

A Semi-empirical Open Shell SCF-MO Method for Transition Metal Complexes

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An application of the Pariser, Parr, Pople method to transition metal complexes is discussed. Open shell systems are handled according to a method given by Roothaan. Formulas for the matrix elements of the self-consistent field operator in the zero differential overlap approximation are derived. The choice of semi-empirical parameters is discussed. An application is made to the copper complexes $\text{Cu}(\text{NH}_3)_6^{2+}$ and $\text{Cu}(\text{H}_2\text{O})_6^{2+}$. The tetragonal distortion from octahedral symmetry in these complexes is discussed and compared to the results from other investigations.

1. INTRODUCTION AND SUMMARY

In theoretical investigations of π -electron systems in organic molecules, the self-consistent field molecular orbital (SCF-MO) method, with the simplifications introduced by Pariser, Parr^{1,2} and Pople,³ has been applied with surprisingly good results during the last years. The relative simplicity of this method makes it suitable for studies of large molecules, where other more elaborate methods become intractable. The applicability of the method is, however, limited by the approximations introduced, especially the so called zero differential overlap (ZDO) approximation. This approximation has been thoroughly discussed by Fischer-Hjalmars,⁴ who has investigated the limitations for its application. It was shown, by means of a transformation to an orthogonal set of basis orbitals, that the ZDO-approximation is equivalent to the neglect of terms, which are of third and higher order in the overlap integrals between the original atomic orbitals. The author concludes that the ZDO-approximation should be able to give reliable results for systems where the overlap integrals do not exceed 0.4. The Pariser, Parr, Pople (PPP) method is semi-empirical. The integrals needed to build up the Hartree-Fock matrix in the atomic orbital representation are determined from certain experimentally known properties of molecules and atoms, which can be related to these integrals. This circumstance outbalances some of the uncertainties which are introduced with the great simplifications made. The PPP-method has hitherto

been applied mainly to π -electron systems. However, there is no inherent property in the method which prevents its application also to other types of bonding, within the limits set up by the ZDO-approximation.

This paper deals with an attempt to apply the PPP-method to molecular complexes containing transition-metal ions. The molecular orbital description of such complexes has hitherto mainly been made with the Wolfsberg-Helmholtz method.⁵ This method is related to the Hückel theory in the sense, that it is based upon an effective one-electron operator. The matrix elements of this operator are chosen empirically. The diagonal elements are determined from the valence state ionization potentials of the metal and the ligands. The relationship between this choice of parameters and the theoretical expression for the one-electron operator is, however, rather unclear. Thus, for example, the terms in the operator describing the potential field from the ligands have no influence on the diagonal elements for the metal ion orbitals. The off-diagonal elements of the energy matrix, the resonance integrals, are related to the diagonal elements by means of the Wolfsberg-Helmholtz formula or the modification introduced by Ballhausen and Gray.⁶ Both these formulas contain one or two constants, which are to be determined empirically from the ligand field spectra of the system. The Wolfsberg-Helmholtz method has its greatest advantage in its simplicity. Since it is mainly used to interpret spectra of transition-metal complexes, the results obtained are often quite reliable. Sometimes, however, they seem to be fortuitous and only a result of an ambiguous choice of the parameters.

The PPP-method retains some of the simplicity of the Wolfsberg-Helmholtz method, while, on the other hand, it avoids the unclearness in the definition of the parameters, since they are given as matrix elements of clearly specified parts of a self-consistent field Hamiltonian. In the case of a closed shell this operator is the ordinary Hartree-Fock operator. A similar operator is introduced for the open shell case in a method developed by Roothaan⁷ for the treatment of open shell systems. This method is, however, only applicable to systems, with certain types of symmetry of the ground state, where the energy can be expressed by means of three parameters introduced into the theory.

It is felt that the PPP-method makes it possible to do more careful interpretations of the properties of the transition metal complexes, and represents a middle course between the method of Wolfsberg and Helmholtz and, many times very untractable, complete theoretical calculations.

Section 2 gives a brief review of Roothaan's method for open shell systems. The matrix elements occurring in this theory have been evaluated in the ZDO approximation and are given in eqns. (4) — (6).

In section 3 we discuss the relation between these matrix elements and the semi-empirical parameters introduced into the theory. The matrix elements are divided into parts, each of which describes a certain type of interaction. An interpolation formula (10) developed in a previous paper⁹ is used for the two-electron integrals. The diagonal elements of the core operator are treated with the Goepfert-Mayer, Sklar technique¹⁰ (eqns. (14) — (15)). Different methods to determine the resonance integrals are discussed (eqns. (16) — (19)). It is found that the use of more appropriate formulas for these integrals,

including more than one semi-empirical parameter, is at the present stage not feasible, on account of lack of experimental information.

Finally in section 4 the method is applied to two copper complexes, $\text{Cu}(\text{NH}_3)_6^{2+}$ and $\text{Cu}(\text{H}_2\text{O})_6^{2+}$.

2. GENERAL FORMALISM IN THE ZDO APPROXIMATION

Since a closed shell system is a special case of the open shell system, the latter will be discussed here as the general case. A method to find self-consistent molecular orbitals for an open shell system has been given by Roothaan.⁷ This method is based upon an expression of the total electronic energy of the following type.

$$E = 2 \sum_k H_k + \sum_{k,l} (2 J_{kl} - K_{kl}) + f [2 \sum_m H_m + f \sum_{m,n} (2a J_{mn} - b K_{mn}) + 2 \sum_{m,k} (2 J_{km} - K_{km})] \quad (1)$$

The summation indices k and l run over the doubly occupied molecular orbitals while m and n run over the open shell orbitals. If these are degenerate, m and n should run over the complete set of degenerate orbitals. The different terms in (1) are matrix elements in the molecular orbital basis of the full Hamiltonian of the system. Thus the elements H_i are the diagonal elements of the one-electron part of the Hamiltonian and J_{ij} and K_{ij} the Coulomb and exchange integrals. f , a , and b are numerical constants. Only ground states for which the energy can be written according to (1), with suitable choices of the constants, can be treated within the formalism discussed here. As an example, we have for a single electron in a non-degenerate orbital outside a closed shell, $f = \frac{1}{2}$, $a = 1$ and $b = 2$. The closed shell case is obtained with $f = 0$. Generally f is the fractional occupation of the open shell, that is, the number of open shell electrons divided with the total number of available spin-orbitals in the shell.

The molecular orbitals (MO:s) φ_i are expressed as linear combinations of atomic orbitals (AO:s) χ_μ .

$$\varphi_i = \sum_\mu c_{i\mu} \chi_\mu \quad (2)$$

This is inserted into (1). According to the variational principle the energy is minimized with respect to the coefficients $c_{i\mu}$, under the restriction that the MO:s are orthonormal. This gives a matrix equation that determines the coefficients $c_{i\mu}$, analogous to the Hartree-Fock equations. The full expression for this equation has been given by Roothaan⁷ and we shall at this stage introduce the ZDO-approximation and only present the simplified equation. This approximation implies that the product of two atomic orbitals is put equal to zero everywhere in space if the two orbitals are located at different atomic centers. The validity of this approximation has been thoroughly discussed by Fischer-Hjalmarsson⁴ and we refer to that article for this discussion. It should only be noted here that the validity is restricted to the case where the overlap integrals are less than 0.4. This is clearly the case for overlap between $3d$ metal orbitals and ligand orbitals. In most cases it is also true for

the 4s orbital. For the 4p orbital, on the other hand, this restriction is not generally fulfilled. It is felt, however, that this should not be a too disturbing fact, since the contribution of the 4p orbitals to the bonding in most cases is weak.

All matrix elements containing products of atomic orbitals centered at different atoms are thus put equal to zero, except for the resonance integrals for which the ZDO-approximation is not applicable. This leads to the following two simplifications. The overlap matrix becomes a unit matrix. The number of two-electron integrals is heavily reduced. The only remaining integrals are the Coulomb integrals and the one-center exchange integrals. The self-consistent field equations are, expressed as a matrix equation

$$\mathbf{F} \mathbf{c}_i = \varepsilon_i \mathbf{c}_i \quad (3)$$

where \mathbf{c}_i is a column vector specifying the MO φ_i , \mathbf{F} is the energy matrix in the AO representation, and ε_i is the corresponding eigenvalue. In order to specify \mathbf{F} we introduce a new set of matrices:

1. The density matrices for the closed (index C) and the open (index O) shell with the elements

$$(P_C)_{\mu\nu} = \sum_k 2 c_{k\mu} c_{k\nu} \quad (4a)$$

$$(P_O)_{\mu\nu} = f \sum_m 2 c_{m\mu} c_{m\nu} \quad (4b)$$

The total density matrix \mathbf{P}_T is the sum of \mathbf{P}_C and \mathbf{P}_O .

2. Closed and open shell Coulomb (\mathbf{J}) and exchange (\mathbf{K}) matrices, with the elements

$$(J_C)_{\mu\nu} = \frac{1}{2} \sum_{\lambda} (P_C)_{\lambda\lambda} \gamma_{\lambda\nu} \delta_{\mu\nu} + (P_C)_{\mu\nu} \kappa_{\mu\nu} \quad (5a)$$

$$(J_O)_{\mu\nu} = \frac{1}{2} \sum_{\lambda} (P_O)_{\lambda\lambda} \gamma_{\lambda\nu} \delta_{\mu\nu} + (P_O)_{\mu\nu} \kappa_{\mu\nu} \quad (5b)$$

$$(K_C)_{\mu\nu} = \frac{1}{2} \sum_{\lambda} (P_C)_{\lambda\lambda} \kappa_{\lambda\nu} \delta_{\mu\nu} + \frac{1}{2} (P_C)_{\mu\nu} (\gamma_{\mu\nu} + \kappa_{\mu\nu}) \quad (5c)$$

$$(K_O)_{\mu\nu} = \frac{1}{2} \sum_{\lambda} (P_O)_{\lambda\lambda} \kappa_{\lambda\nu} \delta_{\mu\nu} + \frac{1}{2} (P_O)_{\mu\nu} (\gamma_{\mu\nu} + \kappa_{\mu\nu}) \quad (5d)$$

Here $\gamma_{\mu\nu}$ is the two-electron Coulomb integral and $\kappa_{\mu\nu}$ the exchange integral. The latter is only different from zero if the AO:s χ_{μ} and χ_{ν} belong to the same center. The total Coulomb and exchange matrices \mathbf{J}_T and \mathbf{K}_T are defined as the sum of the closed and open shell matrices.

3. The total Coulomb and exchange coupling matrices \mathbf{L}_T and \mathbf{M}_T defined by Roothaan. They can be written as matrix products.

$$\mathbf{L}_T = \frac{1}{2} [\mathbf{P}_T \mathbf{J}_O + \mathbf{J}_O \mathbf{P}_T] \quad (6a)$$

$$\mathbf{M}_T = \frac{1}{2} [\mathbf{P}_T \mathbf{K}_O + \mathbf{K}_O \mathbf{P}_T] \quad (6b)$$

By means of (4a) – (6b) the matrix \mathbf{F} occurring in (3) is specified in terms of the density matrices and integrals in the AO representation.

$$\mathbf{F} = \mathbf{H} + 2 \mathbf{J}_T - \mathbf{K}_T + 2 \alpha (\mathbf{L}_T - \mathbf{J}_O) - \beta (\mathbf{M}_T - \mathbf{K}_O) \quad (7)$$

where \mathbf{H} is the matrix, in the AO representation, of the one-electron part of the Hamiltonian for the electronic system. Two new numerical constants, α and β , are introduced in (7). They are related to f , a , and b occurring in (1) in the following way.

$$\alpha = (1 - a)/(1 - f) \quad (8a)$$

$$\beta = (1 - b)/(1 - f) \quad (8b)$$

In the case of one electron in a non-degenerate orbital outside a closed shell we have $\alpha = 0$ and $\beta = -2$. For the closed shell case \mathbf{F} is the usual Hartree-Fock matrix.

Eqn. (3) is solved by an iteration procedure in exactly the same way as in the closed shell case. As a final result self-consistent closed and open shell eigenvectors and density matrices are obtained. It should be noted that the eigenvalues ε_i are not in general "orbital energies" in the meaning used for closed shell systems. However, under the assumption that ionized states can be described with the same MO:s as the ground state, ionization energies w_i for the different MO:s φ_i can be defined. The formulas determining these will be different for different structure of the ground state, that is, different values of f , a , and b . Here we will only give the expressions for w_i in the case of one electron outside a closed shell. We have in this case

$$w_m = -\varepsilon_m + \frac{1}{2} (mm|mm) \quad (9a)$$

where m refers to the open shell orbital and $(mm|mm)$ is the two-electron integral for the orbital φ_m . For the closed shell orbital φ_k we have two expressions depending upon which spin state the ionized molecule is left in.

$${}^3w_k = -\varepsilon_k + \frac{1}{2} (km|km) \quad (9b)$$

$${}^1w_k = -\varepsilon_k + \frac{5}{2} (km|km) \quad (9c)$$

for the triplet and singlet case respectively. Here $(km|km)$ is the exchange integral between the orbitals φ_k and φ_m .

The outlined procedure has been programmed in FORTRAN IV language by the author in collaboration with Dr. Torbjörn Alm. The program handles the excited states by means of configuration interaction where all singly excited states are taken into account. Of course, this cannot be done for the general case. It is, however, possible to treat singlet and triplet states arising from closed shell ground states, and all doublet states occurring, when an electron is excited from a ground state containing one open shell electron. Most molecules and complexes fall within this region.

3. CHOICE OF SEMI-EMPIRICAL PARAMETERS

The number of integrals over atomic orbitals occurring in (7) is heavily reduced by the introduction of the ZDO-approximation. The remaining integrals are of two types, one-electron integrals occurring in the core matrix \mathbf{H} and two-electron integrals of Coulomb and exchange type. As far as possible these integrals are treated as semi-empirical parameters to be determined from measurements on atoms and molecules. For π -electron systems mainly

three sources of experimental information have been used for this purpose. Atomic spectra have been used to determine the one-center two-electron integrals. The one-electron integrals are deduced from the ionization potentials and UV spectra of certain model molecules. A general scheme for the evaluation of semi-empirical parameters for π -electron systems has been given by Fischer-Hjalmar.⁸ The lack of experimental information, together with the increased complexity of the systems, makes this procedure more uncertain for the transition metal complexes. It is thus, as an example, not possible at the present stage, to treat the penetration integrals occurring in the diagonal elements of the core matrix wholly semi-empirically owing to the missing information on ionization potentials for most transition metal complexes.

3a. Two-electron integrals

The one-center two-electron integrals can in most cases be determined from atomic spectral data. The integrals are expressed in terms of Slater-Condon parameters. These are calculated from the energies of different terms and configurations of the atom under consideration. In some cases the spectral information is not able to give all the Slater-Condon parameters. For this case Fischer-Hjalmar⁸ has suggested a method in which empirical and theoretically calculated Slater-Condon parameters are assumed to be proportional. The proportionality constant is calculated from parameters, which are possible to obtain from spectra. Another possibility is to include information from ions of different charges. This has been done in this paper in the application to copper complexes. However, this method has the disadvantage, that it does not take into consideration the charge dependency of the two-electron integrals.

In a previous paper⁹ we have discussed a method for the estimation of the two-center Coulomb integrals. This method has the advantage, that it does not necessitate knowledge about the theoretical values of these integrals as other methods do. The two-center Coulomb integrals between the AO:s χ_μ and χ_ν are expressed in terms of one-center integrals $\gamma_{\mu\mu}$ and $\gamma_{\nu\nu}$ and the distance R between the orbitals.

$$\gamma_{\mu\nu}(R) = \frac{1}{2}(\gamma_{\mu\mu} + \gamma_{\nu\nu}) f(z) \quad (10)$$

where $f(z)$ is a function of the parameter $z = \frac{1}{2}(\gamma_{\mu\mu} + \gamma_{\nu\nu}) R$.

$$f(z) = 1/(z + e^{-z}) \quad (11)$$

This function was discussed in a previous paper,⁹ where it was applied to π -orbitals. If the distance R is defined as the distance between the centers of gravity for the two orbitals the method seems to give appropriate values for the Coulomb integrals also for other types of orbitals.

3b. One-electron integrals

The one-electron part of the operator (7) has the following form

$$H^{\text{core}} = T + U^{\text{core}}(\text{Me}) + \sum_i U^{\text{core}}(L_i) \quad (12)$$

Here T denotes the kinetic energy operator, $U^{\text{core}}(\text{Me})$ the potential field from the metal core and $U^{\text{core}}(\text{L}_i)$ the corresponding field from ligand i . The summation is to be taken over all ligands. These ligands can either be atoms as for example in the metal halogens, dipolar molecules as water or ammonia, or larger molecular entities as in the metal chelates.

We define the parameter α_μ as the diagonal matrix element of H^{core} for the orbital χ_μ .

$$\alpha_\mu = \langle \mu | H^{\text{core}} | \mu \rangle \quad (13)$$

If χ_μ is a metal orbital this parameter is broken up into three parts.

$$\alpha_\mu(\text{Me}) = \langle \mu | T + U^{\text{core}}(\text{Me}) | \mu \rangle - \sum_i \sum_{\nu(i)} n_{\nu(i)} \gamma_{\mu\nu(i)} + \sum_i \langle \mu | U^0(\text{L}_i) | \mu \rangle \quad (14)$$

The first term in this expression gives the interaction between a metal electron and the metal core. This interaction can be estimated from ionization potentials of the metal atom, together with the two-electron integrals deduced from atomic spectral data. The second and third terms give the interaction with the ligands. Here $n_{\nu(i)}$ is the number of electrons associated with the atomic orbital $\chi_{\nu(i)}$ at ligand i . Thus the sum of all $n_{\nu(i)}$ for a certain ligand will give the charge of the core of this ligand. The interaction between a metal orbital and a ligand core is divided into two parts. In the second term the ligand core is reduced to zero charge by means of two-electron integrals according to a method first used by Goeppert-Mayer and Sklar.¹⁰ The third part of (14) represents the penetration between a metal orbital and a neutral ligand. This integral seems at present to be difficult to estimate semi-empirically. The corresponding integrals occurring in the π -electron theory are often incorporated into the one-center term in (14). The parameter defined in this way is then determined from molecular ionization potentials. This method could not be used here because of the lack of experimental information. Some other way to estimate these integrals must be employed. For neutral molecules they are small and can probably, at least as a first approximation, be neglected. For ionic metal complexes, with highly polarized ligands, however, they give an appreciable contribution to the parameters α_μ , and cannot be neglected. One rather crude way to estimate them in this case, which has been applied in the applications of the theory made in this paper, is to consider the ligands as point dipoles.

The core integral $\alpha_{\nu(i)}$ over the ligand orbital $\nu(i)$ can be decomposed in the same way as in (14). We obtain for this case

$$\begin{aligned} \alpha_{\nu(i)}(\text{L}_i) = & \langle \nu(i) | T + U^{\text{core}}(\text{L}_i) | \nu(i) \rangle - \sum_\mu n_\mu \gamma_{\mu\nu(i)} + \langle \nu(i) | U^0(\text{Me}) | \nu(i) \rangle - \\ & - \sum_{j \neq i} \sum_{\nu(j)} n_{\nu(j)} \gamma_{\nu(i)\nu(j)} + \sum_{j \neq i} \langle \nu(i) | U^0(\text{L}_j) | \nu(i) \rangle \end{aligned} \quad (15)$$

The "one-center" part of (15) is not in this case a purely atomic integral, since the atom contributing the ligand electrons is not in general isolated but a part of a ligand molecule. The first term in (15) is therefore not in general to be determined from atomic ionization potentials, but from properly chosen molecular ionization potentials. Examples of this will be given in the applications made later in this paper. The ligand-metal and ligand-ligand interactions

are as in (14) reduced to zero charge by means of the Goeppert-Mayer, Sklar technique. The ligand-ligand penetration term can be handled in the same way as the metal-ligand penetration in (14). In the applications made here the ligand-metal penetration has been neglected. It is probably small, since the metal atom is not polarized. However, it should be emphasized that it is probably a crude approximation to neglect all these terms. Further investigations on this point are desirable.

The off-diagonal elements of the core matrix, the resonance integrals, are denoted $\beta_{\mu\nu}$ and given by

$$\beta_{\mu\nu} = \langle \mu | H^{\text{core}} | \nu \rangle \quad (\mu \neq \nu) \quad (16)$$

Different methods have been used to treat these integrals, all of them containing one or more empirical parameters. These parameters are determined from the spectra of some chosen model molecules. The most frequently used approximation for transition-metal complexes is the equation introduced by Wolfsberg and Helmoltz,⁵ where the resonance integral is assumed to be proportional to the overlap $S_{\mu\nu}$ between the orbitals χ_{μ} and χ_{ν} .

$$\beta_{\mu\nu} = \frac{k}{2} S_{\mu\nu} (W_{\mu} + W_{\nu}) \quad (17)$$

where W_{μ} and W_{ν} are atomic ionization potentials for the orbitals χ_{μ} and χ_{ν} , respectively. In the formalism employed here these quantities should be defined as

$$W_{\mu} = \langle \mu | T + U^+(\text{Me}) | \mu \rangle \quad (18)$$

for the metal orbitals and corresponding expressions for the ligand orbitals. Thus for metal orbitals W_{μ} is defined as the valence state ionization potential of the orbital under consideration and for the ligands as a molecular ionization potential. The constant k is an empirical parameter, which sometimes is given different values for different metal orbitals, when (17) is used in the Wolfsberg-Helmoltz method. A similar expression for the resonance integral has been suggested by Ballhausen and Gray,⁶ where the arithmetic mean value of the ionization potentials is replaced by a geometric mean. It is not easy to give a theoretical interpretation of these formulas for $\beta_{\mu\nu}$. It has, however, been shown by Fischer-Hjalmars⁴ that it is consistent with the ZDO-approximation to use an expression for $\beta_{\mu\nu}$ not very different from (17).

$$\beta_{\mu\nu} = \frac{1}{2} S_{\mu\nu} (A_{\mu} + A_{\nu}) \quad (19)$$

Thus the proportionality between $\beta_{\mu\nu}$ and $S_{\mu\nu}$ is retained. The entities A_{μ} and A_{ν} are, however, not intimately related to ionization potentials, but should be treated merely as semi-empirical parameters. This formula was used in a previous application to π -electron systems⁹ with promising results. However, since there is one parameter associated to each type of atomic orbital, a direct application to transition-metal complexes seems to be difficult to accomplish. Calculations on a series of complexes might, however, give enough information about the resonance integrals, making it possible to estimate these parameters. They have "local" character, in the sense given by the ZDO-approximation, and are therefore transferable from one complex to another once they have been determined.

4. APPLICATION TO COPPER COMPLEXES

In order to test the formalism discussed in the previous sections we have applied it to two copper complexes. Since the method later will be applied to complexes containing copper-nitrogen bonds we have chosen the ionic complex $\text{Cu}(\text{NH}_3)_6^{2+}$ as one of these applications. Discussions of the ligand field spectrum of this and similar complexes have been given by Bjerrum *et al.*¹¹ They used an electrostatic model, where the ligands were replaced by point dipoles. According to their results the ligand field spectrum can be explained only if one assumes for the structure of the complex a slightly distorted octahedron with two of the ammonia molecules at larger distances from the copper ion (Fig. 1). The spectrum of $\text{Cu}(\text{NH}_3)_6^{2+}$ was resolved by Bjerrum *et al.*¹¹ into two absorption bands with frequencies $11\,700\text{ cm}^{-1}$ and $15\,600\text{ cm}^{-1}$. By means of these values a numerical value of the parameter k occurring in the resonance integral (17) has been determined. In order to check this parameter choice calculations have also been performed on the similar complex $\text{Cu}(\text{H}_2\text{O})_6^{2+}$, for which the ligand field spectrum has also been analysed.¹¹

4a. $\text{Cu}(\text{NH}_3)_6^{2+}$

The copper nitrogen distance R_p in the xy -plane (Fig. 1) was assumed to be 2.05 \AA in accordance with measurements on corresponding distances in crystal structures. The axial distance (R_{ax}) is, however, more difficult to estimate and will be treated as a parameter free for variation in the calculations. The complex is treated as a 21 electron problem with 9 electrons contributed by the metal and 2 from each of the lone pairs of the ammonia molecules. The atomic orbitals used are the $3d$ and $4s$ orbitals of copper and one sp^3 hybrid from each nitrogen, altogether 12 orbitals. Usually the $4p$ orbitals of the metal atom are also included in the basis set. There are several reasons not to do this here. The $4p$ orbitals give only a small contribution to the bonding and they do not affect the ligand field spectra since the MO:s contributing to this are different in symmetry. Thus the $4p$ orbitals do not have much significance for the results discussed here. Furthermore the semi-empirical parameters evaluated for these orbitals are very uncertain due to missing experimental information.

The one-center two-electron integrals for the copper orbitals (Table 1) have been evaluated from the spectra of Cu and Cu^+ . The spectral data have been taken from Moore's tables.¹² These integrals are charge dependent and ought to be determined both from the spectrum of Cu and also from the spectrum of Cu^+ . However, the spectral information then becomes incomplete. Calculations on iron to be published later have shown that the charge dependence is weak. The neglect of this is therefore no serious restriction. In a previous paper⁹ a method to calculate two-electron integrals for the elements C, N, and O was discussed and the integrals for π -electrons were tabulated. In Table 2 we have collected all other integrals for the valence electron of these elements, which have been evaluated with the same method. By means of this table we find the value 17.24 eV for the two-electron integral for the sp^3

Table 1. Two-electron integrals for Cu orbitals in eV.

Coulomb integrals		Exchange integrals	
$J(4s,4s) =$	8.32	$K(4s,3d) =$	0.22
$J(4s,3d) =$	9.86	$K(z^2,xz) = K(z^2,yz) =$	0.55
$J(z^2,z^2) = J(x^2 - y^2, x^2 - y^2) =$	17.43	$K(z^2,xy) = K(z^2, x^2 - y^2) =$	1.10
$J(xy,xy) = J(xz,xz) = J(yz,yz) =$	17.43	$K(xz,yz) = K(xy,yz) = K(xy,xz) =$	0.91
$J(z^2,xz) = J(z^2,yz) =$	16.33	$K(xz, x^2 - y^2) = K(yz, x^2 - y^2) =$	0.91
$J(z^2,xy) = J(z^2, x^2 - y^2) =$	15.24	$K(xy, x^2 - y^2) =$	0.37
$J(xz,yz) = J(xy,yz) = J(xy,xz) =$	15.60		
$J(xz, x^2 - y^2) = J(yz, x^2 - y^2) =$	15.60		
$J(xy, x^2 - y^2) =$	16.69		

hybrid on nitrogen. The two-center Coulomb integrals are calculated according to (10) where R is the distance from the center of gravity of the nitrogen sp^3 orbital to the metal atom and corresponding distances for the ligand-ligand interactions.

Table 2. Two-electron integrals for the elements C, N, O in eV.

Elements	C ⁺	C	C ⁻	N ⁺	N	N ⁻	O ⁺	O	O ⁻
$J(2s,2s) = J(2s,2p)$	12.84	11.11	9.38	16.05	14.32	12.59	19.27	17.54	15.81
$J(x,y) = J(x,z) = J(y,z)$	12.34	10.68	9.02	15.43	13.77	12.11	18.52	16.86	15.20
$K(2s,2p)$	2.83	2.59	2.22	3.41	3.06	2.79	3.89	3.66	—
$K(x,y) = K(x,z) = K(y,z)$	0.75	0.65	0.54	0.93	0.83	0.73	1.12	1.02	0.92

The one-electron integrals $\alpha(\text{Me})$ and $\alpha(\text{L}_i)$ are according to (14) and (15) divided into three parts, the one-center term, the interaction with other charges, and the penetration integrals. For the Cu orbitals the first term is easily evaluated by means of two-electron integrals and the ionization potentials for $4s$ and $3d$ respectively. They are found from Moore's tables¹² to be 7.72 eV for $4s$ and 10.65 eV for $3d$. The "one-center" term of the ligand parameter $\alpha(\text{L}_i)$ is divided into two parts.

$$\langle \sigma(i) | T + U^{\text{core}}(\text{L}_i) | \sigma(i) \rangle = \langle \sigma(i) | T + U^+(\text{L}_i) | \sigma(i) \rangle - \gamma_{\sigma(i)\sigma(i)} \quad (20)$$

where σ stands for a nitrogen sp^3 hybrid. The first term in (20), where $U^+(\text{L}_i)$ is the potential from an ammonia molecule with charge plus one, is minus the ionization potential for a lone pair electron in this molecule. This ionization potential has been determined by Joubury and Turner¹³ and was found to be 10.16 eV.

The penetration integrals occurring in (14) and (15) have been roughly estimated as follows. The ligands were treated as point dipoles, the moments of which have been calculated as the sum of the permanent moment of NH_3 (1.47 D)¹⁴ and the moment induced by a charge of plus two at the metal site. This last moment has been calculated with use of the polarizability of the nitrogen atom ($1.13 \times 10^{-24} \text{ cm}^3$).¹⁵ The dipole moments found by this method agree in magnitude with the results obtained by Bjerrum *et al.*¹¹ by means of the electrostatic model. As an example the calculated moment at the distance 2.05 Å is 4.04 D. The penetration integrals have been estimated as the interaction energies between these dipoles and an electronic charge situated at the center of gravity of the orbital in question. The penetration integrals found in this way are of considerable magnitude; as an example, the energy contribution to a $3d$ orbital from a planar dipole is 2.89 eV. It must therefore be emphasized that the method used here to determine these integrals is crude. However, the results of interest in this paper, the ligand field spectra, are not very sensitive to moderate changes in the penetration terms, since they contribute with energies of the same magnitude to each $3d$ orbital. They will, however, be of great importance in discussions of charge-transfer spectra. Furthermore, the special importance of the penetration integrals in ionic complexes should be noticed. For neutral complexes they will be smaller and not have the same influence on the results.

For the determination of the resonance integrals $\beta_{\mu\nu}$ we have used the Wolfsberg-Helmholtz formula (17), where k is treated as an empirical parameter to be determined from the ligand field spectrum. There is no reason to believe that k should have the same value in this formalism as in the Wolfsberg-Helmholtz method. The limited information about the complexes studied here makes it impossible to use the probably more appropriate formula (19). The overlap integrals needed in (17) must be calculated theoretically. For this purpose the self-consistent field atomic orbitals for copper published by Watson¹⁶ have been used. Slater type orbitals have been used for nitrogen. With these orbitals we have found the following overlap integrals at the interatomic distance 2.05 Å, $S(4s, \sigma_i) = 0.2637$, $S(z^2, \sigma_i) = -0.0405$, $S(xy, \sigma_i) = 0.0701$, with σ_i in the symmetry plane of the complex.

From the six atomic orbitals σ_i , belonging to the ligands L_i we can construct symmetry orbitals corresponding to the symmetry group D_{4h} with the axes as in Fig. 1.

$$\begin{aligned}
 \sigma_p(a_{1g}) &= \frac{1}{2}(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4) \\
 \sigma_{ax}(a_{1g}) &= \frac{1}{\sqrt{2}}(\sigma_5 + \sigma_6) \\
 \sigma_{ax}(a_{2u}) &= \frac{1}{\sqrt{2}}(\sigma_5 - \sigma_6) \\
 \sigma_p(b_{2g}) &= \frac{1}{2}(\sigma_1 - \sigma_2 + \sigma_3 - \sigma_4) \\
 \sigma_p(e_u) &= \frac{1}{\sqrt{2}}(\sigma_1 - \sigma_3); \frac{1}{\sqrt{2}}(\sigma_2 - \sigma_4)
 \end{aligned} \tag{21}$$

The MO:s are linear combinations of these symmetry orbitals and metal orbitals $3d$ and $4s$. In Table 3 the MO:s are given together with the eigenvalues of the operator (7) for the case $R_{ax} = 2.25 \text{ \AA}$. From this table we calculate the

Table 3. Molecular orbitals φ_i and eigenvalues ε_i for $\text{Cu}(\text{NH}_3)_6^{2+}$, with $k = 2.9$ and $R_{ax} = 2.25 \text{ \AA}$.

φ_i	ε_i (a.u.)	Orbital coefficients
$1a_{1g}$	-1.1283	$0.5733(4s) - 0.0543(z^2) + 0.7134 \sigma_p(a_{1g}) + 0.3993 \sigma_{ax}(a_{1g})$
$2a_{1g}$	-0.7609	$0.0449(4s) + 0.5618(z^2) - 0.3984 \sigma_p(a_{1g}) + 0.7237 \sigma_{ax}(a_{1g})$
b_{2g}	-0.7534	$0.3907(xy) + 0.9205 \sigma_p(b_{2g})$
e_u	-0.6801	$\sigma_p(e_u)$
a_{2u}	-0.6717	$\sigma_{ax}(a_{2u})$
b_{1g}	-0.6658	$(x^2 - y^2)$
e_g	-0.6066	$(xz), (yz)$
$3a_{1g}$	-0.5045	$0.0341(4s) + 0.8251(z^2) + 0.3020 \sigma_p(a_{1g}) - 0.4783 \sigma_{ax}(a_{1g})$
b_{2g}^*	-0.3242	$0.9205(xy) - 0.3907 \sigma_p(b_{2g})$
$4a_{1g}$	+0.3739	$0.8174(4s) - 0.0272(z^2) - 0.4911 \sigma_p(a_{1g}) - 0.2998 \sigma_{ax}(a_{1g})$

charge on copper to be +1.18. The covalency factor of the odd electron in the orbital b_{2g}^* is 0.85, a value which seems to be in agreement with the results obtained from electron paramagnetic resonance measurements on nitrogen bonded copper chelates by Wiersema and Windle.¹⁷ The covalency factors published by them lie in the range 0.62–0.84. One should expect the corresponding value for $\text{Cu}(\text{NH}_3)_6^{2+}$ to be higher on account of the weaker bonding in this complex.

The spectrum of $\text{Cu}(\text{NH}_3)_6^{2+}$ has been calculated as a function of the distance R_{ax} from the metal position to the axial nitrogens. All singly excited

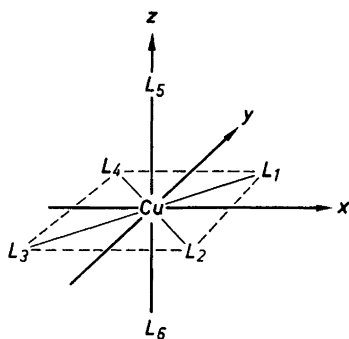


Fig. 1. Structure of the complexes $\text{Cu}(\text{NH}_3)_6^{2+}$ and $\text{Cu}(\text{H}_2\text{O})_6^{2+}$. L_1 – L_6 labels the ligand positions.

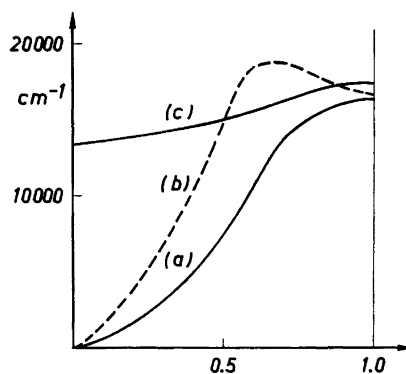


Fig. 2. Ligand field spectrum as a function of tetragonality for $\text{Cu}(\text{NH}_3)_6^{2+}$ with $k = 2.9$. (a): A_{1g} with Cl, (b): A_{1g} without Cl, (c): B_{1g} and E_g .

doublet states, constructable from the MO:s found for the ground state, are taken into account in configurational interaction. In Fig. 2 the ligand field spectrum is given as a function of a tetragonality parameter λ defined as

$$\lambda = \sqrt{1 - (R_p/R_{ax})^2} \quad (22)$$

The tetragonality parameter varies from zero for octahedral to one for square planar symmetry. There are three ligand field transitions, A_{1g} ($3a_{1g} \rightarrow b_{2g}^*$), E_g ($e_g \rightarrow b_{2g}^*$) and B_{1g} ($b_{1g} \rightarrow b_{2g}^*$). However, due to the absence of π -bonding the state E_g and B_{1g} are found to be almost degenerate. They are drawn as one line in the spectrum. These levels are identified with the absorption band with frequency $15\,600\text{ cm}^{-1}$ found by Bjerrum *et al.* The second absorption band at $11\,700\text{ cm}^{-1}$ is attributed to the state A_{1g} . Using these assignments agreement between theory and experiment is obtained with $k = 2.88$ and $R_{ax} = 2.60\text{ \AA}$ ($\lambda = 0.62$). The calculated value of R_{ax} is not in agreement with the tetragonality obtained by Bjerrum *et al.*¹¹ They found the tetragonality to be small with λ around 0.3–0.4. In order to investigate this point more carefully we have also calculated the cohesive energy in the axial bonds as a function of the internuclear distance R_{ax} . This energy is defined as follows

$$E_{\text{coh}}(R_{ax}) = E_{\text{el}}(R_{ax}) + E_{\text{core}}(R_{ax}) - E_{\text{el}}(\infty) - E_{\text{core}}(\infty) \quad (23)$$

The core energy $E_{\text{core}}(R_{ax})$ was calculated as the sum of interactions of the types, charge-charge, charge-dipole, and dipole-dipole. The cohesive energy (Fig. 3) shows a shallow minimum at around 2.20 \AA with a depth of 10 kcal. This tetragonality is in agreement with the previous results¹¹ discussed above. However, this result should be interpreted with caution, since the energy differences occurring in the cohesive energy are of the same order of magnitude as the uncertainties in the calculations. As is seen from Fig. 3 the cohesive energy is positive. Thus, there is no net stabilization. However, this corresponds to the vacuum case. The behaviour of the ammonia molecules at large distances in the solution is difficult to predict. The calculations on $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ indicate, on the other hand, as will be seen later that the higher degree of tetragonality predicted from the spectrum is correct. It is therefore difficult to draw any definite conclusions on this point.

The great importance of configurational mixing for the state A_{1g} should be noticed (Fig. 2). The interaction between this state and the A_{1g} state $2a_{1g} \rightarrow b_{2g}^*$ is strong ($21\,000\text{ cm}^{-1}$ for $R_{ax} = 2.25\text{ \AA}$) and leads to a considerable decrease in energy of A_{1g} . Most calculations done hitherto have not paid any attention to this. If configurational interaction had not been included the obtained degree of tetragonality would have been much lower ($\lambda \approx 0.4$). This might be one of the reasons for the discrepancy with the results of Bjerrum *et al.*¹¹

The obtained value of 2.88 for the parameter k seems to be within the expected limits. One should expect this parameters to be higher in this formalism than in the Wolfsberg-Helmholtz method, on account of the different definition of the resonance integral. The parameter k is almost independent of the degree of tetragonality, and therefore insensitive to moderate changes in

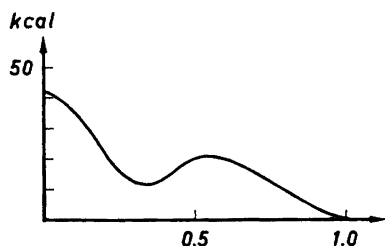


Fig. 3. Cohesive energy for $\text{Cu}(\text{NH}_3)_6^{2+}$ as a function of tetragonality ($k = 2.9$).

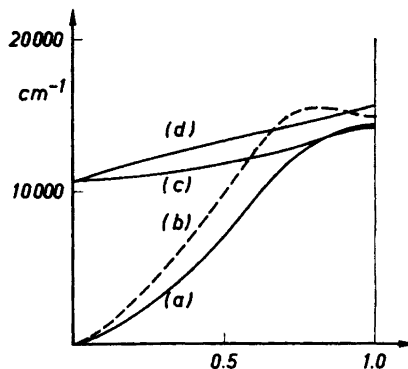


Fig. 4. Ligand field spectrum of $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ as a function of tetragonality with $k = 2.88$. (a): A_{1g} with CI, (b): A_{1g} without CI, (c): B_{1g} , (d): E_g .

this uncertain parameter. If the states B_{1g} and E_g are to fit with the absorption band at $15\,600\text{ cm}^{-1}$ k varies only from 3.07 to 2.88 when R_{ax} varies from 2.05 Å (octahedral symmetry) to 2.60 Å.

4b. $\text{Cu}(\text{H}_2\text{O})_6^{2+}$

In order to test the obtained value of the parameter k this complex has also been investigated. The treatment is quite similar to that discussed above, the only difference being the inclusion of π -bonding. The complex has been treated as a 29-electron problem with bonding between the metal orbitals and both the lone pairs of the planar water molecules (1–4), but only with the σ lone pair of the axial molecules (5–6). The σ lone pairs have been considered as sp^3 -hybrids of oxygen in accordance with the results obtained in an *ab initio* calculation on the water molecule by Ellison and Shull.¹⁸ The π -orbitals of the planar water molecules are supposed to lie in the plane enclosing the four oxygens. They are then able to form a strong π -bond with the metal orbital b_{1g} . The axial ligands are too distant for π -bonding to be of importance. Thus the following four symmetry orbitals must be added to (21) to give the full basis set in this case:

$$\begin{aligned} \pi_p(a_{2g}) &= \frac{1}{2}(\pi_1 - \pi_2 + \pi_3 - \pi_4) \\ \pi_p(b_{1g}) &= \frac{1}{2}(\pi_1 + \pi_2 + \pi_3 + \pi_4) \\ \pi_p(e_u) &= \frac{1}{\sqrt{2}}(\pi_1 - \pi_3); \frac{1}{\sqrt{2}}(\pi_2 - \pi_4) \end{aligned} \quad (24)$$

The metal oxygen distance in the xy -plane is assumed to be 1.97 Å, which is the normal distance in the solid state for bonding of this type. The axial distance has been varied as in the case of $\text{Cu}(\text{NH}_3)_6^{2+}$.

Ionization potentials for the water molecule have been given by Joubury and Turner.¹³ The two lowest potentials are found to be 12.61 eV and 14.23 eV. They have been attributed to the π lone pair and the σ lone pair, respectively, and used to determine the matrix elements (20).

Table 4. Molecular orbitals φ_i and eigenvalues ε_i for $\text{Cu}(\text{H}_2\text{O})_6^{2+}$, with $k = 2.88$ and $R_{\text{ax}} = 2.40 \text{ \AA}$.

φ_i	ε_i (a.u.)	Orbital coefficients
$1a_{1g}$	-1.3292	$0.5408(4s) - 0.0887(z^2) + 0.7772 \sigma_p(a_{1g}) + 0.3093 \sigma_{\text{ax}}(a_{1g})$
b_{2g}	-0.9554	$0.3331(xy) + 0.9429 \sigma_p(b_{2g})$
$2a_{1g}$	-0.8850	$0.0644(4s) + 0.3583(z^2) - 0.3478 \sigma_p(a_{1g}) + 0.8640 \sigma_{\text{ax}}(a_{1g})$
$1e_u$	-0.8848	$\sigma_p(e_u)$
$1b_{1g}$	-0.8555	$0.4113(x^2 - y^2) + 0.9114 \pi_p(b_{1g})$
a_{2u}	-0.8383	$\sigma_{\text{ax}}(a_{2u})$
$2e_u$	-0.8282	$\pi_p(e_u)$
a_{2g}	-0.8262	$\pi_p(a_{2g})$
$2b_{1g}^*$	-0.7061	$0.9114(x^2 - y^2) - 0.4113 \pi_p(b_{1g})$
e_g	-0.6696	$(xz), (yz)$
$3a_{1g}$	-0.6092	$0.0746(4s) + 0.9279(z^2) + 0.1804 \sigma_p(a_{1g}) - 0.3178 \sigma_{\text{ax}}(a_{1g})$
b_{2g}^*	-0.3938	$0.9429(xy) - 0.3331 \sigma_p(b_{2g})$
$4a_{1g}$	0.3203	$0.8354(4s) - 0.4924 \sigma_p(a_{1g}) - 0.2385 \sigma_{\text{ax}}(a_{1g})$

Molecular orbitals and eigenvalues are found in Table 4. The net charge on copper is found to be +1.20 and the covalency factor is 0.89.

The absorption spectrum of $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ has also been analyzed by Bjerrum *et al.*¹¹ They found two absorption bands with maxima at 9400 cm^{-1} and 12700 cm^{-1} , respectively. If the first transition is attributed to the A_{1g} state the axial distance is found to be 2.43 \AA with $k = 2.88$ (Fig. 4). With this value of R_{ax} the states B_{1g} and E_g are expected to absorb at the frequencies 12010 cm^{-1} and 13760 cm^{-1} . The mean value of these energies is 12890 cm^{-1} which is in agreement with the observed peak at 12700 cm^{-1} . Also in this case the tetragonality is unexpectedly high.

It is interesting to compare the spectrum in Fig. 2 with the spectrum of $\text{CuSO}_4(\text{H}_2\text{O})_5$ which has been discussed by Holmes and McClure.¹⁹ In that case the copper atom is surrounded by four water oxygens at a distance of 1.98 \AA and two sulfate oxygens at an average distance of about 2.40 \AA .²⁰ The symmetry is the same as that of $\text{Cu}(\text{H}_2\text{O})_6^{2+}$. An attempt was made by Holmes and McClure¹⁹ to resolve the ligand field spectrum of the complex into three absorption bands. The best fit to the observed absorption curve was obtained with the frequencies 10500 cm^{-1} , 13000 cm^{-1} , and 14500 cm^{-1} . If we, in accordance with Fig. 4, assign these frequencies to the states A_{1g} , B_{1g} , and E_g and choose $R_{\text{ax}} = 2.5 \text{ \AA}$ we obtain the frequencies 10500 cm^{-1} , 12200 cm^{-1} , and 14000 cm^{-1} . It is interesting to notice that the axial distance calculated in this way is in rather good agreement with experiment. Thus it might be possible to give some significance to the tetragonality found for $\text{Cu}(\text{NH}_3)_6^{2+}$

and $\text{Cu}(\text{H}_2\text{O})_6^{2+}$. It should, however, be noticed, that the resolution made by Holmes and McClure¹⁹ is rather uncertain and, further, that the sulphate oxygens are not quite similar to the water oxygens. Holmes and McClure¹⁹ suspected that the A_{1g} state might absorb at lower frequencies. They therefore studied the absorption of $\text{CuSO}_4(\text{D}_2\text{O})_5$ down to $4\,000\text{ cm}^{-1}$. They found no absorption bands in this region. Therefore they concluded that the A_{1g} state should be one of the three bands localized in the near infrared region, in agreement with our results.

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