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A Ligand Field Approach to Orthoaxial Complexes

Perturbation Treatment using Zero-order Functions with Octahedral Basis

By

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First order perturbation considerations are applied to general orthoaxial chromophores. These contain monatomic or linear ligands which are so positioned around the central ion that Cartesian coordinate axes can be placed through the ligands. The zero order functions used are the orbitals of the partially filled shell which are proper basis functions of the regular octahedron and can be thought of as general molecular orbitals of a particular regularly octahedral chromophore. Certain degeneracies not demanded by the proper chromophoric symmetry are rationalized in terms of the holohedrized symmetry, which also determines the number of parameters required for the full parametrization. All the results obtained are, apart from a minor correction given explicitly, formally equivalent to those obtained earlier using the angular overlap model and the electrostatic model. The extra correction required in the present more general treatment is probably unimportant in view of the approximations involved, in particular that of using a basis restricted to five orbitals.

Störungsbetrachtungen erster Ordnung werden auf orthoaxiale Chromophore angewandt. (Einatomige oder lineare Liganden sind so um das Zentralion angeordnet, daß die Achsen eines Cartesischen Koordinatensystems durch die Liganden gehen.) Als Funktionen in nullter Näherung werden die Orbitale der teilweise gefüllten Schale benutzt, die Basiseigenfunktionen des regulären Oktaeders sind und die man sich als allgemeine MO's eines speziellen regulär oktaedrischen Chromophors vorstellen kann. Gewisse Entartungen, die nicht durch die Symmetrie des Chromophors hervorgerufen werden, werden in Ausdrücken der Holoedersymmetrie erklärt, die auch die Zahl der Parameter für die volle Parametrisierung bestimmt. Mit einer geringen Abweichung sind alle Ergebnisse formal äquivalent zu denen des „angular overlap" und des elektrostatischen Modells. Die besondere Abänderung in der vorliegenden allgemeineren Behandlung ist vermutlich unwesentlich im Hinblick auf die enthaltenen Näherungen, besonders bei Benutzung einer auf fünf Orbitale eingeschränkten Basis.

La méthode des perturbations du premier ordre est appliquée aux chromophores orthoaxiaux, ne contenant que des ligandes, atomiques ou linéaires, sur des axes cartésiens de l'ion central. Les fonctions d'ordre zéro sont les orbitales de la couche partiellement occupée qui sont de fonctions propres de base de l'octaèdre régulier, et peuvent être considérées comme orbitales moléculaires générales d'un chromophore octaédrique régulier. Certaines dégénérescences, n'exigées pas de la symétrie du chromophore, sont rationalisées sous termes de symétrie holoédrisée qui détermine aussi le nombre de paramètres nécessaires. Tous les résultats, sauf une correction mineure donnée explicitement, sont équivalents à ceux déjà obtenus à l'aide des modèles électrostatique et à recouvrement angulaire. La correction additionnelle de la présente méthode n'est probablement pas importante, vu les approximations faites, spécialement la restriction à cinq orbitales de base.

1. Introduction

A particular class of chromophores is the orthoaxial one [*12*] which consists of a central ion surrounded by monatomic or linear ligands which are so located around the central ion that a Cartesian coordinate axis can be directed through each ligand as a whole, and not only through the ligating atoms. Such ligands might be described as linearly ligating. Most of the many well characterized complexes of chromium (III), cobalt (III), rhodium (III), and iridium (III) belong, at least to a good approximation*, to this class of chromophores which has been studied extensively before [*1*, *2*, *3* p. 106, *4*, *5*, *7*, *8* p. 123, *11*, *12*, *16*, *17*, *18*].

In a recent paper [*12*] it was discussed on the basis of the angular overlap model [*9*, *10*, *13*] which is a first order perturbation treatment [*13*] based on LCAO-MO ideas. A general orthoaxial chromophore was considered here [*12*] and the concept of the holohedrized symmetry (v.i.) introduced.

In all the earlier papers the one electron energies have been obtained by different perturbation treatments using, as it seems, quite generally, the hydrogenic angular functions for the calculations providing coefficients to the radial integrals which have served as semiempirical parameters.

In the present paper, instead of using functions which are products of hydrogenic angular functions (i.e. with a spherical basis) and unspecified radial functions, we take as our zero order functions such functions as are characterized and limited only by their transformation properties under the octahedral group O_h (i.e. with a cubic basis).

2. Basis for Estimation of Orbital Energy Parameters.
Zero Order Functions

Let us consider a six coordinated orthoaxial chromophore consisting of the central ion M and the ligands A, B, C, D, E, and F. We may now assume that we have made a self-consistent field Hartree-Fock calculation on the regularly octahedral chromophore MX_6, say, where X may or may not be equal to one of the above mentioned ligands.

However, for the parametrization to be described below it is not important that such a Hartree-Fock calculation can be done at all and we shall find it more convenient to think of MX_6 as a cubic average of M $(ABCDEF)$. This is possible because the parameters describing the deviation from cubic symmetry must in any case be taken from experiments.

The orbitals of the partially filled MO shells, which in an LCAO-MO description would be in the main central ion d-orbitals in character, have, also in the most general case, the symmetries e_g and t_{2g} of the octahedral point group O_h. A particular choice of e_g orbitals can be characterized by having the same transformation properties under the octahedron as have $\frac{1}{\sqrt{3}}(2z^2 - x^2 - y^2)$, abbreviated (z^2), and $(x^2 - y^2)$. Similarly the t_{2g} orbitals can be classified** as (xy), (yz),

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[*] Ammonia, for example, is assumed to make up effectively a linearly ligating ligand, its binding properties being associated practically solely with the σ lone pair of the ligating atom.

[**] Our choice of orbitals is equivalent to that of GRIFFITH ([*6*], p. 390), the correspondence being ϑ, ε, ζ, ξ, and η, respectively. An easy way of finding the relative normalization coefficient a of $a\,(2z^2 - x^2 - y^2)$ and $x^2 - y^2$ is to express that the full e_g shell must be totally symmetrical under the octahedral group O_h. As z, x, and y, under these circumstances, are to be equivalent, this means that the coefficient to z^4 and x^4, say, in the sum of the squares of the two orbitals must be the same, or, $4a^2 = a^2 + 1$ and consequently $a = \frac{1}{\sqrt{3}}$.

and (zx). It should be emphasized that the orbitals which are labelled here by a Cartesian notation, may be quite general molecular orbitals, and thus not separable into radial and angular parts. In fact, they are limited only by their transformation properties under the octahedral group.

We now assume that the deviation from regularly octahedral symmetry can be described by a first order perturbation treatment using our above mentioned functions, of symmetry e_g and t_{2g}, which are eigenfunctions of our cubic average system, as our restricted basis of zero order functions. This assumption implies that both those matrix elements of our perturbation which connect our cubic-basis orbitals with other orbitals of the same cubic parentage symmetry, and those connecting them with orbitals of a different parentage symmetry remain of little importance as far as energy is concerned. Further it implies that the interactions between neighbouring ligands are unchanged relative to our regularly octahedral case.

3. Orbital Energies

Let us now consider a matrix element of our perturbing potential V whose form we need not be concerned with except for its sum character which is a consequence of our perturbation description. For the (z^2)-orbital the diagonal matrix element is:

$$\begin{aligned}\langle (z^2) \mid V \mid (z^2)\rangle &= \langle (z^2) \mid (V^{+z} + V^{-z}) + (V^{+x} + V^{-x}) + \\ &+ (V^{+y} + V^{-y}) \mid (z^2)\rangle = \langle (z^2) \mid V^{zc} + V^{xa} + V^{yb} \mid (z^2)\rangle \end{aligned} \tag{1}$$

where e.g. V^{+z} is the perturbation from the positive z-axis and V^{zc} is the sum of the perturbations from the positive and the negative z-axis. If these same perturbations act on the x-axis, their sum will be denoted by V^{xc}. It is always the sum of such perturbations of each Cartesian axis which in an orthoaxial chromophore is important in determining the matrix elements involving the five orbitals (e_g and t_{2g}).

This can be seen from the following argument. A matrix element $\langle \varphi \mid V \mid \psi \rangle$ where φ and ψ are functions with the same parity, will be unchanged on application of the operation of inversion to V (the inversion working on direction as well as on position). This means that if V is written as a sum $\frac{1}{2} V + \frac{1}{2} V$, say, and if inversion is applied on one of these terms, all matrix elements will be unchanged, and thus an apparent center of inversion has been introduced. We have obtained the holohedrized symmetry [*12*].

This means that when we are considering only matrix elements involving our five orbitals mentioned above, or these plus others also of the same, i.e. gerade, parity, the concept of the holohedrized symmetry is applicable to the determination of the number of parameters required for determining the orbital energies. Because of the orthoaxiality [*12*] the lowest possible holohedrized symmetry, which corresponds to different perturbations along the three Cartesian axes, will be D_{2h}.

We now consider the matrix element $\langle (z^2) \mid V^{xc} \mid (z^2)\rangle$ which by the decomposition of (z^2) into a linear combination of (x^2) and $(y^2 - z^2)$, a consequence of the transformation properties of (z^2) under the octahedron, can be written as

$$\begin{aligned}&\langle -\tfrac{1}{2}(x^2) - \tfrac{1}{2}\sqrt{3}\,(y^2 - z^2) \mid V^{xc} \mid -\tfrac{1}{2}(x^2) - \tfrac{1}{2}\sqrt{3}\,(y^2 - z^2)\rangle \\ &= \langle -\tfrac{1}{2}(z^2) - \tfrac{1}{2}\sqrt{3}\,(x^2 - y^2) \mid V^{zc} \mid -\tfrac{1}{2}(z^2) - \tfrac{1}{2}\sqrt{3}\,(x^2 - y^2)\rangle \end{aligned} \tag{2}$$

where a cyclic permutation of the labels z, x, y has led to the last expression which now involves the perturbation V^{zc} at the z axis.

On expansion we get:

$$\tfrac{1}{4}\langle(z^2)\mid V^{zc}\mid(z^2)\rangle+\tfrac{3}{4}\langle(x^2-y^2)\mid V^{zc}\mid(x^2-y^2)\rangle+\tfrac{1}{2}\sqrt{3}\,\langle(z^2)\mid V^{zc}\mid(x^2-y^2)\rangle \quad (3)$$

where the last term vanishes because of the different transformation properties of (z^2) and (x^2-y^2) under $C_4\,(z)$, a transformation which in an orthoaxial chromophore leaves V^{zc} invariant. Defining $\langle(z^2)\mid V^{zc}\mid(z^2)\rangle$ and $\langle(x^2-y^2)\mid V^{zc}\mid(x^2-y^2)\rangle$ as $v_{\sigma c}$ and $v_{\delta c}$, respectively, we have

$$\langle(z^2)\mid V^{xa}\mid(z^2)\rangle=\tfrac{1}{4}\,v_{\sigma a}+\tfrac{3}{4}\,v_{\delta a} \quad (4)$$

and similarly

$$\langle(z^2)\mid V^{yb}\mid(z^2)\rangle=\tfrac{1}{4}\,v_{\sigma b}+\tfrac{3}{4}\,v_{\delta b}\,. \quad (5)$$

The expression for the total diagonal element together with that for the other e_g orbital, obtained in a similar way, then becomes:

$$\begin{aligned}\langle(z^2)\mid V\mid(z^2)\rangle&=v_{\sigma c}+\tfrac{1}{4}\,(v_{\sigma a}+v_{\sigma b})+\tfrac{3}{4}\,(v_{\delta a}+v_{\delta b})\\ \langle(x^2-y^2)\mid V\mid(x^2-y^2)\rangle&=\tfrac{3}{4}\,(v_{\sigma a}+v_{\sigma b})+v_{\delta c}+\tfrac{1}{4}\,(v_{\delta a}+v_{\delta b})\,.\end{aligned} \quad (6)$$

For zx we define $\langle(zx)\mid V^{zc}\mid(zx)\rangle\equiv v_{\pi c}$ and $\langle(zx)\mid V^{yb}\mid(zx)\rangle\equiv v_{\delta' b}$, and by suitable permutations of z, x, y we collect the results

$$\begin{aligned}\langle(zx)\mid V\mid(zx)\rangle&=v_{\pi c}+v_{\pi a}+v_{\delta' b}\\ \langle(yz)\mid V\mid(yz)\rangle&=v_{\pi b}+v_{\pi c}+v_{\delta' a}\\ \langle(xy)\mid V\mid(xy)\rangle&=v_{\pi a}+v_{\pi b}+v_{\delta' c}\,.\end{aligned} \quad (7)$$

If our orbitals had a spherical basis they could also have served as basis functions for a linear point group ($C_{\infty v}$ or $D_{\infty h}$) with the z-axis as the axis of symmetry. The sub-indices used here refer to this situation and pertain to irreducible representations of the holohedrized group $D_{\infty h}$.

The only non-diagonal element which is non-vanishing is that connecting (z^2) and (x^2-y^2) both having the same (a_g) symmetry in the holohedrized D_{2h} group. As seen above, the V^{zc} gives no contribution, but for V^{xa} we get

$$\begin{aligned}\langle(z^2)\mid V^{xa}\mid(x^2-y^2)\rangle&=\langle-\tfrac{1}{2}\,(x^2)-\tfrac{1}{2}\sqrt{3}\,(y^2-z^2)\mid V^{xa}\mid-\\ &\qquad-\tfrac{1}{2}\,(y^2-z^2)+\tfrac{1}{2}\sqrt{3}\,(x^2)\rangle \qquad (8)\\ &=\langle-\tfrac{1}{2}\,(z^2)-\tfrac{1}{2}\sqrt{3}\,(x^2-y^2)\mid V^{za}\mid-\tfrac{1}{2}\,(x^2-y^2)+\tfrac{1}{2}\sqrt{3}\,(z^2)\rangle\\ &=-\tfrac{1}{4}\sqrt{3}\,\langle(z^2)\mid V^{za}\mid(z^2)\rangle+\tfrac{1}{4}\sqrt{3}\,\langle(x^2-y^2)\mid V^{za}\mid(x^2-y^2)\rangle=-\tfrac{1}{4}\sqrt{3}\,(v_{\sigma a}-v_{\delta a})\,.\end{aligned}$$

Similarly we get

$$\langle(z^2)\mid V^{yb}\mid(x^2-y^2)\rangle=\tfrac{1}{4}\sqrt{3}\,(v_{\sigma b}-v_{\delta b}) \quad (9)$$

and therefore

$$\langle(z^2)\mid V\mid(x^2-y^2)\rangle=\tfrac{1}{4}\sqrt{3}\,[(v_{\sigma b}-v_{\sigma a})-(v_{\delta b}-v_{\delta a})]\,. \quad (10)$$

The set of equations (6, 7, 10) are equivalent in form to the set (3, 4) of [*12*] except for the fact that the δ and δ' parameters are not necessarily equal, as they would have been the same as in the case of functions with a spherical basis.

4. Orbital Energy Differences

As indicated, it is a consequence of the orthoaxiality of our chromophore that the orbitals making a basis for e_g are not connected with those of basis t_{2g} by any non-vanishing matrix elements of our perturbation. This circumstance makes it possible to define [*12*] a cubic average energy independently within each of these two groups of orbitals. Calling these energies E_e and E_{t_2} and defining $E_e - E_{t_2}$ as Δ, in accordance with common usage for octahedral chromophores, we get

$$\begin{aligned} E_e - E_{t_2} = \Delta &= \tfrac{1}{2}\,(v_{\sigma c} + v_{\sigma a} + v_{\sigma b}) + \tfrac{1}{2}\,(v_{\delta c} + v_{\delta a} + v_{\delta b}) - \\ &- \tfrac{2}{3}\,(v_{\pi c} + v_{\pi a} + v_{\pi b}) - \tfrac{1}{3}\,(v_{\delta' c} + v_{\delta' a} + v_{\delta' b}) \\ &= \tfrac{1}{3} \sum_{i=c,\,a,\,b} \tfrac{3}{2}\,(v_{\sigma i} - v_{\delta i}) - \tfrac{1}{3} \sum_{i=c,\,a,\,b} 2\,(v_{\pi i} - v_{\delta' i}) + \tfrac{1}{3} \sum_{i=c,\,a,\,b} 3\,(v_{\delta i} - v_{\delta' i})\,. \end{aligned} \tag{11}$$

For $v_{\delta i} = v_{\delta' i}$ (11) is equivalent to eq. (6) of [*12*].

Defining the arguments of these summations as $\Delta_{\lambda i}$ with the appropriate sub-index $\lambda = \sigma$, π or δ, we get*

$$\Delta = \tfrac{1}{3} \sum_{i=c,\,a,\,b} \Delta_{\sigma i} - \tfrac{1}{3} \sum_{i=c,\,a,\,b} \Delta_{\pi i} + \tfrac{1}{3} \sum_{i=c,\,a,\,b} \Delta_{\delta i} \tag{12}$$

which for $c = a = b$ defines a decomposition of Δ for a cubic complex into three terms,

$$\Delta = \Delta_\sigma - \Delta_\pi + \Delta_\delta\,. \tag{13}$$

We shall now, using eqs. (6, 7, and 10), express the orbital energy differences and the non-diagonal element (within our five orbital basis) in terms of our cubic average Δ and of differences between $\Delta_{\lambda i}$ parameters. We abbreviate $\langle z^2 \mid V \mid z^2 \rangle$ as E_{z^2} and use a similar notation for the other diagonal one-electron energies. In the expressions for those energy differences which involve the orbitals E_{z^2} and $E_{x^2-y^2}$, (12) is introduced by adding its left-hand side and subtracting its right-hand side. Thus we obtain the expressions**,

$$\begin{aligned} E_{z^2} - E_{xy} &= \Delta + \tfrac{1}{6}\,(\Delta_{\sigma c} - \Delta_{\sigma a}) + \tfrac{1}{6}\,(\Delta_{\sigma c} - \Delta_{\sigma b}) + \\ &\quad + \tfrac{1}{6}\,(\Delta_{\pi c} - \Delta_{\pi a}) + \tfrac{1}{6}\,(\Delta_{\pi c} - \Delta_{\pi b}) \\ E_{x^2-y^2} - E_{xy} &= \Delta - \tfrac{1}{6}\,(\Delta_{\sigma c} - \Delta_{\sigma a}) - \tfrac{1}{6}\,(\Delta_{\sigma c} - \Delta_{\sigma b}) + \\ &\quad + \tfrac{1}{6}\,(\Delta_{\pi c} - \Delta_{\pi a}) + \tfrac{1}{6}\,(\Delta_{\pi c} - \Delta_{\pi b}) \\ E_{zx} - E_{xy} &= \tfrac{1}{2}\,(\Delta_{\pi c} - \Delta_{\pi b}) \\ E_{yz} - E_{xy} &= \tfrac{1}{2}\,(\Delta_{\pi c} - \Delta_{\pi a}) \\ \langle z^2 \mid V \mid x^2 - y^2 \rangle &= \tfrac{1}{6}\,\sqrt{3}\,[(\Delta_{\sigma c} - \Delta_{\sigma a}) - (\Delta_{\sigma c} - \Delta_{\sigma b})]\,. \end{aligned} \tag{14}$$

We have already mentioned that with the restriction $v_{\delta i} = v_{\delta' i}$ ($i = a, b, c$), Δ from our definition (11, 12), is given by an expression which is equivalent to that which would have been obtained if we had been using zero order functions with a spherical basis. The rest from the expressions (14) has this property even without the above restriction, provided it is remembered that every $\Delta_{\lambda i}$ by (11) implicitly

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* It should be noted that without loss of symmetry in the expressions, $\Delta_{\delta i}$ might as well have been defined with the opposite sign.

** When the two uppermost equations of (14) are compared it is noted that the sign of the π-contributions is the same, but that of the σ-contributions is opposite. Even though each λ-contribution is itself a difference, it is perhaps not unexpected that those marked σ are larger than those marked π. If this is generally so, then the first and the second spin-allowed absorption bands of d^3 and d^6 systems, when their split components are labelled [*12*] by their symmetries in the holohedrized point group D_{2h} will split in such a way that their components occur in opposite order.

contains the $v_{\delta i}$ and $v_{\delta' i}$ parameters. This means that all splittings of cubic energy levels will be described formally in the same way whether we use zero-order functions with a spherical or a cubic basis.

5. The Parametrization of the Orbital Energy Differences

The top equation of (14) contains all the five independent parameters occurring in the whole of (14). These are made up by Δ together with the expressions occurring in the parentheses, two σ-parameters and two π-parameters. Five parameters is just the number required by the most general chromophore of D_{2h} symmetry [*6* p. 197], one for each of the four independent energy differences and one for the nondiagonal element. So again we see the holohedrized symmetry at its insidious restricting work.

We shall consider a few examples of chromophores with higher symmetry.

For $V^{xa} = V^{yb}$ we obtain the tetragonal situation where the symmetry (or the holohedrized symmetry) is D_{4h}. In this case the two σ-parameters become equal, which makes the non-diagonal element vanish. Further the two π-parameters become equal, and we are left with the three parameters required to determine the three energy differences occurring in the D_{4h} symmetry group. It is of special interest to look at the energy difference $E_{x^2-y^2} - E_{xy}$ which, when the functions used have a spherical basis, would be equal to $\Delta_a = \Delta_{\sigma a} - \Delta_{\pi a}$, where Δ_a is the Δ pertaining to a cubic chromophore with $V^{xa} = V^{ya} = V^{za}$.

Here by introducing (12) into the second equation of (14), we get, writing now (13) as

$$\Delta_a = \Delta_{\sigma a} - \Delta_{\pi a} + \Delta_{\delta a} \,, \tag{15}$$

$$E_{x^2-y^2} - E_{xy} = \Delta_a + \tfrac{1}{3}\,\Delta_{\delta c} - \tfrac{1}{3}\,\Delta_{\delta a} \tag{16}$$

containing the expected δ-corrections.

There is a special case of D_{4h} symmetry that we mention as a curiosity. It is the square planar case which in addition to $V^{xa} = V^{yb}$ has $V^{zc} = 0$. Here the cubic average Δ may be written as

$$\Delta = \tfrac{2}{3}\,\Delta_a = \tfrac{2}{3}\,[\Delta_{\sigma a} - \Delta_{\pi a} + \Delta_{\delta a}] \tag{17}$$

and our parameters may be chosen as the three components of Δ_a, the number being again in agreement with the symmetry requirement. However, in this case the similar consideration with functions of spherical basis results in $\Delta_{\delta a}$ equal to zero, and thus leaves only two parameters: the $(x^2 - y^2)$ orbital is three times [*14*, Tab. 1] as much perturbed as the (z^2) orbital. It should be realized that the square planar case, at least if it truly is uncoordinated along the z-axis, is extremely far away from being cubic (and from being spherical) and therefore our five-orbital basis is likely to give a bad approximation even for parametrization of energy level positions. In this case it is probably not irrelevant to include a totally symmetrical orbital among our cubic-basis zero order functions. This would mean to add an orbital transforming as $x^2 + y^2 + z^2$ under O_h (corresponding, in the case where a spherical basis is used, to adding an s orbital to the d set). However, the addition of such an extra orbital will mean addition of one, two and three extra parameters in the cases, cubic, tetragonal, and orthorhombic holohedrized symmetry, respectively. It seems, at least at present, not possible to determine such parameters experimentally.

6. Conclusion

In the present paper we have only been concerned with sum contributions from each Cartesian coordinate axis. It is not at all required, neither by the present treatment nor by the angular overlap model treatment [*12*], that a halide, say, be attributed the same parameters Δ_λ independent of which ligand is situated trans to it. It is only the total perturbation contribution from each axis which effects our orbital energy differences. Recently, WENTWORTH and PIPER [*16*] have proposed a spectral "trans effect" caused by some kind of interaction between ligands trans to each other.

If the single ligand perturbation parameters were independent of the trans-ligand, the usually mentioned relation between the splittings occurring in corresponding trans and cis complexes (symmetry and holohedrized symmetry D_{4h}, respectively) would in our treatment remain equally valid.

Further, for d^3 and d^6 systems, the cubic parentage excited states of orbitally triple degeneracy are each split into a singlet and a doublet in such a way that, for the first spin-allowed cubic absorption band, the diagonal energy of the trans doublet coincides with that of the cis singlet, whereas for the second spin-allowed cubic band, the trans singlet and the cis doublet have the same diagonal energies. This means that if the ligand which gives rise to the name of trans or cis lies below the other ligand of the complex in the spectrochemical series (i.e. has a smaller Δ value), the low energy split component for the first cubic spin-allowed band will approximately coincide for the trans and cis complexes whereas if it lies above, then it is the high energy split component which coincides. Actually the same statement seems, in general, to be valid also for the second band [*15*] because the order of the singlet and the doublet is reversed (see footnote to p. 170).

On the other hand, if the single ligand parameters do depend on the trans-ligand, the connection between the positions of the split bands of cis and trans complexes will be loosened, whereas e.g. the splittings in mono(halido)-pentammine complexes will remain related in the usual way [*12*] to the corresponding cis bis(halido)-tetrammine complexes.

In [*12*] it was pointed out that the diagonal energies of the split components of the first cubic, spin-allowed absorption band, provided no trans-interactions were considered, depended only upon the Δ values of the ligands of the chromophore. This remains true here except for δ-contributions.

If the present parametrization is applied to experimental results on energy level positions [*15*], the δ-contributions are found to be so small that they probably cannot be considered physically significant in view of the unpermitted assumptions of the present treatment. Small δ-contributions, on the other hand, make the formal parametric description of orthoaxial chromophores provided by the angular overlap model [*11*, *12*, *16*, *17*] and by the electrostatic model [*1*, *3*] remain applicable.

Finally, we may say that the present ligand field treatment provides further support for the idea that the success of such approaches is connected with the fact that their results essentially are derived on the basis of symmetry arguments.

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