 + z_3 + z_4$	σ-bonding σ-bonding
$A_{1u}a_{1u}$	-	-	
$A_{2g}a_{2g}$	-	$x_1 - x_2 + x_3 - x_4$	no-bonding
$A_{2u}a_{2u}$	p_z	$-(y_1 - y_2 + y_3 - y_4)$	π-bonding
$B_{1g}b_{1g}$	$d_{x^2-y^2}$	$x_1 + x_2 - x_3 - x_4$	π-bonding
$B_{1u}b_{1u}$	-	$y_1 + y_2 - y_3 - y_4$	no-bonding
$B_{2g}b_{2g}$	d_{xy}	$s_1 - s_2 - s_3 + s_4$ $z_1 - z_2 - z_3 + z_4$	σ-bonding σ-bonding
$B_{2u}b_{2u}$	-	-	
$E_g x$	d_{yz}	$-(y_1 + y_2 + y_3 + y_4)$	π-bonding
$E_g y$	d_{xz}	$-(y_1 - y_2 - y_3 + y_4)$	π-bonding
$E_u x$	p_x	$s_1 + s_2 - s_3 - s_4$ $z_1 + z_2 - z_3 - z_4$ $x_1 + x_2 + x_3 + x_4$	σ-bonding σ-bonding π-bonding
$E_u y$	p_y	$s_1 - s_2 + s_3 - s_4$ $z_1 - z_2 + z_3 - z_4$ $-(x_1 - x_2 - x_3 + x_4)$	σ-bonding σ-bonding π-bonding

(a) Overlap integrals S_{ij}

The overlap integrals S_{ij} are of the form

$$\langle \phi_M \mid \sum_\alpha c_\alpha \phi_\alpha \rangle = \sum_\alpha \langle \phi_M \mid \phi_\alpha \rangle c_\alpha \qquad (2.18)$$

These integrals, known as "group overlap integrals", must first be expressed in the more simple overlap integrals $\langle s_M \mid s_\alpha \rangle$, $\langle p\sigma_M \mid p\sigma_\alpha \rangle$, $\langle p\pi_M \mid p\pi_\alpha \rangle$, ... etc.

This can be done in a manner somewhat analogous to that proposed by Ballhausen (11). We apply a coordinate transformation subsequent to which the metal orbitals are described with the help of a right-handed coordinate system with the z-axis directed to ligand α.

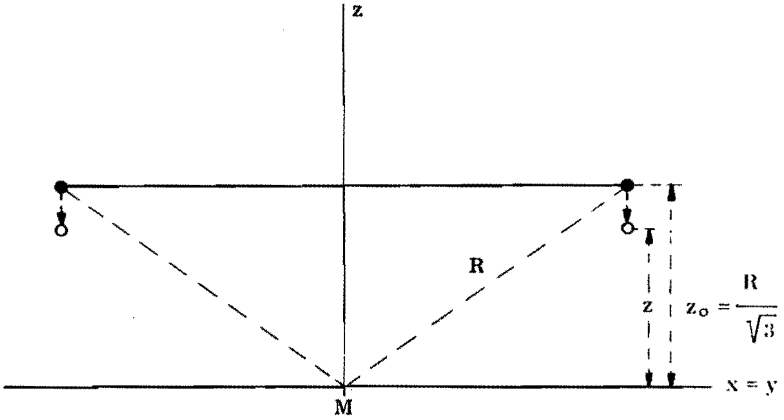


Fig. 2.6 Deformation of a tetrahedral complex

Table II-6 Character Table for D_{2d}

D_{2d}	E	C_2^z	$2C_2$	$2S_4$	$2\sigma_d$
A_1	1	1	1	1	1
A_2	1	1	-1	1	-1
B_1	1	1	1	-1	-1
B_2	1	1	-1	-1	1
E	2	-2	0	0	0

Denoting the original system of axes by x, y, z and the new system by x', y', z', the position of x', y', z' with regard to x, y, z can, for example, be given by

$$\begin{aligned} x' &= a_1 x + b_1 y + c_1 z \\ y' &= a_2 x + b_2 y + c_2 z \\ z' &= a_3 x + b_3 y + c_3 z \end{aligned} \qquad (2.19)$$

The transformation of the axes is now given by

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = A \begin{pmatrix} x \\ y \\ z \end{pmatrix} \text{ with } A = \begin{pmatrix} a_1 & b_1 & c_1 \\ a_2 & b_2 & c_2 \\ a_3 & b_3 & c_3 \end{pmatrix} \qquad (2.20)$$

Table II-7 Classification of the atomic orbitals in the D_{2d}-symmetry

Representation of D_{2d}	Metal orbitals	Ligand orbitals	Type of bonding
A_1a_1	s d_{z^2}	$s_1+s_2+s_3+s_4$ $z_1+z_2+z_3+z_4$ $y_1+y_2-y_3-y_4$	σ-bonding σ-bonding
A_2a_2	-	$x_1-x_2+x_3-x_4$	no-bonding
B_1b_1	$d_{x^2-y^2}$	$x_1+x_2-x_3-x_4$	π-bonding
B_2b_2	p_z d_{xy}	$s_1-s_2-s_3+s_4$ $z_1-z_2-z_3+z_4$ $y_1-y_2+y_3-y_4$	σ-bonding σ-bonding π-bonding
E_x	p_x d_{yz}	$s_1+s_2-s_3-s_4$ $z_1+z_2-z_3-z_4$ $x_1+x_2+x_3+x_4$ $y_1+y_2+y_3+y_4$	σ-bonding σ-bonding π-bonding π-bonding
E_y	p_y d_{xz}	$s_1-s_2+s_3-s_4$ $z_1-z_2+z_3-z_4$ $x_1-x_2-x_3+x_4$ $y_1-y_2-y_3+y_4$	σ-bonding σ-bonding π-bonding π-bonding

We can also express x, y, z in x', y', z', i.e.

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix} = A^{-1} \begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} \qquad (2.21)$$

The wave functions can be written as

$$\psi = f(r)\ H(x,y,z) \qquad (2.22)$$

Substituting the expressions (2.21) for x, y, z we obtain the wave functions in the new coordinate system x', y', z'.

Example:

In a tetrahedral complex the overlap integral for the symmetry Eε is given by

$$\langle d_{x^2-y^2} \,|\, N_\varepsilon\,(x_1+x_2-x_3-x_4)\rangle = N_\varepsilon\,\langle d_{x^2-y^2} \,|\, (x_1+x_2-x_3-x_4)\rangle$$

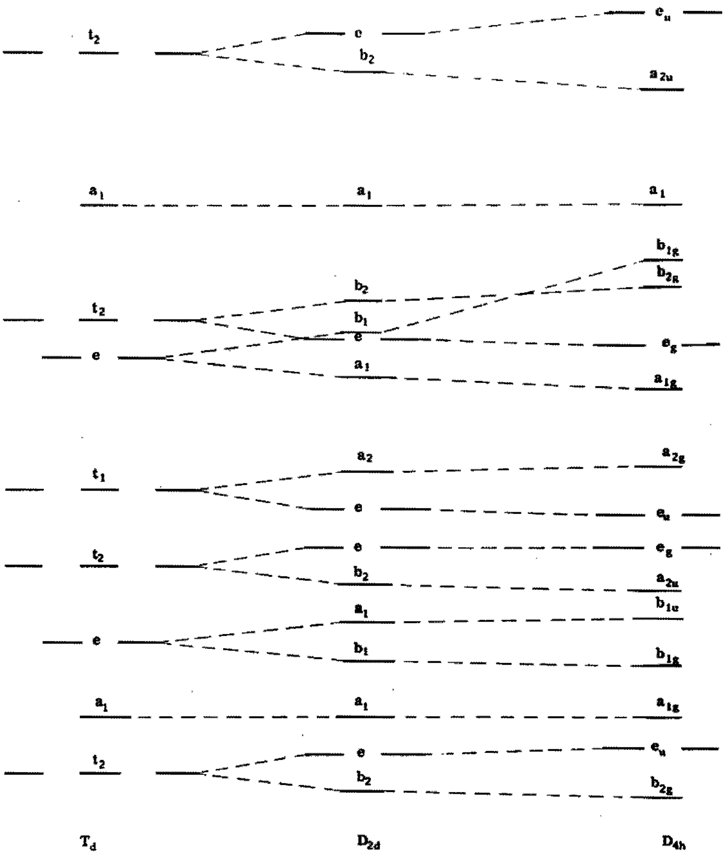


Fig. 2.7 Qualitative scheme of the one-electron energies in a complex with D_{2d} - symmetry

N_ε is a normalisation constant for the ligand function.

(1) $\langle d_{x^2-y^2} | x_1 \rangle$: $\alpha = L_1$

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} & 0 \\ \frac{1}{\sqrt{6}} & \frac{1}{\sqrt{6}} & -\frac{2}{\sqrt{6}} \\ \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{3}} \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

hence

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{6}} & \frac{1}{\sqrt{3}} \\ -\frac{1}{\sqrt{2}} & \frac{1}{\sqrt{6}} & \frac{1}{\sqrt{3}} \\ 0 & -\frac{2}{\sqrt{6}} & \frac{1}{\sqrt{3}} \end{pmatrix} \begin{pmatrix} x' \\ y' \\ z' \end{pmatrix}$$

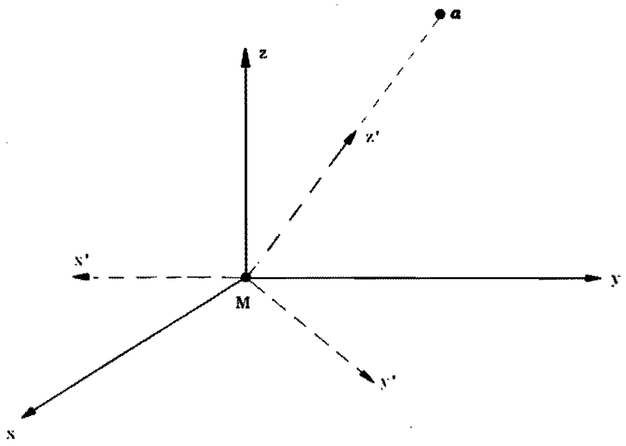


Fig. 2.8 Transformation of coordinates necessary for the calculation of group-overlap integrals

As a consequence

$$x = \frac{1}{\sqrt{2}}x' + \frac{1}{\sqrt{6}}y' + \frac{1}{\sqrt{3}}z' \qquad \text{etc.}$$

Now

$$\begin{aligned}
d_{x^2-y^2} &= f(r).\ \frac{\sqrt{3}}{2}(x^2-y^2) = \\
&= f(r)\ \frac{\sqrt{3}}{2}\ \left(\frac{1}{\sqrt{2}}x' + \frac{1}{\sqrt{6}}y' + \frac{1}{\sqrt{3}}z'\right)^2 - \left(\frac{-1}{\sqrt{2}}x' + \frac{1}{\sqrt{6}}y' + \frac{1}{\sqrt{3}}z'\right)^2 = \\
&= f(r).\ \frac{\sqrt{3}}{2}x'\left(\frac{2}{\sqrt{6}}y' + \frac{2}{\sqrt{3}}z'\right) = \\
&= \frac{1}{\sqrt{3}}d_{x'y'} + \frac{\sqrt{2}}{\sqrt{3}}d_{x'z'}
\end{aligned}$$

and

$$\begin{aligned}
\langle d_{x^2-y^2} | x_1 \rangle &= \frac{1}{\sqrt{3}}\langle d_{x'y'} | x_1 \rangle + \frac{\sqrt{2}}{\sqrt{3}}\langle d_{x'z'} | x_1 \rangle = \\
&= \frac{1}{\sqrt{3}}\langle d\delta | p\pi \rangle + \frac{\sqrt{2}}{\sqrt{3}}\langle d\pi | p\pi \rangle = \\
&= \frac{\sqrt{2}}{\sqrt{3}}\langle d\pi | p\pi \rangle
\end{aligned}$$

Analogously

$$(2) \quad \langle d_{x^2-y^2} \,|\, x_2 \rangle = \frac{\sqrt{2}}{\sqrt{3}} \langle d\pi \,|\, p\pi \rangle$$

$$(3) \quad -\langle d_{x^2-y^2} \,|\, x_3 \rangle = \frac{\sqrt{2}}{\sqrt{3}} \langle d\pi \,|\, p\pi \rangle$$

$$(4) \quad -\langle d_{x^2-y^2} \,|\, x_4 \rangle = \frac{\sqrt{2}}{\sqrt{3}} \langle d\pi \,|\, p\pi \rangle$$

which leads to

$$\langle d_{x^2-y^2} \,|\, \chi_E \rangle = 4N_\varepsilon \frac{\sqrt{2}}{\sqrt{3}} \langle d\pi \,|\, p\pi \rangle$$

In this way all group overlap integrals are expressed in terms of normal overlap integrals. The Tables II-8, II-9 and II-10 give the results for tetrahedral, octahedral and square planar complexes respectively.

The problem yet to be solved is the calculation of the simple overlap integrals

$$\langle n\ l\ m \,|\, n'\ l'\ m' \rangle$$

These are integrals in six variables: r_A, r_B, θ_A, θ_B, φ_A and φ_B which are, however, not independent. The most convenient way of dealing with them is to change them into other variables and choose elliptical coordinates, thus producing three independent variables

Table II-8 Group overlap integrals in tetrahedral complexes

$$G_{A_1}(s,\sigma) = 4N_{A_1} \langle s|\sigma \rangle$$

$$G_E(d,p\pi) = 4N_E \left(\frac{2}{3}\right)^{\frac{1}{2}} \langle d\pi | p\pi \rangle$$

$$G_{T_2}(d,\sigma) = \frac{4}{\sqrt{3}} N_{T_2}(\sigma) \langle d\sigma | \sigma \rangle$$

$$G_{T_2}(p,\sigma) = \frac{4}{\sqrt{3}} N_{T_2}(\sigma) \langle p\sigma | \sigma \rangle$$

$$G_{T_2}(d,p\pi) = 4 \left(\frac{2}{3}\right)^{\frac{1}{2}} N_{T_2}(\pi) \langle d\pi | p\pi \rangle$$

$$G_{T_2}(p,p\pi) = -4 \left(\frac{2}{3}\right)^{\frac{1}{2}} N_{T_2}(\pi) \langle p\pi | p\pi \rangle$$

Table II-9 Group overlap integrals in octahedral complexes

$$G_{A_{1g}}(s,\sigma) = 6\,N_{A_{1g}} \langle s|\sigma\rangle$$

$$G_{E_g}(d,\sigma) = 2\sqrt{3}\,N_{E_g} \langle d\sigma|\sigma\rangle$$

$$G_{T_{1u}}(p,\sigma) = 2\,N_{T_{1u}}(\sigma) \langle p\sigma|\sigma\rangle$$

$$G_{T_{1u}}(p,\pi) = 4\,N_{T_{1u}}(\pi) \langle p\pi|p\pi\rangle$$

$$G_{T_{2g}}(d,\pi) = 4\,N_{T_{2g}} \langle d\pi|p\pi\rangle$$

Table II-10 Group overlap integrals in square planar complexes

$$G_{A_{1g}}(s,\sigma) = 4\,N_{A_{1g}} \langle s|\sigma\rangle$$

$$G_{A_{1g}}(d,\sigma) = -2\,N_{A_{1g}} \langle d\sigma|\sigma\rangle$$

$$G_{A_{2u}}(p,\pi) = 4\,N_{A_{2u}} \langle p\pi|p\pi\rangle$$

$$G_{B_{1g}}(d,\pi) = 4\,N_{B_{1g}} \langle d\pi|p\pi\rangle$$

$$G_{B_{2g}}(d,\sigma) = 2\sqrt{3}\,N_{B_{2g}} \langle d\sigma|\sigma\rangle$$

$$G_{E_g}(d,\pi) = 2\sqrt{2}\,N_{E_g} \langle d\pi|p\pi\rangle$$

$$G_{E_u}(p,\sigma) = 2\sqrt{2}\,N_{E_u}(\sigma) \langle p\sigma|\sigma\rangle$$

$$G_{E_u}(p,\pi) = 2\sqrt{2}\,N_{E_u}(\pi) \langle p\pi|p\pi\rangle$$

$$\xi = \frac{r_A + r_B}{R}$$

$$\eta = \frac{r_A - r_B}{R}$$

$$\varphi = \varphi_A = \varphi_B$$ (See fig. 2.9)

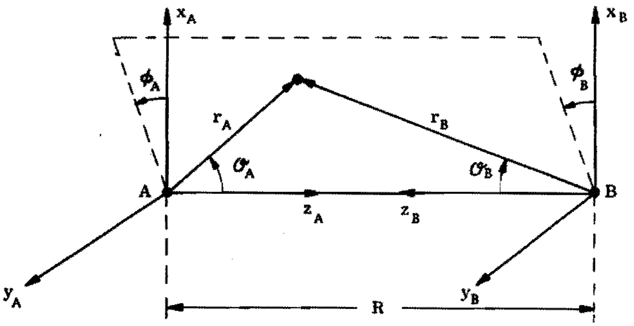


Fig. 2.9 Coordinate system used in the calculation of overlap integrals

The following now holds

$$r_A = \frac{R}{2}(\xi + \eta)$$

$$r_B = \frac{R}{2}(\xi - \eta)$$

$$\cos\theta_A = \frac{1 + \xi\eta}{\xi + \eta} \qquad \sin^2\theta_A = \frac{\xi^2 + \eta^2 - \xi^2\eta^2 - 1}{(\xi + \eta)^2}$$

$$\cos\theta_B = \frac{1 - \xi\eta}{\xi - \eta} \qquad \sin^2\theta_B = \frac{\xi^2 + \eta^2 - \xi^2\eta^2 - 1}{(\xi - \eta)^2}$$

$$d\tau = \left(\frac{R}{2}\right)^3 (\xi - \eta)^2 \; d\xi \, d\eta \, d\varphi \tag{2.23}$$

with

$$\xi \text{ from } 1 \rightarrow \infty$$
$$\eta \text{ from } -1 \rightarrow 1$$
$$\varphi \text{ from } 0 \rightarrow 2\pi$$

With the help of the equations (2.23) we now express the wave functions (2.4) in terms of ξ, η and φ. If it is assumed that R_{nl} has the form $r^{n-1}e^{-ar}$ (Slater functions) and if we use the expressions

$$\rho = \frac{R}{2}(a_A + a_B)$$
$$\tau = \frac{a_A - a_B}{a_A + a_B} \tag{2.24}$$

the overlap integrals are written as a linear combination of the integrals

$$A_k(\rho) = \int_1^{\infty} \xi^k e^{-\rho\xi} d\xi$$
$$B_k(\rho\tau) = \int_{-1}^{1} \eta^k e^{-\rho\tau\eta} d\eta \tag{2.25}$$

See Ref. (12)

These integrals can be calculated in a relatively simple manner and have moreover been tabulated before (13, 14, 15).
The calculation of the overlap integrals will now present no serious difficulties.

(b) The integrals H_{ij}

The integrals H_{ij} have the form

$$\langle \phi_M | H | \phi'_M \rangle$$
$$\text{or} \quad \langle \phi_M | H | \sum_{\alpha} \phi_{\alpha} \rangle \tag{2.26}$$
$$\text{or} \quad \langle \sum_{\alpha} \phi_{\alpha} | H | \sum_{\alpha'} \phi_{\alpha'} \rangle$$

The second and the third type of integrals have to be expressed again in integrals of the type $\langle n_A l_A m_A | H | n'_B l'_B m'_B \rangle$ and $\langle n_A l_A m_A | H | n'_A l'_A m'_A \rangle$ by a coordinate transformation as discussed in part (a) of this section. Because H is invariant under these transformations, the expressions for the H_{ij} integrals are identical to those encountered with the group overlap integrals. For instance, in a tetrahedral complex for the symmetry Eε

$$\langle d_{x^2-y^2} | H | \chi_E \rangle = 4 N_{\varepsilon} \frac{\sqrt{2}}{\sqrt{3}} \langle d\pi | H | p\pi \rangle$$

The Tables II-8, II-9 and II-10 then give the necessary relations.

We shall first limit the discussion to the integrals H_{ii}

$$\langle \phi_i \mid H \mid \phi_i \rangle$$

ϕ_i being a one-electron function either of the metal ion or of a ligand. The operator H is defined according to (2.6) and so the integral can be split up as follows:

$$
\begin{aligned}
\langle \phi_i \mid H \mid \phi_i \rangle \; = \; & \langle \phi_i(1) \left| \frac{-\nabla^2}{2} \right| \phi_i(1) \rangle && (1) \\
& - \sum_{\alpha} \langle \phi_i(1) \left| \frac{Z\alpha}{r_{\alpha 1}} \right| \phi_i(1) \rangle && (2) \\
& && (2.27) \\
& + \sum_{j \neq i} \langle \phi_i(1) \left| \frac{\phi_j(2)\, \phi_j(2)}{r_{12}} \right| \phi_i(1) \rangle && (3) \\
& - \sum_{j \neq i} \delta(s_i, s_j) \langle \phi_i(1) \left| \frac{\phi_j(2)\, \phi_j(1)}{r_{12}} P_{12} \right| \phi_i(1) \rangle && (4)
\end{aligned}
$$

(1) This term is equal to the kinetic energy of an electron in orbital ϕ_i and is a one-electron integral.

If ϕ_i has the form

$$\phi_i = \mid n, l, m \rangle = (2a)^{n+\frac{1}{2}} \left[(2n)! \right]^{-\frac{1}{2}} r^{n-1} e^{-ar} Y_{lm}(\theta, \varphi) \qquad (2.28)$$

the integral (1) can be solved in an analytical form.

(2) This term gives the potential energy of an electron in orbital ϕ_i in the electrostatic field of the nuclei. The summation over α furnishes two types of integrals:

(a) Orbital ϕ_i belongs to nucleus α. With ϕ_i as of (2.28) the solution of the integral can be effected in an analytical form. This integral is usually combined with integral (1); if so, one finds

$$\langle n, l, m \left| -\frac{\nabla^2}{2} - \frac{Z\alpha}{r} \right| n, l, m \rangle = \left[1 - 2\, \frac{n(n-1) - l(l+1)}{n(2n-1)} \right] \frac{a^2}{2} - \frac{Z\alpha a}{n} \qquad (2.29)$$

and the integral can be calculated straight away.

(b) The orbital ϕ_i does not belong to the nucleus α:

$$\langle \phi_i^A(1) \left| \frac{Z\beta}{r_{\beta 1}} \right| \phi_i^A(1) \rangle$$

By applying the expressions (2.23) and (2.24) this integral can be reduced to a combination of A_k and B_k-integrals (2.25).

(3) This term contains what are known as the Coulomb integrals that represent the Coulomb repulsion between the charge clouds of the electrons in orbitals ϕ_i and ϕ_j. There are again two types of integrals:

   (a) ϕ_i and ϕ_j belong to the same nucleus. In this case the Coulomb integrals can be expressed in the Condon-Shortley F^k-integrals as given, for instance, by Griffith (Ref.(4), chapter 4). The F^k-integrals have the form

$$\left\langle R_{n_i l_i}(1)\, R_{n_j l_j}(2) \left| \frac{r_<^{\,k}}{r_>^{\,k+1}} \right| R_{n_i l_i}(1)\, R_{n_j l_j}(2) \right\rangle \tag{2.30}$$

   Substitution of Slater functions for R_{nl} leads to an analytical soluble form.

   (b) ϕ_i and ϕ_j belong to different nuclei. Substitution of (2.23) and (2.24) reduces the Coulomb integrals to a combination of A_k and B_k-integrals (See Roothaan, Ref.(16)).

(4) The last term contains what are known as the Exchange integrals. Again we distinguish two cases:

   (a) ϕ_i and ϕ_j belong to the same nucleus. The exchange integrals can now be expressed in the Condon-Shortley G^k-integrals

$$\left\langle R_{n_i l_i}(1)\, R_{n_j l_j}(2) \left| \frac{r_<^{\,k}}{r_>^{\,k+1}} \right| R_{n_j l_j}(1)\, R_{n_i l_i}(2) \right\rangle \tag{2.31}$$

   (b) ϕ_i and ϕ_j belong to different nuclei. The integrals now become much more complicated. An approximated method of solving these integrals is given by Ruedenberg (17).

Further information for the computation of the various integrals may be found in (18, 19, 20, 21).

At least in principle it is now possible to calculate the matrix elements H_{ii} explicitely starting from the one-electron wave functions. In practice, however, the computation entails a huge amount of effort.

Even more difficult is the computation of the integrals H_{ij} with $i \neq j$. These matrix elements contain integrals with functions that belong to three different nuclei, for instance,

$$\left\langle \phi_i^{A}(1)\, \phi_j^{B}(2) \left| \frac{1}{r_{12}} \right| \phi_k^{C}(1)\, \phi_j^{B}(2) \right\rangle$$

It is practically impossible to find an analytical solution here. One must apply a numerical approximation and this is always very time-consuming.

Now there exist several approximate methods that are based on the use of empirical parameters to avoid the computational work. One of the best known is the one proposed by Wolfsberg and Helmholz (22), which uses the H_{ii} as parameters. These H_{ii} integrals are chosen equal to the Valence State Ionisation Energies (23, 24) of the relevant ion and subsequently are corrected by trial and error in such a way that the energies of the first and second excitation acquire the correct values. The H_{ij}-integrals are then approximated by empirical averaging over H_{ii} and H_{jj}:

$$H_{ij} = FG_{ij} (H_{ii} + H_{jj}) / 2 \tag{2.32}$$

Here G_{ij} is a group overlap integral and F a constant chosen so that reasonably correct values of H_{ij} are obtained for simple molecules. One assumes

$$\begin{aligned} F &= 1.67 \text{ for } \sigma\text{-bonding} \\ F &= 2.00 \text{ for } \pi\text{-bonding} \end{aligned} \tag{2.33}$$

The data necessary for the solution of the secular determinant are now known and the energies can be calculated.

The results of the Wolfsberg-Helmholz method are reasonably satisfactory, but the approximation suffers from the fact that it is predominantly empirical.

A slightly different method is proposed by Ballhausen *et al.*(25) for the vanadyl ion. They assume

$$H_{ij} = -2\, G_{ij} \sqrt{H_{ii}\, H_{jj}} \tag{2.34}$$

which is certainly a somewhat more acceptable assumption because the integral H_{ij} tends to decrease rapidly if the difference between H_{ii} and H_{jj} increases (See Chapter III).

Far less empirical is the method published by Sugano and Shullman (26). With this method the efforts made in obtaining numerical solutions are much greater. They finally calculate $\Delta = E(2t_{2g}) - E(3e_g)$ for NiF_6^{4-} from first principles with the satisfactory result that the theoretical value is found to agree with the experimental one.

REFERENCES

1. L. Pauling: The Nature of the Chemical Bond. New York (1960).
2. H. Hartmann, E. Ilse: Z. Phys. Chem. (Leipzig) 197, (1951), 239.
3. L.E. Orgel: An Introduction to Ligand Field Chemistry. London (1962).
4. J.S. Griffith: The Theory of Transition Metal Ions. Cambridge (1961).
5. J.H. van Vleck: J. Chem. Phys. 3, (1935), 803, 807.
6. J. Owen, K.H. Stevens: Nature 171, (1953), 836.
7. E.U. Condon, G.H. Shortley: The Theory of Atomic Spectra. Cambridge (1953).
8. G. Racah: Phys. Rev. 61, (1942), 186; 62, (1942), 438; 63, (1943), 367; 76, (1949), 1352.
9. V. Heine: Group Theory in Quantum Mechanics. New York (1960).
10. D.R. Bates: Quantum Theory, volume II. New York (1962).
11. C.J. Ballhausen: Introduction to Ligand Field Theory. New York (1962).

12. R.S. Mulliken *et al.*: J. Chem. Phys. 17, (1949), 1248.

13. M. Kotani *et al.*: Tables of Molecular Integrals. Maruzen Co. Ltd. Japan (1955).

14. H. Preuss: Integraltafeln zur Quantenchemie, vols. 1, 2, 4. Berlin (1956, 1957, 1960).

15. J. Miller: Quantum Chemistry Integrals and Tables. Texas (1959).

16. C.C.J. Roothaan: J. Chem. Phys. 19, (1951), 1445.

17. K. Ruedenberg: J. Chem. Phys. 19, (1951), 1459.

18. K. Ruedenberg: J. Chem. Phys. 19, (1951), 1433.

19. E.A. Magnusion, C. Zauli: Proc. Phys. Soc. 78, (1961), 53.

20. A. Lofthus: Mol. Phys. 5, (1962), 105; 6, (1963), 115.

21. S.O. Lundquist, P.O. Löwdin: Arkiv Fysik 3, (1951), 147.

22. M. Wolfsberg, L. Helmholz: J. Chem. Phys. 20, (1952), 837.

23. R.S. Mulliken: J. Chem. Phys. 2, (1934), 784.

24. W. Moffith: Repts. Progr. Phys. 17, (1954), 173.

25. C.J. Ballhausen, H.B. Gray: Inorg. Chem. 1, (1962), 111.

26. R.G. Shullman, S. Sugano: Phys. Rev. 130, (1963), 517.

27. F.A. Cotton: Chemical Applications of Group Theory. New York (1963).

CHAPTER III

MOLECULAR ORBITAL CALCULATION ON THE GROUND STATE OF THE TETRAHEDRAL TETRACHLOROCUPRATE (II) ION

III-1 INTRODUCTION AND LITERATURE DATA

The following molecular orbital calculation assumes the complex $CuCl_4^{2-}$ to possess a tetrahedral structure. The wave functions of the atoms in the complex are then classified according to the irreducible representations of the group T_d as has been explained in Chapter II. Subsequently the matrix elements of the secular determinant can be calculated, and by evaluating the secular determinant a number of eigenvalues of the energies is obtained.

There is, however, a complicating factor here. The wave functions of the electrons are dependent on the charge distribution in the complex, for instance, the wave function of a 3d-electron turns out to be different in the d^9 and d^{10}-configuration of Cu, etc. Consequently also the H_{ij} and S_{ij}-integrals become dependent on the charge distribution. In the calculation given in the following, the H_{ij} and S_{ij}-integrals are computed as functions of this charge distribution. To determine the correct eigenvalues an iteration process is then applied, viz.

(1) An estimate is made of the initial charge distribution, ρ.

(2) The H_{ij} and S_{ij}-integrals pertaining to this charge distribution ρ are calculated and substituted in the secular determinant.

(3) Evaluation of the secular determinant then produces the energy-eigenvalues and the relevant eigenfunctions.

(4) From the eigenfunctions a new charge distribution, ρ', is calculated.

If ρ and ρ' differ too much the cycle is repeated with ρ' as initial charge distribution.

Little can be said at present about the tendency towards convergence of this iteration process and about the tolerance of ρ. It is supposed that when the initial ρ and the final ρ' are within certain limits found to be equal, ρ represents the correct charge distribution and the eigenvalues of the determinant belonging to this charge distribution are considered to be the correct one-electron energies in our approximation.

The wave functions applied in the calculation are summarised in the Tables III-1 and III-2. The functions of chlorine were obtained from a paper by Watson and Freeman (1). They are Self Consistent Field (SCF)-functions approximated by linear combinations of Slater functions.

Table III-1 One-electron Wave Functions of Chlorine *

The radial part of the one-electron wave functions of chlorine will be given by the following sum

$$R_{nl} = \sum_i c_i N_i r^{n_i-1} e^{-a_i r}$$

3s-functions

	Cl			Cl^-		
i	c_i	n_i	a_i	c_i	n_i	a_i
1	0.03227	1	18.9832	0.04601	1	18.9832
2	0.05472	1	14.7941	0.03205	1	14.7941
3	0.04605	2	14.7181	0.06034	2	14.7181
4	-0.05545	2	9.6220	-0.07895	2	9.6220
5	-0.21002	2	6.7665	-0.18010	2	6.7665
6	-0.20191	3	6.3407	-0.21416	3	6.2190
7	0.29052	3	3.3742	0.40045	3	3.2450
8	0.71292	3	2.2999	0.59959	3	2.1679
9	0.14068	3	1.4375	0.16295	3	1.3550

3p-functions

	Cl			Cl^-		
i	c_i	n_i	a_i	c_i	n_i	a_i
1	-0.01295	2	13.7900	-0.01158	2	13.7900
2	-0.03982	2	8.8355	-0.03902	2	8.8355
3	-0.26254	2	5.3987	-0.23912	2	5.3987
4	0.12225	3	4.0186	0.10277	3	4.0186
5	0.35932	3	2.4367	0.38612	3	2.4367
6	0.56879	3	1.7380	0.49189	3	1.6382
7	0.09941	3	0.8720	0.20319	3	0.8219

* These functions are from a paper by R.E. Watson and A.J. Freeman. For the other functions and for further data see this paper (Ref.(1)).

Table III-2 One-electron Wave Functions of Copper *

The radial part of the one-electron wave functions is given by

$$R_{nl} = \sum_i c_i N_i r^{n_i-1} e^{-a_i r}$$

3d-functions

i	d^{10}			d^{9}		
	c_i	n_i	a_i	c_i	n_i	a_i
1	0.5933	3	5.95	0.6062	3	5.95
2	0.5744	3	2.30	0.5371	3	2.50

4s-functions

i	$d^{10}s^{2}$			$d^{10}s$		
	c_i	n_i	a_i	c_i	n_i	a_i
1	-0.00569	1	28.365	-0.01111	1	28.365
2	0.01899	2	11.025	0.03716	2	11.025
3	-0.04475	3	5.11	-0.08862	3	5.11
4	1.00084	4	1.00	1.00330	4	1.25
	$d^{9}s^{2}$			$d^{9}s$		
1	-0.01992	1	28.365	-0.02693	1	28.365
2	0.06677	2	11.025	0.09042	2	11.025
3	-0.1620	3	5.11	-0.2223	3	5.11
4	1.0107	4	1.55	1.0201	4	1.75

4p-functions

i	$d^{10}p^{2}$			$d^{10}p$		
	c_i	n_i	a_i	c_i	n_i	a_i
1	0.00150	2	11.95	0.01040	2	11.95
2	-0.00486	3	4.815	-0.03428	3	4.815
3	1.00001	4	0.51	1.00053	4	0.89
	$d^{9}p^{2}$			$d^{9}p$		
1	0.02714	2	11.95	0.03813	2	11.95
2	-0.09050	3	4.815	-0.12818	3	4.815
3	1.00368	4	1.22	1.00736	4	1.38

* Some of these functions are from Ref.(2). For other copper-functions and for further data see Ref.(2).

The 1s, 2s, 3s, 3d and 4p functions of copper are from Richardson *et al.* (2), as is the 4s function of the $d^9 s^2$-configuration of Cu. The other 4s functions were selected in such a way that the trend of the coefficients a (of $r^{n-1} e^{-ar}$) runs parallel to that of the coefficients of the 4p functions. The 4s functions have been normalised, and orthogonalised with respect to the 1s, 2s and 3s functions of Cu. The Cu-functions are also approximations of SCF-functions but are less accurate than Watson's functions. However, they are more easily applicable and their accuracy is good enough for our purpose. The overlap between a Cu-function of Richardson and an appropriate Cu-function of Watson is only slightly different from 1. A discussion of the accuracy of the functions can be found in the papers cited. Fig. 3.1 shows the radial part of some of them.

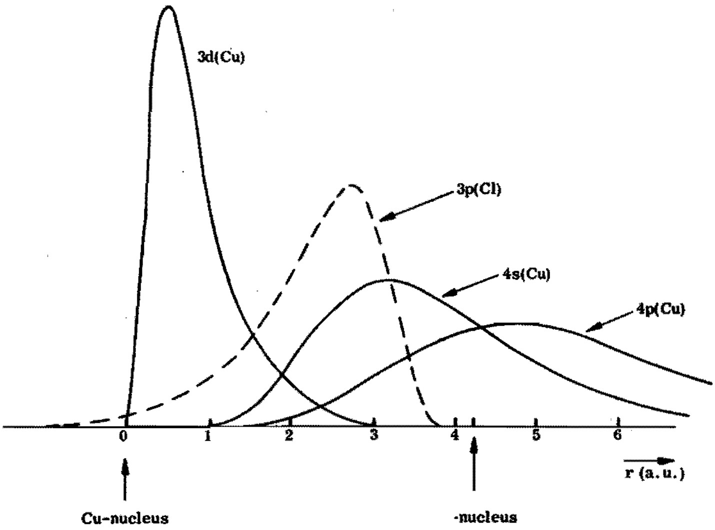


Fig. 3.1 Radial part of some atomic wave functions.

From X-ray measurements by Helmholz and Kruh (3) the distance between Cu and Cl in Cs_2CuCl_4 is found to be 2.22 Å, or in atomic units: 4.194 a.u. For tetrahedral $CuCl_4^{2-}$ the Cl-Cl distance is then 6.849 a.u. These distances Cu-Cl and Cl-Cl are kept constant throughout the following computations.

III-2 OVERLAP INTEGRALS

To calculate the overlap integrals between functions belonging to a certain irreducible representation of T_d (Table II-3), we must first compute a number of simple diatomic overlap integrals. The integrals that have to be calculated are (written as $\langle \phi_{Cu} | \phi_{Cl} \rangle$):

$$\begin{array}{lll}
\langle 4s \mid 3s \rangle & \langle 4s \mid 3p\sigma \rangle & \\
\langle 4p\sigma \mid 3s \rangle & \langle 4p\sigma \mid 3p\sigma \rangle & \langle 4p\pi \mid 3p\pi \rangle \\
\langle 3d\sigma \mid 3s \rangle & \langle 3d\sigma \mid 3p\sigma \rangle & \langle 3d\pi \mid 3p\pi \rangle
\end{array}$$

The functions ϕ are taken according to (2.4) with

$$R_{nl} = N_{nl}\, r^{n-1}\, e^{-ar} \tag{3.1}$$

and

$$N_{nl} = \frac{(2a)^{n+\frac{1}{2}}}{((2n)\,!)^{\frac{1}{2}}} \tag{3.2}$$

Now

$$\langle n_1 l_1 m \mid n_2 l_2 m \rangle = N_1 N_2 \int r_1^{n_1-1}\, r_2^{n_2-1}\, e^{-a_1 r_1}\, e^{-a_2 r_2}\, F(\theta_1,\theta_2,\varphi_1,\varphi_2)\, d\tau \tag{3.3}$$

in which $m = 0$ for σ-overlap

$m = 1$ for π-overlap.

We now change to elliptical coordinates ξ and η using the formulas (2.23) and (2.24). We shall not try to give a general formula for the overlap integrals but instead distinguish three separate cases.

(a) l_1 and l_2 both are 0 or 1 (s or p-functions).

Formula (3.3) then gives:

$$\langle n_1 l_1 m \mid n_2 l_2 m \rangle = \left(\frac{R}{2}\right)^{n_1+n_2+1} (-1)^m \frac{\{(2l_1+1)(2l_2+1)\}^{\frac{1}{2}}}{2^{m+1}}\, N_1 N_2 \, .$$

$$. \int_1^{\infty} \int_{-1}^{1} (\xi+\eta)^{n_1-l_1} (\xi-\eta)^{n_2-l_2} (1+\xi\eta)^{l_1-m} (1-\xi\eta)^{l_2-m} (1-\xi^2)^m (1-\eta^2)^m \, e^{-\rho\xi}\, e^{-\rho\tau\eta}\, d\xi\, d\eta \tag{3.4}$$

Expressing the latter integral in the A_n and B_n-integrals of (2.25), we find:

$$\langle n_1 l_1 m \mid n_2 l_2 m \rangle = \left(\frac{R}{2}\right)^{n_1+n_2+1} \frac{\{(2l_1+1)(2l_2+1))^{\frac{1}{2}}}{2^{m+1}}\, N_1 N_2 \, .$$

$$. \sum_{k_1=0}^{n_1-l_1} \sum_{k_2=0}^{n_2-l_2} \sum_{k_3=0}^{l_1-m} \sum_{k_4=0}^{l_2-m} \sum_{k_5=0}^{m} \sum_{k_6=0}^{m} (-1)^{m'} \binom{n_1-l_1}{k_1} \binom{n_2-l_2}{k_2} \binom{l_1-m}{k_3} \binom{l_2-m}{k_4} \binom{m}{k_5} \binom{m}{k_6} A_q(\rho)\, B_r(\rho\tau) \tag{3.5}$$

in which

$$m' = m + k_2 + k_4 + k_5 + k_6$$

$$q = n_1 + n_2 - l_1 - l_2 - k_1 - k_2 + k_3 + k_4 + 2k_5$$

$$r = k_1 + k_2 + k_3 + k_4 + 2k_6$$

$$\binom{v}{w} = \frac{v!}{w!\,(v-w)!}$$

(b) $l_1 = 0$ or 1, $l_2 = 2$, $m = 0$.

Formula (3.3) now gives:

$$\langle n_1 l_1 \sigma \mid 3d\sigma \rangle = \frac{\sqrt{5}}{4}\left(\frac{R}{2}\right)^{n_1+4} (2l_1+1)^{\frac{1}{2}} N_1 N_{3d}\,.$$

$$\sum_{k_1=0}^{n_1-l_1} \binom{n_1-l_1}{k_1} \left[3\sum_{k_2=0}^{l_1+2} \binom{l_1+2}{k_3} \sum_{k_3=0}^{1} (-1)^{k_3} \binom{1}{k_3} A_q(\rho)\, B_r(\rho\tau) - \sum_{k_2=0}^{l_1} \binom{l_1}{k_2} \sum_{k_3=0}^{3} (-1)^{k_3} \binom{3}{k_3} A_s(\rho)\, B_r(\rho\tau) \right] \qquad (3.6)$$

with

$$q = n_1 + 1 - l_1 - k_1 + k_2 - k_3$$

$$r = k_1 + k_2 + k_3$$

$$s = n_1 + 3 - l_1 - k_1 + k_2 - k_3$$

(c) $l_1 = 0$ or 1, $l_2 = 2$, $m = 1$.

This integral $\langle n_1 l_1 \pi \mid 3d\pi \rangle$ equals integral (3.5) multiplied by a factor $\sqrt{3}$.

The integrals $A_q(\rho)$ and $B_r(\rho\tau)$ are easily calculated with the help of some recursion formulas. The following relations hold:

$$A_o(\rho) = \frac{e^{-\rho}}{\rho} \qquad (3.7)$$

$$A_q(\rho) = A_o(\rho) + \frac{q}{\rho} A_{q-1}(\rho) \qquad (3.8)$$

Somewhat more complicated are the $B_r(\rho\tau)$ integrals. It can be shown that

$$B_o(\rho\tau) = \frac{e^{\rho\tau} - e^{-\rho\tau}}{\rho\tau} \qquad (3.9)$$

Suppose

$$C(\rho\tau) = \frac{-e^{\rho\tau} - e^{-\rho\tau}}{\rho\tau}$$

then we find

$$B_r(\rho\tau) = B_o(\rho\tau) + \frac{r}{\rho\tau} B_{r-1}(\rho\tau) \qquad \text{for r even}$$

$$B_r(\rho\tau) = C(\rho\tau) + \frac{r}{\rho\tau} B_{r-1}(\rho\tau) \qquad \text{for r odd} \qquad (3.10)$$

With the help of the equations (3.5) to (3.10) it is now relatively easy to set up a computer programme for the simple diatomic overlap integrals. This program was written in FORTRAN, the calculations were performed with an IBM 1620 Data Processing System.

The functions of Cu and Cl to be used are linear combinations of a number of functions (n, l, m) (See Table III-1 and III-2). To find, for instance, the overlap integral between a Cu(3dσ) function and a Cl(3pσ) function we have to combine a number of simple overlap integrals. This part of the calculation may be included in the computer programme. The total programme (M.O. BEREKENING 270E OVERLAP-INT) then produces directly the numerical value of the overlap between a function of Cu and of Cl, or between two functions of different Cl atoms. Table III-3 gives the values of the overlap integrals for those orbitals that are relevant in our special problem.

Once in the possession of these overlap integrals we can now calculate the normalisation constants for the ligand functions. Using Table III-4 we obtain the normalisation constants of Table III-5.

The integrals that appear in the secular determinant (2.11) are the group overlap integrals; it has been shown in Chapter II how these integrals can be expressed in simple diatomic overlap integrals. Table II-8 shows for Cu-functions and combinations of ligand functions the relations between the group overlap integrals and the simple diatomic overlap integrals.

Similar relations pertaining to different combinations of ligand functions belonging to the same representation of T_d are given in Table III-6.

Finally, all the group overlap integrals for the secular determinant can be computed, the results being grouped in Table III-7. With Table III-7 we now have at our disposal the group overlap integrals for a limited number of charge distributions.

In the following iteration process it will, however, be necessary to know the overlap integrals for all charge distributions intermediate between those given above.

We can calculate these integrals from the values given in Table III-7 by interpolation. Take as an example the group overlap integral between the 3dσ-function of Cu and the 3s-combination of the ligands. For a charge distribution Cu(d^9)-Cl this integral is equal to 0.05216, for a charge distribution Cu(d^{10})-Cl it is 0.07070.

Interpolation gives the formula to find the value of the integral for the charge distribution Cu(d^{10-A})-Cl as

$$0.07070 - 0.01854A$$

In a similar way the effect of a charge variation on Cl can also be approximated and we find finally that the integral for the charge distribution Cu(d^{10-A})-Cl^{-D} equals

Table III-3 Simple Diatomic Overlap Integrals

Cu-orbital		Cl-orbital	Overlap (Cl)	Overlap (Cl^-)
d^{10}	$3d\sigma$	3s	0.05685	0.05719
	$3d\sigma$	$3p\sigma$	0.08186	0.07620
d^9	$3d\sigma$	3s	0.04199	0.04237
	$3d\sigma$	$3p\sigma$	0.06493	0.06063
$d^{10}s^2$	4s	3s	0.31205	0.32995
	4s	$3p\sigma$	0.15525	0.20322
$d^{10}s$	4s	3s	0.30547	0.32222
	4s	$3p\sigma$	0.24456	0.30100
d^9s^2	4s	3s	0.26212	0.27704
	4s	$3p\sigma$	0.29554	0.35303
d^9s	4s	3s	0.22757	0.24149
	4s	$3p\sigma$	0.30132	0.35706
$d^{10}p^2$	$4p\sigma$	3s	0.22075	0.23449
	$4p\sigma$	$3p\sigma$	-0.09108	-0.12512
$d^{10}p$	$4p\sigma$	3s	0.44237	0.45966
	$4p\sigma$	$3p\sigma$	0.05081	0.03258
d^9p^2	$4p\sigma$	3s	0.45045	0.46429
	$4p\sigma$	$3p\sigma$	0.21700	0.20581
d^9p	$4p\sigma$	3s	0.41857	0.43082
	$4p\sigma$	$3p\sigma$	0.26409	0.25240
d^{10}	$3d\pi$	$3p\pi$	0.04359	0.04684
d^9	$3d\pi$	$3p\pi$	0.03216	0.03472
$d^{10}p^2$	$4p\pi$	$3p\pi$	0.13473	0.19003
$d^{10}p$	$4p\pi$	$3p\pi$	0.24082	0.30552
d^9p^2	$4p\pi$	$3p\pi$	0.23544	0.28733
d^9p	$4p\pi$	$3p\pi$	0.21626	0.26160
Cl_a-orbital		Cl_b-orbital	Overlap (Cl)	Overlap (Cl^-)
	3s	3s	0.00776	0.01205
	3s	$3p\sigma$	0.03062	0.05882
	$3p\sigma$	$3p\sigma$	0.05550	0.09834
	$3p\pi$	$3p\pi$	0.01408	0.03417

Table III-4 Normalisation Constants for the Ligand Orbitals in a Tetrahedral Complex

$$N_{A_1}(s) = 0.5\ \{1 + 3\langle s_1 | s_2\rangle\}^{-\frac{1}{2}}$$

$$N_{A_1}(z) = 0.5\ \{1 + 2\langle p\sigma_1 | p\sigma_2\rangle + \langle p\pi_1 | p\pi_2\rangle\}^{-\frac{1}{2}}$$

$$N_E = 0.5\ \{1 + \tfrac{1}{2}\langle p\sigma_1 | p\sigma_2\rangle - \tfrac{1}{2}\langle p\pi_1 | p\pi_2\rangle\}^{-\frac{1}{2}}$$

$$N_{T_1} = 0.5\ \{1 - \tfrac{1}{2}\langle p\sigma_1 | p\sigma_2\rangle - \frac{3}{2}\langle p\pi_1 | p\pi_2\rangle\}^{-\frac{1}{2}}$$

$$N_{T_2}(s) = 0.5\ \{1 - \langle s_1 | s_2\rangle\}^{-\frac{1}{2}}$$

$$N_{T_2}(z) = 0.5\ \{1 - \frac{2}{3}\langle p\sigma_1 | p\sigma_2\rangle - \frac{1}{3}\langle p\pi_1 | p\pi_2\rangle\}^{-\frac{1}{2}}$$

$$N_{T_2}(x,y) = 0.5\ \{1 + \frac{1}{6}\langle p\sigma_1 | p\sigma_2\rangle + \frac{11}{6}\langle p\pi_1 | p\pi_2\rangle\}^{-\frac{1}{2}}$$

Table III-5 Normalisation Constants for the Ligand Orbitals in Tetrahedral $CuCl_4^{2-}$

Normalisation Constant	Cl	Cl^-
$N_{A_1}(s)$	0.49428	0.49120
$N_{A_1}(z)$	0.47139	0.45068
N_E	0.49662	0.49629
N_{T_1}	0.51269	0.52717
$N_{T_2}(s)$	0.50195	0.50304
$N_{T_2}(z)$	0.51076	0.52043
$N_{T_2}(x,y)$	0.49146	0.48134

Table III-6 Group Overlap Integrals between different Combinations of Ligand Functions

A_1	$\langle \chi(s) \| \chi(z) \rangle$	$= 4\sqrt{6}\, N_{A_1}(s)\, N_{A_1}(z)\, \langle s_1 \| p\sigma_2 \rangle$
T_2	$\langle \chi(s) \| \chi(z) \rangle$	$= \frac{-4}{3}\sqrt{6}\, N_{T_2}(s)\, N_{T_2}(z)\, \langle s_1 \| p\sigma_2 \rangle$
	$\langle \chi(s) \| \chi(x,y) \rangle$	$= \frac{-8}{3}\sqrt{3}\, N_{T_2}(s)\, N_{T_2}(x,y)\, \langle s_1 \| p\sigma_2 \rangle$
	$\langle \chi(z) \| \chi(x,y) \rangle$	$= \frac{-8}{3}\sqrt{2}\, N_{T_2}(z)\, N_{T_2}(x,y)\, \{\langle p\sigma_1 \| p\sigma_2 \rangle - \langle p\pi_1 \| p\pi_2 \rangle\}$

$$0.07070 - 0.01854A + 0.00522D + 0.00110AD$$

Evidently this makes possible the calculation of all group overlap integrals for a general charge distribution $Cu(d^{10-A}s^{B}p^{C})$-$(Cl^{-D})_4$. We thus find the relations of Table III-8. With these formulas the overlap integrals for any of the intermediate charge distributions in $CuCl_4^{2-}$ (refered to above) can be computed reasonably accurately (3 to 4 significant figures).

III-3 H_{ii} INTEGRALS

In the H_{ii} integral

$$\langle \psi_i | H | \psi_i \rangle$$

H is the Hamilton operator (2.6) and ψ_i is either a wave function of the central ion or a linear combination of wave functions of the ligands (Table II-3).

Let us first discuss the integral

$$\langle \phi_i | H | \phi_i \rangle \tag{3.11}$$

in which ϕ_i is simply a wave function of one of the atoms in the molecule. The integral (3.11) can be split up as follows:

$$\begin{aligned}\langle \phi_i | H | \phi_i \rangle = {} & \langle \phi_i(1) | h_o(1) | \phi_i(1) \rangle + \sum_{j \neq i} \langle \phi_i(1) | \frac{\phi_j(2)\,\phi_j(2)}{r_{12}} | \phi_i(1) \rangle \\ & - \sum_{j \neq i} \delta(s_i, s_j) \langle \phi_i(1) | \frac{\phi_j(2)\,\phi_j(1)}{r_{12}} | \phi_i(2) \rangle - \sum_{\beta} \langle \phi_i(1) | \frac{Z_\beta}{r_{\beta 1}} | \phi_i(1) \rangle \\ & + \sum_{k \neq i} \langle \phi_i(1) | \frac{\phi_k(2)\phi_k(2)}{r_{12}} | \phi_i(1) \rangle - \sum_{k \neq i} \delta(s_i, s_k) \langle \phi_i(1) | \frac{\phi_k(2)\,\phi_k(1)}{r_{12}} | \phi_i(2) \rangle\end{aligned} \tag{3.12}$$

Table III-7 Group Overlap Integrals in Tetrahedral $CuCl_4^{2-}$

	Cu-orbital	Cl-orbital	G(Cl)	$G(Cl^-)$
A_1	$d^{10}s^2$ 4s	3s -comb.	0.61696	0.64829
	$d^{10}s$ 4s	3s -comb.	0.60395	0.63310
	d^9s^2 4s	3s -comb.	0.51824	0.54433
	d^9s 4s	3s -comb.	0.44993	0.47448
	$d^{10}s^2$ 4s	3pσ-comb.	0.29273	0.36437
	$d^{10}s$ 4s	3pσ-comb.	0.46113	0.53968
	d^9s^2 4s	3pσ-comb.	0.55726	0.63297
	d^9s 4s	3pσ-comb.	0.56816	0.64020
E	d^{10} 3d	3pπ-comb.	0.07070	0.07600
	d^9 3d	3pπ-comb.	0.05216	0.05628
T_2	d^{10} 3d	3s -comb.	0.06590	0.06644
	d^9 3d	3s -comb.	0.04867	0.04922
	$d^{10}p^2$ 4p	3s -comb.	0.25590	0.27241
	$d^{10}p$ 4p	3s -comb.	0.51280	0.53399
	d^9p^2 4p	3s -comb.	0.52217	0.53938
	d^9p 4p	3s -comb.	0.48521	0.50049
	d^{10} 3d	3pσ-comb.	0.09655	0.09158
	d^9 3d	3pσ-comb.	0.07659	0.07287
	$d^{10}p^2$ 4p	3pσ-comb.	-0.10743	-0.15038
	$d^{10}p$ 4p	3pσ-comb.	0.05993	0.03916
	d^9p^2 4p	3pσ-comb.	0.25596	0.24735
	d^9p 4p	3pσ-comb.	0.31151	0.30335
	d^{10} 3d	3pπ-comb.	0.04039	0.04251
	d^9 3d	3pπ-comb.	0.02980	0.03151
	$d^{10}p^2$ 4p	3pπ-comb.	-0.21626	-0.29874
	$d^{10}p$ 4p	3pπ-comb.	-0.38654	-0.48030
	d^9p^2 4p	3pπ-comb.	-0.37791	-0.45170
	d^9p 4p	3pπ-comb.	-0.34712	-0.41125
	Cl-orbital	Cl-orbital		
A_1	3s -comb.	3pσ-comb.	0.06990	0.12689
T_2	3s -comb.	3pσ-comb.	-0.02564	-0.05029
	3s -comb.	3pπ-comb.	-0.03489	-0.06578
	3pσ-comb.	3pπ-comb.	-0.03921	-0.06062

Table III-8 Group Overlap Integrals in tetrahedral $CuCl_4^{2-}$ as a function of the charge distribution $(Cu(d^{10-A}s^Bp^C)-(Cl^{-D})_4)$

A_1	$G(4s\text{-}3s \text{ comb.}) = 0.59094 - 0.20932A + 0.01301B + 0.02697D + 0.05530AB - 0.00524AD + 0.00218BD$
	$G(4s\text{-}3p\sigma \text{ comb.}) = 0.62953 - 0.05048A - 0.16840B + 0.07288D + 0.15750AB - 0.00451AD + 0.00367BD$
	$G(3s \text{ comb.}\text{-}3p\sigma \text{ comb.}) = 0.06990 + 0.05699D$
E	$G(3d\text{-}3p\pi \text{ comb.}) = 0.07070 - 0.01854A + 0.00522D - 0.00110AD$
T_2	$G(3d\text{-}3s \text{ comb.}) = 0.06590 - 0.01723A + 0.00054D + 0.00001AD$
	$G(3d\text{-}3p\sigma \text{ comb.}) = 0.09655 - 0.01996A - 0.00497D + 0.00125AD$
	$G(3d\text{-}3p\pi \text{ comb.}) = 0.04039 - 0.01039A + 0.00212D - 0.00041AD$
	$G(4p\text{-}3s \text{ comb.}) = 0.76970 - 0.32145A - 0.25690C + 0.02588D + 0.29386AC + 0.00069AD - 0.00468CD$
	$G(4p\text{-}3p\sigma \text{ comb.}) = 0.22729 + 0.13976A - 0.16736C - 0.02033D + 0.11182AC + 0.01262AD - 0.00045CD$
	$G(4p\text{-}3p\pi \text{ comb.}) = -0.55683 + 0.24049A + 0.17028C - 0.08409D - 0.20107AC + 0.02962AD - 0.00966CD$
	$G(3s \text{ comb.}\text{-}3p\sigma \text{ comb.}) = -0.02564 - 0.02466D$
	$G(3s \text{ comb.}\text{-}3p\pi \text{ comb.}) = -0.03489 - 0.03089D$
	$G(3p\sigma \text{ comb.}\text{-}3p\pi \text{ comb.}) = 0.03921 - 0.02141D$

Here

$$h_o = -\frac{\nabla^2}{2} - \frac{Z\alpha}{r_{\alpha 1}} \qquad (3.13)$$

α is the atom to which the function ϕ_i belongs; the summation j extends over all occupied orbitals of atom α;
the summation β extends over all other atoms in the molecule;
the summation k extends over all occupied orbitals of these atoms β.

The h_o and $\frac{\phi_j^2}{r_{12}}$ integrals will be calculated exactly; for the $\frac{1}{r_{\beta 1}}$ and the $\frac{\phi_k^2}{r_{12}}$ integrals we shall have to find the best approximation attainable within the limits of our aim. Because the H operator is written in atomic units - as are the wave functions - the H_{ii} and H_{ij} integrals will also be expressed in these units.

(a) h_o integrals

If the function ϕ_i is a function from Table III-1 or III-2, the integral that has to be solved is of the type

$$I_{ij} = \langle N_i \, r^{n_i-1} \, e^{-a_i r} \, Y_{lm}(\theta,\varphi) \,|\, h_o \,|\, N_j \, r^{n_j-1} \, e^{-a_j r} \, Y_{lm}(\theta,\varphi) \rangle$$

After substitution of (3.13) this integral can be written in an analytical form (4)

$$I_{ij} = -N_i N_j \left[\left\{ \frac{(n_i+n_j)!}{(a_i+a_j)^{n_i+n_j+1}} - \frac{2n_i(n_i+n_j-1)!}{a_i(a_i+a_j)^{n_i+n_j}} + \frac{(n_i(n_i-1)-l(l+1))}{a_i^{2}} \; \frac{(n_i+n_j-2)!}{(a_i+a_j)^{n_i+n_j-1}} \right\} . \right.$$

$$\left. . \frac{a_i^{2}}{2} + Z \frac{(n_i+n_j-1)!}{(a_i+a_j)^{n_i+n_j}} \right] \qquad (3.14)$$

To carry out the calculation a computer programme was written (M.O. BEREKENING 270E HO-INT). For wave functions as given in the Tables III-1 and III-2 this computer programme gives the h_o integrals direct. Table III-9 contains the h_o integrals for the Cu-functions.

Table III-9 h_o integrals for the Copper Functions

φ_i	$\langle \varphi_i \,\vert\, -\frac{\nabla^2}{2} - \frac{Z_{Cu}}{r} \,\vert\, \varphi_i \rangle$
3d (d^9)	- 32.19117
3d (d^{10})	- 30.98197
4s ($d^{10}s^2$)	- 7.16691
4s ($d^{10}s$)	- 8.90836
4s ($d^9 s^2$)	- 10.93153
4s ($d^9 s$)	- 12.23333
4p ($d^{10}p^2$)	- 3.66019
4p ($d^{10}p$)	- 6.33308
4p ($d^9 p^2$)	- 8.59362
4p ($d^9 p$)	- 9.65974

(b) $\frac{\phi_j^2}{r_{12}}$ integrals

As has been discussed in Chapter II, this part of the energies is given by two types of integrals:

$$\text{Coulomb integrals : } J(\phi_i, \phi_j) = \left\langle \frac{\phi_i(1)\phi_j(2)\phi_j(2)\phi_i(1)}{r_{12}} \right\rangle \tag{3.15}$$

$$\text{Exchange integrals: } K(\phi_i, \phi_j) = \left\langle \frac{\phi_i(1)\phi_j(2)\phi_j(1)\phi_i(2)}{r_{12}} \right\rangle \tag{3.16}$$

Condon and Shortley applied a method to calculate these integrals by expanding $\frac{1}{r_{12}}$ in a series (Ref.(5))

$$\frac{1}{r_{12}} = \sum_{k=0}^{\infty} \left| \frac{r_<^k}{r_>^{k+1}} \right| P_k(\cos\omega) \tag{3.17}$$

Here $r_<$ is the smaller of r_1 and r_2, $r_>$ is the larger of them. $P_k(\cos\omega)$ is a Legendre polynominal that can be expressed in terms of the functions Y_{lm} (See Chapter II)

$$P_k(\cos\omega) = \frac{4}{2k+1} \sum_{m=-k}^{k} Y_{lm}(1)\, \bar{Y}_{lm}(2) \tag{3.18}$$

See Ref.(6).

If $\phi_i = R_{n_i l_i}(r) Y_{l_i m_i}(\theta, \varphi) \tau_{s_i}$ the formulas (3.15) and (3.16)

become respectively

$$J(\phi_i, \phi_j) = \sum_{k=0}^{\infty} \left\langle R_{n_i l_i}(1) R_{n_j l_j}(2) \left| \frac{r_<^k}{r_>^{k+1}} \right| R_{n_j l_j}(2)\, R_{n_i l_i}(1) \right\rangle \cdot$$

$$\cdot \left\langle Y_{l_i m_i}(1) Y_{l_j m_j}(2) \middle| P_k(\cos\omega) \middle| Y_{l_j m_j}(2) Y_{l_i m_i}(1) \right\rangle \left\langle \tau_{s_i}(1)\, \tau_{s_j}(2) \middle| \tau_{s_j}(2) \tau_{s_i}(1) \right\rangle$$

or

$$J(\phi_i, \phi_j) = \sum_{k=0}^{\infty} F^k\, a^k . \tag{3.19}$$

and

$$K(\phi_i, \phi_j) = \sum_{k=0}^{\infty} \left\langle R_{n_i l_i}(1) R_{n_j l_j}(2) \left| \frac{r_<^k}{r_>^{k+1}} \right| R_{n_i l_i}(2) R_{n_j l_j}(1) \right\rangle \cdot$$

$$\cdot \left\langle Y_{l_i m_i}(1) Y_{l_j m_j}(2) \middle| P_k(\cos\omega) \middle| Y_{l_i m_i}(2) Y_{l_j m_j}(1) \right\rangle \left\langle \tau_{s_i}(1) \tau_{s_j}(2) \middle| \tau_{s_i}(2) \tau_{s_j}(1) \right\rangle$$

or

$$K(\phi_i,\phi_j) = \sum_{k=0}^{\infty} G^k b^k \delta(s_i,s_j) \qquad (3.20)$$

In these formulas a^k and b^k are the integrals over θ and φ, for instance

$$a^k = \frac{4\pi}{2k+1}\sum_{m=-k}^{k}\langle Y_{l_im_i}(1)\,|\,Y_{km}(1)\,|\,Y_{l_im_i}(1)\rangle\langle Y_{l_jm_j}(2)\,|\,Y_{km}(2)\,|\,Y_{l_jm_j}(2)\rangle$$

Defining

$$c^k(l_im_il_jm_j) = \left(\frac{4\pi}{2k+1}\right)^{\frac{1}{2}}\langle Y_{l_im_i}\,|\,Y_{k\,m_i-m_j}\,|\,Y_{l_jm_j}\rangle$$

it can be shown (see Ref.(6)) that

$$a^k = c^k(l_im_il_im_i).c^k(l_jm_jl_jm_j)$$

and

$$b^k = \{c^k(l_im_il_jm_j)\}^2$$

The coefficients c^k are only dependent on l_i, m_i, l_j, m_j and k and have been tabulated for s, p, d, and f-electrons. See Ref.(5) pp. 178, 179 and Ref.(6) p. 77.

The integrals F^k and G^k are the radius-dependent parts of the integrals and have to be calculated for each atom. Of the a^k and b^k coefficients only a very limited number differs from zero, hence, the F^k and G^k integrals have only to be calculated for those cases.

The Coulomb and Exchange integrals necessary for our problem can be expressed in F^k and G^k integrals using the Tables of the Ref. (5) and (6). The resulting expressions are tabulated in Table III-10.

To compute the F^k and G^k integrals occurring in this Table for the functions given in Table III-2, we have to solve integrals of the form

$$I = \langle R_{m_1}(1)\,R_{n_1}(2)\,\left|\,\frac{r_<^k}{r_>^{k+1}}\,\right|\,R_{m_2}(1)\,R_{n_2}(2)\rangle \qquad (3.21)$$

with

$$R_{m_i}(1) = N_{m_i}\,r_1^{m_i-1}\,e^{-a_ir_1}$$

$$R_{n_i}(2) = N_{n_i}\,r_2^{n_i-1}\,e^{-b_ir_2}$$

Table III-10 Coulomb and Exchange Interactions between electrons of the same atom

ϕ_i	ϕ_j	$J(\phi_i,\phi_j) - K(\phi_i,\phi_j)$
3d	ms^2	$2F^0(3d,ms) - \frac{1}{5}G^2(3d,ms)$
3d	mp^6	$6F^0(3d,mp) - \frac{6}{15}G^1(3d,mp) - \frac{9}{35}G^3(3d,mp)$
3d	$3d^9$	$9F^0(3d,3d) - \frac{2}{7}F^2(3d,3d) - \frac{2}{7}F^4(3d,3d)$
4s	ms^2	$2F^0(4s,ms) - G^0(4s,ms)$
4s	mp^6	$6F^0(4s,mp) - G^1(4s,mp)$
4s	$3d^{10}$	$10F^0(4s,3d) - G^2(4s,3d)$
4p	ms^2	$2F^0(4p,ms) - \frac{1}{3}G^1(4p,ms)$
4p	mp^6	$6F^0(4p,mp) - G^0(4p,mp) - \frac{2}{5}G^2(4p,mp)$
4p	$3d^{10}$	$10F^0(4p,3d) - \frac{2}{3}G^1(4p,3d) - \frac{3}{7}G^3(4p,3d)$
3d	4s	$F^0(3d,4s) - \frac{1}{10}G^2(3d,4s)$ *
3d	4p	$F^0(3d,4p) - \frac{1}{15}G^1(3d,4p) - \frac{3}{70}G^3(3d,4p)$ *
4s	4s	$F^0(4s,4s)$ *
4s	4p	$F^0(4s,4p) - \frac{1}{3}G^1(4s,4p)$ *
4p	4p	$F^0(4p,4p) - \frac{4}{75}F^2(4p,4p)$ *

* These interactions are averaged over the different functions $|lm_l\rangle$ that are possible for a certain value of l.

Hence

$$I = N_{m_1} N_{m_2} N_{n_1} N_{n_2} \int_o^{\infty}\int_o^{\infty} r_1^{m_1+m_2-2}\, r_2^{n_1+n_2-2}\, e^{-(a_1+a_2)r_1}\, e^{-(b_1+b_2)r_2}$$

$$\frac{r_<^{k}}{r_>^{k+1}}\, r_1^2 r_2^2\, dr_1 dr_2$$

or

$$I = N_{m_1} N_{m_2} N_{n_1} N_{n_2} \int_o^{\infty}\int_o^{\infty} r_1^{M} r_2^{N} e^{-Ar_1}\, e^{-Br_2}\, \frac{r_<^{k}}{r_>^{k+1}}\, dr_1 dr_2 \tag{3.22}$$

$$M = m_1 + m_2$$
$$N = n_1 + n_2$$
$$A = a_1 + a_2$$
$$B = b_1 + b_2$$

The integral (3.22) can be expressed in an analytical form

$$I = \frac{N_{m_1} N_{m_2} N_{n_1} N_{n_2}}{A^M B^{N+1}} \quad \frac{P^M}{(1+P)^{M-k}} \,.$$

$$\cdot \left[(N+k)!\,(M-k-1)! - \sum_{I=0}^{N+k-1} \{(N+k)! - (N-k-1)!\} \prod_{l=0}^{2k} (I-2l) \frac{(M+I-k-1)!}{I!\,(1+P)^I} \right] \tag{3.23}$$

in which

$$P = A/B$$

$$\prod_{l=0}^{2k} (I-l) = I(I-1)\,(I-2)\ldots\ldots.(I-2k)$$

With the help of this formula FORTRAN programmes were written for the F^k and G^k integrals (M.O. BEREKENING 270E FK-INT and M.O. BEREKENING 270E GK-INT respectively) giving the F^k and G^k integrals for the functions of Table III-2. Table III-11 contains a number of these integrals necessary in the calculation.

By using the appropriate part of formula (3.12), the energy ε_i of an electron in the orbital ϕ_i of the free ion can be calculated. In fact, for the free ions we have

$$\varepsilon_i = (h_o)_i + \sum_{j \neq i} J(\phi_i, \phi_j) - \sum_{j \neq i} \delta(s_i, s_j)\, K(\phi_i, \phi_j) \tag{3.25}$$

TABLE III - 11 F^k and G^k integrals for Cu

ϕ_i	ϕ_j	F^0	G^0	G^1	G^2
$4s(d^{10}s^2)$	1s	0.25056	0.00011		
	2s	0.25023	0.00015		
	3s	0.24974	0.00046		
	4s	0.20077	-		
	2p	0.25028		0.00018	
	3p	0.24969		0.00063	
	$4p(d^{10}p^2)$	0.12385		0.04057	
	$4p(d^{10}p)$	0.18850		0.13395	
	$3d(d^{10})$	0.24916	0.00920		0.00657
$4s(d^{10}s)$	1s	0.31458	0.00042		
	2s	0.31338	0.00058		
	3s	0.31148	0.00163		
	4s	0.25048	-		
	2p	0.31352		0.00068	
	3p	0.31134		0.00222	
	$4p(d^{10}p^2)$	0.12601		0.02244	
	$4p(d^{10}p)$	0.20326		0.12096	
	$3d(d^{10})$	0.30969	0.02141		0.01633
$4s(d^9s^2)$	1s	0.39391	0.00135		
	2s	0.39008	0.00184		
	3s	0.38402	0.00479		
	4s	0.30862	-		
	2p	0.39048		0.00217	
	3p	0.38364		0.00649	
	$4p(d^9p^2)$	0.26925		0.17783	
	$4p(d^9p)$	0.29023		0.20672	
	$3d(d^9)$	0.38091	0.02698		0.02500
$4s(d^9s)$	1s	0.44913	0.00247		
	2s	0.44216	0.00332		
	3s	0.43120	0.00823		
	4s	0.34622	-		
	2p	0.44289		0.00394	
	3p	0.43054		0.01112	
	$4p(d^9p^2)$	0.27863		0.16268	
	$4p(d^9p)$	0.30310		0.20065	
	$3d(d^9)$	0.42607	0.03689		0.03643

TABLE III - 11 (CONTINUED)

ϕ_i	ϕ_j	F^0	F^2	F^4	G^0	G^1	G^2	G^3
$4p(d^{10}p^2)$	1s	0.12751				0.00000		
	2s	0.12750				0.00000		
	3s	0.12750				0.00001		
	2p	0.12750			0.00000		0.00000	
	3p	0.12749			0.00001		0.00001	
	4p	0.10246	0.05741		-		-	
	$3d(d^{10})$	0.12748	0.00405			0.00021		0.00014
$4p(d^{10}p)$	1s	0.22279				0.00008		
	2s	0.22265				0.00008		
	3s	0.22237				0.00038		
	2p	0.22268			0.00008		0.00009	
	3p	0.22234			0.00030		0.00038	
	4p	0.17872	0.10027		-		-	
	$3d(d^{10})$	0.22204	0.01970			0.00456		0.00314
$4p(d^9p^2)$	1s	0.30701				0.00052		
	2s	0.30610				0.00052		
	3s	0.30418				0.00230		
	2p	0.30614			0.00054		0.00060	
	3p	0.30394			0.00184		0.00235	
	4p	0.24431	0.13766		-		-	
	$3d(d^9)$	0.30299	0.03925			0.01164		0.00875
$4p(d^9p)$	1s	0.34870				0.00102		
	2s	0.34692				0.00102		
	3s	0.34316				0.00430		
	2p	0.34719			0.00105		0.00118	
	3p	0.34291			0.00343		0.00441	
	4p	0.27552	0.15564		-		-	
	$3d(d^9)$	0.34121	0.05335			0.01853		0.01423
$3d(d^{10})$	1s	1.38825					0.00129	
	2s	1.36730					0.00164	
	3s	1.08299					0.00463	
	2p	1.37415				0.16489		0.09584
	3p	1.06560				0.62186		0.37870
	3d	0.96306	0.43615	0.26968				
$3d(d^9)$	1s	1.45357					0.00138	
	2s	1.43113					0.00177	
	3s	1.12434					0.00495	
	2p	1.43847				0.17725		0.10303
	3p	1.10558				0.66241		0.40500
	3d	1.10314	0.48059	0.29975				

The one-electron energies, calculated according to formula (3.25) for the different configurations of Cu, are tabulated in Table III-12. This Table has been derived from the Tables III-9, 10 and 11.

Analogously to the procedure applied in the calculation of the overlap integrals, the one-electron energies for any configuration of the free ion can be approximated as functions of A, B, C and D (from $Cu(d^{10-A}s^{B}p^{C})(Cl^{-D})_4$) by interpolation. These functions for Cu are mentioned in Table III-13. It was not required to compute the one-electron energies of Cl since these have been published by Watson (1). Their values also appear in the Tables III-12 and III-13.

Table III-12 One-electron Energies of the Free Ions

	Configuration	ϕ_i	ε_i
Copper	d^9	3d	-1.31515
	d^{10}	3d	-0.64741
	d^9s	4s	-0.57508
	d^9s^2	4s	-0.56174
	$d^{10}s$	4s	-0.20536
	$d^{10}s^2$	4s	-0.18262
	d^9p	4p	-0.39609
	d^9p^2	4p	-0.38672
	$d^{10}p$	4p	-0.11313
	$d^{10}p^2$	4p	-0.09064
Chlorine *	Cl	3s	-1.0717
	Cl^-	3s	-0.7356
	Cl	3p	-0.5051
	Cl^-	3p	-0.1518

* The one-electron energies of chlorine are from Ref.(1).

(c) Interaction of the Electrons of a Certain Atom with the Other Atoms in the Molecule

The interaction of an electron in an orbital ϕ_i of a certain atom with all other atoms in a molecule is given by

$$- \sum_{\beta} \langle \phi_i(1) | \frac{Z_\beta}{r_{\beta 1}} | \phi_i(1) \rangle + \sum_{k} \langle \phi_i(1) | \frac{\phi_k(2)\phi_k(2)}{r_{12}} | \phi_i(1) \rangle$$

$$- \sum_{k} \langle \phi_i(1) | \frac{\phi_k(2)\phi_k(1)}{r_{12}} | \phi_i(2) \rangle \, \delta(s_i, s_k) \qquad (3.26)$$

as can be seen by comparison with (3.12).

β represents a summation over all other nuclei in the molecule, k represents a summation over all occupied orbitals belonging to these nuclei.

Table III-13 One-electron Energies of the Free Ions as functions of the charge distribution

Copper

$$\varepsilon_{3d} = - 0.64741 + 0.37021B + 0.31660C - 0.06053B^2 - 0.08912C^2 - A\{0.66774 - 0.09623B - 0.06283C - 0.01652B^2 - 0.05090C^2\}$$

$$\varepsilon_{4s} = - 0.22810 + 0.02274B - 0.02868BC + 0.27261C - 0.07258C^2 + 0.01175BC^2 - A\{0.36030 + 0.00943B - 0.01282BC - 0.03104C - 0.05246C^2 + 0.00977BC^2\}$$

$$\varepsilon_{4p} = - 0.13562 + 0.02249C + 0.27261B - 0.07258BC - 0.02868B^2 + 0.01175B^2C - A\{0.26982 + 0.01313C - 0.03104B - 0.05246BC - 0.01282B^2 + 0.00977B^2C\}$$

Chlorine

$$\varepsilon_{3s} = - 1.0717 + 0.3361D$$

$$\varepsilon_{3p} = - 0.5051 + 0.3533D$$

As has been discussed previously (Chapter II, Section 9) the computation of the Coulomb and the Exchange integrals in (3.26) is extremely difficult.
The interaction of an electron of a certain atom with the other atoms in the molecule will therefore in the following be approximated by

$$\sum_{\beta} \langle \phi_i(1) | \frac{Z'_\beta}{r_{\beta 1}} | \phi_i(1) \rangle \qquad (3.27)$$

In other words, we assume that an electron of a certain atom "sees" the other atoms as point charges. This is the basic approximation in our calculation of the H_{ii} integrals and, at first sight, it seems a rather drastic approximation. Of course, the electron sees the nuclei of other atoms as point charges. If we have to do with electrons of other atoms with small n and l (1s, 2s, 2p, etc.), the situation will be similar because the orbitals of these electrons will be close to the nucleus of the atom to which they belong.

The approximation can be expected to become less accurate for orbitals with higher n and l. The orbitals of these electrons are more extended in space. Consequently, the Coulomb integrals deviate from the point charge model, and, moreover, the Exchange integrals become significant since the function $\phi_i(1)\,\phi_k(2)$ is not necessarily small.

However, an inspection of Table III-15 (and also of Table III-11) reveals that the deviation from the point charge model is surprisingly small and therefore one may hope - and we believe with some justification - that our approximation is a useful one.

The calculation of the integrals (3.27) can now be split into two operations because Z'_β is not a function of the coordinates

(1) Calculation of the integrals

$$\langle \phi_i(1) \left| \frac{1}{r_{\beta 1}} \right| \phi_i(1) \rangle \qquad (\frac{1}{r_\beta} \text{ integral}) \tag{3.28}$$

(2) Calculation of the effective charges Z'_β

(1) Calculation of the $\frac{1}{r_\beta}$ integrals

These integrals are of the type

$$\langle \phi_{Cu} \left| \frac{1}{r_{Cl}} \right| \phi_{Cu} \rangle, \ \langle \phi_{Cl} \left| \frac{1}{r_{Cu}} \right| \phi_{Cl} \rangle \quad \text{or} \quad \langle \phi_{Cl} \left| \frac{1}{r_{Cl'}} \right| \phi_{Cl} \rangle$$

They can be expressed in elementary integrals of the type

$$\langle ns_a \left| \frac{1}{r_b} \right| ns_a \rangle, \ \langle np\sigma_a \left| \frac{1}{r_b} \right| np\sigma_a \rangle, \ \langle np\pi_a \left| \frac{1}{r_b} \right| np\pi_a \rangle, \ \text{etc.}$$

analogously to the reduction of group overlap integrals to simple diatomic overlap integrals. The transformations to be applied are the same in the two cases and we thus find expressions for the $\frac{1}{r_\beta}$ integrals; they are given in Table III-14.

Using the same notation as for the overlap integrals and also applying the functions of the Tables III-1 and III-2 we find

$$\langle n_1 lm \left| \frac{1}{r_2} \right| n'_1 lm \rangle = N_1 N_1' \int r_1^{\,n_1+n_1'-2}\, e^{-(a_1+a_1')\,r_1}\, \frac{1}{r_2}\, F(\theta,\varphi)\, d\tau \tag{3.29}$$

Table III-14 Expressions for the $\frac{1}{r_\beta}$-integrals

(1) Interaction of Cu-electrons with unit point charges on the 4 Cl-ligands

ϕ_i	$\sum\limits_{\beta} \langle \phi_i \vert \frac{1}{r_\beta} \vert \phi_i \rangle$
4s	$4 \langle 4s \vert \frac{1}{r_{Cl}} \vert 4s \rangle$
4p	$\frac{4}{3} \langle 4p\sigma \vert \frac{1}{r_{Cl}} \vert 4p\sigma \rangle + \frac{8}{3} \langle 4p\pi \vert \frac{1}{r_{Cl}} \vert 4p\pi \rangle$
$3d_{z^2}, 3d_{x^2-y^2}$	$\frac{8}{3} \langle 3d\pi \vert \frac{1}{r_{Cl}} \vert 3d\pi \rangle + \frac{4}{3} \langle 3d\delta \vert \frac{1}{r_{Cl}} \vert 3d\delta \rangle$
$3d_{xy}, 3d_{xz}, 3d_{yz}$	$\frac{4}{3} \langle 3d\sigma \vert \frac{1}{r_{Cl}} \vert 3d\sigma \rangle + \frac{8}{9} \langle 3d\pi \vert \frac{1}{r_{Cl}} \vert 3d\pi \rangle +$ $\frac{16}{9} \langle 3d\delta \vert \frac{1}{r_{Cl}} \vert 3d\delta \rangle$

(2) Interaction of Cl-electrons with unit point charges on the Cu-nucleus and on the other Cl-ligands

ϕ_i	$\sum\limits_{\beta} \langle \phi_i \vert \frac{1}{r_\beta} \vert \phi_i \rangle$
3s	$\langle 3s \vert \frac{1}{r_{Cu}} \vert 3s \rangle + 3 \langle 3s \vert \frac{1}{r_{Cl}} \vert 3s \rangle$
$3p_z$	$\langle 3p\sigma \vert \frac{1}{r_{Cu}} \vert 3p\sigma \rangle + 2 \langle 3p\sigma \vert \frac{1}{r_{Cl}} \vert 3p\sigma \rangle +$ $\langle 3p\pi \vert \frac{1}{r_{Cl}} \vert 3p\pi \rangle$
$3p_x, 3p_y$	$\langle 3p\pi \vert \frac{1}{r_{Cu}} \vert 3p\pi \rangle + \frac{1}{2} \langle 3p\sigma \vert \frac{1}{r_{Cl}} \vert 3p\sigma \rangle +$ $\frac{5}{2} \langle 3p\pi \vert \frac{1}{r_{Cl}} \vert 3p\pi \rangle$

Changing to elliptical coordinates ξ, η, and φ, we now define

$$I(n_1, n_1', l, m, p) = N_1 N_1' \left(\frac{R}{2}\right)^{n_1+n_1'} \frac{2l+1}{2^{m+1}} \cdot$$

$$\cdot \int_1^{\infty} \int_{-1}^{1} (\xi+\eta)^{n_1+n_1'-2l-1+p} (1-\xi^2)^m (\eta^2-1)^m (1+\xi\eta)^{2(l-m)-p} e^{-\rho\xi} e^{-\rho\eta} \, d\xi \, d\eta \tag{3.30}$$

In terms of this integral (3.30) we get the following expressions for the relevant $\frac{1}{r_\beta}$ integrals

$$\left.\begin{aligned}
\langle n_1 s \left|\frac{1}{r_2}\right| n_1' s \rangle &= I(n_1, n_1', 0, 0, 0) \\
\langle n_1 p\sigma \left|\frac{1}{r_2}\right| n_1' p\sigma \rangle &= I(n_1, n_1', 1, 0, 0) \\
\langle n_1 p\pi \left|\frac{1}{r_2}\right| n_1' p\pi \rangle &= I(n_1, n_1', 1, 1, 0) \\
\langle n_1 d\sigma \left|\frac{1}{r_2}\right| n_1' d\sigma \rangle &= \frac{9}{4} I(n_1, n_1', 2, 0, 0) - \frac{3}{2} I(n_1, n_1', 2, 0, 2) \\
&\quad + \frac{1}{4} I(n_1, n_1', 2, 0, 4) \\
\langle n_1 d\pi \left|\frac{1}{r_2}\right| n_1' d\pi \rangle &= 3\, I(n_1, n_1', 2, 1, 0) \\
\langle n_1 d\delta \left|\frac{1}{r_2}\right| n_1' d\delta \rangle &= \frac{3}{2} I(n_1, n_1', 2, 2, 0)
\end{aligned}\right\} \tag{3.31}$$

If

$$u = n_1 + n_1' - 2l - 1 + p$$

$$v = 2(l-m) - p$$

then (3.30) can be expressed in A and B integrals according to

$$I(n_1, n_1', l, m, p) = N_1 N_1' \left(\frac{R}{2}\right)^{n_1+n_1'} \frac{2l+1}{2^{m+1}} \cdot$$

$$\cdot \sum_{k_1=0}^{u} \sum_{k_2=0}^{m} \sum_{k_3=0}^{m} \sum_{k_4=0}^{v} \binom{u}{k_1}\binom{m}{k_2}\binom{m}{k_3}\binom{v}{k_4} (-1)^{k_2+k_3} A_r(\rho) \, B_s(\rho) \tag{3.32}$$

with

$$r = u - k_1 + 2k_2 + k_4$$

$$s = k_1 + 2(m - k_3) + k_4$$

A method for the computation of the A_r and B_s integrals has been given in Section 2 of this Chapter.

On the basis of formula (3.32) a FORTRAN computer programme was written (M.O. BEREKENING 270E 1/RB-INT). This programme, in connection with the relations (3.31), gives the numerical values of the $\frac{1}{r_\beta}$ integrals as shown in Table III-15.

The interaction of an electron of a certain atom in the molecule with unit point charges on the other atoms of the molecule is now known. Evidently these interactions depends on the charge distribution in the complex (since the size of the orbitals depend on the charge distribution) and therefore are again functions of A, B, C, and D (from $Cu(d^{10-A}s^Bp^C)(Cl^{-D})_4$). These functions are given in Table III-16.

(2) Calculation of effective charges Z'_β

The only thing left to be done is the calculation of the effective charges Z'_β. Consider two electrons, No. 1 in orbital ϕ_1 on atom A and No. 2 in orbital ϕ_2 on atom B. ϕ_1 and ϕ_2 are taken spherically symmetrical, which is correct for s-orbitals and for completely filled p and d-shells, but is only an approximation for partly filled p and d-shells. However, since the relevant p and d-shells are as good as filled (d^{10} for Cu and p^6 for Cl) the approximation is justified.

We now have to calculate how electron 2 screens electron 1 from nucleus B. Take a volume element $d\tau$. "The part of electron 1" contained by $d\tau$ equals

$$\phi_1^2 \, d\tau$$

We now suppose that this part of electron 1 is screened from nucleus B by the part of electron 2 that is in a sphere round B with radius r_β :

$$y(2) = \int_0^{r_\beta} R_2^2 \, r^2 \, dr \qquad (\phi_2 \text{ is spherically symmetrical})$$

So the total screening of electron 1 from nucleus B by electron 2 is given by

$$S_2(1) = \int \phi_1^2 \, y(2) \, d\tau \tag{3.33}$$

Since it is difficult to compute the integral (3.33) we shall try to find an approximation. Consider the function R^2r^2 (Fig. 3.2). We see that both for low and high values of r this function is practically zero. So we may suppose that electron 2 is in a "spherical shell" between concentric spheres with radii $r_{min.}$ and $r_{max.}$ (These radii can be determined by drawing two intersecting straight lines (see Fig. 3.2) thus forming a triangle with the r-axis in such a way that the triangle covers the surface under the R^2r^2 function as well as possible. Actual manipulation shows that this is easy to do).

Table III-15 Values of the $\frac{1}{r_\beta}$ integrals

ϕ_A	β	$\langle \phi_A \| \frac{1}{r_\beta} \| \phi_A \rangle$
4s $(d^{10}s^{2})$	Cl	0.21005
4s $(d^{10}s)$	Cl	0.22758
4s $(d^{9}s^{2})$	Cl	0.23548
4s $(d^{9}s)$	Cl	0.23741
$4p\sigma(d^{10}p^{2})$	Cl	0.14463
$4p\sigma(d^{10}p)$	Cl	0.24704
$4p\sigma(d^{9}p^{2})$	Cl	0.28081
$4p\sigma(d^{9}p)$	Cl	0.28316
$4p\pi(d^{10}p^{2})$	Cl	0.11668
$4p\pi(d^{10}p)$	Cl	0.17240
$4p\pi(d^{9}p^{2})$	Cl	0.19872
$4p\pi(d^{9}p)$	Cl	0.20662
$3d\sigma(d^{10})$	Cl	0.24356
$3d\sigma(d^{9})$	Cl	0.24185
$3d\pi(d^{10})$	Cl	0.24065
3d (d^{9})	Cl	0.24084
$3d\delta(d^{10})$	Cl	0.23308
$3d\delta(d^{9})$	Cl	0.23387
3s (Cl)	Cu	0.23832
3s (Cl^{-})	Cu	0.23508
$3p\sigma$(Cl)	Cu	0.25910
$3p\sigma(Cl^{-})$	Cu	0.26500
$3p\pi$(Cl)	Cu	0.22741
$3p\pi(Cl^{-})$	Cu	0.22960
Point charges on Cu and Cl		0.23843
3s (Cl)	Cl'	0.14611
3s (Cl^{-})	Cl'	0.14414
$3p\sigma$(Cl)	Cl'	0.15067
$3p\sigma(Cl^{-})$	Cl'	0.15418
$3p\pi$(Cl)	Cl'	0.14344
$3p\pi(Cl^{-})$	Cl'	0.14552
Point charges on Cl and Cl'		0.14599

Table III-16 Interaction of an electron in an orbital of a certain atom with the other atoms of the complex

(1) Cu-electrons

4s	$(0.98046 - 0.02308A - 0.07012B + 0.06241AB)\,Z'_{Cl}$
4p	$(1.07430 - 0.12155A - 0.28516C + 0.26096AC)\,Z'_{Cl}$
3d(e)	$(0.95304 - 0.00070A)\,Z'_{Cl}$
$3d(t_2)$	$(0.95253 + 0.00156A)\,Z'_{Cl}$

(2) Cl-electrons

3s	$(0.23832 - 0.00323D)\,Z'_{Cu} + (0.43834 - 0.00591D)\,Z'_{Cl}$
$3p\sigma$	$(0.25910 + 0.00590D)\,Z'_{Cu} + (0.44479 + 0.00910D)\,Z'_{Cl}$
$3p\pi$	$(0.22742 + 0.00218D)\,Z'_{Cu} + (0.43395 + 0.00695D)\,Z'_{Cl}$

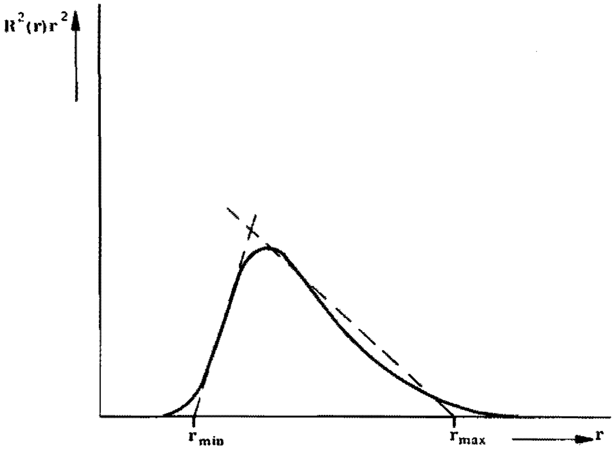


Fig. 3.2 Determination of r_{min} and r_{max}.

For the system of two orbitals we now get Fig. 3.3 and with the help of it, we can distinguish three cases -

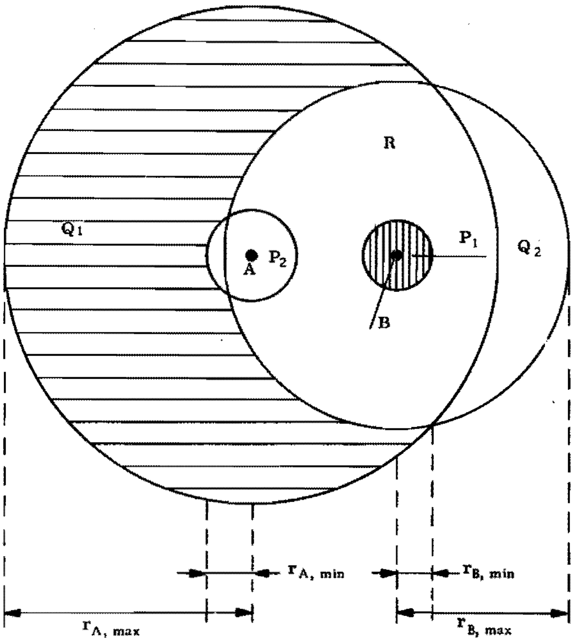


Fig. 3.3 Determination of Z_{eff}.

(a) $y(2) = 0$ in a region within a sphere with radius $r_{min.}$ of electron 2, denoted in the diagram by P_1 (shaded vertically);

(b) $y(2) = 1$ in a region outside a sphere with radius $r_{max.}$ of electron 2, denoted by Q_1 (shaded horizontally);

(c) $y(2)$ has a value between 0 and 1 within the shell between the spheres with radii $r_{min.}$ and $r_{max.}$ (region R).

Since

$$S_2(1) = \int_{P_1} \phi_1^2\, y(2)\, d\tau + \int_{Q_1} \phi_1^2\, y(2)\, d\tau + \int_R \phi_1^2\, y(2)\, d\tau$$

we now find

$$S_2(1) = 0 + \int_{Q_1} \phi_1^2\, d\tau + \int_R \phi_1^2\, y(2)\, d\tau$$

which may be approximated by

$$\frac{\overline{\phi_1^{\,2}}^{\,Q_1}\,.\,\mathrm{vol}\ Q_1}{V_1} + \frac{\overline{\phi_1^{\,2}\ y(2)}^{\,R}\,.\,\mathrm{vol}\ R}{V_1} \qquad (3.34)$$

where $\overline{\phi_1^{\,2}}^{\,Q_1}$ is the mean value of the function $\phi_1^{\,2}$ in the region Q_1, etc.

V_1 is the volume of the spherical shell of electron 1.

Analogously we find for the screening of electron 2 from nucleus A by electron 1

$$\frac{\overline{\phi_2^{\,2}}^{\,Q_2}\,.\,\mathrm{vol}\ Q_2}{V_2} + \frac{\overline{\phi_2^{\,2}\ y(1)}^{\,R}\,.\,\mathrm{vol}\ R}{V_2} \qquad (3.35)$$

Table III-17 gives the values of $r_{min.}$ and $r_{max.}$ used in the calculation, Table III-18 shows the screening constants calculated by this method. We may expect that these factors satisfactorily reproduce the screening effects of the electrons (*)

Table III-17 r_{min} and r_{max} of Cu- and Cl-functions

Atom	ϕ	r_{min}	r_{max}
Cu	4s	1.5	6.4
Cu	4p	2.0	7.5
Cu	3d	0.0	2.0
Cl	3s	0.5	3.5
Cl	3p	0.5	4.3

(*) Note

Using the same principles we can calculate the mutual screening of two orbitals belonging to the same nucleus. Assume, for instance, ϕ_1 = 3s(Cl) and ϕ_2 = 3p(Cl), then we find with the method described above

$$S_2(1) = 0.39 \quad \text{and} \quad S_1(2) = 0.60$$

Hence a 3p electron of Cl is screened more by a 3s electron than reversely, and this is what is expected. The method of Slater (7) yields 0.35 for the two screening constants.

Table III-18 Shielding Constants in $CuCl_4^{2-}$

$\phi(1)$	$\phi(2)$	$S_2(1)$	$S_1(2)$
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

With the screening constants thus obtained, it is easy to calculate the effective charges Z'_β of an atom for an electron of another atom. These Z'_β are given in Table III-19 as functions of A, B, C, and D. The interaction between an electron of a certain atom and the other atoms in a molecule is then completely determined from data given in the Tables III-16 and III-19.

Table III-19 Effective Charges in $CuCl_4^{2-}$

(1) For Cu-electrons

4s $Z'_{Cl} = 0.92D - 0.55$

4p $Z'_{Cl} = 0.91D - 0.55$

$3d(t_2)$ $Z'_{Cl} = 0.96D - 0.22$

3d(e) $Z'_{Cl} = 0.96D - 0.22$

(2) For Cl-electrons

3s $Z'_{Cu} = 1.15 - 0.99A + 0.43B + 0.51C$
$Z'_{Cl} = 0.99D - 0.05$

$3p\sigma$ $Z'_{Cu} = -1.25 - 0.98A + 0.38B + 0.49C$
$Z'_{Cl} = 0.98D - 0.10$

$3p\pi$ $Z'_{Cu} = -1.25 - 0.98A + 0.38B + 0.49C$
$Z'_{Cl} = 0.98D - 0.10$

(d) H_{ii} integrals

We now have to calculate the H_{ii} integrals from the integrals computed so far. This presents no difficulties in the case of the orbitals of the central ion. Assume ϕ_i to be an orbital of the central ion, then in our approximation

$$H_{ii} = \varepsilon_i + \sum_{\beta} \langle \phi_i \left| \frac{Z_{Cl}}{r_{Cl_\beta}} \right| \phi_i \rangle \qquad (3.36)$$

Both ε_i (Table III-12) and the $\frac{1}{r_{Cl}}$ integrals (Tables III-16 and III-19) are completely known and the H_{ii} integral can be written down straight away.

The situation is somewhat complicated for the ligand orbitals. These orbitals have been constructed as linear combinations of the atomic orbitals (Table II-3) and this fact has to be allowed for when calculating the energies of the orbitals. Take, for instance, a ligand orbital of Table II-3

$$\chi_i = N_i (C_1\phi_1 + C_2\phi_2 + C_3\phi_3 + C_4\phi_4)$$

in which ϕ_k is an atomic orbital belonging to the ligand k. Now

$$H_{ii} = \langle \chi_i \left| H \right| \chi_i \rangle = N_i^2 \sum_{k=1}^{4} \sum_{l=1}^{4} C_k C_l \langle \phi_k \left| H \right| \phi_l \rangle \qquad (3.37)$$

In this formula ϕ_k and ϕ_l can be two atomic orbitals belonging to different Cl nuclei and therefore we have to define the orientation of the orbitals in relation to the position of the two nuclei. That is why we have to apply a transformation of the type as already discussed in the case of the group overlap integrals. Since H is invariant under all operations of T_d the results of these transformations must be analogous to those found for the group overlap integrals. We can therefore use Table III-4 and find for example for the A_1 representation

$$\langle \text{s-comb.} \left| H \right| \text{s-comb.} \rangle = \{N_{A_1}(s)\}^2 \{4\langle s_1 \left| H \right| s_1 \rangle + 12\langle s_1 \left| H \right| s_2 \rangle\}$$

$$\langle p_z\text{-comb.} \left| H \right| p_z\text{-comb.} \rangle = \{N_{A_1}(z)\}^2 \{4\langle p_1 \left| H \right| p_1 \rangle + 8\langle p\sigma_1 \left| H \right| p\sigma_2 \rangle + 4\langle p\pi_1 \left| H \right| p\pi_2 \rangle\}$$

In this way we find two types of integral

(1) integrals $\langle \phi_k \left| H \right| \phi_k \rangle$. These are of the type $\langle s_1 \left| H \right| s_1 \rangle$, $\langle p\sigma_1 \left| H \right| p\sigma_1 \rangle$, etc., and can be calculated immediately from

$$\langle \phi_k \left| H \right| \phi_k \rangle = \varepsilon_k + \sum_{\beta'} \langle \phi_k \left| \frac{Z'_{Cl}}{r_{Cl_{\beta'}}} \right| \phi_k \rangle + \langle \phi_k \left| \frac{Z'_{Cu}}{r_{Cu}} \right| \phi_k \rangle$$

(2) integrals $\langle \phi_k | H | \phi_l \rangle$, with $k \neq l$, for instance, $\langle s_1 | H | s_2 \rangle$, $\langle p\sigma_1 | H | p\sigma_2 \rangle$, and so on. ϕ_k and ϕ_l now belong to different Cl nuclei. This type of integral presents another complication. We shall not attempt an exact computation of these integrals because the three and four centre integrals that arise in this computation are too laborious to carry out. Therefore we shall apply an approximating method as used by Wolfsberg, Helmholz (8) and Gray, Ballhausen (9)

$$\langle \phi_k | H | \phi_l \rangle = -FS_{kl} \sqrt{\langle \phi_k | H | \phi_k \rangle \langle \phi_l | H | \phi_l \rangle} \qquad (3.38)$$

with F = 1.67 for σ-bonding
F = 2.00 for π-bonding.

For a discussion of this approximation see the following Section. Because ϕ_k and ϕ_l are completely identical, except for the fact that they belong to different nuclei (e.g. $p\sigma_1$ and $p\sigma_2$),

$$\langle \phi_k | H | \phi_k \rangle = \langle \phi_l | H | \phi_l \rangle$$

and therefore

$$\langle \phi_k | H | \phi_l \rangle = FS_{kl} \langle \phi_k | H | \phi_k \rangle \qquad (3.39)$$

Since the integrals $\langle \phi_k | H | \phi_k \rangle$ are independent of k we find, for instance, for the A_1 representation

$$\langle \text{s-comb.} | H | \text{s-comb.} \rangle = \{N_{A_1}(s)\}^2 (4+12.1,67 \langle s_1 | s_2 \rangle) \langle s_1 | H | s_1 \rangle$$

$$\langle p_z\text{-comb.} | H | p_z\text{-comb.} \rangle = \{N_{A_1}(z)\}^2 (4+8.1,67 \langle p\sigma_1 | p\sigma_2 \rangle + 4.2,00 \; p\pi_1 | p\pi_2 \rangle \cdot \langle p_1 | H | p_1 \rangle$$

Table III-20 gives the final H_{ii} integrals as functions of the charge distribution.

III-4 CALCULATION OF H_{ij} INTEGRALS

In Chapter II we already saw that an accurate calculation of H_{ij} integrals entails a large amount of difficulties. The three and four centre integrals in the H_{ij} integrals often have to be approximated numerically and this process consumes a great deal of time.

Wolfsberg and Helmholz (8) already noticed that for homonuclear diatomic molecules of the first and second row of elements in the periodical table, the H_{ij} integrals may be approximated fairly accurately by the formula

Table III-20 H_{ii} integrals of tetrahedral $CuCl_4^{2-}$

We define:

$$E_{3s} = \varepsilon_{3s} + (0.23832 + 0.00323D)(-1.15 - 0.99A + 0.43B + 0.51C) + (0.43834 - 0.00591D)(0.99D - 0.05)$$

$$E_{3p\sigma} = \varepsilon_{3p} + (0.25910 + 0.00590D)(-1.25 - 0.98A + 0.38B + 0.49C) + (0.44479 + 0.00910D)(0.98D - 0.10)$$

$$E_{3p\pi} = \varepsilon_{3p} + (0.22742 + 0.00218D)(-1.25 - 0.98A + 0.38B + 0.49C) + (0.43395 + 0.00695D)(0.98D - 0.10)$$

We now have the following expressions for the H_{ii} integrals

A_1 representation:

Cu-4s: $\varepsilon_{4s} + (0.98046 - 0.02308A - 0.07012B + 0.06241AB).(0.92D - 0.55)$

pσ-comb. of ligands: $(1.07830 + 0.05599D)\, E_{3p\sigma}$

s-comb. of ligands: $(1.01500 + 0.00080D)\, E_{3s}$

E representation

Cu-3d: $\varepsilon_{3d} + (0.95304 - 0.00070A)(0.96D - 0.22)$

pπ-comb. of ligands: $(1.01826 + 0.01403D)\, E_{3p\pi}$

T_1 representation

pπ-comb. of ligands: $(0.96836 - 0.05176D)\, E_{3p\pi}$

T_2 representation

Cu-4p: $\varepsilon_{4p} + (1.07430 - 0.12155A - 0.28516C + 0.26096AC).(0.91D - 0.55)$

Cu-3d: $\varepsilon_{3d} + (0.95253 + 0.00156A)(0.96D - 0.22)$

pπ-comb. of ligands: $(1.03090 + 0.03728D)\, E_{3p\pi}$

pσ-comb. of ligands: $(0.96937 - 0.02903D)\, E_{3p\sigma}$

s-comb. of ligands: $(0.99484 - 0.00289D)\, E_{3s}$

$$H_{ij} = F\,G_{ij}\,\frac{H_{ii} + H_{jj}}{2} \tag{3.40}$$

with

$$F = 1.67 \text{ for } \sigma\text{-bonding}$$
$$F = 2.00 \text{ for } \pi\text{-bonding}$$

In fact this approximation runs parallel to an approximation of the charge distribution given by Mulliken (10)

$$\phi_i \phi_j = \tfrac{1}{2}\, S_{ij}\,(\phi_i\phi_i + \phi_j\phi_j) \tag{3.41}$$

This approximation of the charge distribution can be used reasonably well for integrals $\langle \phi_i \mid Op \mid \phi_j \rangle$ in which the operator is of such a form that the integral can also be written $\langle Op \mid \phi_i \phi_j \rangle$, for instance, if the operator is $\frac{e^2}{r_{12}}$ or $\frac{Z}{r}$ (potential energy, Coulomb and exchange integrals). The approximation is less applicable to integrals in which it is not allowed to commute the operator with a function, for instance, if the operator is ∇^2 (kinetic energy integral).

Hence, the H_{ij} integrals remain a point of discussion, but since the approximation formula gives fairly good results for simple molecules, one might expect that the use of the same formula in our problem will not introduce large errors.

Ballhausen and Gray (9) prefer the geometric mean $\sqrt{H_{ii}\,H_{jj}}$ instead of $\frac{1}{2}(H_{ii} + H_{jj})$ because, as it turns out for simple molecules, the integral H_{ij} decreases rapidly when the difference in energy of the orbitals increases. Indeed, this fact is rendered better by

$$H_{ij} = -F\,G_{ij}\,\sqrt{H_{ii}\,H_{jj}} \tag{3.42}$$

III-5 EVALUATION OF THE SECULAR DETERMINANT

As has been shown in Chapter II, we have to solve the following secular determinants for a tetrahedral complex:

$\underline{A_1 \text{ symmetry}}$: A 3 x 3 determinant. The eigenvalues of this determinant will be indicated by EA(1), EA(2) and EA(3) with EA(1) $\langle$ EA(2) $\langle$ EA(3). The eigenvectors of the determinant are

V_1 : CA(1, 1) , CA(2, 1) , CA(3, 1)
V_2 : CA(1, 2) , CA(2, 2) , CA(3, 2)
V_3 : CA(1, 3) , CA(2, 3) , CA(3, 3)

giving the eigenfunctions

$$\begin{aligned}
\psi_A(1) &= CA(1,1)\,\phi_{4s} + CA(2,1)\,\chi_{p\sigma} + CA(3,1)\,\chi_{3s} \\
\psi_A(2) &= CA(1,2)\,\phi_{4s} + CA(2,2)\,\chi_{p\sigma} + CA(3,2)\,\chi_{3s} \\
\psi_A(3) &= CA(1,3)\,\phi_{4s} + CA(2,3)\,\chi_{p\sigma} + CA(3,3)\,\chi_{3s}
\end{aligned}$$

E symmetry : two identical 2 x 2 secular determinants, giving the eigenvalues and eigenfunctions

EE(1) $\psi_E(1) = CE(1,1)\phi_{3d} + CE(2,1)\chi_{p\pi}$
EE(2) $\psi_E(2) = CE(1,2)\phi_{3d} + CE(2,2)\chi_{p\pi}$

T_1 symmetry : three identical 1 x 1 determinants giving

EU and $\psi_{T_1} = \chi_{p\pi}$

T_2 symmetry : three identical 5 x 5 determinants with the eigenvalues and eigenfunctions as follows

ET(1) $\psi_{T_2}(1) = CT(1,1)\,\phi_{4p} + CT(2,1)\,\phi_{3d} + CT(3,1)\,\chi_{p\pi} + CT(4,1)\,\chi_{p\sigma} + CT(5,1)\,\chi_s$
ET(2)
ET(3) etc.
ET(4)
ET(5)

The computer programme, with the help of which the eigenvalues and the eigenvectors of the secular determinant will be determined, can be split up into three parts:

(1) For a given charge distribution (A, B, C, and D), all H_{ij} and S_{ij} integrals are calculated.
(2) The secular determinants are solved by using the H_{ij} and S_{ij} integrals calculated in part (1).
(3) With the eigenfunctions found in part (2) a new charge distribution is calculated (new A, B, C, and D).

(1) As stated before, we shall characterise a charge distribution by A, B, C, and D from $Cu(d^{10-A}s^{B}p^{C})\text{-}(Cl^{-D})_4$. In the Tables III-8 and III-20, we find how the S_{ij} and H_{ii} integrals depend on these A, B, C, and D. Using these Tables the S_{ij} and the H_{ii} integrals are calculated for initial A, B, C, and D in this part of the computer programme. Subsequently the corresponding H_{ij} integrals are computed in the manner that has been discussed in Section 4 of this Chapter. (This first part of the programme was written in FORTRAN.)

(2) The basic programme for the evaluation of the secular determinant in our calculation is an S.P.S. (Symbolic Programming System) computer programme made by Veltkamp and Clement (12). This programme is practically analogous to the ALGOL procedure published by Wilkinson (11). A description of this programme and of the subroutines used in it are to be found in Refs.(11) and (12).
The basic computer programme cited here, computes the eigenvalues λ and the eigenvectors $\underline{c}$ of the equation

$$(\mathcal{H} - \lambda I)\,\underline{c} = 0 \tag{3.43}$$

in which $\mathcal{H}$ is a symmetrical matrix and I is the unit matrix.
However in our particular problem we have to compute the eigenvalues and eigenvectors of

$$(H - \lambda S)\,\underline{c} = 0 \tag{3.44}$$

in which H and S are both symmetrical matrices. Equation (3.44) must first be reduced to an equation of the type (3.43). Multiplication of (3.41) by the matrix $S^{-\frac{1}{2}}$ gives

$$(S^{-\frac{1}{2}} H - \lambda S^{\frac{1}{2}})\,\underline{c} = 0$$

or

$$(S^{-\frac{1}{2}} H S^{-\frac{1}{2}} S^{\frac{1}{2}} - \lambda S^{\frac{1}{2}})\,\underline{c} = 0$$

or

$$(S^{-\frac{1}{2}} H S^{-\frac{1}{2}} - \lambda I)\, S^{\frac{1}{2}}\,\underline{c} = 0$$

or

$$(\mathcal{H} - \lambda I)\,\underline{d} = 0 \tag{3.45}$$

with

$$\mathcal{H} = S^{-\frac{1}{2}} H S^{-\frac{1}{2}}$$

and

$$\underline{d} = S^{\frac{1}{2}}\,\underline{c}$$

As H is a symmetrical matrix, $\mathcal{H}$ is also a symmetrical matrix. Now equation (3.45) can be solved by the basic eigenvalue computer programme; the eigenvalues found then are also the eigenvalues of (3.44). The eigenvectors of (3.44) can be determined by multiplying the eigenvectors of (3.45) by the matrix $S^{-\frac{1}{2}}$.

We can now act in the following way:

(a) The matrix $S^{-\frac{1}{2}}$ is determined as follows:

Compute the eigenvalues of S with the help of the basic eigenvalue computer programme: $\mu_1, \ldots\ldots, \mu_n$.
From these eigenvalues we can construct the matrix

$$M = \begin{pmatrix} \mu_1 & & 0 \\ & \ddots & \\ 0 & & \mu_n \end{pmatrix} .$$

Compute, by means of the same programme, the eigenvectors of S : $\underline{v}_1, \ldots\ldots, \underline{v}_n$. From these vectors we construct the matrix

$$V = \begin{pmatrix} v_{11} & \cdots\cdots & v_{n1} \\ \vdots & & \\ v_{1n} & \cdots\cdots & v_{nn} \end{pmatrix}$$

Because

$$S\,\underline{v}_i = u_i\underline{v}_i = \underline{v}_i u_i$$

it may be seen that

$$S\,V = V\,M \qquad \text{also holds,}$$

or

$$S = V\,M\,V^{-1} = V\,M\,V^T$$

V^T is the transpose of the matrix V.
From this can be concluded

$$S^{-\frac{1}{2}} = V\,M^{-\frac{1}{2}}\,V^T$$

The matrix $M^{-\frac{1}{2}}$ is easily computed

$$M^{-\frac{1}{2}} = \begin{pmatrix} \mu_1^{-\frac{1}{2}} & & O \\ & \ddots & \\ O & & \mu_n^{-\frac{1}{2}} \end{pmatrix}$$

So $S^{-\frac{1}{2}}$ is also easily found.

(b) With the help of $S^{-\frac{1}{2}}$ we calculate

$$\mathcal{H} = S^{-\frac{1}{2}}\,H\,S^{-\frac{1}{2}}$$

(c) Using the basic eigenvalue computer programme we compute the eigenvalues and eigenvectors of

$$(\mathcal{H} - \lambda\,I)\,\underline{d} = 0$$

The eigenvalues $\lambda_1, \ldots\ldots, \lambda_n$ are also the eigenvalues of our initial secular determinant.

(d) The eigenvectors of the initial secular determinant can now be calculated by applying the transformation

$$\underline{c}_i = S^{-\frac{1}{2}}\,\underline{d}_i \qquad i = 1, \ldots\ldots, n$$

The result is an orthonormal set of eigenvectors.

From the complete procedure (a) to (d) an S.P.S. computer programme was written. The matrices H and S used in this programme are to be taken from the results of part (1).
In this way the secular determinants appertaining to the symmetries A_1, E, and T_2 are solved successively. The corresponding eigenvalues and eigenvectors are stored in places of the computer memory that have beforehand been fixed by the FORTRAN programme (part (1)) and can be used in part (3) of the programme.

(3) From the eigenfunctions found in part (2) of the programme we must now compute a new charge distribution.

Suppose we have a molecular orbital

$$\chi = C_A \phi_A + C_B \phi_B \qquad (\chi \text{ is normalised})$$

in which ϕ_A and ϕ_B are atomic orbitals of the nuclei A and B resp. If the molecular orbital χ contains electrons, we may distribute the charge of these electrons over the two nuclei A and B. The charge distribution of an electron in χ is given by $|\chi|^2$, so we suppose the charge ρ_A, belonging to nucleus A, to be proportional to C_A^2 and in the same way ρ_B, belonging to nucleus B, to be proportional to C_B^2. If there are n_χ electrons in orbital χ then

$$\rho_A + \rho_B = n_\chi$$

so

$$\rho_A = \frac{C_A^2}{C_A^2 + C_B^2} n_\chi \qquad (3.46)$$

$$\rho_B = \frac{C_B^2}{C_A^2 + C_B^2} n_\chi$$

The distribution of the charge over A and B, as carried out here, remains somewhat arbitrary because it is never possible to determine unequivocally which part of the charge belongs to nucleus A and which to B.
Mulliken (13) gives another suggestion for the distribution of the charge. Since

$$|\chi|^2 = C_A^2 |\phi_A|^2 + 2C_A C_B |\phi_A \phi_B| + C_B^2 |\phi_B|^2$$

Mulliken supposes

$$\rho_A = n_\chi (C_A^2 + C_A C_B S(\phi_A, \phi_B))$$

$$\rho_B = n_\chi (C_B^2 + C_A C_B S(\phi_A, \phi_B))$$

As χ is normalised, $\rho_A + \rho_B = n_\chi$ also holds in this case. Now ρ_A and ρ_B contain two terms:

(1) a term proportional to C_A^2 : the nett charge (according to Mulliken);

(2) an overlap contribution to the charge which is proportional to $C_A C_B$.

The overlap contribution may also be negative, viz. if C_A and C_B have different signs.
In some cases, the overlap contribution is larger than the nett charge; so in such circumstances ρ may also become negative. Physically this is inconceivable. Mulliken supposes that negative ρ's will only appear exceptionally. Unfortunately however in the calculation concerning the ground state of $CuCl_4^{2-}$ using Mulliken's method we found some negative ρ's (see following section). Therefore, from now on formula (3.46) is used to determine the A, B, C, and D from the molecular orbitals.

We take the configuration (2.17a) as the ground state of $CuCl_4^{2-}$.

Determination of A (from $3d^{10-A}$ of Cu)

The 3d orbitals of Cu appear in the molecular orbitals with E and T_2 symmetry. As the orbitals with E symmetry are completely filled, they contribute four d-electrons. The levels with T_2 symmetry are only partly filled

$$(1t_2)^6\,(2t_2)^6\,(3t_2)^6\,(4t_2)^5\,(5t_2)^0$$

These orbitals contribute to the d-electrons

$$\begin{aligned} SD = {} & 6\,\{CT(2,1)\}^2 \Big/ \Big[\sum_{i=1}^{5}\{CT(i,1)\}^2\Big] + \\ & 6\,\{CT(2,2)\}^2 \Big/ \Big[\sum_{i=1}^{5}\{CT(i,2)\}^2\Big] + \\ & 6\,\{CT(2,3)\}^2 \Big/ \Big[\sum_{i=1}^{5}\{CT(i,3)\}^2\Big] + \\ & 5\,\{CT(2,4)\}^2 \Big/ \Big[\sum_{i=1}^{5}\{CT(i,4)\}^2\Big] \end{aligned} \qquad (3.48)$$

Hence

$$10 - A = 4 + SD$$

or $\qquad$ (3.49)

$$A = 6 - SD$$

Determination of B (from $4s^B$ of Cu)

The 4s orbitals of Cu only appear in the molecular orbitals with A_1 symmetry. These orbitals are not completely filled:

$$(1a_1)^2\,(2a_1)^2\,(3a_1)^0$$

Therefore we obtain

$$B = 2\,\{CA(1,1)\}^2 \,/\, \left[\sum_{i=1}^{3} \{CA(i,1)\}^2\right] + 2\,\{CA(1,2)\}^2 \,/\, \left[\sum_{i=1}^{3} \{CA(i,2)\}^2\right] \tag{3.50}$$

Determination of C (from $4p^C$ of Cu)

The 4p orbitals of Cu have T_2 symmetry, so we find analogously to the results for 3d electrons

$$\begin{aligned} C = {} & 6\,\{CT(1,1)\}^2 \,/\, \left[\sum_{i=1}^{5} \{CT(i,1)\}^2\right] + \\ & 6\,\{CT(1,2)\}^2 \,/\, \left[\sum_{i=1}^{5} \{CT(i,2)\}^2\right] + \\ & 6\,\{CT(1,3)\}^2 \,/\, \left[\sum_{i=1}^{5} \{CT(i,3)\}^2\right] + \\ & 5\,\{CT(1,4)\}^2 \,/\, \left[\sum_{i=1}^{5} \{CT(i,4)\}^2\right] \end{aligned} \tag{3.51}$$

Determination of D (from Cl^{-D})

After the determination of A, B, and C the determination of D is quite easy because we known the total charge in the complex $CuCl_4^{2-}$. It is easily seen that

$$D = \frac{1}{4}(3 + A - B - C) \tag{3.52}$$

We now have new values for A, B, C, and D. In general these new A, B, C, and D will differ from the initial A, B, C, and D. We can now use the calculated A, B, C, and D for a new calculation cycle etc., hoping that after some iterations we will get a better approximation to the correct A, B, C, and D. It then turns out that the process often oscillates around the correct values of A, B, C, and D. However we can help the process to converge.

Suppose we take A_o, B_o, C_o as initial values of A, B, and C (D is always fully determined by (3.52)) and, after a first calculation, obtain A_1, B_1, and C_1 as new values of A, B, and C. A second calculation (with A_1, B_1, and C_1 as initial values for A, B, and C) gives us A_2, B_2, and C_2.

We can now find a better approximation of the correct values of A, B, and C with the δ^2-process of Aitken (14).

Suppose

$$\Delta A_o = A_1 - A_o, \quad \Delta A_1 = A_2 - A_1$$

and

$$\Delta^2 A_o = \Delta A_1 - \Delta A_o$$

then a better approximation of A is

$$A = A_o - \frac{(\Delta A_o)^2}{\Delta^2 A_o} \tag{3.53}$$

Analogously we can find better approximations of B and C.
The A, B, and C found in this way are taken as new A_o, B_o, and C_o etc.
It turns out that, if the first A_o, B_o, and C_o are not excessively far from the correct A, B, and C, the convergence of the process is good and we can obtain values for A, B, and C that are constant up to six figures.
(This part (3) of the computer programme has also been written in FORTRAN.)

III-6 RESULTS

When we carry out the calculation for the ground state of tetrahedral $CuCl_4^{2-}$ as described in the preceding Sections, we obtain the following values for A, B, C, and D

$A = 0.5408$
$B = 0.1160$
$C = 0.5063$
$D = 0.7296$

This combination of A, B, C, and D is found to be the only one that remains constant throughout the calculation.

The values of A, B, C, and D given here deviate somewhat from the values of A, B, C, and D in a fully ionic bonding ($A = 1$, $B = C = 0$, $D = 1$). This means that covalency effects are really of importance in the bonding of $CuCl_4^{2-}$. Instead of one Cu^{+2} and four Cl^- ions we now have one $Cu^{+0.92}$ and four $Cl^{-0.73}$.
The high value of C is also remarkable and reveals the important role of the 4p orbitals.

The eigenvalues and eigenfunctions belonging to the computed charge distribution are reported in Table III-21 (for the notation see Section III-5).
In this Table the H_{ii} integrals also appear.

The results prompt us to making 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 III-21 Eigenvalues and Eigenfunctions belonging to the ground state of tetrahedral $CuCl_4^{2-}$

A_1 symmetry

	ϕ →	4s	χ(z)	χ(s)
	H_{ii} → εmo ↓	-0.16996	-0.40468	-0.87306
$3a_1$	0.23604	1.5590	-0.9496	-0.5014
$2a_1$	-0.39578	0.0378	0.9833	-0.1468
$1a_1$	-0.90749	-0.2733	0.1852	1.1000
	EA(i)	CA(1, i)	CA(2, i)	CA(3, i)

E symmetry

	ϕ →	3d	χ(x, y)
	H_{ii} → εmo ↓	-0.34082	-0.35662
2e	-0.32351	0.8361	-0.6046
1e	-0.37105	0.5521	0.7990
	EE(i)	CE(1, i)	CE(2, i)

T_1 symmetry

$E(T_1) = -0.32267$

T_2 symmetry

	ϕ →	4p	3d	χ(x, y)	χ(z)	χ(s)
	H_{ii} → εmo ↓	-0.13640	-0.34048	-0.36688	-0.34286	-0.85342
$5t_2$	0.14177	1.4480	0.0860	0.5550	-0.3770	-0.5718
$4t_2$	-0.30961	-0.0573	0.7069	-0.3953	-0.6897	-0.0872
$3t_2$	-0.35835	-0.0044	0.7101	0.2265	0.6134	0.0014
$2t_2$	-0.37125	0.0165	0.0644	0.9105	-0.3810	0.0349
$1t_2$	-0.91174	-0.3510	-0.0020	-0.1558	0.0772	1.1640
	ET(i)	CT(1, i)	CT(2, i)	CT(3, i)	CT(4, i)	CT(5, i)

With A = 1, B = C = 0 and D = 1, we find for the H_{ii} integrals

HA(3, 3)= -0.23417 HE(2, 2)= -0.61042 HT(5, 5)= -0.06245
HA(2, 2)= -0.38943 HE(1, 1)= -0.32910 HT(4, 4)= -0.60912
HA(1, 1)= -0.84536 HT(3, 3)= -0.34055
HT(2, 2)= -0.32284
T_1 : E= -0.29222 HT(1, 1)= -0.82551

From these values we see that 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^{2+} ion and four Cl^- ions, some charge of the filled ligand orbitals with high energy will flow to the partly filled d-orbitals with low energy. At the same time, the energy of the ligand orbitals decreases and the energy of the central ion orbitals rises. At the computed charge distribution the energy of the ligand orbitals is below that of the central ion orbitals (*)

(*) Note
If this were not the case, the complex $CuCl_4^{2-}$ might not be stable. In the (hypothetical) complex CuI_4^{2-} for instance, one may expect that the ligand energies remain above the energies of the central ion orbitals and this may be the reason why Cu(II) is reduced to Cu(I).

(b) For the splitting of the "d-orbitals" we find the following

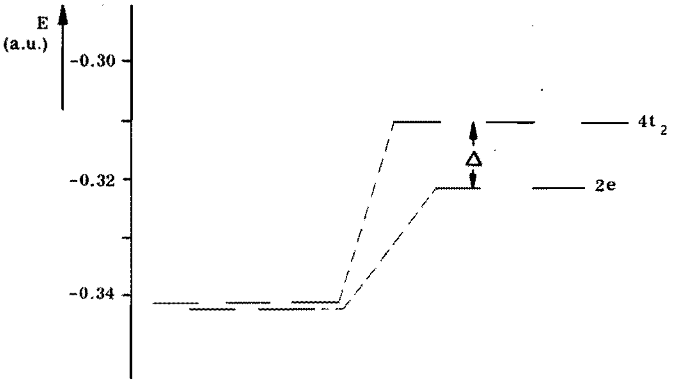


Fig. 3.4 Splitting of the d-orbitals in tetrahedral $CuCl_4^{2-}$

Before the formation of the molecular orbitals, the splitting of the d-orbitals is very small:

$$0.00034 \text{ a.u.} = 74 \text{ cm}^{-1}$$

After the formation the splitting is much larger:

$$0.01390 \text{ a.u.} = 3050 \text{ cm}^{-1}.$$

The splitting has the right sign ($4t_2$ above 2e) and also a very reasonable value. From optical spectra and from crystal field calculations a value of 3500 to 4000 cm^{-1} for Δ is expected (15).

In the pure crystal field picture (A = 1, B = C = 0, D = 1) we find

$$\Delta' = H_{ii}(3d_{t_2}) - H_{ii}(3d_e) = 0.00130 \text{ a.u.} = 285 \text{ cm}^{-1}.$$

Clearly there is no stabilisation of d-electrons; on the contrary, the d-electrons are destabilised by a large amount. The stabilisation of the complex must be found in the bonding orbitals.

(c) From the eigenfunctions we can see that a large amount of mixing occurs not only in the $4t_2$ orbitals but also in the 2e orbitals. Probably the mixing given by the molecular orbital theory is too large, as is not exceptional with this theory. We shall discuss the effect later on. The large mixing causes the anti-bonding orbitals to be situated relatively high. An example is afforded by the t_1 orbitals. The energy of these ligand orbitals is as high as that of the 2e orbitals. However, the t_1 orbitals are strongly anti-bonding ligand orbitals as can be seen from Table III-4.

(d) From Table III-21 we see that there are two molecular orbitals with positive energies: $3a_1$ and $5t_2$. This is conceivable since the energy of all other orbitals is calculated by placing the electron in the field of (n-1) other electrons, while in the case of $3a_1$ and $5t_2$ the energy is calculated by placing a (fictitious) electron in the field of n other electrons. Therefore the energies of these orbitals are higher than those of the others (16).

(e) Chemists often work with the concepts of bonding and anti-bonding molecular orbitals. In this connection they introduce a quantity known as the "overlap population" (13). Suppose we have a molecular orbital composed of central ion and ligand functions.

We then define:

$$\text{O.P.} = 2 \sum_i \sum_j c_i c_j S_{ij}$$

where the summation i extends over the central-ion functions and the summation j over the ligand functions occurring in the molecular orbital.

Mulliken shows that in most cases a positive overlap population corresponds to a bonding effect of the molecular orbital and a negative overlap population to an anti-bonding effect. This view if founded on the fact that with a positive overlap population, charge is concentrated between the nuclei, thus giving a bonding effect.

However, in our calculation we must use these considerations with some reserve. The 4p function of copper has its highest density not between the Cu

and Cl nuclei but on the other side of the Cl nucleus (see Fig. 3.1), and the same holds to a certain extent for the 4s function.
Normally, most overlap is found between the two nuclei but with the 4s and 4p functions this is not the case. So with these functions a positive overlap population need not correspond with a concentration of charge between the Cu and Cl nuclei but, on the contrary, a concentration of charge may be caused by a negative overlap population. Hence, although we find a negative overlap population in the $1a_1$ (-0.36) and the $1t_2$ (-0.70), these orbitals may be bonding orbitals.

(f) The evaluation of the secular determinant and the determination of A, B, C, and D is carried out very accurately by the computer. The errors introduced by the approximations of the preceding Sections are much larger than the computational errors.

A further discussion of the results will be given later on, when the results of the calculations on other systems are available.

REFERENCES

1. R.E. Watson, A.J. Freeman: Phys. Rev. 123, (1961), 521.
2. J.W. Richardson *et al.*: J. Chem. Phys. 36, (1962), 1057; 38, (1963), 796.
3. L. Helmholz, R.F. Kruh: J. Am.Chem.Soc. 74, (1952), 1176.
4. C.C.J. Roothaan: J.Chem.Phys. 19, (1951), 1445.
5. E.U. Condon, G.H. Shortley: The Theory of Atomic Spectra. Cambridge (1953).
6. J.S. Griffith: The Theory of Transition Metal Ions. Cambridge (1961).
7. J.C. Slater: Phys.Rev. 36, (1930), 57.
8. M. Wolfsberg, L. Helmholz: J.Chem.Phys. 20, (1952), 837.
9. H.B. Gray, C.J. Ballhausen: Inorg.Chem. 1, (1962), 111.
10. R.S. Mulliken: Journ.Chim.Phys. 46, (1949), 497, 675.
11. J.H. Wilkinson: Num.Mat. 4, (1962), 354.
12. G.W. Veltkamp, N.M. Clement: Rekengroep Onderafdeling Wiskunde, Bull. No. 25, 8 July 1963. Techn. Univ. Eindhoven.
13. R.S. Mulliken: J.Chem.Phys. 23, (1953), 1833.
14. A.C. Aitken: Proc.Roy.Soc.Edin. 46, (1926), 289.
15. C. Furlani, G. Morpurgo: Theor.Chim.Acta 1, (1963), 102.
16. J.C. Slater: Quantum Theory of Molecules and Solids. New York (1963).

CHAPTER IV

MOLECULAR ORBITAL CALCULATION ON THE GROUND STATE OF THE SQUARE PLANAR TETRACHLOROCUPRATE (II) ION

IV-1 INTRODUCTION

The calculation on the ground state of the square planar configuration of $CuCl_4^{2-}$ is completely analogous to the calculation on tetrahedral $CuCl_4^{2-}$ as discussed in the preceding Chapter. An attempt will be made to use the results of the preceding calculation as much as possible. This causes the calculation on square planar $CuCl_4^{2-}$ to be less accurate on some points, but this additional inaccuracy will not prevent us from comparing the calculation on the tetrahedral complex with that on the square planar one.

As a first approximation we assume the distance Cu-Cl in the square planar $CuCl_4^{2-}$ to be equal to that in the tetrahedral complex, viz. 4.194 a.u. The distance Cl-Cl then becomes 5.931 a.u. for neighbouring ligands and 8.388 a.u. for opposite ligands. We expect that in actual reality the distances are somewhat larger than given here because in a square planar complex the ligands repel each other more strongly than in tetrahedral complexes.

The one-electron atomic wave functions in the calculation are taken as in the preceding problem. We must now classify these one-electron wave functions according to the irreducible representations of the group D_{4h}. In Chapter II we already discussed this problem, Table II-5 giving the result of this classification. The following calculation is performed for the configuration

$$\text{IC}\ (1a_{1g})^2 (1b_{2g})^2 (1e_u)^4 (2a_{1g})^2 (2b_{2g})^2 (2e_u)^4 (1e_g)^4 (1b_{1g})^2 (1a_{2u})^2 (3e_u)^4 (1b_{1u})^2 (a_{2g})^2 (3a_{1g})^2 (2e_g)^4 (2b_{1g})^2 (3b_{2g})^1 \qquad (4.1)$$

At the end of the calculation it will be seen that this configuration turns out to be the ground state of the square planar $CuCl_4^{2-}$.

IV-2 OVERLAP INTEGRALS

To evaluate the group overlap integrals S_{ij}, we need simple diatomic overlap integrals of the type $\langle s | s \rangle$, $\langle p\sigma | p\sigma \rangle$, etc. We take the simple diatomic overlap integrals equal to those found in the calculation on tetrahedral $CuCl_4^{2-}$ (Table III-3). This is correct for the overlap integrals of Cu functions and Cl

functions since the distance Cu-Cl has been kept constant. For the simple diatomic overlap integrals of two wave functions of neighbouring Cl ligands we likewise take the numerical values of the preceding calculation.
This is not correct here since the Cl-Cl distance has changed, but we expect that the error will not be large. The overlap integrals for functions of opposite Cl ligands will be neglected. The error introduced here often counteracts the previous one, and since the numerical values of the ligand-ligand overlap integrals are small, the total error will not be large.

The relations between the group overlap integrals in square planar complexes and the simple diatomic overlap integrals are given in Table II-10 for overlap integrals of copper functions and combinations of ligand functions. The relations for overlap integrals of different combinations of ligand functions are shown in Table IV-1.

Table IV-1 Group Overlap Integrals between different Combinations of Ligand Functions in a Square Planar Complex

$$A_{1g} \quad \langle \chi(s) | \chi(z) \rangle = 4\sqrt{2} N_{A_{1g}}(s) N_{A_{1g}}(z) \langle s_1 | p\sigma_2 \rangle$$

$$B_{2g} \quad \langle \chi(s) | \chi(z) \rangle = -4\sqrt{2} N_{B_{2g}}(s) N_{B_{2g}}(z) \langle s_1 | p\sigma_2 \rangle$$

$$E_u \quad \langle \chi(s) | \chi(z) \rangle = 0$$

$$\langle \chi(s) | \chi(x,y) \rangle = \sqrt{2} \langle s_1 | p\sigma_2 \rangle$$

$$\langle \chi(z) | \chi(x,y) \rangle = \langle p\sigma_1 | p\sigma_2 \rangle - \langle p\pi_1 | p\pi_2 \rangle$$

The normalisation constants of the combinations of ligand orbitals may also be expressed in simple diatomic overlap integrals; Table IV-2 gives these expressions together with the numerical values of the normalisation constants used in the following calculation.

The group overlap integrals can now be computed for different charge distributions and analogously to the previous calculation we can, by interpolation, construct formulas that represent the group overlap integrals as functions of the charge distribution.

Table IV-2 Normalisation Constants for the Ligand Orbitals in Square Planar $CuCl_4^{2-}$

Norm. Constant	Expression	Cl	Cl^-
$N_{A_{1g}}(s)$	$0.5\{1+2\langle s_1 \mid s_2\rangle\}^{-\frac{1}{2}}$	0.49616	0.49008
$N_{A_{1g}}(z)$	$0.5\{1+\langle p\sigma_1 \mid p\sigma_2\rangle+\langle p\pi_1 \mid p\pi_2\rangle\}^{-\frac{1}{2}}$	0.48346	0.46982
$N_{A_{2g}}(x)$	$0.5\{1-\langle p\sigma_1 \mid p\sigma_2\rangle-\langle p\pi_1 \mid p\pi_2\rangle\}^{-\frac{1}{2}}$	0.51838	0.53685
$N_{A_{2u}}(y)$	$0.5\{1+2\langle p\pi_1 \mid p\pi_2\rangle\}^{-\frac{1}{2}}$	0.49310	0.48374
$N_{B_{1g}}(x)$	$0.5\{1+\langle p\sigma_1 \mid p\sigma_2\rangle+\langle p\pi_1 \mid p\pi_2\rangle\}^{-\frac{1}{2}}$	0.48346	0.46982
$N_{B_{1u}}(y)$	$0.5\{1-2\langle p\pi_1 \mid p\pi_2\rangle\}^{-\frac{1}{2}}$	0.50719	0.51801
$N_{B_{2g}}(s)$	$0.5\{1-2\langle s_1 \mid s_2\rangle\}^{-\frac{1}{2}}$	0.50393	0.50613
$N_{B_{2g}}(z)$	$0.5\{1-\langle p\sigma_1 \mid p\sigma_2\rangle-\langle p\pi_1 \mid p\pi_2\rangle\}^{-\frac{1}{2}}$	0.51838	0.53685
$N_{E_g}(y)$	0.5	0.50000	0.50000
$N_{E_u}(s)$	0.5	0.50000	0.50000
$N_{E_u}(z)$	0.5	0.50000	0.50000
$N_{E_u}(x)$	0.5	0.50000	0.50000

IV-3 H_{ii} AND H_{ij} INTEGRALS

To compute the H_{ii} integrals we again divide these integrals into two parts

(a) the one-electron energies of the free ion,

(b) the interaction of an electron of a certain atom with all other atoms in the molecule.

In this calculation part (a) is of course the same as in the calculation on tetrahedral $CuCl_4^{2-}$. Part (b), however, differs. In Chapter III the interaction of an electron of a certain atom with all other atoms in the molecule was approximated by

$$\sum_\beta \langle \phi_i(1) \left| \frac{Z'_\beta}{r_{\beta 1}} \right| \phi_i(1) \rangle$$

For interactions between copper and chlorine we will take the integrals $\langle \phi_i(1) \left| \frac{1}{r_{\beta 1}} \right| \phi_i(1) \rangle$ ($\frac{1}{r_\beta}$-integrals) equal to those found in Chapter III, since the distance Cu-Cl is kept constant in our calculations. The Z'_β also remain the same in our calculation, so that in the square planar complex the interaction between an electron of Cu and the ligands or between an electron of the ligands and Cu is exactly equal to that in the tetrahedral complex.

This is not the case with interactions of an electron of a ligand with the other ligands because the Cl-Cl distance changes. From Table III-15 we can see that the $\frac{1}{r_\beta}$-integrals deviate only little from the point charge model, i.e.

$$\langle \phi_i \left| \frac{1}{r_{Cl}} \right| \phi_i \rangle \simeq \frac{1}{r_{Cl-Cl}} \qquad (4.2)$$

This formula will now be used to approximate the $\frac{1}{r_\beta}$-integrals for the square planar case. We then obtain for neighbouring ligands

$$\langle \phi_i \left| \frac{1}{r_{Cl}} \right| \phi_i \rangle = \frac{1}{5.9312} = 0.16860 \qquad (4.3)$$

and for opposite ligands

$$\langle \phi_i \left| \frac{1}{r_{Cl}} \right| \phi_i \rangle = \frac{1}{8.388} = 0.11922 \qquad (4.4)$$

Furthermore, the Z'_β for neighbouring ligands will be taken equal to the effective charges for Cl-Cl used in the previous calculation. As regards opposite ligands we suppose that the electrons of a ligand screen their nucleus completely from an opposite ligand (Table III-18 indicates that this is a good approximation), so in this case

$$Z'_\beta = -D \qquad (4.5)$$

where D has the same meaning as in the preceding Chapter (Cl^{-D}). It is now possible to calculate the H_{ii} integrals as functions of the charge distribution in the manner described in Section III-4. The H_{ij} integrals are in this calculation evaluated with the help of formula (3.42).

IV-4 EVALUATION OF THE SECULAR DETERMINANT

In Chapter II we already discussed what types of determinants have to be solved for square planar complexes. The eigenvalues and eigenfunctions belonging to these determinants will be defined as follows:

$\underline{A_{1g}}$ symmetry

EA(i) $\psi_A(i)=CA(1,i)\phi_{4s}+CA(2,i)\phi_{3d}+CA(3,i)\chi_\sigma+CA(4,i)\chi_s$

$\underline{A_{2g}}$ symmetry

$E(A_{2g})$ $\psi(A_{2g})=\chi_\pi$

$\underline{A_{2u}}$ symmetry

EC(i) $\psi_c(i)=CC(1,i)\phi_{4p}+CC(2,i)\chi_\pi$

$\underline{B_{1g}}$ symmetry

EB(i) $\psi_B(i)=CB(1,i)\phi_{3d}+CB(2,i)\chi_\pi$

$\underline{B_{1u}}$ symmetry

$E(B_{1u})$ $\psi(B_{1u})=\chi_\pi$

$\underline{B_{2g}}$ symmetry

ED(i) $\psi_D(i)=CD(1,i)\phi_{3d}+CD(2,i)\chi_\sigma+CD(3,i)\chi_s$

$\underline{E_g}$ symmetry

EE(i) $\psi_E(i)=CE(1,i)\phi_{3d}+CE(2,i)\chi_\pi$

$\underline{E_u}$ symmetry

EF(i) $\psi_F(i)=CF(1,i)\phi_{4p}+CF(2,i)\chi_\pi+CF(3,i)\chi_\sigma+CF(4,i)\chi_s$

The determinants are evaluated with a computer programme that is completely analogous to the programme used for tetrahedral complexes. Only where necessary has the programme been adjusted to the special problem. Part (3) of the computer programme (the determination of the new A, B, and C from the computed eigenfunctions) has to be altered considerably. To determine the new A, B, and C, we start from the configuration (4.1).

Determination of A ($3d^{10-A}$ of Cu)

The d-electrons of Cu play a role in the molecular orbitals with A_{1g}, B_{1g}, B_{2g} and E_g symmetry. The orbitals with B_{1g} and E_g symmetry are completely filled, which gives us six d-electrons. The orbitals with A_{1g} and B_{2g} symmetry are only partly filled:

$$(1a_{1g})^2\,(2a_{1g})^2\,(3a_{1g})^2\,(4a_{1g})^0$$

and

$$(1b_{2g})^2\,(2b_{2g})^2\,(3b_{2g})^1$$

respectively.

If we suppose

$$\begin{aligned} SA_1 = {} & 2\,\{CA(2,1)\}^2 \Big/ \Big[\sum_{i=1}^{4} \{CA(i,1)\}^2\Big] + \\ & 2\,\{CA(2,2)\}^2 \Big/ \Big[\sum_{i=1}^{4} \{CA(i,2)\}^2\Big] + \\ & 2\,\{CA(2,3)\}^2 \Big/ \Big[\sum_{i=1}^{4} \{CA(i,3)\}^2\Big] \end{aligned}$$

and

$$SA_2 = \{CD(1,3)\}^2 \Big/ \Big[\sum_{i=1}^{3} \{CD(i,3)\}^2\Big]$$

then

$$10 - A = 6 + SA_1 + 2 - SA_2$$

or

$$A = 2 - SA_1 + SA_2 \tag{4.6}$$

Determination of B ($4s^B$ of Cu)

The 4s electrons of Cu only occur in the molecular orbitals with A_{1g} symmetry. We thus find

$$\begin{aligned} B = {} & 2\,\{CA(1,1)\}^2 \Big/ \Big[\sum_{i=1}^{4} \{CA(i,1)\}^2\Big] + \\ & 2\,\{CA(1,2)\}^2 \Big/ \Big[\sum_{i=1}^{4} \{CA(i,2)\}^2\Big] + \\ & 2\,\{CA(1,3)\}^2 \Big/ \Big[\sum_{i=1}^{4} \{CA(i,3)\}^2\Big] \end{aligned} \tag{4.7}$$

Determination of C ($4p^C$ of Cu)

The 4p electrons of Cu occur in the molecular orbitals with A_{2u} and E_u symmetry. These molecular orbitals are only partly filled:

$$(1a_{2u})^2 (2a_{2u})^o$$

and

$$(1e_u)^4 (2e_u)^4 (3e_u)^4 (4e_u)^o$$

It is easy to see that

$$\begin{aligned} C = {} & 2\{CC(1,1)\}^2 / \left[\sum_{i=1}^{2} \{CC(i,1)\}^2 \right] + \\ & 4\{CF(1,1)\}^2 / \left[\sum_{i=1}^{4} \{CF(i,1)\}^2 \right] + \\ & 4\{CF(1,2)\}^2 / \left[\sum_{i=1}^{4} \{CF(i,2)\}^2 \right] + \\ & 4\{CF(1,3)\}^2 / \left[\sum_{i=1}^{4} \{CF(i,3)\}^2 \right] \end{aligned} \tag{4.8}$$

In this calculation D is also computed with the help of formula (3.52).

IV-5 RESULTS

The calculation concerning the ground state of square planar $CuCl_4^{2-}$ gives us the following values of A, B, C, and D

$A = 0.4999$
$B = 0.1333$
$C = 0.6707$
$D = 0.6990$

So in this case we find on copper a charge of +0.80 and on each of the chlorine ligands -0.70.

The eigenfunctions and eigenvalues belonging to this charge distribution can be found in Table IV-3.

Some of the remarks made on the results of the calculation on tetrahedral complexes also hold in this case. Of course, the splitting of the d-orbitals is totally different here.

Table IV-3 Eigenvalues and Eigenfunctions belonging to the ground state of square planar $CuCl_4^{2-}$

A_{1g} symmetry

	ϕ →	4s	$3d_{z^2}$	$\chi\sigma$	χs
	H_{ii} → ε_{mo} ↓	-0.16820	-0.32312	-0.37521	-0.85492
$4a_{1g}$	0.40209	1.7280	0.0486	-1.1620	-0.6440
$3a_{1g}$	-0.31533	-0.0448	0.9696	-0.2930	0.0859
$2a_{1g}$	-0.37801	0.0720	0.2568	0.9040	-0.0780
$1a_{1g}$	-0.88871	-0.2839	-0.0055	0.1835	1.1190
	EA(i)	CA(1, i)	CA(2, i)	CA(3, i)	CA(4, i)

A_{2g} symmetry

$E(A_{2g}) = -0.29552$

A_{2u} symmetry

	ϕ →	$4p_z$	$\chi\pi$
	H_{ii} → ε_{mo} ↓	-0.15691	-0.34476
$2a_{2u}$	0.01050	1.1410	-0.7836
$1a_{2u}$	-0.35931	0.2310	0.8616
	EC(i)	CC(1, i)	CC(2, i)

B_{1g} symmetry

	ϕ →	$3d_{x^2-y^2}$	$\chi\pi$
	H_{ii} → ε_{mo} ↓	-0.31418	-0.35242
$2b_{1g}$	-0.29969	0.9145	-0.4794
$1b_{1g}$	-0.36309	0.4114	0.8808
	EB(i)	CB(1, i)	CB(2, i)

B_{1u} symmetry

$$E(B_{1u}) = -0.30778$$

B_{2g} symmetry

	$\phi \rightarrow$	$3d_{xy}$	χ_σ	χ_s
	$H_{ii} \rightarrow$ $\varepsilon_{mo} \downarrow$	-0.31479	-0.31463	-0.83059
$3b_{2g}$	-0.27296	0.7707	-0.7594	-0.1325
$2b_{2g}$	-0.33928	0.6588	0.6702	-0.0073
$1b_{2g}$	-0.83060	0.0043	-0.0038	0.9993
	ED(i)	CD(1, i)	CD(2, i)	CD(3, i)

E_g symmetry

	$\phi \rightarrow$	$3d_{xz,\,yz}$	χ_π
	$H_{ii} \rightarrow$ $\varepsilon_{mo} \downarrow$	-0.32072	-0.32743
$2e_g$	-0.30438	0.7872	-0.6626
$1e_g$	-0.34169	0.6192	0.7510
	EE(i)	CE(1, i)	CE(2, i)

E_u symmetry

	$\phi \rightarrow$	$4p_{x,\,y}$	χ_π	χ_σ	χ_s
	$H_{ii} \rightarrow$ $\varepsilon_{mo} \downarrow$	-0.14238	-0.32743	-0.34860	-0.84303
$4e_u$	0.26940	1.6240	-0.5461	-0.4045	-0.8014
$3e_u$	-0.31795	-0.0113	0.9348	-0.4251	-0.0671
$2e_u$	-0.35362	0.0042	0.3747	0.9045	-0.0299
$1e_u$	-0.92617	-0.4440	0.1573	0.1072	1.2550
	EF(i)	CF(1, i)	CF(2, i)	CF(3, i)	CF(4, i)

We now obtain the following picture

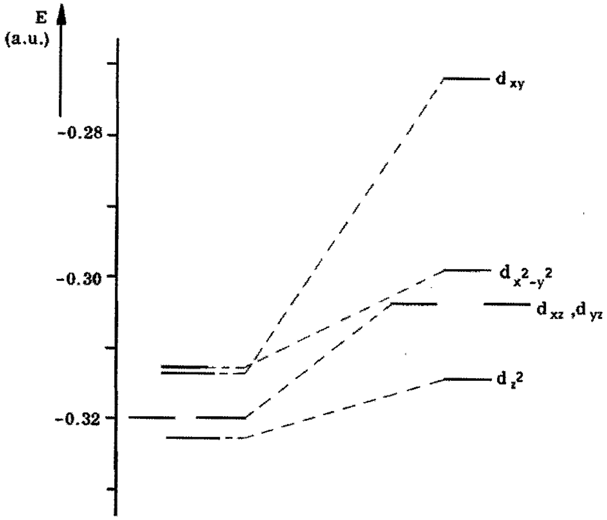


Fig. 4.1 Splitting of the d-orbitals in square planar $CuCl_4^{2-}$

The relative splitting of the d-orbitals is correct. See, for example, Ref.(1), page 24 (we use a different coordinate system from the one in Ref.(1), so $d_{x^2-y^2}$ and d_{xy} have to be interchanged to make possible a satisfactory comparison). The maximum splitting $(E(d_{xy}) - E(d_{z^2}))$ is equal to

$$0.0424 \text{ a.u.} = 9300 \text{ cm}^{-1}.$$

This value is a very reasonable one for square planar complexes (2).

IV-6 COMPARISON OF THE CALCULATIONS ON TETRAHEDRAL AND SQUARE PLANAR $CuCl_4^{2-}$

Comparing the results of the calculations on tetrahedral and square planar $CuCl_4^{2-}$ we observe the following points:

(a) The charge distribution in the tetrahedral complex differs somewhat from that in the square planar complex. On the central ion we find in the two cases a charge of +0.92 and +0.80 respectively. So in the square planar complex there is more negative charge on the central ion.
This is understandable since in the square planar complex the distance between the ligands is smaller and therefore the electrons of the ligands will repel each other more strongly. Consequently some negative charge will be projected to the central ion.

(b) The splitting of the d-orbitals can be compared as follows

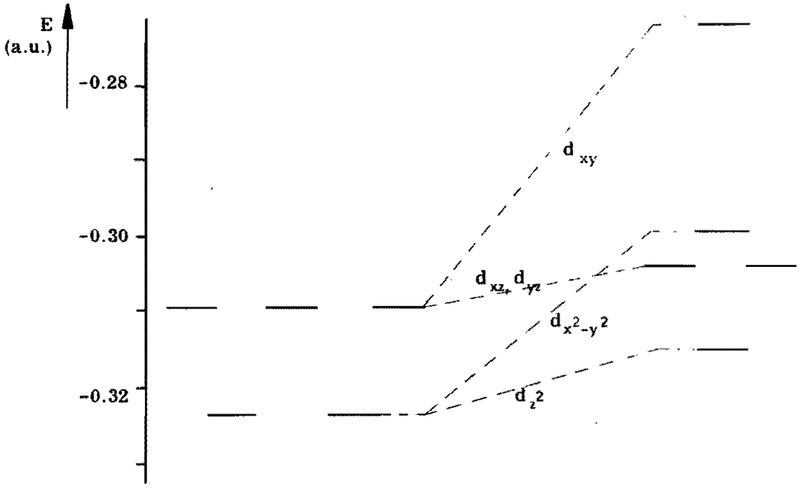


Fig. 4.2 Tetrahedral and Square Planar $CuCl_4^{2-}$

From this figure we see that the splitting of the d-orbitals is different for the two types of surrounding. X-ray analysis shows the actual structure of $CuCl_4^{2-}$ to be a distorted tetrahedron (intermediate between the tetrahedral and the square planar structure) and we now see that a small amount of distortion of the tetrahedron may already cause a considerable change in the positions of the energy levels.

(c) Adding the energies of all occupied molecular orbitals, we obtain

for tetrahedral $CuCl_4^{2-}$ -18.717 a.u.

for square planar $CuCl_4^{2-}$ -18.003 a.u.

This does not mean, however, that the tetrahedral structure is more stable than the square planar structure because the total energy of a complex is not equal to the sum of the orbital energies. In the sum of the orbital energies the energy of repulsion between the electrons has been counted twice, so to obtain the correct total energy we have to subtract this repulsion term. We shall discuss this in a following chapter.

REFERENCES

1. L.E. Orgel: An Introduction to Ligand Field Chemistry. London (1962).

2. C. Furlani, G. Morpurgo: Theor. Chim. Acta. 1, (1963), 102.

CHAPTER V

MOLECULAR ORBITAL CALCULATION ON THE GROUND STATE OF THE OCTAHEDRAL HEXACHLOROCUPRATE (II)ION

V-1 CALCULATION OF S_{ij} AND H_{ij} INTEGRALS

The calculation concerning the ground state of octahedral $CuCl_6^{4-}$ resembles very much the calculation on the square planar complex as discussed in Chapter IV. For the two calculations we have used the same approximations. So the Cu-Cl distance in $CuCl_6^{4-}$ is supposed to be 4.194 a.u.; consequently the Cl-Cl distance is 5.931 a.u. for neighbouring ligands and 8.388 a.u. for opposite ligands.

In the present calculation we have to classify the one-electron wave functions of the central ion and of the ligands according to the irreducible representations of the octahedral group O_h.
Table II-6 gives the results of this classification. In Chapter II we expected the configuration

$$IC\,(1e_g)^4\,(1a_{1g})^2\,(1t_{1u})^6\,(2e_g)^4\,(2a_{1g})^2\,(2t_{1u})^6\,(1t_{2g})^6\,(3t_{1u})^6\,(t_{2u})^6\,(t_{1g})^6\,(2t_{2g})^6\,(3e_g)^3 \qquad (5.1)$$

to be the ground state of $CuCl_6^{4-}$.

The overlap integrals in the octahedral complex are calculated under similar restrictions as the overlap integrals in square planar $CuCl_4^{2-}$. Table V-1 gives the formulas of the normalisation constants of the ligand functions, Table V-2 gives the relations between the group overlap integrals and the simple diatomic overlap integrals for combinations of ligand functions.

The evaluation of the H_{ii} integrals is performed with the same approximations as used in the calculation of the H_{ii} integrals in square planar $CuCl_4^{2-}$. The calculation of the H_{ij} integrals is carried out with the help of formula (3.42). However, since some of the H_{ii} integrals are positive in $CuCl_6^{4-}$ (for instance, for 4p(Cu)) the expression $\sqrt{H_{ii}\,H_{jj}}$ may become imaginary, in which case $\sqrt{H_{ii}\,H_{jj}}$ is replaced by $\frac{1}{2}(H_{ii} + H_{jj})$.

Table V-1 Normalisation Constants of the Ligand Orbitals in Octahedral Complexes.

$$
\begin{aligned}
N_{A_{1g}}(s) &= \{6 + 24 \langle s_1 | s_2 \rangle\}^{-\frac{1}{2}} \\
N_{A_{1g}}(z) &= \{6 + 12 \langle p\sigma_1 | p\sigma_2 \rangle + 12 \langle p\pi_1 | p\pi_2 \rangle\}^{-\frac{1}{2}} \\
N_{E_g}(s) &= \{4 - 8 \langle s_1 | s_2 \rangle\}^{-\frac{1}{2}} \\
N_{E_g}(z) &= \{4 - 4 \langle p\sigma_1 | p\sigma_2 \rangle - 4 \langle p\pi_1 | p\pi_2 \rangle\}^{-\frac{1}{2}} \\
N_{T_{1g}}(x,y) &= \{4 - 4 \langle p\sigma_1 | p\sigma_2 \rangle - 4 \langle p\pi_1 | p\pi_2 \rangle\}^{-\frac{1}{2}} \\
N_{T_{1u}}(s) &= \{2\}^{-\frac{1}{2}} \\
N_{T_{1u}}(z) &= \{2\}^{-\frac{1}{2}} \\
N_{T_{1u}}(x,y) &= \{4 + 8 \langle p\pi_1 | p\pi_2 \rangle\}^{-\frac{1}{2}} \\
N_{T_{2g}}(x,y) &= \{4 + 4 \langle p\sigma_1 | p\sigma_2 \rangle - 4 \langle p\pi_1 | p\pi_2 \rangle\}^{-\frac{1}{2}} \\
N_{T_{2u}}(x,y) &= \{4 - 8 \langle p\pi_1 | p\pi_2 \rangle\}^{-\frac{1}{2}}
\end{aligned}
$$

Table V-2 Group Overlap Integrals between different Combinations of Ligand Functions in an Octahedral Complex

$$
\begin{aligned}
A_{1g} \quad & \langle \chi(s) | \chi(z) \rangle = 12\sqrt{2}\, N_{A_{1g}}(s)\, N_{A_{1g}}(z) \langle s_1 | p\sigma_2 \rangle \\
E_g \quad & \langle \chi(s) | \chi(z) \rangle = -4\sqrt{2}\, N_{E_g}(s)\, N_{E_g}(z) \langle s_1 | p\sigma_2 \rangle \\
T_{1u} \quad & \langle \chi(s) | \chi(z) \rangle = 0 \\
& \langle \chi(s) | \chi(x,y) \rangle = 4\, N_{T_{1u}}(x,y) \langle s_1 | p\sigma_2 \rangle \\
& \langle \chi(z) | \chi(x,y) \rangle = 2\sqrt{2}\, N_{T_{1u}}(x,y) \{\langle p\sigma_1 | p\sigma_2 \rangle - \langle p\pi_1 | p\pi_2 \rangle\}
\end{aligned}
$$

V-2 EVALUATION OF THE SECULAR DETERMINANT

For octahedral complexes we have to solve the following secular determinants:

symmetry A_{1g}	3 x 3 determinant
symmetry E_g	3 x 3 determinant
symmetry T_{1g}	1 x 1 determinant
symmetry T_{1u}	4 x 4 determinant
symmetry T_{2g}	2 x 2 determinant
symmetry T_{2u}	1 x 1 determinant

The computer programme used for the evaluation of these secular determinants is completely analogous to the programme that has been discussed in the previous Chapters. Only where necessary is the programme modified to make it suitable for the present calculation on $CuCl_6^{4-}$. The determination of A, B, and C is carried out correspondingly to the configuration (5.1) with the procedure described in the preceding calculations. In this calculation

$$D = \frac{1}{6}(5 + A - B - C) \tag{5.2}$$

V-3 RESULTS

For the ground state of the octahedral $CuCl_6^{4-}$ we find the following charge distribution

$A = 0.926$
$B = 0.515$
$C = 0.466$
$D = 0.824$

With these values we get a charge of +0.94 on copper, and of -0.82 on each of the ligands. Although in $CuCl_6^{4-}$ there are two extra Cl^- ligands with respect to $CuCl_4^{2-}$, the negative charge on the central ion is lower. Possibly this points to the fact that covalency effects are less important in octahedral complexes than in tetrahedral or square planar complexes. The one-electron energies and the molecular orbitals of $CuCl_6^{4-}$ are shown in Table V-3. The results lead us to the following remarks:

(a) The one-electron energies of $CuCl_6^{4-}$ are surprisingly high with respect to the one-electron energies of $CuCl_4^{2-}$. This is caused by the presence of two extra ligands, which has an unfavourable effect on the one-electron energies. We regard these high energies as an indication of the instability of the $CuCl_6^{4-}$ complex.

(b) From the molecular orbitals of Table V-3 we see that the mixing in the orbitals with a predominantly 3d character ($3e_g$ and $2t_{2g}$) is very small with respect to the comparable mixing in the tetrahedral complex. The splitting of these orbitals is as follows

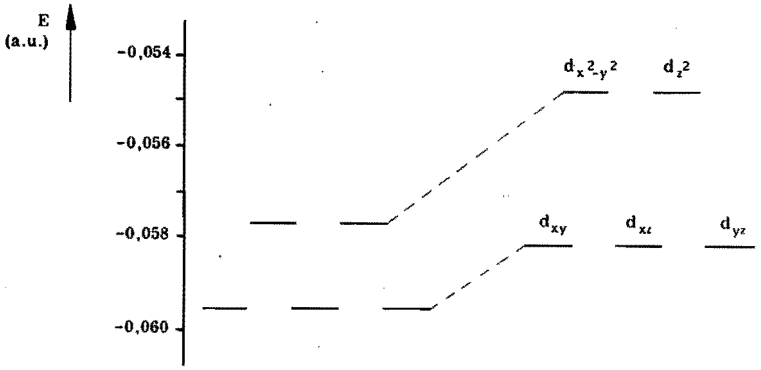


Fig. 5.1 Splitting op the d-orbitals in $CuCl_6^{4-}$

Table V-3 Eigenvalues and Eigenfunctions belonging to the ground state of octahedral $CuCl_6^{4-}$

A_{1g} symmetry

	ϕ →	4s	χ(z)	χ(s)
	H_{ii} → ε_{mo} ↓	-0.01254	-0.10988	-0.57491
$3a_{1g}$	0.50901	2.122	-1.682	-0.837
$2a_{1g}$	-0.12662	0.383	0.719	-0.214
$1a_{1g}$	-0.59072	-0.258	0.109	1.117
	EA(i)	CA(1,i)	CA(2,i)	CA(3,i)

E_g symmetry

	ϕ →	3d	χ(z)	χ(s)
	H_{ii} → ε_{mo} ↓	-0.05771	-0.08589	-0.55010
$3e_g$	-0.05477	0.997	-0.274	-0.051
$2e_g$	-0.08548	0.154	0.972	0.425
$1e_g$	-0.55152	-0.043	0.038	1.004
	EE(i)	CE(1, i)	CE(2, i)	CE(3, i)

T_{1g} symmetry

$E(T_{1g}) = -0.06187$

T_{1u} symmetry

	ϕ →	4p	χ(x, y)	χ(z)	χ(s)
	H_{ii} → ε_{mo} ↓	0.04464	-0.07306	-0.09591	-0.55875
$4t_{1u}$	0.39282	1.619	-0.477	-0.453	-0.799
$3t_{1u}$	-0.06989	-0.137	0.984	-0.516	0.004
$2t_{1u}$	-0.10390	-0.188	0.464	0.905	0.056
$1t_{1u}$	-0.57306	-0.194	0.037	0.076	1.104
	EU(i)	CU(1, i)	CU(2, i)	CU(3, i)	CU(4, i)

T_{2g} symmetry

	ϕ →	3d	χ(x, y)
	H_{ii} → ε_{mo} ↓	-0.05974	-0.07468
$2t_{2g}$	-0.05822	0.975	-0.296
$1t_{2g}$	-0.07561	0.232	0.957
	ET(i)	CT(1, i)	CT(2, i)

T_{2u} symmetry

$E(T_{2u}) = -0.06456$

The relevant positions of the orbitals are correct. We find 850 cm^{-1} as the numerical value of the splitting. However, we expect for octahedral complexes a larger splitting: 8,000-10,000 cm^{-1} (1). There is no possebility of experimental verification of this value, since no CuCl_6^{4-} complex is known. There is, however, a situation in which Cu is surrounded by six Cl-ligands, namely in a CuCl_2 crystal. In this crystal Cu is found in a distorted octahedron of Cl, with 4 Cl ligands at a distance of 2.3 Å and 2 Cl ligands at 3.0 Å (2). We may wonder why the copper ion is stable in this environment. 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 CuCl_2 crystal.

V-4 CALCULATION ON Cu IN A CuCl_2 CRYSTAL

In the following calculation we use an idealised cubic structure of CuCl_2 instead of the actual structure (Fig. 5.2). We derive the structure from the NaCl structure by replacing half of the Na-atoms by Cu leaving the remaining sites vacant (This idealised structure resembles the actual structure of CuCl_2 apart from the distortion). As a second approximation we suppose the shortest Cu-Cl distance to be 4.194 a.u. (as in the CuCl_4^{2-} complex). From the CuCl_2 crystal we take a CuCl_6 unit and to this unit we apply a molecular orbital calculation. In our approximation, the classification of the one-electron wave functions is, of course, identical with that in CuCl_6^{4-}. Also, the overlap integrals in the CuCl_6 unit are

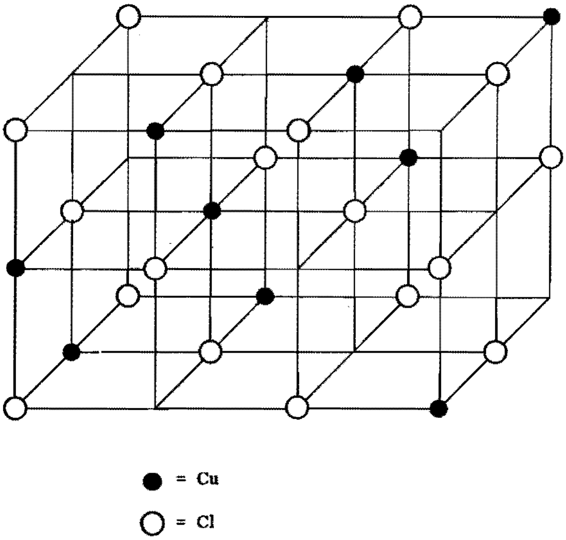


Fig. 5.2 CuCl_2 crystal

the same as in $CuCl_6$. However, the H_{ii} integrals attain a different value, for we suppose that the electrons of the $CuCl_6$ unit are not only affected by atoms of this unit but also by atoms situated outside the $CuCl_6$ unit. This is not surprising. For instance, a Cl atom will not only be affected by the Cu atom of the $CuCl_6$ unit to which it belongs, but also by other Cu atoms that are to be found at the same distance. Of course, the same holds for Cu atoms. The situation is simplified by the fact that the influences of different atoms situated at greater distances cancel. For at larger distances, the shielding constants of all electrons may be taken equal to 1.00, and then we get an effective charge of -D on Cl and of +2D on Cu. On an average there are at a certain distance two Cl atoms to each Cu atom. Taking the $\frac{1}{r\beta}$ integrals for atoms at a distance r equal to $\frac{1}{r}$ (which is a satisfactory approximation for large r) we see that the contribution of the atoms at the distance r to the H_{ii} integrals is approximately equal to

$$N_r\left(\frac{+2D}{r} + 2\frac{-D}{r}\right) = 0$$

(with N_r being the number of Cu atoms at the distance r).
For this reason the influence (on the H_{ii} integrals) of all atoms at twice 4.194 a.u. or more from the $CuCl_6$ unit is ignored. The Cu atom in the particular $CuCl_6$ unit is now affected by the following atoms:

Atom	Distance r_o = 4.194 a.u.	Effective Charge
6 Cl	r_o	See Table III-16
6 Cu	$r_o\sqrt{2}$	-1-A+0.8B+0.7C (*)
8 Cl	$r_o\sqrt{3}$	D

and each of the Cl atoms by

Atom	Distance	Effective Charge
3 Cu	r_o	See Table III-16
12 Cl	$r\sqrt{2}$	See Table III-16
4 Cu	$r_o\sqrt{3}$	-1-A+0.95B+0.9C (*)
1 Cl	$2r_o$	D (**)

(*) These effective charges are estimated with the help of the effective charges of Table III-16.

(**) This extra Cl is added to obtain charge neutrality.

The $\frac{1}{r_\beta}$ integrals that are not calculated in the preceding Chapters, are approximated by $\frac{1}{r}$. Now the H_{ii} integrals can be calculated as functions of the charge distribution. The H_{ii} integrals are then obtained by formula (3.42). The determination of A, B, and C is carried out for the configuration (5.1), just as in the case of $CuCl_6^{4-}$. Now D is obtained from

$$D = \tfrac{1}{2}(1 + A - B - C) \tag{5.3}$$

We now obtain the following charge distribution

$A = 0.768$
$B = 0.445$
$C = 1.242$
$D = 0.041$

This results in a charge of +0.08 on Cu and a charge of -0.04 on Cl. The molecular orbital energies and the molecular orbital wave functions belonging to this charge distribution are given in Table V-4. From these results we see the following:

Table V-4 Eigenvalues and Eigenfunctions belonging to the ground state of a $CuCl_6$ unit in a $CuCl_2$ crystal

A_{1g} symmetry

	$\phi \rightarrow$	4s	$\chi(z)$	$\chi(s)$
	$H_{ii} \rightarrow$ $\varepsilon_{mo} \downarrow$	-1.424	-1.842	-2.014
$3a_{1g}$	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
	EA(i)	CA(1, i)	CA(2, i)	CA(3, i)

E_g symmetry

	$\phi \rightarrow$	3d	$\chi(z)$	$\chi(s)$
	$H_{ii} \rightarrow$ $\varepsilon_{mo} \downarrow$	-1.360	-1.589	-1.953
$3e_g$	-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
	EE(i)	CE(1, i)	CE(2, i)	CE(3, i)

T_{1g} symmetry

$$E(T_{1g}) = -1.546$$

T_{1u} symmetry

	$\phi \rightarrow$	4p	$\chi(x,y)$	$\chi(z)$	$\chi(s)$
	$H_{ii} \rightarrow$ $\varepsilon_{mo} \downarrow$	-1.389	-1.687	-1.686	-1.974
$4t_{1u}$	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
	EU(i)	CU(1, i)	CU(2, i)	CU(3, i)	CU(4, i)

T_{2g} symmetry

	$\phi \rightarrow$	3d	$\chi(x,y)$
	$H_{ii} \rightarrow$ $\varepsilon_{mo} \downarrow$	-1.359	-1.721
$2t_{2g}$	-1.324	0.977	-0.288
$1t_{2g}$	-1.742	0.223	0.960
	ET(i)	CT(1, i)	CT(2, i)

T_{2u} symmetry

$$E(T_{2u}) = -1.589$$

(a) The charge differences in the $CuCl_2$ crystal are very small. This is mainly caused by the considerable occupation of the 4p orbitals of copper which is a result of the large mixing of the 4p orbitals in the $1t_{1u}$ molecular orbital. Perhaps this must be ascribed to the fact that the energies of the 4p orbitals and of the ligand orbitals are of the same order of magnitude (-1.4 and -1.7 respectively), which was not the case in the previous calculations (See also Chapter VIII).

(b) In the $CuCl_2$ crystal, all one-electron energies are very low with respect to the corresponding energies in $CuCl_6^{4-}$. This is understandable since the effect of the six Cl ligands on the energies of the Cu electrons is counteracted in the $CuCl_2$ crystal by other Cu atoms. Moreover, the negative charge of the Cl ligands in the $CuCl_2$ crystal is smaller than in the $CuCl_6^{4-}$ complex. The values of the one-electron energies in the $CuCl_2$ crystal are even lower than the energies in $CuCl_4^{2-}$ (which may be an explanation of the stability of the octahedral crystalline structure of $CuCl_2$).

(c) From the molecular orbitals of Table V-4 we see that the mixing in the $3e_g$ and the $2t_{2g}$ orbitals (with a predominantly 3d character) is larger than in $CuCl_6^{4-}$, but smaller than in $CuCl_4^{2-}$. On the other hand the role of the 4s and 4p orbitals is very important in the $CuCl_2$ crystal.

(d) For the splitting of the 3d orbitals we now find:

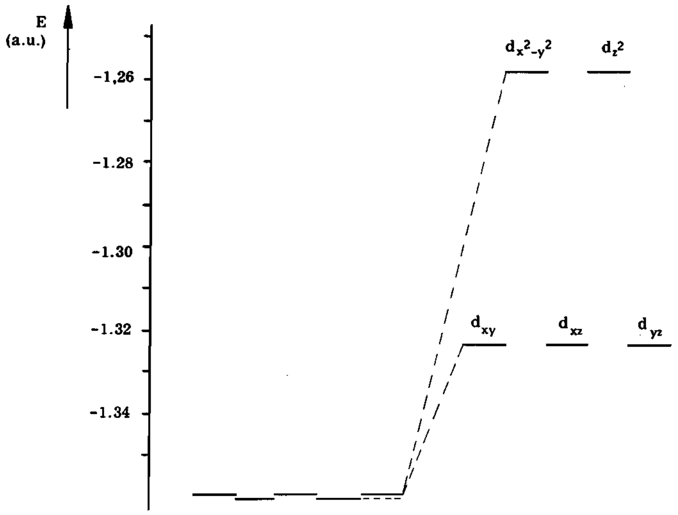


Fig. 5.3 Splitting of the d-orbitals in a $CuCl_2$ crystal

The relative positions of the orbitals are again correct but the numerical value of the splitting has become much higher than in $CuCl_6^{4-}$, viz. 14,300 cm^{-1}. On the one hand this is caused by the fact that the absolute values of all energies are larger; another and more important cause is the larger mixing in the relevant orbitals in the case of $CuCl_2$. However, the splitting found here is almost certainly too high; we expect a value of 8,000-10,000 cm^{-1} (1). The high value of the splitting in our calculation may be the result of the approximations we have made. So we took, for instance, the Cu-Cl distance too short.

As a result of this very rough calculation we may state that, although the $CuCl_6^{4-}$ ion seems unstable, copper in an octahedral environment of Cl may be considerably more stable in a $CuCl_2$ crystal.

REFERENCES

1. C.K. Jorgensen: Absorption Spectra and Chemical Bonding. Oxford (1962).
2. A.F. Wells: Structural Inorganic Chemistry. Oxford (1962).

CHAPTER VI

EXCITED STATES AND TOTAL ENERGIES

VI-1 MOLECULAR ORBITAL CALCULATION ON THE EXCITED STATE ^2E OF TETRAHEDRAL $CuCl_4^{2-}$

If an electron in a molecule passes from one molecular orbital to another, the charge distribution in the molecule may change and, consequently, so may the molecular orbitals. To get an impression about the magnitude of these effects, let us try to perform a molecular orbital calculation on an excited state of the tetrahedral $CuCl_4^{2-}$ complex. For this purpose we choose the first excited state of the complex, the ^2E state.

As a first approximation we assume the distances between the nuclei in the excited complex to be the same as those in the ground state of $CuCl_4^{2-}$. For the first excited state this assumption may be said to be reasonable.
The distribution of the electrons among the molecular orbitals in the ^2E state is given by formula (2.17b).
For the calculation on the ^2E state we now use the results of our calculation on the ground state of tetrahedral $CuCl_4^{2-}$ as far as possible. The two calculations are completely identical except for the determination of A, B, C, and D from the molecular orbitals. In the case of the ^2E state we determine A, B, C, and D on the basis of formula (2.17b).

We now find the following charge distribution in the ^2E state:

$A = 0.5629$
$B = 0.1120$
$C = 0.5012$
$D = 0.7372$

This charge distribution results in a charge of +0.95 on Cu and of -0.74 on each of the ligands. The one-electron energies and molecular orbitals belonging to this charge distribution are to be found in Table VI-1.

Comparing the results of the calculation on the ground state with those of the calculation on the first excited state, we notice the following points:

(a) The charge distribution in the complex changes somewhat by the transition of an electron from $2e \longrightarrow 4t_2$ and this is not surprising since the 2e molecular orbital consists for about 65% of metal orbitals and the $4t_2$ for about 50%.
If the molecular orbitals before and after the transition were identical, the change in the charge distribution would have been much larger. With the molecular orbitals from Table III-21 we would have found

Table VI-1 Eigenvalues and Eigenfunctions belonging to the excited state ^2E of tetrahedral $CuCl_4^{2-}$

A_1 symmetry

	$\phi \rightarrow$	4s	$\chi(\sigma)$	$\chi(s)$
	$H_{ii} \rightarrow$ $\varepsilon_{mo} \downarrow$	-0.1717	-0.4055	-0.8733
$3a_1$	0.2320	1.552	-0.949	-0.494
$2a_1$	-0.3966	0.042	0.981	-0.148
$1a_1$	-0.9061	-0.266	0.181	1.097
	EA(i)	CA(1, i)	CA(2, i)	CA(3, i)

E symmetry

	$\phi \rightarrow$	3d	$\chi(\pi)$
	$H_{ii} \rightarrow$ $\varepsilon_{mo} \downarrow$	-0.3504	-0.3569
2e	-0.3293	0.778	-0.679
1e	-0.3750	0.631	0.736
	EE(i)	CE(1, i)	CE(2, i)

T_1 symmetry

$E(T_1) = -0.3228$

T_2 symmetry

	$\phi \rightarrow$	4p	3d	$\chi(\pi)$	$\chi(\sigma)$	$\chi(s)$
	$H_{ii} \rightarrow$ $\varepsilon_{mo} \downarrow$	-0.1367	-0.3500	-0.3672	-0.3433	-0.8536
$5t_2$	0.1388	1.444	0.086	0.549	-0.384	-0.567
$4t_2$	-0.3134	-0.057	0.641	-0.420	-0.738	-0.088
$3t_2$	-0.3643	-0.009	0.764	0.136	0.572	-0.010
$2t_2$	-0.3717	0.015	0.116	0.917	-0.352	0.034
$1t_2$	-0.9108	-0.347	0.000	-0.153	0.078	1.161
	ET(i)	CT(1, i)	CT(2, i)	CT(3, i)	CT(4, i)	CT(5, i)

	$^2T_2$	^2E
A	0.5408	0.6566
B	0.1160	0.1160
C	0.5063	0.5092
D	0.7296	0.7578

We see, however, that in actual practice the charge distribution changes only little since the coefficients in the molecular orbitals also change slightly.

(b) The change in the coefficients in the molecular orbitals is small, namely at most ten per cent. This is the reason why in the calculation to be carried out in the following Chapter, we shall use the same coefficients in the molecular orbitals before and after the transition.

(c) All one-electron energies of the ^2E state differ a little from the energies of the ground state. The relative positions of the energies remain the same in both cases.

VI-2 TOTAL ENERGIES

As we have stated before, it is not correct to consider the sum of the one-electron energies to be the total energy of the system. This is also clear if we compare the sum of the one-electron energies of the ^2E state with that of the ground state. We thus find:

^2E	-18.791 a.u.
$^2T_2$	-18.717 a.u.

So the sum of the one-electron energies is lower in the ^2E state than in the ground state but from optical spectra and from E.P.R. spectra we know fairly certainly that the total energy of the ^2E state is higher than that of the ground state.
The total energy of a molecule is given by (1):

$$E_{tot} = \Sigma\, \varepsilon_{mo} - \sum_{i>j} I_{ij} + \sum_{\alpha>\beta} I_{\alpha\beta} \qquad (6.1)$$

where

I_{ij} is interaction between the electrons i and j;
$I_{\alpha\beta}$ is interaction between the nuclei α and β.

We now assume the following:

(a) In the sum of the one-electron energies we only insert the filled molecular orbitals occurring in our calculation.
Hence, we suppose the energies of the lower-lying orbitals to provide a constant contribution to the total energy of the system since in our calculations for $^2T_2$ and ^2E we keep the distances between the atoms constant. The remaining sum is denoted by $\Sigma'\varepsilon_{mo}$.

(b) On account of the restriction made under (a) the summation $\sum_{i>j} I_{ij}$ has only to be carried out for electrons occurring in the relevant orbitals: $\sum'_{i>j} I_{ij}$.

(c) Since the distances between the atoms in the molecule are kept constant, the term $\sum_{\alpha>\beta} I_{\alpha\beta}$ produces a constant contribution to the total energy.

We now obtain:

$$E_{tot} = \text{Constant} + \sum{}' \varepsilon_{mo} - \sum_{i>j}{}' I_{ij} \tag{6.2}$$

Applying the same approximations as used in the calculation of the H_{ii} integrals, we can compute the interactions between the electrons, thus obtaining the following values

Relevant electrons of	Relevant electrons of	Interaction (a.u.) $^2T_2$	^2E
central ion	central ion	40.752	40.588
central ion	ligands	72.450	72.326
ligand α	ligand α	47.206	47.278
ligand α	other ligands	51.103	51.201
	I_{tot}	211.511	211.393
	$\sum' \varepsilon_{mo}$	-18.717	-18.791
	E_{tot} - Constant	-230.228	-230.184

We now find indeed that the total energy of $^2T_2$ is lower than that of ^2E. The energy difference is found to be

$$0.044 \text{ a.u.} = 9600 \text{ cm}^{-1}$$

The expected value is 4000 cm^{-1} (see Chapter III).

However, from the discussion given above it is easily seen that the interactions between the electrons form the main contribution in determining the total energy. To compute these interactions we had to make some drastic approximations (see Chapter III) and therefore we may not expect the numerical values of the interactions to be accurate. Since in calculating the energy difference two of these large interactions are subtracted, it is, indeed, surprising that the difference found is so close to the expected value. However, it is clearly senseless to compute energy differences in this way since, for instance, a change of 1% in A or D may cause a change of 0.01 a.u. (25%) in the energy difference.

If we want to discuss the energy differences of the ground state and the excited states, we can consider the one-electron energies of the ground state and allow only qualitatively for the interactions between the electrons.

So we expect the ^2E state to be a lower lying state than $^2T_1$ since in the latter state the electron hole is on the ligands, and therefore the electron interactions will be larger in the $^2T_1$ state than in the ^2E state.

REFERENCES

1. J.C. Slater: Quantum Theory of Molecules and Solids, Vol. I. New York, (1963).

CHAPTER VII

SPECTRA OF THE TETRACHLOROCUPRATE (II) ION

VII-1 LITERATURE DATA

The optical absorption spectrum of the $CuCl_4^{2-}$ ion has been investigated by various authors. In some cases the spectrum was measured of a solution of the complex in acetonitril or nitromethane (1, 2, 3); other workers measured the spectrum of microcrystals of Cs_2CuCl_4 (4) or used the KBr disc technique to obtain the spectrum of $CuCl_4^{2-}$ (5). Unfortunately, the spectra measured by various authors do not always yield identical positions and intensities of the optical absorption bands. Since both the positions and the intensities can supply important information of the complex, we have repeated the measurement of the optical spectrum.

Data concerning the electron paramagnetic resonance spectrum of the $CuCl_4^{2-}$ ion were not found in the literature.

VII-2 PREPARATION OF THE COMPLEXES

The preparation of the complexes of $CuCl_4^{2-}$ has been described in detail in the literature. For our investigation we prepared two types of complexes:

(a) $[(C_2H_5)_4N]_2CuCl_4$ by mixing equivalent amounts of $CuCl_2$ and $2(C_2H_5)_4NCl$ in alcoholic solution. Addition of ether to this solution causes the precipitation of the desired complex (1, 6). Analysis of the complex yields

Cu	found	13.5 %	calculated	13.64 %
Cl	found	30.3 %	calculated	30.44 %

(b) Cs_2CuCl_4 by solving $CuCl_2$ with an excess of CsCl in water and evaporating the water until crystallisation of yellow Cs_2CuCl_4 needles starts (5). The result was:

Cu	found	13.4 %	calculated	13.48 %
Cl	found	30.2 %	calculated	30.10 %

VII-3 THE MEASUREMENT OF THE OPTICAL SPECTRUM

When measuring the spectrum of $CuCl_4^{2-}$ in solution we must take into account two effects -

(a) Interaction of the solvent with the complex leading to the formation of species as $CuCl_3S^-$ (exchange of a chloride ion by a solvent molecule S) or $CuCl_4S_2^{2-}$ (formation of a complex with a higher coordination number);

(b) Absorption of light by the solvent. Most solvents (as acetonitril, nitromethane, etc.) have absorption bands in the near infrared. This may cause difficulties if $CuCl_4^{2-}$ has an absorption band in the same region.

To avoid these effects we at first tried to obtain a spectrum of $CuCl_4^{2-}$ with the disc technique (7). However, this method failed when we used KBr as disc-material since there was some exchange of Cl^- of $CuCl_4^{2-}$ with Br^- ions (8). Unfortunately, it proved very difficult to make a disc with KCl. The discs were always somewhat opaque. Only the positions of the near infrared band of $CuCl_4^{2-}$ could be determined with some accuracy in spectra obtained by this method. Intensity measurements could not be performed.

A reasonably good spectrum was obtained from $\left[(C_2H_5)_4N\right]_2CuCl_4$ dissolved in acetonitril. The solution was saturated with $(C_2H_5)_4NCl$ to give an excess of Cl^- ions so that effect (a) could not disturb the measurement. Nor did (b) seriously affect the determination of the spectrum. We made use of a Zeiss spectrophotometer PMIV QII. Fig. 7.1 gives the spectrum we found, Table VII-1 gives

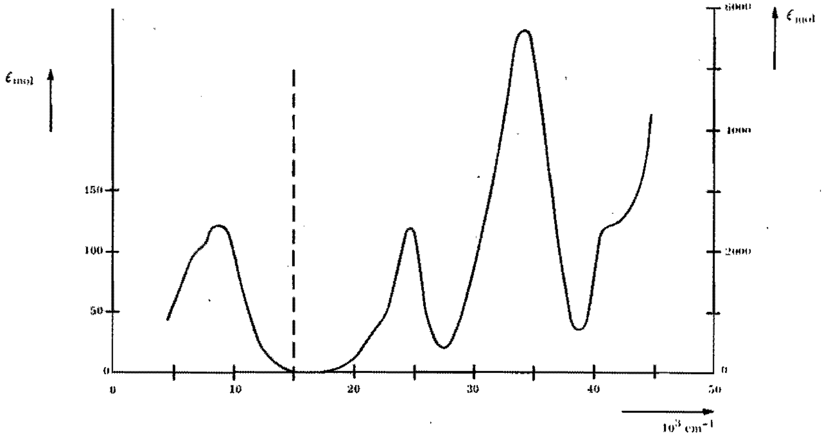


Fig. 7.1 Optical Absorption Spectrum of the $CuCl_4^{2-}$ ion

numerical values of the positions and the intensities of the absorption bands. The intensities are expressed in the oscillator strength f, a quantity that can be calculated from the spectrum by the formula:

$$f = 4.32\ 10^{-9} \int \varepsilon_{\gamma} d\gamma \qquad (7.1)$$

in which

γ = wave number

ε_{γ} = molar extenction of the complex at the wave number γ.

See Ref. (9, 10).

When electromagnetic radiation is absorbed by a molecule, the molecule changes from a state with total energy E_o to a state with total energy E_1 and the following relation holds:

$$h\gamma_t = E_1 - E_o \tag{7.2}$$

where

h = Planck's constant

γ_t = frequency of the radiation.

Since we measure the frequency of our radiation in energy units (cm^{-1}), we may write

$$\gamma = E_1 - E_o \tag{7.3}$$

where

γ = wave number of the radiation

E_o and E_1 are expressed in cm^{-1}.

Thus to obtain the positions of an absorption band, we have to subtract two total energies. In the preceding chapter, we saw, however, that it is too difficult a proposition to compute the total energy of the system from the one-electron molecular orbital energies. Therefore the best we can do is to estimate the positions of the absorption bands from the one-electron energies of the ground state.

In the theory of the absorption spectra of transition metal ions two types of transitions are distinguished, viz. crystal field transitions and charge transfer transitions.

(a) Crystal field transitions

In our molecular orbital picture, these are transitions between molecular orbitals that have predominantly a 3d character. For perfectly tetrahedral $CuCl_4^{2-}$, we only expect one crystal field transition: $^2T_2 \rightarrow {}^2E$. However, X-ray analysis shows $CuCl_4^{2-}$ to be a distorted tetrahedron. In reality, $CuCl_4^{2-}$ possesses a D_{2d} symmetry with a structure between the tetrahedral and the square planar structure, and as we can see from Fig. 4.2 we may expect three crystal field transitions. Using group theory we can prove that one of these transitions is forbidden. We can classify the 3d orbitals of the central ion according to the irreducible representations of D_{2d}:

d_{z^2} - A_1

$d_{x^2-y^2}$ - B_1

d_{xy} - B_2

d_{xz}, d_{yz} - E

The ground state of $CuCl_4^{2-}$ is $^2B_2$ since d_{xy} is the orbital with the highest energy. As the dipole moment operator $e\underline{r}$ transforms according to $E + B_2$ in the D_{2d} symmetry and as $B_2\,(E + B_2) = E + A_1$

we expect that only transitions to ^2E and $^2A_1$ are allowed.

Therefore the transition $^2B_2 \rightarrow {}^2B_1$ is symmetry forbidden.
Indeed, we find only two crystal field transitions in the absorption spectrum of $CuCl_4^{2-}$. Yet there is a difficulty. Since we know the deviation of $CuCl_4^{2-}$ from the tetrahedral structure to be small, we expect the transition $^2B_2 \rightarrow {}^2E$ to occur at a low wave number (1,000 or 2,000 cm^{-1} or so). This is not the case, but from our calculations we cannot understand the reason of this discrepancy. We limited ourselves to calculations on the T_d and D_{2d} symmetry and found the results corresponding with the D_{2d} symmetry by interpolation. A calculation as made by Furlani (3) shows, however, that linear interpolation is not always correct.

(b) Charge transfer transitions

A charge transfer transition is caused by the electron transfer from a molecular orbital with ligand character to a molecular orbital with central ion character. If a tetrahedral complex is distorted to the D_{2d} symmetry, its energy levels split up as follows:

$A_1 \rightarrow A_1$
$E \rightarrow A_1 + B_1$
$T_1 \rightarrow E + A_2$
$T_2 \rightarrow E + B_2$

From group theoretical arguments, we can see that the following transitions are allowed:

Transition in complex with T_d symmetry	Corresponding transition in complex with D_{2d} symmetry
$^2T_2 \rightarrow {}^2A_1$	$^2B_2 \rightarrow a^2A_1$
$^2T_2 \rightarrow {}^2E$	$^2B_2 \rightarrow b^2A_1$
$^2T_2 \rightarrow {}^2T_1$	$^2B_2 \rightarrow a^2E$
$a^2T_2 \rightarrow b^2T_2$	$^2B_2 \rightarrow b^2E$

(The prefixes a and b are added to distinguish states with the same symmetry).

We cannot predict the positions of the charge transfer transitions quantitatively, we can only estimate these positions and with the help of Table III-21 say something about the sequence in which they appear. So we expect the first charge transfer band to be caused by the transfer of an electron from the no-bonding t_1 to the $4t_2$ molecular orbital; in the D_{2d} symmetry this is the transition

$$^2B_2 \rightarrow a^2E$$

In the following transition an electron will go from $3t_2$ to $4t_2$, or in the D_{2d} symmetry: $^2B_2 \rightarrow b^2E$

For the third charge transfer band there are three possibilities:

$$2t_2 \rightarrow 4t_2 \quad \text{corresponding to } {}^2B_2 \rightarrow c^2E$$

$$1e \rightarrow 4t_2 \quad \text{corresponding to } {}^2B_2 \rightarrow a^2A_1$$

and somewhat less likely

$$2a_1 \rightarrow 4t_2 \quad \text{corresponding to } {}^2B_2 \rightarrow b^2A_1.$$

VII-5 INTENSITIES OF THE OPTICAL ABSORPTION BANDS IN $CuCl_4^{2-}$

We shall give here only the main lines for the calculation of the intensities of the optical absorption bands. All details can be found in Ref. (11).

It is possible to compute the absolute intensities of the absorption bands with the help of the wave functions obtained from the molecular orbital calculation of $CuCl_4^{2-}$ and so we can check these wave functions.

In the previous Section we saw that the intensities can be expressed in the oscillator strength f, which can be calculated from the observed spectrum. On the other hand, f can be connected with the transition probability of the system from one certain energy level to another. The relation is given by (10, 12, 13):

$$f = 1.085\ 10^{11}\ \Upsilon\ P \qquad (7.4)$$

$$P = Av_{I}\ \Sigma_{II}\ \left| \langle \Psi_I \,|\, \underline{r} \,|\, \Psi_{II} \rangle \right|^2 \qquad (7.5)$$

with

Υ = wave number of the absorption band or the mean wave number of a broad band (in cm^{-1})

Ψ_I = total wave function of the ground state

Ψ_{II} = total wave function of the excited state

$\underline{r}$ = position vector, we take for this a vector that points from the origin of the main coordinate system (central ion) to the integration point.

If the ground state is n-fold degenerate and the excited state is m-fold degenerate, we have to calculate n x m integrals

$$\langle \Psi_{I,i} \,|\, \underline{r} \,|\, \Psi_{II,j} \rangle \ .$$

To evaluate P, all these integrals are squared, added, and the sum is divided by n (So we have summed over the excited states and averaged over the ground states). The wave functions ψ_I and ψ_{II} are wave functions of the whole system and they may be written as determinantal wave functions that are composed of the one-electron wave functions of the filled molecular orbitals. To calculate the transition probabilities for $CuCl_4^{2-}$, we shall use the following approximations

(a) We assume the complex $CuCl_4^{2-}$ to be perfectly tetrahedral and ignore the distortions of this structure;

(b) we suppose that the one-electron molecular orbitals are the same before and after the transition (see Chapter VI).

Then in the ground state Ψ_I of $CuCl_4^{2-}$ we have a hole in, say, the molecular orbital ψ_I, and in the excited state Ψ_{II} we have a hole in ψ_{II}. We can now prove by simple algebra and by using the orthonormality relations of the molecular orbitals that

$$\langle \Psi_I | \underline{r} | \Psi_{II} \rangle = \langle \psi_{II} | \underline{r} | \psi_I \rangle \cdot \tag{7.6}$$

So to calculate the f-values we can make use of the one-electron molecular orbitals. The integrals $\langle \psi_{II} | \underline{r} | \psi_I \rangle$ have only to be calculated for the transitions that are allowed (see preceding Section).

Since a molecular orbital ψ is of the form

$$\psi = c_1 \phi_M + c_2 \chi_L$$

we obtain three types of integrals

$$\langle \phi_M | \underline{r} | \phi'_M \rangle$$
$$\langle \phi_M | \underline{r} | \chi_L \rangle$$
$$\langle \chi_L | \underline{r} | \chi'_L \rangle$$

(a) $\langle \phi_M | \underline{r} | \phi'_M \rangle$ is an integral of functions that belong to only one nucleus. For these integrals an analytical form is easily derived and a computer programme written.

(b) $\langle \phi_M | \underline{r} | \chi_L \rangle$ is an integral of functions that belong to two different nuclei. We can write

$$\chi_L = \sum_\alpha c_\alpha \phi_\alpha$$

in which the summation α extends over all ligands. The integral now becomes

$$\sum_\alpha c_\alpha \langle \phi_M | \underline{r} | \phi_\alpha \rangle$$

This integral is completely analogous to the overlap integrals and may be evaluated in the same manner (with A_n and B_n integrals, etc.).

(c) $\langle \chi_L | \underline{r} | \chi'_L \rangle$ may be written as

$$\sum_{\alpha_1} \sum_{\alpha_2} c_{\alpha_1} c'_{\alpha_2} \langle \phi_{\alpha_1} | \underline{r} | \phi'_{\alpha_2} \rangle$$

The integral will be calculated using a coordinate system as given in Fig. 7.2.

The vector $\underline{r}$ may be replaced by

$$\underline{r} = \underline{r}_o + \underline{r}'$$

this giving

$$\sum_{\alpha_1} \sum_{\alpha_2} c_{\alpha_1} c'_{\alpha_2} \langle \phi_{\alpha_1} | \underline{r}_o + \underline{r}' | \phi'_{\alpha_2} \rangle = \tag{7.7}$$

$$\sum_{\alpha_1} \sum_{\alpha_2} c_{\alpha_1} c'_{\alpha_2} \underline{r}_o \langle \phi_{\alpha_1} | \phi'_{\alpha_2} \rangle + \sum_{\alpha_1} \sum_{\alpha_2} c_{\alpha_1} c'_{\alpha_2} \langle \phi_{\alpha_1} | \underline{r}' | \phi'_{\alpha_2} \rangle$$

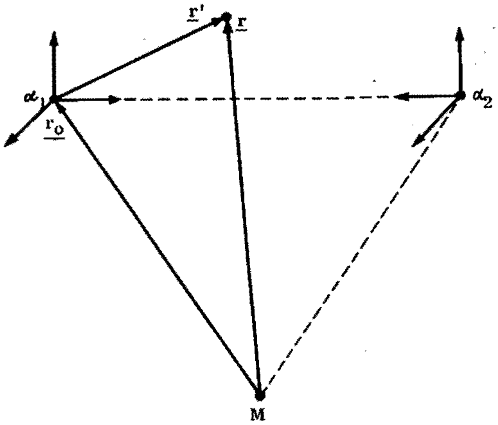


Fig. 7.2

The first term of (7.7) can be written down immediately, since the overlap integrals have already been calculated. The second term of (7.7) contains integrals of the same type as dealt with under (b).

All elementary integrals have been computed for different charge distributions, and by means of interpolation formulas have been obtained giving the integrals as functions of the charge distribution (A, B, C, and D). Substitution of the numerical values of A, B, C, and D and of the coefficients of the molecular orbitals as found for the ground state of tetrahedral $CuCl_4^{2-}$, then produces the integrals $\langle \psi_I | \underline{r} | \psi_{II} \rangle$. With these integrals the quantity P can now be calculated according to formula (7.5).

Taking the absorption bands in the sequence proposed in the preceding Section, we obtain the f-values as reported in Table VII-1. From these results we may conclude the following.

(1) For all transitions the calculated f-values are a factor 2 too high with respect to the experimental f-values. The cause of this is not evident but may no doubt partly be ascribed to the fact that formula (7.4) is valid for gases, whereas our absorption spectra have been measured in solution.

(2) The intensity of the crystal field transition is at least a factor 10 lower as compared with the charge transfer transitions.

Table VII-1 Optical Absorption Spectrum of $CuCl_4^{2-}$

Transition	Energy (cm^{-1})	ε_{max}	Experimental f	Theoretical f
$2e \rightarrow 4t_2$	6000 8500	shoulder 122	0.0037	0.0075
$t_1 \rightarrow 4t_2$	24500	2400	0.040	0.080
$3t_2 \rightarrow 4t_2$	34000	5700	0.120	0.184
$1e \rightarrow 4t_2$	41000	shoulder	0.032	0.052
$2t_2 \rightarrow 4t_2$				0.234
$2a_1 \rightarrow 4t_2$				0.316

(3) The sequence of the absorption bands as estimated from the one-electron molecular orbital energies, seems to be correct, hence

first the crystal field transition $2e \rightarrow 4t_2$

followed by three charge transfer transitions

(1) $t_1 \rightarrow 4t_2$

(2) $3t_2 \rightarrow 4t_2$

(3) $1e \rightarrow 4t_2$

The third charge transfer transition can now be identified with $1e \rightarrow 4t_2$ since the other two possibilities require a much higher f-value.

(4) The largest contribution to the intensity of the charge transfer bands is not given by a typical charge transfer (electron transfer from ligands to central ion) but by the transfer from one ligand function to another. The following Table shows this clearly.

Transition	Most important of the terms determining the intensity (m.o. coefficients included)
$2e \rightarrow 4t_2$	$\langle \chi(x,y) \mid \underline{r} \mid \chi(x,y) \rangle$
$t_1 \rightarrow 4t_2$	$\langle \chi(x,y) \mid \underline{r} \mid \chi(x,y) \rangle$
$3t_2 \rightarrow 4t_2$	$\langle \chi(z) \mid \underline{r} \mid \chi(z) \rangle$
$1e \rightarrow 4t_2$	$\langle \chi(x,y) \mid \underline{r} \mid \chi(x,y) \rangle$
$2t_2 \rightarrow 4t_2$	$\langle \chi(z) \mid \underline{r} \mid \chi(z) \rangle$ and $\langle \chi(x,y) \mid \underline{r} \mid \chi(x,y) \rangle$
$2a_1 \rightarrow 4t_2$	$\langle \chi(z) \mid \underline{r} \mid \chi(z) \rangle$

If the integrals $\langle \chi_L \,|\, \underline{r} \,|\, \chi'_L \rangle$ had been ignored f-values, twenty times too low would have been found.

(5) The intensity of the crystal field transition is preponderantly determined by the amount of mixing of the 3d orbitals with the ligand functions.
Although the 4p orbitals have the same symmetry as three 3d orbitals, they hardly affect the intensity of the crystal field band.

(b) A better agreement of the experimental with the theoretical values may be obtained if we assume that the mixing found in our molecular orbital calculation is somewhat too high.

VII-6 ELECTRON PARAMAGNETIC RESONANCE IN $CuCl_4^{2-}$ COMPLEXES

A Experimental

The principles of electron paramagnetic resonance (E.P.R.) have been described extensively in the literature (14, 15). If a complex of a transition metal ion is placed in a magnetic field, it can absorb electromagnetic radiation of microwave frequencies. This absorption only occurs if the complex possesses one or more unpaired electrons. These unpaired electrons then change from one spin state to another. Since $CuCl_4^{2-}$ possesses one unpaired electron we may expect that the complex shows paramagnetic resonance.

The E.P.R. measurements have been carried out with a Varian V4502 EPR spectrometer.

We first tried to measure the E.P.R. spectrum of solid $\left[(C_2H_5)_4N\right]_2CuCl_4$. At room temperature we did not observe a resonance spectrum for this complex but when we lowered the temperature to that of liquid nitrogen, we found a spectrum as given in Fig. 7.3. At the temperature of liquid hydrogen, the peaks of the spectrum became even sharper. The effect points to the appearance of spin lattice relaxation (16). This relaxation also explains the absence of a resonance spectrum at room temperature, the effect is, however, out of the scope of this thesis.

The condition for paramagnetic resonance is given by

$$h\nu = g\beta H \tag{7.8}$$

where

h = Planck's constant
ν = frequency of electromagnetic radiation
g = gyromagnetic ratio
β = Bohr magneton
H = magnetic field strength

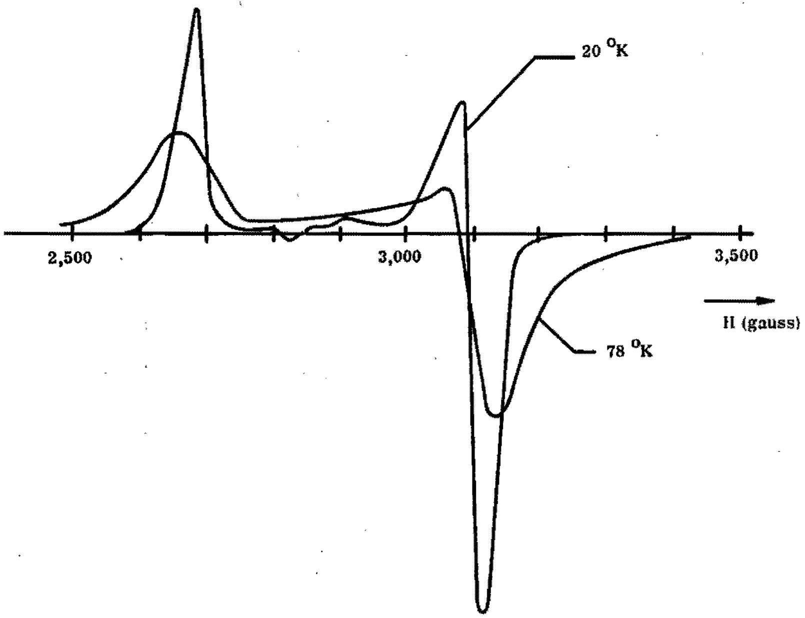


Fig. 7.3 E.P.R. Spectrum of the $CuCl_4^{2-}$ ion

As all quantities except g can be obtained from the E.P.R. spectrum, we can now calculate the numerical value of g. The form of the spectrum of $CuCl_4^{2-}$ indicates that we are dealing with an anisotropic g-factor (16) and so we obtain from the E.P.R. spectrum

$$g_{\parallel} = 2.45$$
$$g_{\perp} = 2.10$$

The E.P.R. spectrum of $\left[(C_2H_5)_4N\right]_2CuCl_4$ (or of Cs_2CuCl_4) does not show a hyperfine structure, but this may be ascribed to the fact that we carried out our measurements on a solid.

A double integration of the spectrum of Fig. 7.3 gives us the area of the absorption peak. From this area we can estimate the number of unpaired spins in the solid. We found this to be about one unpaired spin per $CuCl_4^{2-}$ complex.

B Calculation of the g-values

For the energy level scheme of distorted $CuCl_4^{2-}$ as given in Fig. 7.4, the g-values can be calculated with formulas given by Gray, Ballhausen (17) and by Van Reyen (Ref.(16), p.48):

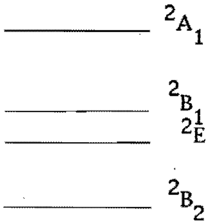


Fig. 7.4

$$g_{\parallel} = 2\left(1 - \frac{4\lambda}{\Delta_B}\alpha\beta\right) \qquad (7.9)$$

$$g_{\perp} = 2\left(1 - \frac{\lambda}{\Delta_E}\alpha^2\right) \qquad (7.10)$$

where

λ = spin orbit coupling constant of a 3d electron
$\Delta_B = E(^2B_1) - E(^2B_2)$
$\Delta_E = E(^2E) - E(^2B_2)$

An assumption made here is that the molecular orbitals of the distorted complex do not deviate much from the molecular orbitals in perfectly tetrahedral $CuCl_4^{2-}$ and that in this latter case

$$\psi_{T_2} = \alpha \,.\, 3d + \text{ligand functions}$$

$$\psi_E = \beta \,.\, 3d + \text{ligand functions}$$

From the Tables III-21 and IV-5 we see that the coefficients α and β indeed do not change much:

	T_d	D_{4h}
α	0.707	0.771 and 0.787
β	0.836	0.914 for b_1 symmetry

(the a_1 symmetry is not important for the g-values).
In the derivation of the formulas (7.9) and (7.10), terms in $(\frac{\lambda}{\Delta})^2$, etc. are ignored. Moreover, it is assumed that contributions of the spin orbit interaction arising from motions of the electrons in the ligands can be ignored.
We now take the following numerical values

$\lambda = -800\ cm^{-1}$ (from Ref. (9))
$\Delta_E = 6000\ cm^{-1}$ (from the optical spectrum)
$\Delta_B = 7000\ cm^{-1}$ (estimated from Δ_E, Fig. 4.2 and Ref. (3))
$\alpha = 0.71$
$\beta = 0.84$

and then obtain:

$g_{\parallel} = 2.54$
$g_{\perp} = 2.13$

The calculated g-values are somewhat too high but they do not deviate much from the experimental values. So we get the impression that our coefficients α and β are fairly satisfactory. To give a better agreement of the theoretical with the experimental g-values, we would have to lower the values of α and β a little but this seems unrealistic since we expect (as has been stated in Chapter III and as can also be seen from the intensity calculations for the optical spectrum) that the values of α and β are already low. The discrepancy between the theoretical and the experimental values must now be presumed to be affected by the inaccuracy of Δ_E and Δ_B and by the neglect of spin orbit interaction when the unpaired electron moves on the ligands.

It is however, obvious that a fairly large mixing must be present in the relevant molecular orbitals, for if there were no mixing then we would find the following values:

$$g_{\parallel} = 2.91$$

$$g_{\perp} = 2.26$$

and these would be far too high.

REFERENCES

1. C. Furlani, G. Morpurgo: Z.physik.Chem. 28, (1961), 93.
2. F.A. Cotton *et al.*: J.Am.Chem.Soc. 83, (1961), 4690.
3. C. Furlani, G. Morpurgo: Theor.Chim.Acta 1, (1963), 102.
4. S. Yamada, R. Tsuchida: Bull.Chem.Soc.Japan 27, (1954), 436.
5. B. Morosin, K. Lawson: Mol.Spectr. 12, (1964), 98.
6. R.S. Nyholm, N.S. Gill: J.Chem.Soc. (1959), 3997.
7. A. Tolk: Thesis, Utrecht, (1959).
8. P. Ros: Rec.Trav.Chim. 82, (1963), 823.
9. J.S. Griffith: The Theory of Transition Metal Ions. Cambridge (1961).
10. C.J. Ballhausen: Introduction to Ligand Field Theory. New York (1962).
11. A.P.J.J. van der Avoird: Internal Report of the Inorganic Chemistry Department. Techn. University, Eindhoven (1964).
12. R.S. Mulliken, C.A. Rieke: Repts.Progr.Phys. 8, (1941), 231.
13. C.J. Ballhausen: Progress in Inorganic Chemistry 2, (1960), 251.
14. G.E. Pake: Paramagnetic Resonance, New York, (1962).
15. D.J.E. Ingram: Spectroscopy at Radio and Microwave Frequencies, London, (1955).
16. L.L. van Reyen: Thesis, Eindhoven, (1964).
17. C.J. Ballhausen, H.B. Gray: Inorg. Chem. 1, (1962), 111.

CHAPTER VIII

CONCLUSIONS

In the Introduction (Chapter I) we made it our object to perform a molecular orbital calculation on $CuCl_4^{2-}$ and to use empirical parameters as sparingly as possible. Already then we expected that such a calculation must necessarily contain certain approximations. At the end of our investigation we can now survey on what points we had to introduce these approximations. The most important of them will be summarised here.

(a) The first approximation we made was the choice of the molecular orbitals as linear combinations of atomic orbitals; we only selected a limited number of atomic orbitals to describe the orbitals of the electrons in the molecule. On account of this restriction our molecular orbitals may deviate somewhat from the actual ones (Ref. (1), p. 97). Another inaccuracy inherent in the simple LCAO method is the under-estimation of the repulsion of the electrons (Ref. (2)). In each molecular orbital found in our calculation we had to place two electrons with opposite spins. Assume we have a molecular orbital

$$\psi = \phi_A + \phi_B$$

and that it is occupied by two electrons. The chance that the two electrons are present on the same nucleus is then as large as the chance that they are on different nuclei. In reality, the repulsion of the electrons causes a preference for the latter case.

(b) A second approximation consisted in the choice of the radial parts of the wave functions of the atomic orbitals. These radial parts were written as linear combinations of Slater functions, thus approximating Hartree Fock functions. Although these approximations are not always very accurate, this will not affect our calculation unduly since, in principle, any function may be used to describe the molecular orbitals.

(c) The H_{ij} and S_{ij} integrals were calculated as functions of the charge distribution by interpolation between a number of computed values. For integrals that are strongly dependent on the charge distribution, this interpolation may introduce inaccuracies.

(d) In the calculation of the H_{ii} integrals of a certain atom we approximated the other atoms in the molecule by point charges and had to calculate a Z_{eff}. Of course, this is a rigorous approximation, but crude as it may be, it remains faithful to a model discussion and avoids the smuggling in of experimental data.

(e) In the calculation of the H_{ij} integrals we used an empirical formula which has proved to be satisfactory for small molecules. There exists no *a priori* knowledge whether the agreement will be as satisfactory for the systems considered here.

(f) To obtain the charge distribution in the molecule from the calculated molecular orbitals we had to use a rather arbitrary approximation (Chapter III, Section 4).

(g) In the molecular orbital calculations on square planar and octahedral copper complexes we introduced a number of additional approximations concerning the distances of the atoms in the molecule, the $\frac{1}{r_B}$ integrals, etc.

In view of the number of approximations we may not expect our calculations to be accurate. However, we are in a position to check our results with data that have been obtained in a different way, and find satisfactory agreement.

Let us consider the following points.

(a) The splitting of the d-orbitals of the central ion always turns out to have the correct sign, and also quantitatively we find reasonable values (except perhaps in the $CuCl_6^{4-}$ case). On this point our results are more satisfactory than those of the crystal field calculations.

(b) The mixing of the d-orbitals of the central ion with ligand orbitals seems to be correct. In other investigations large mixing is found in tetrahedral halide complexes (Ref.(3), p. 172) but in octahedral halide complexes the mixing seems to be smaller (3, 4). This is also clearly shown by our calculations (compare the Tables III-21, IV-3, V-2 and V-3).

(c) We cannot compute the positions of the absorption bands of the optical spectrum from the results of our calculations. We can, however, predict the sequence in which the transitions occur.

(d) The intensities of the optical absorption bands, calculated with the help of the functions found in the molecular orbital calculation, although somewhat too high, agree rather well with the experimental intensities.

(e) With the help of our molecular orbital functions we can obtain E.P.R. g-values that approximate the experimental g-values very closely.

(f) The method applied does not allow of a satisfactory calculation concerning the total energies and the stabilities of the complexes. We can, however, find a number of qualitative indications. It appears, for instance, that a $CuCl_6^{4-}$ complex is very unstable, whereas Cu in an octahedral surrounding in a $CuCl_2$ crystal is stable. Some indications may be derived from our results to the effect that tetrahedral $CuCl_4^{2-}$ will be more stable than square planar $CuCl_4^{2-}$ but that anyhow the difference seems small.

(g) With the molecular orbitals found in our calculation it is possible to compute a charge distribution. We already saw that this charge distribution can deviate greatly from the charge distribution that may be obtained from the ionic model: Cu^{2+} and Cl^{-}. In the calculation of the charge distribution from the molecular orbitals we considered the electrons in the 4s and 4p orbitals of copper to belong to the charge on copper, and as far as we are concerned with the computation of integrals this seems correct. However, with this charge distribution we do not get a good insight into the amount of charge that we can find on different sites in the complex. From Fig. 3.1 we can see that the 4s and 4p orbitals of copper have their largest density in the neighbourhood of the Cl nucleus, and if we wish to calculate the amount of charge on a certain site in the molecule, the proper way seems to reckon the 4s and 4p electrons among the charge on Cl. We then get quite another impression of the charge distribution. The following Table shows the new results.

	Charge on	
	Cu site	Cl site
Tetrahedral $CuCl_4^{2-}$	+ 1.54	- 0.89
Square planar $CuCl_4^{2-}$	+ 1.50	- 0.88
$CuCl_6^{4-}$	+ 1.93	- 0.99
$CuCl_2$ crystal	+ 1.77	- 0.88

The new charge distribution resembles much more the charge distribution of the ionic model. Nevertheless, the Table clearly shows that covalency effects are important, especially in tetrahedral and square planar $CuCl_4^{2-}$. Taking into account the approximations we made, we may consider the results to be surprisingly satisfactory. The calculations that we performed fulfil the purpose set out in Chapter I completely. Moreover hardly any empirical quantities were used, the only exception being the calculation of the H_{ij} integrals from the H_{ii} and S_{ij} integrals which was based on an empirical formula. Evidently several improvements may be introduced. For instance, the calculation of the H_{ii} and H_{ij} integrals can be performed with greater precision if a larger and faster computer is available. Other approximations that are perhaps of equal importance, such as used, for instance, in the calculation of the charge distribution from the molecular orbitals, cannot be improved by the use of a larger computer, but they require a more penetrating theoretical study. However, with this investigation we have shown that a rather useful molecular orbital calculation can be performed with relatively simple means and that the results of this calculation may clarify our insight in a number of problems that are connected with the bonding and the physical properties of inorganic complexes.

REFERENCES

1. J.C. Slater: Quantum Theory of Molecules and Solids, Vol. I. New York, (1963).
2. C.A. Coulson: Valence. Oxford, (1961).
3. C.J. Ballhausen: Introduction to Ligand Field Theory. New York, (1962).
4. R.G. Shullman, S. Sugano: Phys. Rev. 130, (1963), 517.

SUMMARY

The last few years first principle calculations on molecules have been used more and more to provide insight into various physical properties of the molecule. Attempts have been made to obtain in this way information on the situation of the energy levels of the molecule, on the optical absorption spectrum, on the magnetic properties, on the stability, etc. Complexes of transition metal ions, i.e. ions with a partly filled d-shell, are in this connection of special interest.
Since S.C.F. calculations become very complicated in the case of systems with a partly filled shell, only molecular orbital calculations have been performed on these complexes. However, molecular orbital calculations on inorganic complexes are not simple either, the greatest difficulties arising in calculating the integrals $\langle \phi_i | H | \phi_i \rangle$ and $\langle \phi_i | H | \phi_j \rangle$. Usually therefore these integrals are determined empirically from ionisation energies.

This thesis describes a method to carry out a molecular orbital calculation on inorganic complexes that restricts the use of empirical quantities as much as possible. In the investigation the integrals $\langle \phi_i | H | \phi_i \rangle$ are computed from the wave functions (given in the literature) by:

(a) computing the one-electron energies of the free atoms or ions. This computation can be carried out exactly since the wave functions are given;

(b) approximating the interaction of an electron of a certain atom in the molecule with the other atoms of the molecule by a point-charge model. The integrals and the effective charges then arising may be computed from the wave functions.

In this way the integrals $\langle \phi_i | H | \phi_i \rangle$ are computed as functions of the charge distribution in the molecule. The integrals $\langle \phi_i | H | \phi_j \rangle$ are then calculated from the integrals $\langle \phi_i | H | \phi_i \rangle$ with the help of an empirical formula. Applying an iteration process it is then possible to find a consistent charge distribution of the complex.

The calculation described here is performed on some copper complexes because the fact that Cu^{2+} possesses nine 3d-electrons (and therefore has only one hole in the 3d-shell) simplifies the calculation considerably, while on the other hand the optical and magnetic spectra provide ample information on the complexes. To investigate the influence of the environment of the central ion on the properties of the complex, the calculation is carried out on the following species:

tetrahedral $CuCl_4^{2-}$
square planar $CuCl_4^{2-}$
octahedral $CuCl_6^{4-}$
an octahedral $CuCl_6$ unit from a cubic $CuCl_2$ crystal.

In all these cases the molecular orbital calculation yields qualitatively the correct splitting of the d-orbitals of copper; quantitatively satisfactory results are also found, viz. 3,050 cm^{-1} for tetrahedral $CuCl_4^{2-}$; 9,300 cm^{-1} for square planar $CuCl_4^{2-}$; 850 cm^{-1} for $CuCl_6^{4-}$ and 14,300 cm^{-1} for the $CuCl_2$ crystal.
Moreover the calculations show that in some cases the charge distribution in the complex deviates considerably from the charge distribution according to the ionic model. This points to the fact that covalency effects are important in such complexes.
The calculation on $CuCl_6^{4-}$ indicates this complex to be unstable, whereas Cu in an octahedron of Cl may be quite stable in a $CuCl_2$ crystal.

The intensities of the optical absorption bands are calculated with the help of the one-electron molecular orbitals found for tetrahedral $CuCl_4^{2-}$. The agreement of the calculated and the experimental values is quite good. So we find, for instance, the calculated ratio between the intensities of the crystal field and the charge transfer transitions to be equal to the experimental one.

The g-values of electron spin resonance are also calculated with the help of the wave functions of tetrahedral $CuCl_4^{2-}$. The calculated g-values ($g_{\parallel} = 2.54$ and $g_{\perp} = 2.13$) approximate the experimental g-values ($g_{\parallel} = 2.45$ and $g_{\perp} = 2.10$) closely.

SAMENVATTING

Gedurende de laatste jaren blijkt steeds meer dat het belangrijk is om te proberen inzicht te verkrijgen in verschillende fysische eigenschappen van een molecule met behulp van een a priori berekening aan dat molecule. Men probeert op deze wijze gegevens te verkrijgen over b.v. de ligging van de energieniveaus van het molecule, over het optische absorptiespectrum, over de magnetische eigenschappen, over de stabiliteit, enz. De belangstelling gaat hierbij vooral uit naar complexen van overgangsmetaalionen, dus van ionen die een niet geheel gevulde d-schil hebben. Daar voor systemen met niet geheel gevulde schillen S.C.F. berekeningen zeer gecompliceerd worden, heeft men voor deze complexen tot nu toe alleen "molecular orbital" berekeningen uitgevoerd. Maar ook deze berekeningen zijn niet eenvoudig; de grote moeilijkheid waarop men stuit is de berekening van de integralen $\langle \phi_i |H| \phi_i \rangle$ en $\langle \phi_i |H| \phi_j \rangle$. Deze integralen worden dan meestal (empirisch) bepaald uit de ionisatie-energieën.

In dit proefschrift wordt een methode beschreven waarmen men een "molecular orbital" berekening voor anorganische complexen kan uitvoeren die het gebruik van empirische gegevens zoveel mogelijk beperkt.
De integralen $\langle \phi_i |H| \phi_i \rangle$ worden in dit werk uit de gegeven golffuncties berekend door:

(a) de één-elektron energieën voor de vrije atomen of ionen te berekenen, hetgeen omdat de golffuncties bekend zijn, exact kan gebeuren;

(b) de interactie van een elektron van een bepaald atoom in het molecule met de andere atomen van het molecule te benaderen met een puntladingsmodel. De daarbij voorkomende integralen en effectieve ladingen kunnen weer uit de golffuncties berekend worden.

Op deze manier worden de integralen $\langle \phi_i |H| \phi_i \rangle$ als functies van de ladingsverdeling in het molecule berekend. De integralen $\langle \phi_i |H| \phi_j \rangle$ worden met behulp van een empirische formule bepaald uit de nu bekende $\langle \phi_i |H| \phi_i \rangle$. Door het toepassen van een iteratie-procedure kan nu een consistente ladingsverdeling voor het complex gevonden worden.

De hierboven omschreven berekening is uitgevoerd voor enkele koper-complexen omdat het feit dat Cu^{2+} een d^9-systeem is (en dus slechts één gat in de d-schil heeft) de berekening aanzienlijk vereenvoudigt, terwijl er anderzijds voldoende informatie over deze complexen te verkrijgen is uit optische en magnetische spectra.

Om de invloed van de omringing van Cu^{2+} na te gaan, is de berekening voor de volgende gevallen uitgevoerd:

tetraedrisch $CuCl_4^{2-}$
vlak vierkant $CuCl_4^{2-}$
octaedrisch $CuCl_6^{4-}$
een octaedrische $CuCl_6$ eenheid uit een kubisch $CuCl_2$ kristal.

In al deze gevallen geeft de "molecular orbital" berekening kwalitatief de juiste opsplitsing van de d-banen van koper en ook kwantitatief worden zeer aannemelijke resultaten gevonden: 3050 cm^{-1} voor tetraedrisch $CuCl_4^{2-}$; 9300 cm^{-1} voor vlak vierkant $CuCl_4^{2-}$; 850 cm^{-1} voor $CuCl_6^{4-}$ en 14300 cm^{-1} voor het $CuCl_2$-kristal.

De berekeningen tonen verder aan dat de ladingsverdeling in sommige gevallen (b.v. $CuCl_4^{2-}$) aanzienlijk afwijkt van de ladingsverdeling die men volgens het ion-model verwacht. Dit wijst erop dat covalentie-effecten in deze complexen belangrijk zijn.

De berekening aan $CuCl_6^{4-}$ doet verwachten dat dit complex instabiel zal zijn, terwijl daarentegen Cu met een zesomringing van Cl in een $CuCl_2$-kristal zeer stabiel schijnt te zijn.

Met de één-elektron golffuncties die voor tetraedrisch $CuCl_4^{2-}$ gevonden zijn, worden de intensiteiten voor de optische absorptie-overgangen van het tetraedrische complex berekend. De overeenkomst van de berekende en de experimentele waarden blijkt goed te zijn. Zo wordt b.v. voor de verhouding van de intensiteiten van de kristalveld-overgang en de charge transfer overgangen de uit het experiment gevonden waarde berekend.

Eveneens worden met de golffuncties voor tetraedrisch $CuCl_4^{2-}$ de g-waarden voor elektronenspinresonantie bepaald. De berekende g-waarden ($g_{\parallel} = 2.54$ en $g_{\perp} = 2.13$) benaderen de experimentele waarden ($g_{\parallel} = 2.45$ en $g_{\perp} = 2.10$) zeer goed.

DANKWOORD

Gaarne wil ik op deze plaats mijn dank betuigen aan allen die aan het verschijnen van dit proefschrift hun medewerking hebben verleend.

In het bijzonder wil ik danken Mej. M. Kuyer en haar staf voor het verrichten van de analyses; de heer A.P.J.J. van der Avoird voor zijn werk bij het berekenen van de intensiteiten; Mej. N.M. Clement voor het samenstellen van het S.P.S. gedeelte van de computerprogramma's en de heer H.J.A. van Beckum voor de correctie van het Engels.

De directie van het Koninklijke/Shell Laboratorium te Amsterdam ben ik erkentelijk voor de gelegenheid die zij mij heeft geboden om dit werk te voltooien.

LEVENSBERICHT

De schrijver van dit proefschrift werd op 24 juli 1939 te Raamsdonksveer geboren. Zijn middelbare opleiding ontving hij aan het Willem van Oranje College te Waalwijk. In 1957 behaalde hij daar het H.B.S.-B diploma.

Van 1957 tot 1962 studeerde hij in de afdeling der Scheikundige Technologie aan de Technische Hogeschool te Eindhoven. In juni 1962 legde hij met goed gevolg het ingenieursexamen af. Hij studeerde af bij prof. dr. G.C.A. Schuit op het onderwerp: "Kinetiek en mechanisme van de Wacker-reactie".
Na zijn afstuderen trad hij bij de groep Anorganische Chemie van de T.H.E. in dienst als wetenschappelijk assistent. Sinds 1 mei 1964 is hij verbonden aan het Koninklijke/Shell Laboratorium te Amsterdam.

Het volgen van twee cursussen van prof. C.A. Coulson in Oxford heeft hem een waardevolle bijdrage geleverd tot zijn studie in de theoretische chemie.

STELLINGEN

1. Schmidt veronderstelt dat voor de ontleding van het geactiveerde complex in de oxydatie van ethyleen tot aceetaldehyde een OH$^-$ion nodig is. Deze hypothese is niet houdbaar.
   J. Schmidt: Chem. and Ind. (1962), 54.
   J. Schmidt: Angew. Chem. 74, (1962), 93.

2. Stouthamer neemt aan dat tijdens de hydrogenering van vetzuren tot vetalcoholen onder invloed van Cu-houdende katalysatoren CuH aanwezig is. Deze veronderstelling zou beter gefundeerd zijn als hij overeenkomst had gevonden tussen de optische absorptiespectra van het reactiemengsel en van b.v. CuH opgelost in pyridine.
   B. Stouthamer: Proefschrift Delft (1964).
   H.W. van der Linden, B. Stouthamer, J.C. Vlugter: Chem. Weekblad 60, (1964), 254.

3. De wijze waarop Cossee de katalytische activiteit van chloriden van verschillende overgangsmetalen vergelijkt, is aan bedenkingen onderhevig.
   P. Cossee: J. Catalysis 3, (1964), 80.

4. De kinetische benadering van de vethydrolyse zoals die door Sturzenegger en Sturm is uitgevoerd mag alleen worden toegepast bij homogene reacties.
   A. Sturzenegger, H. Sturm: Ind. Eng. Chem. 43, (1951), 510.

5. Bates houdt bij de bespreking van de spectra van overgangsmetaalionen in glazen niet voldoende rekening met selectieregels.
   T. Bates: Modern Aspects of the Vitreous State 2, (1962), 195.

6. De formule die Jørgensen voor de oscillatorsterkte van een optische dipoolovergang geeft, is onjuist.
   C.K. Jørgensen: Absorption Spectra and Chemical Bonding in Complexes, Oxford (1962).

7. De veronderstelling van Blasse dat $\Delta_O \simeq \Delta_T$ mag alleen met grote voorzichtigheid toegepast worden.
   G. Blasse: Proefschrift Leiden (1964).

8. Het is mogelijk dat susceptibiliteit en demagnetisatie invloed uitoefenen op resonantieproeven zoals die door Poulis e.a. uitgevoerd zijn. Dit blijkt echter nergens in de door Poulis gegeven resonantiediagrammen.
   N.J. Poulis e.a.: Physica 23, (1957), 907.
   N.J. Poulis, W. van der Lugt: Physica 25, (1959), 1313.
   N.J. Poulis, W. van der Lugt: Physica 27, (1961), 733.

9. Het is te betwijfelen of door het meten van elektronenspinresonantie bij hoge temperaturen voldoende informatie verkregen kan worden over de omringing van overgangsmetaalionen.

10. Bij het doceren van de groepentheorie worden twee verschillende methoden gevolgd:
    (a) de groepentheorie wordt zuiver wiskundig behandeld en eerst later worden fysische toepassingen besproken;
    (b) men begint met het bespreken van fysische toepassingen en behandelt aan de hand daarvan alleen die stukken van de groepentheorie die nodig zijn.

    De eerste methode verdient de voorkeur.
    (a) F.A. Cotton: Chemical Applications of Group Theory, New York, (1962).
    (b) S.L. Altmann in D.R. Bates: Quantum Theory, vol. II, New York, (1962).

11. Voor studenten die fundamenteel chemisch of fundamenteel technologisch willen afstuderen is niet alleen de toepassing van de wiskunde, maar vooral ook de wiskundige wijze van denken van belang.

13 oktober 1964

P. ROS