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MOLECULAR ORBITAL CALCULATIONS ON COPPER CHLORIDE COMPLEXES

P. ROS*, A. VAN DER AVOIRD** AND G. C. A. SCHUIT

Department of Inorganic Chemistry, Technological University, Eindhoven (The Netherlands)

The quantum theoretical calculations performed on transition metal complexes extend over a range of different complexities. The simplest approach, from the computational point of view, is the Wolfsberg–Helmholz method[1], which makes use of experimentally obtained data, such as ionization potentials. The most rigorous procedure that, at the moment, lies within the field of possibilities is a "*ab initio*" LCAO-SCF calculation. However, an approach of this type is so complex that it has not yet been undertaken without some approximations.

The aim of the present calculation is not to test the validity of some approximations usually introduced in the MO-calculations as *e.g.* R. Fenske does in his paper *Parameter Free Molecular Orbital Calculations for Metal Complexes.*

It is rather meant to provide a method of doing calculations on transition metal complexes without introducing measured parameters and still to avoid excessive computations. The experience obtained in the Wolfsberg–Helmholz method is used in estimating some of the occurring integrals.

The calculation is based on the LCAO-SCF method: the wave function for the complex is written as a single determinant composed of the filled molecular one-electron orbitals, which are linear combinations of atomic orbitals. Minimization of the one-electron energies leads to the secular equations involving the general elements $H_{ij} = \langle \phi_i | H | \phi_j \rangle$ and $S_{ij} = \langle \phi_i | \phi_j \rangle$; ϕ_i and ϕ_j are atomic orbitals. Since the effective one-electron Hamiltonian H depends on the molecular orbitals an iterative procedure is followed.

In this calculation on copper chloride complexes the atomic orbital set consisted of the 3d, 4s and 4p orbitals of the central copper ion and the 3s and 3p orbitals of the chlorine ligands. The radial parts of these orbitals were obtained from Hartree–Fock calculations on atoms and ions by Watson and Freeman[2] and by Richardson *et al.*[3], for several atomic and ionic configurations. From these radial functions variable atomic orbitals were constructed, depending on para-

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* Present address: Koninklijke/Shell-Laboratorium, Amsterdam (The Netherlands).
** Present address: Battelle Institute, Advanced Studies Center, 7, route de Drize, 1227 Carouge/Geneva (Switzerland).

meters which describe the electronic configuration in the complex. As this electronic configuration was not known, these parameters were also varied in the MO-SCF iteration. Thereby a self-consistent electronic configuration of the complex and the corresponding atomic orbitals were obtained.

Calculations were performed on tetrahedral (T_d) and square planar (D_{4h}) $CuCl_4^{2-}$ and octahedral (O_h) $CuCl_6^{4-}$ ions keeping the Cu–Cl distance constant. The complex $CuCl_4^{2-}$ exists in a tetragonally distorted tetrahedral form (D_{2d}), a distorted octahedron occurs in solid $CuCl_2$. The atomic orbitals were classified according to the irreducible representations of the symmetry groups indicated and the secular equations were simplified thereby. The matrix elements that we were left with were evaluated using two approximations.

The first one concerns the diagonal elements H_{ii}. In the Wolfsberg–Helmholz method they are replaced by Valence State Ionization Energies. These were calculated after a simplification of the Hamiltonian.

The Hartree–Fock one-electron operator for electron 1 in orbital ϕ_i may be written as follows (in atomic units):

$$H = -\frac{\nabla_1{}^2}{2} - \frac{z_\alpha}{\mathrm{r}_{\alpha 1}} + \sum_{j \neq i} \int \frac{\phi_j{}^*(2)\phi_j(2)}{r_{12}} \mathrm{d}\tau_2 -$$

$$\sum_{\substack{j \neq i \\ \text{equal spin}}} \int \frac{\phi_j{}^*(2)\phi_j(1)}{r_{12}} \mathrm{d}\tau_2 \cdot P_{12} - \sum_{\beta \neq \alpha} \frac{z_\beta}{r_{\beta 1}} +$$

$$\sum_k \int \frac{\phi_k{}^*(2)\phi_k(2)}{r_{12}} \mathrm{d}\tau_2 - \sum_{\substack{k \\ \text{equal spin}}} \int \frac{\phi_k{}^*(2)\phi_k(1)}{r_{12}} \mathrm{d}\tau_2 \cdot P_{12}$$

where the orbitals ϕ_j are located on nucleus α, the orbitals ϕ_k on the other nuclei β.

Those parts of the matrix elements H_{ii} with the first four terms of H only yield one-ceter one- and two-electron integrals, such as occur in atomic problems. Using atomic orbitals whose radial parts were given as linear combinations of Slater type orbitals, these integrals were easily calculated. The last three terms of the Hamiltonian were approximated by

$$-\sum_{\beta \neq \alpha} \frac{z'_\beta}{r_{\beta 1}}.$$

This means physically that the influence of a nucleus β and the electrons belonging to β on an electron in orbital ϕ_i on α was approximated by an effective point charge z'_β. Taking rather simple geometrical forms for the charge distributions a screening constant was calculated for each electron on β. z'_β was found by subtracting from the core charge z_β the amount due to the screening of the outer electrons. The second line of H then yielded one-electron two-center integrals. They were evaluated using elliptical coordinates as were the overlap integrals S_{ij}.

The second approximation concerns the non-diagonal elements H_{ij}. Following the experience obtained in the Wolfsberg–Helmholz method they were written as

$$H_{ij} = -FS_{ij}\sqrt{H_{ii} \cdot H_{jj}}$$

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

according to Gray and Ballhausen[4].

The formulae for the matrix elements having been worked out, the iteration was performed. The molecular orbital functions and one-electron energies obtained where checked by comparison with the optical spectrum (Fig. 1). Assuming that with an electronic transition of low energy the total electronic configuration of the complex does not change very much one can obtain the excitation energies, and therewith the positions of the bands in the optical spectrum as differences of one-electron energies.

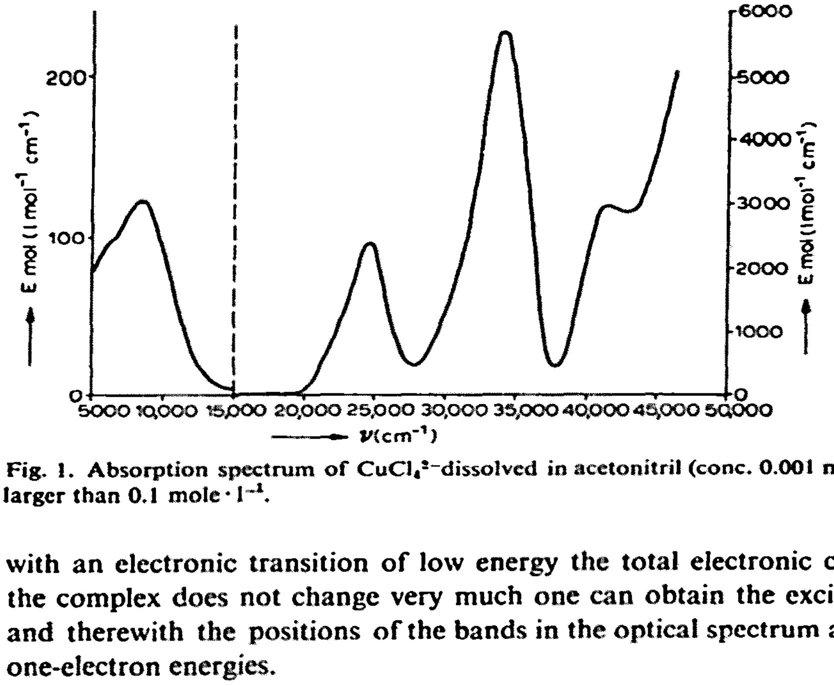

Fig. 1. Absorption spectrum of $CuCl_4^{2-}$-dissolved in acetonitril (conc. 0.001 mole · l^{-1}, Cl^- conc. larger than 0.1 mole · l^{-1}.

The $CuCl_4^{2-}$ complex is a tetragonally distorted tetrahedron. Its structure is intermediate between a tetrahedral and a square planar form, far on the tetrahedral side. The calculation yielded the positions of the crystal field bands rather well. For the charge transfer bands the agreement was less good.

With the one-electron wave functions the electric dipole transition probabilities were evaluated. Group theory was used to find the transitions allowed in each symmetry and their polarizations. In the ground state of the tetrahedral complex there is just one hole in the $4t_2$ orbital; so the ground state has a symmetry $^2T_2$. The allowed transitions with the calculated and measured oscillator strengths are given in Table 1. The calculated values were about a factor 2 too large, but the

TABLE 1

Electron transition	$\nu_{max} = \nu(\text{cm}^{-1})$	$\varepsilon_{max}(\text{l mol}^{-1}\text{cm}^{-1})$	*Exp. f*	*Theor. f*
Crystal field	6,000 8,500	Shoulder 122	0.0037	0.0075
$2e \rightarrow 4t_2$				
First charge transfer				
$t_1 \rightarrow 4t_2$	24,500	2400	0.040	0.080
Second charge transfer				
$3t_2 \rightarrow 4t_2$	34,000	5700	0.120	0.184
Third charge transfer				
$1e \rightarrow 4t_2$	41,000	~1800	0.032	0.052
$2t_2 \rightarrow 4t_2$				0.234
$2a_1 \rightarrow 4t_2$				0.316

relative agreement was so good that it was possible to assign the third charge transfer band to the transition $^2E \leftarrow {}^2T_2(1e \rightarrow 4t_2)$; from the one-electron energies we could not yet decide which one of three possible transitions causes the third charge transfer band.

Finally three remarks may be made:

1. The Wolfsberg–Helmholz method makes use of Valence State Ionization Energies, whereby some assumptions are made about the electronic configurations of the complexes that are difficult to verify. An extension of this method is the method of Differential Ionization Energies: From measured ionization energies for different ionized states a continuous Ionization Energy function is constructed and substituted for the diagonal matrix elements. The optimal electronic configuration is obtained by iteration. In the present method, instead of these empirically obtained parameters, variable atomic orbitals constructed from atomic SCF-orbitals for different configurations, are introduced in the iteration. Excessive complexity is avoided by some approximations. A more detailed description of the method and the results is given in ref. 5.

2. The stable charge distribution in the ground state of tetrahedral CuCl_4^{2-} is: $\text{Cu}^{+0.92}\,4\text{Cl}^{-0.73}$. These numbers are obtained by adding to the positive core charges the negative charges of the electrons in the respective atomic orbitals. Comparison to the purely ionic form $\text{Cu}^{+2.00}4\text{Cl}^{-1.00}$ shows that the bonding in the complex seems to have a considerable covalent contribution. However the charge distribution according to the atomic orbitals is somewhat misleading since *e.g.* the Cu 4s and 4p orbitals have maximum densities in the neighbourhood of the Cl-nuclei. A more spatial separation of charge yields $\text{Cu}^{+1.54}\,4\text{Cl}^{-0.89}$.

3. The calculated transition probabilities are almost entirely determined by integrals over ligand functions only. When π-bonding is neglected, (see *e.g.* Ballhausen and Liehr[6]), the oscillator strengths obtained for transitions to non-bonding metal orbitals, that would otherwise be π-bonding, are much too small.

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