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ENERGY LEVELS OF ORTHOAXIAL  
CHROMOPHORES AND THE INTERRELATION  
BETWEEN CUBIC PARENT  
CONFIGURATIONS

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## Synopsis

The Angular Overlap Model, i.e. an LCAO MO approximation equivalent to a contact term perturbation model, is applied to orthoaxial octahedral chromophores. These may contain six different ligands but always in such a way that the three Cartesian axes can be directed through the ligands. The Angular Overlap Model gives the energies of the central ion orbitals in terms of radial parameters essentially describing the  $\sigma$  and  $\pi$  anti-bonding (bonding) effects. The results are formally equivalent with those of an electrostatic model for which no restrictions have been posed on the choice of the radial parameters. For example, it is found that the contribution from two ligands which are *trans* to each other always can be expressed as a sum contribution from each of them. The concept of holohedrized symmetry is introduced.

The general expression for the orbital energy of a  $d$ -electron in these systems has been given together with its characterization as a sum of a low symmetry contribution, which has always  $D_{2h}$  symmetry or higher, and a cubic average contribution. All non-diagonal elements connecting cubic parentage orbitals,  $e_g$  and  $t_{2g}$ , vanish in orthoaxial chromophores.

The energies of the first two spin-allowed transitions in  $d^3$  and low-spin  $d^6$  systems have been given within the approximation of pure cubic sub-configurations. The energy levels of maximum spin-multiplicity originating in all possible cubic  $d^q$  sub-configurations have been divided into four classes within each of which the energies are interrelated in a simple way. By application of some simple operators,  $\mathfrak{P}$  [Pauli] and  $\mathfrak{V}$  [van Vleck], it is possible from a function, corresponding to an energy level, of each class to generate all the others of that class.

## 1. Introduction

In some recent papers [1-5] a model was developed to calculate, on a semiempirical basis, the orbital energies in chromophores containing partially filled electronic shells. This model, called the *Angular Overlap Model* [5], attempts to account for the covalency between the central ion and the ligands using an approximated LCAO MO approach. We have assumed, as have MULLIKEN [6] and WOLFSBERG and HELMHOLZ [7, and ref. [8] p. 93], that the antibonding contribution to the energy of a given central ion orbital is proportional to the square of its group overlap integral with the ligands\*. It has further been assumed that the central ion orbitals are separable into angular and radial parts, the latter being equal for all  $l$ -orbitals of an  $l^q$  configuration, the former, of course, being hydrogenic. The ligands are assumed not to overlap with each other.

On the basis of these assumptions it was shown [1, 5] that the Angular Overlap Model is mathematically equivalent with a contact term perturbation model if the matrix elements in the case of  $\lambda > 0$  (e.g. for  $\pi$  and  $\delta$  overlaps) are evaluated for certain functions which are simple transformations of the central ion orbitals (ref. [5]).

This mathematical equivalence leads to an extension of the model to cover also chromophores in which the ligands are not equal.

The antibonding energy of a central ion orbital is expressed as a product of an angular and a radial part. This is taken as a semiempirical parameter that is calculated from the hydrogenic angular functions. The expression of the general matrix element is

$$\sum_{\lambda\omega} \sum_{j=1}^N e_{\lambda j} F_{\lambda\omega}[M, A_j] F_{\lambda\omega}[M', A_j] \quad (1)$$

where  $e_{\lambda j}$  is the radial contribution from the ligand  $j$  associated with its  $\sigma$  ( $\lambda = 0$ ),  $\pi$  ( $\lambda = 1$ ) or  $\delta$  ( $\lambda = 2$ ) overlap with the central ion  $l$ -shell containing the orbitals  $M$  and  $M'$ .  $A_j$  is the ligand orbital whose overlap is considered and could be further specified by the indices  $\lambda\omega$ , where  $\omega$ , for

\* Or rather the sum of the squares of all its possible group overlap integrals [5] corresponding to a given  $\lambda$ , a different constant of proportionality applying to each  $\lambda$ .



$\lambda > 0$ , specifies the particular  $\lambda$ -orbital within the  $\pi$  sets or  $\delta$  sets. In the present paper we assume that the ligands are so constituted that the components of the  $\pi$  and  $\delta$  sets are degenerate\*. This is strictly true if for each ligand the central ion and ligand atoms are placed on a straight line e.g. CN, Cl, and probably a good approximation for a number of other ligands, e.g.  $\text{NH}_3$ .

The first summation in (1) covers the  $(2l+1)$  combinations of  $\lambda\omega$ , the second the contribution from the  $N$  ligands in the chromophore. The  $F_{\lambda\omega}$  terms are the angular overlap integrals which for each ligand form a unitary matrix [5], in which each row is characterized by an  $M$  central ion orbital and each column by an  $A_{j\lambda\omega}$  ligand orbital.

Because of the unitariness of the  $F$ -matrices, the following sum rule is valid

$$\sum_{M,j} (F_{\lambda\omega}[M,A_j])^2 = N \quad (2)$$

where there is one equation for each  $\lambda\omega$  set. This rule states that for a given central ion  $l$  shell containing the orbitals  $M$  and a given  $\lambda\omega$  set of ligand orbitals the sum of the squares of the angular overlap integrals with all the ligands  $j$  is equal to the number of ligands  $N$ .

In the general case, the non-diagonal elements (1) will be non-vanishing. If, however, at the same time the central ion basis functions chosen (in our case the usual real (Cartesian) sets of  $l$ -orbitals) are proper symmetry functions of the molecular point group and are distributed over the different symmetry classes in such a way that no two orbitals belong to the same row of an irreducible representation, the non-diagonal elements will be zero. This case was treated in our last paper [5].

In the present paper we are concerned with the orbital energies of octahedral, quadratic and linear chromophores in which the ligands may all be different. Furthermore, the energy levels of the octahedral chromophores are studied and a comparison is made of the low symmetry splittings of some cubic configurations corresponding to a different number of electrons in the partially filled  $l$ -shell.

It is found that, as for the electrostatic model, the Angular Overlap Model provides accidental degeneracies. These can be given the physical interpretation that a particular orbital feels the effect of two ligands aligned with the central ion just as if the sum of these effects was coming from only one side of the central ion.

\* In a forthcoming paper we shall be concerned with cases in which the same classification of ligand orbitals remains useful even though the degeneracies are lifted.

We introduce here the concept of *holohedrized symmetry* where any interaction occurring at  $(x, y, z)$  is divided into two halves, one half moved to  $(-x, -y, -z)$  and the other remaining at  $(x, y, z)$ .

It has often been said, qualitatively, that the electrostatic model which uses arbitrarily chosen radial parameters is so successful in explaining experimental results because the model is fundamentally based on the symmetry properties of the wavefunctions. The present paper provides a somewhat more quantitative justification of this statement by showing that a model, essentially on an MO basis, leads to the same results as the electrostatic model for which no restrictions have been posed on the choice of radial parameters.

## 2. Orthoaxial chromophores

In regularly octahedral chromophores the Cartesian  $d$ -orbitals are separated by symmetry into the class  $e_g(O_h)$ , consisting of  $d_{z^2}$ ,  $d_{x^2-y^2}$ , which is able to form  $\sigma$ -bonds, and the class  $t_{2g}(O_h)$ , consisting of  $d_{xy}$ ,  $d_{zx}$ ,  $d_{yz}$ , which can form  $\pi$ -bonds. This classification remains valid if a Cartesian coordinate system with the origin at the central ion nucleus can be placed in such a way that the axes are directed\* through the ligand nuclei.

We suggest that chromophores belonging to this class be called *orthoaxial*.

By application of the angular overlap matrix [5], or directly by inspection of the angular distribution of the Cartesian  $d$ -orbitals, it is seen that the angular overlap integral is the same along the positive and the negative directions of any of the Cartesian axes. This has the same consequence as in the electrostatic model [9], and it means that for each Cartesian axis it is the sum of the radial contributions of the ligands on that axis which is important in determining its antibonding (bonding) effect on the  $d$ -orbitals.

Because of this result, it is the holohedrized symmetry of an orthoaxial chromophore, which determines the energy levels to this approximation. The holohedrized symmetry may be higher than the actual symmetry and cannot be lower than  $D_{2h}$ .

\* It is also correct for linear chromophores, with, say, the  $z$ -axis as the symmetry axis, in which case the  $\sigma$  and  $\pi$ -contributions from  $d_{x^2-y^2}$  and  $d_{xy}$ , respectively, vanish. These orbitals are always  $\delta$ -bonding [5] in orthoaxial chromophores, and only  $\delta$ -bonding in the linear case.

For polyatomic, non-linear ligands [27] the  $\pi$  and  $\delta$  orbitals are no longer degenerate and for such systems  $e_g(O_h)$  and  $t_{2g}(O_h)$  may mix.

### 3. Orbital energies

The sum of the radial  $\lambda$ -antibonding contributions from the  $q$ -axis has in this paper been denoted by  $e_{\lambda q}$  ( $\lambda = \sigma, \pi, \delta$ ;  $q = z, x, y$ ). In terms of these radial parameters the non-vanishing matrix elements of the contact term potential  $V$  of the Angular Overlap Model [5] are the diagonal elements,

$$\left. \begin{aligned} \langle d_{z^2} | V | d_{z^2} \rangle &= e_{\sigma z} + \frac{1}{4}(e_{\sigma x} + e_{\sigma y}) + \frac{3}{4}(e_{\delta x} + e_{\delta y}) \\ \langle d_{x^2-y^2} | V | d_{x^2-y^2} \rangle &= \frac{3}{4}(e_{\sigma x} + e_{\sigma y}) + e_{\delta z} + \frac{1}{4}(e_{\delta x} + e_{\delta y}) \\ \langle d_{zx} | V | d_{zx} \rangle &= e_{\pi z} + e_{\pi x} + e_{\delta y} \\ \langle d_{yz} | V | d_{yz} \rangle &= e_{\pi y} + e_{\pi z} + e_{\delta x} \\ \langle d_{xy} | V | d_{xy} \rangle &= e_{\pi x} + e_{\pi y} + e_{\delta z} \end{aligned} \right\} \quad (3)$$

and one non-diagonal element,

$$\langle d_{z^2} | V | d_{x^2-y^2} \rangle = \frac{1}{4} \sqrt{3} [(e_{\sigma y} - e_{\delta y}) - (e_{\sigma x} - e_{\delta x})] = \frac{1}{4} \sqrt{3} [e'_{\sigma y} - e'_{\sigma x}] \quad (4)$$

all the other nine non-diagonal elements vanishing. Since it is always energy differences which can be observed [27] the substitution

$$e'_{\lambda q} = e_{\lambda q} - e_{\delta q} \quad (5)$$

has been introduced into eq. (4). Because of the peculiarity of the orthoaxial chromophores that no mixing occurs between those  $d$ -orbitals which are  $\sigma$ -antibonding, and those which are  $\pi$ -antibonding (bonding), it is possible to define a cubic average contribution to the orbital energy within each of these orbital sets. These cubic average energies  $E$  have been characterized by sub-indices referring to the symmetry notations  $e_g$  and  $t_{2g}$  of the point group  $O_h$ .

$$\left. \begin{aligned} E_{e_g} &= \frac{1}{2} [e_{\sigma z} + e_{\delta z} + e_{\sigma x} + e_{\delta x} + e_{\sigma y} + e_{\delta y}] \\ E_{t_{2g}} &= \frac{2}{3} [e_{\pi z} + e_{\pi x} + e_{\pi y}] + \frac{1}{3} [e_{\delta z} + e_{\delta x} + e_{\delta y}] \end{aligned} \right\} \quad (6)$$

For six-coordinated orthoaxial chromophores, these cubic averages are convenient zero points for the orbital energies which in terms of the reduced parameters of eq. (5) are expressed as:



$$\left. \begin{array}{l}
 e_g \left\{ \begin{array}{l}
 E_{z^2} = \frac{1}{2}e'_{\sigma z} - \frac{1}{4}e'_{\sigma x} - \frac{1}{4}e'_{\sigma y} \\
 E_{x^2-y^2} = -\frac{1}{2}e'_{\sigma z} + \frac{1}{4}e'_{\sigma x} + \frac{1}{4}e'_{\sigma y}
 \end{array} \right. \\
 t_{2g} \left\{ \begin{array}{l}
 E_{zx} = \frac{1}{3}e'_{\pi z} + \frac{1}{3}e'_{\pi x} - \frac{2}{3}e'_{\pi y} \\
 E_{yz} = \frac{1}{3}e'_{\pi z} - \frac{2}{3}e'_{\pi x} + \frac{1}{3}e'_{\pi y} \\
 E_{xy} = -\frac{2}{3}e'_{\pi z} + \frac{1}{3}e'_{\pi x} + \frac{1}{3}e'_{\pi y}
 \end{array} \right.
 \end{array} \right\} \quad (7)$$

where the cubic parentage symmetries are stated to the left. There are two characteristic features of these energies of deviation from cubic symmetry. Firstly, the sum of the coefficients for each orbital is zero. Secondly, the energies of the orbitals which are  $t_{2g}$  orbitals in the regular octahedron are interrelated, as they should be, by a cyclic permutation of the labels  $z, x, y$ .

#### 4. Comparison with the electrostatic model

The expression, eq. (7), for the energies of deviation from the cubic average do not formally disagree with the corresponding expressions of the electrostatic point charge or point dipole model. For the point-dipole model, for example, the relations are

$$\left. \begin{array}{l}
 e_{\sigma q} = \mu_q \left[ B_0 + \frac{2}{7}B_2 + \frac{6}{21}B_4 \right] \\
 e_{\pi q} = \mu_q \left[ B_0 + \frac{1}{7}B_2 - \frac{4}{21}B_4 \right] \\
 e_{\delta q} = \mu_q \left[ B_0 - \frac{2}{7}B_2 + \frac{1}{21}B_4 \right]
 \end{array} \right\} \quad (8)$$

or, in the reduced form:

$$\left. \begin{array}{l}
 e'_{\sigma q} = \mu_q \left[ \frac{4}{7}B_2 + \frac{5}{21}B_4 \right] \\
 e'_{\pi q} = \mu_q \left[ \frac{3}{7}B_2 - \frac{5}{21}B_4 \right]
 \end{array} \right\} \quad (9)$$

where  $q$  represents either  $z, x$ , or  $y$ . Here  $\mu_q$  is the sum of the absolute values of the dipoles of the ligands situated on the  $q$ -axis.

$\mu_q$  multiplied by the radial integrals [10],  $B_o, B_2$ , and  $B_4$ , whose sub-indices refer to the degree of the term in the expansion into spherical harmonics, apart from certain constants make up the radial parameters of the electrostatic model.

It is perhaps worthwhile to express  $\mu_q B_2$  and  $\mu_q B_4$  in terms of our  $e'_q$  parameters. From (9) we obtain:

$$\left. \begin{aligned} \mu_q B_2 &= e'_{\sigma q} + e'_{\pi q} \\ \frac{5}{3} \mu_q B_4 &= 3e'_{\sigma q} - 4e'_{\pi q} = 2 \cdot \Delta_q \end{aligned} \right\} \quad (10)$$

where\* we have introduced in the last expression the term,  $\Delta_q$ , which is the orbital energy difference between  $e_q$  and  $t_{2q}$  orbitals in a cubic (or when holohedrized, cubic) chromophore whose sum-contributions to  $e'_\sigma$  and  $e'_\pi$  are the same from all three axes.

One of the reasons for the criticism of the electrostatic model has been the unreasonable values which had to be chosen for the radial parameters [11]. The expressions of the angular overlap model which are formally equivalent to those of the electrostatic model, because both models are based on the symmetry [27] of the  $d$ -orbitals and of the chromophores, contain radial parameters, whose physical interpretation is entirely different from that of the radial parameters of the electrostatic model. However, because of the expressions (9), an electrostatic contribution might be included in our radial parameters.

According to our description the total perturbation of the central ion orbitals contains a further contribution (eq. 7) in addition to the cubic average (eq. 6). We should mention here that in some cases it may be useful to have another cubic reference state. For example, in their treatment of tetragonal complexes,  $\mu_x = \mu_y$ , BALLHAUSEN and MOFFITT [12] used the radial parameters  $Dq$ ,  $Ds$ , and  $Dt$  which can be translated to the point dipole and angular overlap parameters as follows:

$$\left. \begin{aligned} Dq &= \frac{1}{12} \mu_x \cdot B_4 = \frac{1}{20} (3e'_{\sigma x} - 4e'_{\pi x}) = \frac{1}{10} \Delta_x \\ Ds &= \frac{1}{7} [\mu_x - \mu_z] B_2 = \frac{1}{7} [e'_{\sigma x} + e'_{\pi x} - e'_{\sigma z} - e'_{\pi z}] \\ Dt &= \frac{1}{21} [\mu_x - \mu_z] B_4 = \frac{1}{35} [3e'_{\sigma x} - 4e'_{\pi x} - 3e'_{\sigma z} + 4e'_{\pi z}] \end{aligned} \right\} \quad (11)$$

\* It should here be recalled that our  $e_{\lambda q}$  parameters make up the sum of the two radial contributions from each end of the  $q$  axis. This is the cause of the factor 2 in front of  $\Delta_q$  in eq. (10).



The formulation in terms of  $Dq$ ,  $Ds$  and  $Dt$  destroys the baricenter (center of gravity) rule for the  $Dt$  elements but has the advantage of making a comparison with the cubic complex of  $\mu_x$ -type more evident.

### 5. Energy levels of $d^3$ and $d^6$ systems and the consequences of the holohedrized symmetry

The energy levels in tetragonal chromophores have been discussed by a number of authors [9, 12, 13, 14] using the electrostatic parameter description and by GRIFFITH and ORGEL [15], YAMATERA [16, 17] and McCLURE [18] using an interpretation of the radial parameters similar to the present one.

These earlier results have been augmented by considering

- 1) a general orthoaxial chromophore of the lowest possible symmetry, i.e.  $C_1$ , although its holohedrized symmetry, as mentioned in section 2, cannot be lower than  $D_{2h}$ ,
- 2) the non-diagonal elements connecting the pure cubic configuration split components of the two spin-allowed absorption bands, and
- 3) the accidental degeneracies in the light of the concept of the holohedrized perturbation field.

We shall be concerned, as earlier authors have been, with the transitions which by their cubic parentage can be characterized by  $t_{2g}^3 \rightarrow t_{2g}^2 e_g$  and  $t_{2g}^6 \rightarrow t_{2g}^5 e_g$ . However, because the cubic configurations are not pure (except for  ${}^4T_{2g}$  ( $t_{2g}^2 e_g$ )), even when taking into account our non-diagonal elements a correction must be made before a proper comparison with experimental results is possible.

The procedure of YAMATERA [16, 17] has been adopted for characterizing the one-electron transitions. The orbitals and energy levels have been labelled as symmetry functions (rep.) of the point group  $D_{2h}$ , the notation being selected so that  $z, x$  and  $y$  transform as  $b_{1u}, b_{2u}$  and  $b_{3u}$ , respectively.

The ground levels of  $d^3$  and low-spin  $d^6$  systems, whose cubic parentages are  ${}^4A_2$  and  ${}^1A_1$ , have an orbital symmetry  $A$  under the point group  $D_2$ . The first two spin-allowed transitions in order of increasing energy lead to levels whose cubic parentages are  ${}^4T_2$  and  ${}^4T_1$  in  $d^3$ , and  ${}^1T_1$  and  ${}^1T_2$  in  $d^6$  systems. The components of both  $T_1$  and  $T_2$  in the point group  $D_2$  are distinguishable as  $B_1, B_2$  and  $B_3$ . Also in the following, we often omit the parity designation.

The transitions  $A \rightarrow B_1$  to the two  $B_1$  components of the cubic spin-allowed absorption bands can in either case be characterized as combinations of the one-electron transitions  $d_{xy} \rightarrow d_{x^2-y^2}$  and  $d_{xy} \rightarrow d_{z^2}$ . We have taken the energies of these transitions as our diagonal one-electron operator energies, which can be read directly from (3).

The corresponding non-diagonal element is given in (4) and the energy matrix can be written for  $A \rightarrow B_1$ :

$$\begin{bmatrix} e'_{\sigma z} + \frac{1}{4}(e'_{\sigma x} + e'_{\sigma y}) - (e'_{\pi x} + e'_{\pi y}) + a - C & \frac{1}{4}\sqrt{3}(e'_{\sigma y} - e'_{\sigma x}) \\ \frac{1}{4}\sqrt{3}(e'_{\sigma y} - e'_{\sigma x}) & \frac{3}{4}(e'_{\sigma x} + e'_{\sigma y}) - (e'_{\pi x} + e'_{\pi y}) - C \end{bmatrix} \quad (12)$$

where the eigenvalues directly correspond to the energies of the  $A \rightarrow B_1$  transitions.  $a$  and  $C$  are parameters expressing the interelectronic repulsion energy\* relative to that of the ground level. In terms of Racah parameters  $a$  is equal to  $12B$  for  $d^3$  systems for which the Racah parameter  $C$  disappears in equ. (12) and  $a$  is  $16B$  for  $d^6$  systems [19] (see also Table V).

The corresponding energy matrices for the  $A \rightarrow B_2$  and  $A \rightarrow B_3$  transitions can now be obtained by cyclic permutations. With our choice of labelling the  $D_2$  symmetry functions ( $x:b_2$ , see beginning of this section)

the permutation  $\begin{matrix} x & y \\ y & z \\ z & x \end{matrix}$  will lead to the  $A \rightarrow B_2$  matrix and  $\begin{matrix} x & z \\ y & x \\ z & y \end{matrix}$  to the

$A \rightarrow B_3$  matrix.

In Tables I, II and III results have been given for typical systems for which some chloro-ammines have served as examples. Throughout ammonia has been abbreviated to  $N$  and has been assumed not to have any  $\pi$ -antibonding contribution. In Tables I and II the energy levels have been characterized by their symmetry (irreducible representations, rep.) in different ways: their cubic parentage symmetry, their symmetry relative to our general reference point group  $D_{2h}$  and their symmetry relative to their proper point group. Table I contains the chromophores for which the  $D_{2h}$  functions are themselves also proper symmetry functions of the true chromophore point group. Table II contains those for which linear combinations of the  $D_{2h}$  functions are required to make up proper basis functions of the chromophore

\* The description of the interelectronic repulsion [19] in terms of Racah parameters involves the additional assumption that the deformation of the central ion orbitals by the mixing with ligand orbitals can be accounted for by a nephelauxetic effect, i.e. a common reduction of the Racah parameters of all the energy levels [20]. For the third band of  $d^3$  systems [21] this is known to be an assumption which cannot be brought into accordance with experiment.



point group. These linear combinations have been given except for their normalization constants. The accidental degeneracies  $B_2, B_3$  in *cis*  $N_4Cl_2$  and  $B_1, B_2, B_3$  in *fac.*  $N_3Cl_3$  have been pointed out previously [9, 17, 18], although it has not been mentioned that this degeneracy also remains after consideration of the non-diagonal elements. If the holohedrized symmetry (see end of introduction) is used these accidental degeneracies become a necessary consequence. If the artificial center of inversion is appreciated the holohedrized symmetry of the examples of Table I becomes  $D_{4h}, D_{4h}$  and  $D_{2h}$  and those of Table II  $D_{4h}$  and  $O_h$ , respectively.

Table III contains the diagonal splittings, derived from Tables I and II, splittings which when referred to the first and second spin-allowed absorption band have the same expression for  $d^3$  and  $d^6$  systems.

The well known rule that *trans*  $N_4Cl_2$  has a diagonal splitting twice that of the mono complex  $N_5Cl$ , which itself has  $-1$  times the splitting of the *cis*  $N_4Cl_2$  complex is illustrated. For *mer.*  $N_3Cl_3$  the  $B_1(D_{2h})$  component, which has the same position as all the components of the pseudo cubic *fac.*  $N_3Cl_3$  lies between the  $B_2$  and  $B_3$  components whose energy difference [18] is equal to the splitting of the *trans*  $N_4Cl_2$  complex. This result has been applied to recognize a triammine as the facial isomer on the basis of a consideration of positions and widths of its absorption bands [22].

It has to our knowledge not been pointed out before that the diagonal contribution to the position of the split components of the first absorption band depends only on the relative positions of the ligands in the spectrochemical series. The expression for the orbital energy difference in a regularly octahedral chromophore is  $\Delta = 3e'_\sigma - 4e'_\pi$ , so that, for example, the splitting in our *trans* complex (table I) can be expressed as  $\frac{1}{2} (\Delta_N - \Delta_{Cl})$ .

It is seen that the  $E$  component will lie below the orbitally non-degenerate component because  $Cl^-$  comes earlier (i.e. has a smaller  $\Delta$ -value than ammonia) in the spectrochemical series. For the second band the  $\sigma$  and  $\pi$  contributions cannot be expressed in terms of  $\Delta$  values and a two-dimensional spectrochemical series becomes necessary for describing the splittings in general terms [18, 26].

No genuine example exists in which a well defined splitting of both spin-allowed absorption bands has been observed. We shall therefore not attempt any comparison with experiments here but refer to the discussion\* given by McCLURE [18].

\* Added in proof. For a recent contribution, see WENTWORTH, R. A. D. and PIPER, T. S., 1965, *Inorg. Chem.*, **4** 709.



There exist many cases, e.g. tetrahedral chromophores  $MX_4$ , where the center of inversion is absent, and where the concept of holohedrized symmetry is nevertheless applicable to a surprisingly good approximation. The non-diagonal elements connecting  $3d$  and  $4p$  orbitals seem unimportant for the position of the energy levels in such cases, thus imitating the holohedrized situation where non-diagonal elements between orbitals of opposite parity vanish.

Two molecules can have the same symmetries but have entirely different holohedrized symmetries. This would be the case, e.g. for  $AsH_3$  and  $NH_3$  if the angles H-As-H were all  $90^\circ$ . Then the holohedrized symmetry would be  $O_h$  (like the *fac.*  $N_3Cl_3$  isomer) and  $D_{3d}$ , respectively. Even this idealized form of  $AsH_3$  has the actual symmetry  $C_{3v}$ , not higher than that of  $NH_3$ .

## 6. Interrelation between low symmetry splittings of energy levels belonging to different cubic sub-configurations

The well known Pauli hole equivalence principle relates an  $l^q$  configuration to an  $l^{4l+2-q}$  configuration. The latter behaves in a certain sense as a full shell into which  $q$  positively charged electrons have entered. All composite wavefunctions will have the same expression and the absolute value\* of all matrix elements involving only angular coordinates will be the same, the sign being occasionally reversed.

A similar relation between the energy levels of different cubic configurations has been studied by VAN VLECK [23] who found some regularities among the levels of maximum spin multiplicity. Thus the cubic ligand field perturbation energies were found, except for the sign, to be the same with the pairs  $d^q-d^{5-q}$ , and  $d^{5+q}-d^{10-q}$ .

Here the cubic sub-configurations  $t_{2g}^a e_g^b$  will be divided into four classes\*\* characterized by the irreducible representations attributed to the cubic energy levels of highest spin multiplicity to which they give rise.

In Table IV these classes of cubic configurations have been characterized by the irreducible representations of  $O_h$  which they contain. Further for each class the simplest configuration and the orbitals which specify a particular level are given together with the level's energy. This is the deviation from the cubic average energy and contains independent contributions from each of the two sub-shells (eq. 6 and 7). The level corresponds to that row

\* With the exception of certain constant contributions to the interelectronic repulsion energy thoroughly discussed by GRIFFITH [25].

\*\* The classes A. and D. of ref. [11] constitute one of our four classes. The same is true for B. and C.

of the  $O_h$  irreducible representation which transforms as the  $D_{2h}$  representation given. For the classes  $T$  and  $T'$  the energies of the  $B_1$  component(s) of the  $D_{2h}$  reference point group have been given, as before, and for the class  $T'$  the non-diagonal element can be found in eq. (4). The energies of the  $B_2$  and  $B_3$  components can again be obtained by cyclic permutations of  $(z, x, y)$ .

From the levels specified in Table IV all other levels belonging to the same class can be generated by the operators  $\mathfrak{P}$  (Pauli) and  $\mathfrak{B}$  (van Vleck). These operators, which commute and which both have squares equal to identity, have, for the present purpose, been considered as working solely on sub-shells, and, in particular, on wavefunctions having extreme  $M_S$  values.  $\mathfrak{P}$  transforms a configuration into its complement relative to the full configuration,  $\mathfrak{B}$  into its complement relative to that half configuration, either the first half or the second half, to which it already belongs.

The results from operations with  $\mathfrak{P}$  and  $\mathfrak{B}$  depend on the number of times (i. e. on their exponents) they are applied. (1) The energy contribution from a sub-shell changes sign if the sum of the exponents to all the operators ( $\mathfrak{P}$  and  $\mathfrak{B}$ ) working on that sub-shell is odd. Conversely, if the sum is even, the sign remains unchanged. (2) For  $\Gamma = A$  or  $T$ , a level  $\Gamma_1$  (or  $\Gamma_2$ ) is converted into  $\Gamma_2$  (or  $\Gamma_1$ ) if the sum of the exponents to  $\mathfrak{B}$ , counted for both sub-configurations, is odd. If this is even, the symmetry of the level remains unaltered. The application of  $\mathfrak{P}$  never alters the symmetry of the level. (3) For the class  $T'$ , in which two different cubic levels occur, a specified configuration corresponding to an upper level is transformed into one of a lower level (and vice versa) if the sum of all exponents to  $\mathfrak{P}$  and  $\mathfrak{B}$ , counted for both sub-shells, is odd. If the sum is even, a specified configuration of an upper (lower) level remains that of an upper (lower) level.

As an example of the application of these operators they have been used to generate the perturbation energies belonging to

$$\left. \begin{aligned} & t_2^2 e^4 T_2 (B_1: d_{zx} d_{yz} d_{x^2-y^2}) \\ \text{and} & t_2^5 e^3 T_1 (B_1: d_{zx}^2 d_{yz}^2 d_{xy} d_{x^2-y^2}) \end{aligned} \right\} \quad (13)$$

We are concerned with the class  $T'$  because two levels of maximum spin multiplicity originate from each of the configurations.  $t_2 e^3 T_1$  (upper level), or specified,  $d_{xy} d_{x^2-y^2}$ , is the simplest function of the class  $T'$  (Table IV) which therefore has been chosen to generate all the other functions of that class.

For the  $B_1$  ( $D_{2h}$ ) functions we have:



$$\left. \begin{aligned} \mathfrak{B}(t_2)(e) : {}^3T_1 \text{ (upper level)} &= t_2^2 e : {}^4T_2 \text{ (lower level) or} \\ \mathfrak{B}(d_{xy})(d_{x^2-y^2}) &= d_{zx}d_{yz}d_{x^2-y^2} \text{ (lower level)} \end{aligned} \right\} \quad (14)$$

$$\left. \begin{aligned} \mathfrak{B}(t_2)(e) : {}^3T_1 \text{ (upper level)} &= t_2^5 e : {}^3T_1 \text{ (lower level) or} \\ \mathfrak{B}(d_{xy})(d_{x^2-y^2}) &= d_{zx}^2 d_{yz}^2 d_{xy} d_{x^2-y^2} \text{ (lower level)} \end{aligned} \right\} \quad (15)$$

The energy in both cases is  $-E_{xy} + E_{x^2-y^2}$ , the sign being reversed on the  $t_2$  contribution (relative to that of the starting function) because the operators working on the  $t_2$  sub-shell ( $\mathfrak{B}$  and  $\mathfrak{B}$ , respectively) have been applied an odd number of times (rule 1). For the  $d^3$  case  $\mathfrak{B}$  has been applied an odd number of times and therefore the  $T_1$  level has gone into a  $T_2$  level (rule 2). For both  $d^3$  and  $d^6$  cases the total number of applications of operators is odd and our original function which was an upper level function has therefore been transformed to functions which belong to lower levels (rule 3). These particular results could, of course, have been obtained directly from the specified configurations (to the right in eq. (13)) provided these had been obtained by other methods.

It should be emphasized that the half of the configurations belonging to the  $T'$  class, which has the maximum spin multiplicity 3, contributes for each spin triplet also a spin singlet level whose orbital symmetry and one electron operator energy is exactly that of the corresponding spin triplet level. This is actually the relation between the spin quartet levels of  $d^3$  systems and the singlet levels of  $d^6$  systems. The ground levels are related similarly, but their  $D_{2h}$  perturbation energy vanish.

The two electron operator energies which separate the  $T_1$  and  $T_2$  levels, which originate from each configuration of the  $T'$  class and its corresponding spin-singlet levels, are given in Table V.

## 7. Some reservations

We have mentioned the regularities which relate the spectra of  $d^3$  and low-spin- $d^6$  systems, among others. A further similarity [24] is also expected for the systems  $d^3$  and  $d^8$  within our approximation of pure cubic sub-configurations. However, because of the lower energy difference between  $e$  and  $t_2$ , the cubic sub-configurations are much less pure in the typical example of Ni(II).

It should further be added that if the experimental results for  $d^3$  and  $d^6$  systems were to be discussed it would also be necessary for these to introduce



a correction for the impurity of the cubic sub-configurations. However, the non-cubic contributions to this mixing can be shown to be negligibly small, and the cubic contribution can, at least in principle, be calculated from the results of TANABE and SUGANO [19].

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### Legend of Tables I and II

One electron operator contribution to the position of the two spin-allowed absorption bands of some simple orthoaxial chromophores. The ground levels serve as zero points of energy. Each level is characterized by different symmetry designations, referring to the cubic parentage, the  $D_{2h}$  common reference and the chromophore point group. The phases of the corresponding wavefunctions are interrelated in such a way that a cyclic permutation of  $(z, x, y)$  brings  $B_1(D_{2h})$  functions into  $B_2$  functions and  $B_2$  functions into  $B_3$  functions. The  $B_1$  and  $B_2$  designations in  $C_{2v}$  symmetry are those usually found in the literature, but of course can be permuted without any physical consequence. The three nitrogen atoms of *mer.*  $N_3Cl_3$  have been placed in the  $zx$ -plane\*. In table II the linear combinations of the  $D_{2h}$  functions, required for forming basis functions of the proper chromophore point group, are given. From the form of the linear combinations of the  $D_2$  functions, which make up the levels  $A_2(C_{2v})$  and  $B_2(C_{2v})$  in the chromophore *cis*  $N_4Cl_2$ , it can be seen that the degeneracy of these levels remains after consideration of the non-diagonal elements.

\* In the case of *cis*  $N_4Cl_2$  we have chosen  $B_1(C_{2v})$  to be symmetrical with respect to the symmetry plane containing the two Cl.

TABLE I.

Chromophore Atoms on the z-axis of $D_{2h}$ Point group		$N_5Cl$ N-Cl $C_{4v}$		$trans N_4Cl_2$ Cl-Cl $D_{4h}$		$mer. N_3Cl_3$ N-Cl $C_{2v}$					
$O_h$ rep.	$D_{2h}$ rep.	$C_{4v}$ rep.	energies	$D_{4h}$ rep.	energies	$C_{2v}$ rep.	energies				
$d^3$ $4A_{2g}$ $1A_{1g}$ $4T_{2g}$ $1T_{1g}$ $4T_{1g}$ $1T_{2g}$	$d^6$ $A_g$ $B_{1g}$ $B_{2g}$ $B_{3g}$ $B_{1g}$ $B_{2g}$ $B_{3g}$ $B_{1g}$ $B_{2g}$ $B_{3g}$	$d^3$ $B_1$ $B_2$ $E$ $A_2$ $E$ $E$ $B_1$ $B_2$ $B_3$	$d^6$ $A_1$ $A_2$ $E$ $2e'_\sigma N + e'_\sigma Cl$ $11 \frac{1}{4} e'_\sigma N + \frac{1}{4} e'_\sigma Cl - e'_\pi Cl$ $0$ $-\frac{1}{4} \sqrt{3}(e'_\sigma N - e'_\sigma Cl)$ $+\frac{1}{4} \sqrt{3}(e'_\sigma N - e'_\sigma Cl)$	$d^3$ $B_{1g}$ $B_{2g}$ $E_g$ $A_{2g}$ $E_g$ $E_g$ $B_{2g}$ $B_{1g}$	$d^6$ $0$ $3e'_\sigma N$ $3 \frac{3}{4} e'_\sigma N + \frac{3}{4} e'_\sigma Cl - e'_\pi Cl$ $2e'_\sigma N + 2e'_\sigma Cl$ $0$ $-\frac{1}{2} \sqrt{3}(e'_\sigma N - e'_\sigma Cl)$ $+\frac{1}{2} \sqrt{3}(e'_\sigma N - e'_\sigma Cl)$	$d^3$ $A_1$ $A_2$ $B_2$ $B_1$ $A_2$ $B_2$ $B_1$	$d^6$ $0$ $3 \frac{3}{2} e'_\sigma N + \frac{2}{2} e'_\sigma Cl - 2e'_\pi Cl$ $3 \frac{3}{4} e'_\sigma N + \frac{9}{4} e'_\sigma Cl - 3e'_\pi Cl$ $9 \frac{3}{4} e'_\sigma N + \frac{3}{4} e'_\sigma Cl - e'_\pi Cl$ $3 \frac{3}{2} e'_\sigma N + \frac{3}{2} e'_\sigma Cl - 2e'_\pi Cl$ $0$ $-\frac{1}{2} \sqrt{3}(e'_\sigma N - e'_\sigma Cl)$ $+\frac{1}{4} \sqrt{3}(e'_\sigma N - e'_\sigma Cl)$				
								Diagonal energies		Non-diagonal energies	



TABLE II.

Cromophore Atoms on the $z$ -axis of $D_{2h}$ Point group		<i>cis</i> $N_4Cl_2$ N-N $C_{2v}$		<i>fac</i> $N_3Cl_3$ N-Cl $C_{3v}$		energies	
$O_h$ rep.	$D_{2h}$ rep.	$C_{2v}$ rep.	$D_{2h}$ rep. combination making up $C_{2v}$ rep.	energies	$C_{3v}$ rep.		$D_{2h}$ rep. combination making up $C_{3v}$ rep.
$d^3$	$d^6$	$d^3$	$d^6$		$d^3$	$d^6$	
$4A_{2g}$	$1A_{1g}$	$B_1$	$A_g$	0	$A_2$	$A_1$	0
		$A_1$	$B_{1g}$	$\frac{3'}{2}e_{\sigma N} + \frac{3'}{2}e_{\sigma Cl} - 2e'_{\pi Cl}$	$A_1$	$B_{1g} + B_{2g} + B_{3g}$	$\frac{3'}{2}e_{\sigma N} + \frac{3'}{2}e_{\sigma Cl} - 2e'_{\pi Cl}$
$4T_{2g}$	$1T_{1g}$	$A_2$	$B_{2g} - B_{3g}$	$\frac{9'}{4}e_{\sigma N} + \frac{3'}{4}e_{\sigma Cl} - e'_{\pi Cl}$	$E$	$B_{2g} + B_{3g} - 2B_{1g}$	$\frac{3'}{2}e_{\sigma N} + \frac{3'}{2}e_{\sigma Cl} - 2e'_{\pi Cl}$
		$B_2$	$B_{2g} + B_{3g}$	$\frac{9'}{4}e_{\sigma N} + \frac{3'}{4}e_{\sigma Cl} - e'_{\pi Cl}$	$E$	$B_{2g} - B_{3g}$	$\frac{3'}{2}e_{\sigma N} + \frac{3'}{2}e_{\sigma Cl} - 2e'_{\pi Cl}$
		$B_1$	$B_{1g}$	$\frac{5'}{2}e_{\sigma N} + \frac{1'}{2}e_{\sigma Cl} - 2e'_{\pi Cl}$	$A_2$	$B_{1g} + B_{2g} + B_{3g}$	$\frac{3'}{2}e_{\sigma N} + \frac{3'}{2}e_{\sigma Cl} - 2e'_{\pi Cl}$
$4T_{1g}$	$1T_{2g}$	$A_2$	$B_{2g} - B_{3g}$	$\frac{7'}{4}e_{\sigma N} + \frac{5'}{4}e_{\sigma Cl} - e'_{\pi Cl}$	$E$	$B_{2g} + B_{3g} - 2B_{1g}$	$\frac{3'}{2}e_{\sigma N} + \frac{3'}{2}e_{\sigma Cl} - 2e'_{\pi Cl}$
		$B_2$	$B_{2g} + B_{3g}$	$\frac{7'}{4}e_{\sigma N} + \frac{5'}{4}e_{\sigma Cl} - e'_{\pi Cl}$	$E$	$B_{2g} - B_{3g}$	$\frac{3'}{2}e_{\sigma N} + \frac{3'}{2}e_{\sigma Cl} - 2e'_{\pi Cl}$
				0			0
		$B_{1g}$		$\frac{1}{4}\sqrt{3}(e_{\sigma N} - e_{\sigma Cl})$			0
		$B_{2g}$		$\frac{1}{4}\sqrt{3}(e_{\sigma N} - e_{\sigma Cl})$			0
		$B_{3g}$		$-\frac{1}{4}\sqrt{3}(e_{\sigma N} - e_{\sigma Cl})$			0

Diagonal energies

Non-diagonal energies

TABLE III.  
 Diagonal splittings of the spin-allowed absorption bands of  $d^3$  and  $d^6$  orthoaxial chromophores  
 for which further details are given in tables I and II.

	$D_{2h}$ designations	<i>cis</i> N <sub>4</sub> Cl <sub>2</sub>	N <sub>5</sub> Cl	<i>trans</i> N <sub>4</sub> Cl <sub>2</sub>	<i>mer.</i> N <sub>3</sub> Cl <sub>3</sub>
First absorption band	$B_{1g} - B_{2g}$	$\frac{3}{4}e\sigma_N + \frac{3}{4}e\sigma_{Cl} - e\pi_{Cl}$	$\frac{3}{4}e\sigma_N - \frac{3}{4}e\sigma_{Cl} + e\pi_{Cl}$	$\frac{3}{2}e\sigma_N - \frac{3}{2}e\sigma_{Cl} + 2e\pi_{Cl}$	$\frac{3}{4}e\sigma_N - \frac{3}{4}e\sigma_{Cl} + e\pi_{Cl}$
	$B_{1g} - B_{3g}$	$-\frac{3}{4}e\sigma_N + \frac{3}{4}e\sigma_{Cl} - e\pi_{Cl}$	$\frac{3}{4}e\sigma_N - \frac{3}{4}e\sigma_{Cl} + e\pi_{Cl}$	$\frac{3}{2}e\sigma_N - \frac{3}{2}e\sigma_{Cl} + 2e\pi_{Cl}$	$-\frac{3}{4}e\sigma_N + \frac{3}{4}e\sigma_{Cl} - e\pi_{Cl}$
Second absorption band	$B_{1g} - B_{2g}$	$\frac{3}{4}e\sigma_N - \frac{3}{4}e\sigma_{Cl} - e\pi_{Cl}$	$\frac{3}{4}e\sigma_N + \frac{3}{4}e\sigma_{Cl} + e\pi_{Cl}$	$-\frac{3}{2}e\sigma_N + \frac{3}{2}e\sigma_{Cl} + 2e\pi_{Cl}$	$-\frac{3}{4}e\sigma_N + \frac{3}{4}e\sigma_{Cl} + e\pi_{Cl}$
	$B_{1g} - B_{3g}$	$\frac{3}{4}e\sigma_N - \frac{3}{4}e\sigma_{Cl} - e\pi_{Cl}$	$-\frac{3}{4}e\sigma_N + \frac{3}{4}e\sigma_{Cl} + e\pi_{Cl}$	$-\frac{3}{2}e\sigma_N + \frac{3}{2}e\sigma_{Cl} + 2e\pi_{Cl}$	$\frac{3}{4}e\sigma_N - \frac{3}{4}e\sigma_{Cl} - e\pi_{Cl}$

TABLE IV.

Cubic sub-configurations classified according to their energy levels of maximum spin-multiplicity. Within each generating function (column 4) the  $m_s$  values of the one electron component functions should be the same (either  $+\frac{1}{2}$  or  $-\frac{1}{2}$ ). The energies of these particular functions are given in column 6 with reference to eq. (7).

class	$O_h$ -rep.	Simplest configurations	Specification of row of rep.	$D_{2h}$ rep.	energy
A	$A_{1g}$ or $A_{2g}$	$t_{2g}^o e_g^o$		$A_g$	0
E	$E_g$	$t_{2g}^o e_g$	$d_{x^2-y^2}$	$A_g$	$E_{x^2-y^2}$
T	$T_{1g}$ or $T_{2g}$	$t_{2g} e_g^o$	$d_{xy}$	$B_{1g}$	$E_{xy}$
T'	$T_{1g}$ and $T_{2g}$	$t_{2g} e_g$	$d_{xy} d_{x^2-y^2}$	$B_{1g}$	$E_{x^2-y^2} + E_{xy}$

TABLE V.

Energy differences in units of  $B$  between the  $T_1$  and  $T_2$  levels of class  $T'$ , and between the singlet levels which correspond to the triplet levels of  $T'$ .

	$S = 0$	1	3/2
$d^2, d^8$	4	12	—
$d^3, d^7$	—	—	12
$d^4, d^6$	-16	-8	—
$d^5$	—	—	-8