

THE ANGULAR OVERLAP MODEL OF THE LIGAND FIELD THEORY AND APPLICATIONS

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ABSTRACT

The Angular Overlap Model, AOM, is historically reviewed. Solid and surface harmonics are discussed in relation to the model and chosen as real basis functions for the two-dimensional as well as the three-dimensional rotation group. The concepts of angular overlap integrals and group angular overlap integrals are described. Further the angular overlap operators and the surface angular overlap operators are developed.

The AOM endeavours to parametrize the non-spherical part of the ligand field. The assumptions which are necessary for this parametrization are enumerated by considering it (1) as a perturbation model (2) as an overlap model. The two points of view give identical results, and for linearly ligating ligands the AOM is, in a formal parametrical sense, equivalent to the point charge electrostatic model, when all parameters of both models are taken into account.

The expanded radial function model for parametrizing the interelectronic repulsion is discussed and the field strength series described. Finally the two-dimensional spectrochemical series is used as an illustration of the application of AOM to experiment.

1. INTRODUCTION

THE present day stage of development is always interesting to view in the light of its history. It is possible here to view the angular overlap model of the ligand field in this way, but an attempt to go through the whole history of ligand field models would be out of place.

For those who have a broad idea about the development, it may, however, be worth while making a brief enumeration of some events and of some names of scientists who contributed. The electrostatic model as well as the group-theoretical simplification of its application was proposed in Bethe's now famous 1929 paper¹, which apparently was not much read until more than fifteen years later. There are various reasons for this. One reason is the advancement of nuclear physics at that time, which occupied the working power of more and more of the physicists. Another reason is the poor

mathematical education that chemists in general had at that time. This made Pauling's intelligible valence bond description of complex chemistry dominate the theoretical consideration of this field for twenty five years.

It is true that Bethe's ideas were elaborated and used by magnetophysicists during that time, but it was not until 1940 that the first attempt² was made by Finkelstein and Van Vleck to consider excited states by application of Bethe's model. These authors assigned the spin-forbidden transitions in chromium alum but characterized the rise in absorption, which we now know is caused by the spin-allowed bands, as absorption edges. Their work apparently did not influence the further development which took place with Ilse and Hartmann³⁻⁵ and with Orgel^{6,7} closely followed by Bjerrum, Ballhausen and Jørgensen⁸⁻¹², and by Tanabe and Sugano¹³. Only some of the pioneer papers of all these authors have been cited here, but already with that of Tanabe and Sugano the whole formalism was essentially complete.

The criticism of the electrostatic model from a physical point of view developed very shortly after, and a whole section of a book by Jørgensen¹⁴ has been devoted to this purpose. In a more mathematical form the criticism was formulated by Freeman and Watson¹⁵.

Even though the parameters of the electrostatic model have been shown to be without physical significance, the symmetry basis of the model, so beautifully illuminated in Griffith's book¹⁶, has given the parameters so long a life in the chemical literature that one can still meet them today.

The angular overlap model of the ligand field qualifies itself by combining the full symmetry basis of the electrostatic model with a perspicuous connection with molecular orbital concepts. For the special case of so-called linearly ligating ligands the restricted angular overlap model and the electrostatic model, considered as mathematical formalisms, are equivalent¹⁷.

2. THE HISTORY OF THE ANGULAR OVERLAP MODEL

In a historical perspective it can probably be justified to say that the angular overlap model was first proposed by Yamatera^{18,19}, although he applied the model only to six coordinated orthoaxial chromophores (section 6b) based upon the octahedron, and did not realize the more general aspects of the model. Apparently independently the same model was developed for the same chromophores by McClure²⁰. The model has parameters which represent the energetic consequences of σ - and π -bond formation upon the central ion d -orbitals. For a regularly octahedral chromophore the d -orbital level splits into an upper lying $e(O_h)$ -level of proper symmetry for σ -bonding and a lower lying $t_2(O_h)$ -level of symmetry for π -bonding. The usual spectrochemical parameter Δ , which expresses the difference in energies h of the $e(O_h)$ and the $t_2(O_h)$ orbitals,

$$\Delta \equiv h(e) - h(t_2) \quad (1)$$

is interpreted within the model as the difference between a σ -bonding and a π -bonding contribution

$$\Delta = \Delta_\sigma - \Delta_\pi \quad (2)$$

Δ_σ is here positive because it represents the energetic effects of the $e(O_h)$ orbitals becoming σ -antibonding. The same is expected to be true of Δ_π .

except for certain ligands of π -accepting character, such as for example 2,2'-bipyridine. McClure²⁰ had an idea which, on the basis of equation 2, may be expressed as the possibility of a bisection of each Δ value into a σ and a π part, thus giving rise to a two-dimensional spectrochemical series (section 6c). A determination of Δ_σ and Δ_π is not possible in a regularly octahedral chromophore where only their difference is observable, because there are only two distinct orbital energies and therefore only one energy difference to observe. However, in chromophores of lower symmetry it is, in principle, possible to determine the individual parameters Δ_σ and Δ_π and this has also been done in certain cases²¹.

The development of the angular overlap model for application to general chromophores took place in stages and without direct connection with Yamatera's and McClure's work. Rather the results obtained by these authors came out as special cases of the application of the more general model to their particular chromophore systems²². The first generalization was made for σ -bonding in f -electron systems by Jørgensen, Pappalardo and Schmidtke²³, who developed the model from a molecular orbital point of view, but pointed out that it was equivalent to a contact term perturbation model. These authors used symmetry adapted ligand orbital linear combinations and considered only systems for which the same symmetry type occurred only once within the f -orbital manifold, thus avoiding the introduction of non-diagonal matrix elements. Perkins and Crosby²⁴, also considering σ -bonding in f -electron systems, showed a formalism which led to an expression for the non-diagonal elements and proposed, especially for computer calculators, not to worry about symmetry adaptation. Schäffer and Jørgensen²⁵ gave the model the name of the angular overlap model and, in principle, generalized it to apply to an l -electron system of any symmetry, taking into account σ -, π -, δ -, and ϕ -bonding. They further proved that the model had the character of a first order perturbation model and showed by the introduction of the orthogonal angular overlap matrix the validity of certain interesting sum-rules for the coefficients of the semiempirical parameters of the model. The angular overlap matrix was calculated for p and d functions. The symmetry basis for the model was discussed in other papers^{26, 27} and the relation between the angular overlap operators²⁸ and the irreducible representations (reps) of the three-dimensional rotation group demonstrated. The formal equivalence with the electrostatic model for chromophores containing linearly ligating ligands was shown in some special cases^{22, 29, 30} and proved to be of general validity¹⁷. Finally the angular overlap matrices for f and g functions and the corresponding rep matrices for the rotation group were calculated³¹.

The relation between the angular overlap model and the molecular orbital model of Wolfsberg and Helmholz³² has been discussed on several occasions by Jørgensen³³⁻³⁶.

3. THE SPHERICAL HARMONIC BASIS FUNCTIONS

(a) Importance of angular part of central atom orbitals

It is common to the angular overlap model and to the electrostatic model (section 6a) that the central ion orbitals are written as products of an angular

function $A(\vartheta, \varphi)$ and a radial function $R(r)$. The angular function is a hydrogen atom function, but no restrictions of this kind are imposed upon the radial function. However, it is only when one tries to place the results of the model as a part of a greater whole that considerations of the explicit form of the radial functions come in, since matrix elements over these functions are taken as the semiempirical parameters of the model. The coefficients to these semiempirical parameters are matrix elements taken over the angular functions, which therefore have a particular importance.

(b) The use of real orbitals

The pictorial character of the angular overlap model which made the intuitive basis for its development, is based upon the use of real spherical harmonics as basis functions. Although this does not exclude the use of a complex set of basis functions²⁷, the real functions are easier to visualize. Therefore this section will be devoted to presenting some of the relevant algebraical and geometrical properties of these functions.

(c) Surface harmonics and solid harmonics

As will appear from the applications, in addition to the surface spherical harmonics which make up the angular functions themselves, it is useful to consider also the solid spherical harmonics belonging to them³⁷⁻³⁹. With the relations:

$$\begin{aligned} z &= r \cos \vartheta \\ y &= r \sin \vartheta \sin \varphi \\ x &= r \sin \vartheta \cos \varphi \end{aligned} \tag{3}$$

between the Cartesian and the polar coordinates the general hydrogen atom angular function, corresponding to the azimuthal quantum number l , can be written as a surface harmonic of the form

$$A_l(\vartheta, \varphi) = \sum_i k_i x^a y^b z^c r^{-l} \quad (l = a + b + c) \tag{4}$$

subject to the equation of Laplace

$$\nabla^2 \left[\sum_i k_i x^a y^b z^c \right] = 0 \tag{5}$$

characterizing

$$\sum_i k_i x^a y^b z^c = r^l A_l \tag{6}$$

as the corresponding solid spherical harmonic. ∇^2 of equation 5 is the differential operator $\partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2$. The ratios between the coefficients k_i are determined³⁷⁻³⁹ by equation 5, their absolute value by a normalization condition, and their sign by a phase convention. It can be shown that there exist $2l + 1$ linearly independent functions A_l which can be chosen to be mutually orthogonal. Such $2l + 1$ functions can serve as basis functions for the $(2l + 1)$ -dimensional irreducible representation of the three-dimensional rotation group, spanning the same space as that of the

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usual complex spherical harmonics Y_l^m . These complex spherical harmonics Y_l^m also constitute a standard complex set of basis functions for the two-dimensional rotation group C_∞ as expressed in the second column of *Table 1*.

Table 1. Characterization of spherical harmonics in terms of their properties as basis functions for the two-dimensional rotation group C_∞ .

This group, being a commutative group, has only one-dimensional irreducible representations (reps), corresponding to the complex spherical harmonics Y_l^m , characterized by the integers l and m ($-l \leq m \leq l$; $l > 0$). However, for $m \neq 0$, these reps fall into pairs, $\lambda = |m|$, whose matrices, when transformed to refer to the real functions λs and λc with $\sin(\lambda\varphi)$ and $\cos(\lambda\varphi)$ -dependence, are non-diagonal (see also equation 65) and thus form the pseudo two-dimensional reps of C_∞ , whose characters χ are given in this table.

Rep. of C_∞	m	λ	λt	χ
σ	0	0	0	1
π	$\begin{Bmatrix} 1 \\ -1 \end{Bmatrix}$	1	$\begin{Bmatrix} 1s \\ 1c \end{Bmatrix}$	$2 \cos \varphi$
δ	$\begin{Bmatrix} 2 \\ -2 \end{Bmatrix}$	2	$\begin{Bmatrix} 2s \\ 2c \end{Bmatrix}$	$2 \cos 2\varphi$
φ	$\begin{Bmatrix} 3 \\ -3 \end{Bmatrix}$	3	$\begin{Bmatrix} 3s \\ 3c \end{Bmatrix}$	$2 \cos 3\varphi$
\cdot	\cdot	\cdot	\cdot	\cdot
\cdot	\cdot	\cdot	\cdot	\cdot
\cdot	\cdot	\cdot	\cdot	\cdot
\cdot	\cdot	\cdot	\cdot	\cdot

The functions to be used in the present paper are the usual real linear combinations of the Y_l^m functions which form a standard real set²⁷ of basis functions for C_∞ as well as for the three-dimensional rotation group.

(d) σ -Functions or zonal harmonics

The function Y_l^0 is common to the two basis sets and can, normalized to unity, be written

$$Y_l^0 = [(2l + 1)/4\pi]^{\frac{1}{2}} P_l(\cos \vartheta) = [(2l + 1)/4\pi]^{\frac{1}{2}} (l\sigma) \tag{7}$$

where $P_l = (l\sigma)$ is the so-called Legendre function, Legendre coefficient, zonal spherical harmonic, or axial spherical harmonic. The function $(l\sigma)$ is normalized to $4\pi(2l + 1)^{-1}$ and can be expressed as

$$P_l = (l\sigma) = \left[\cos^l \vartheta - \frac{l(l-1)}{2 \times 2} \cos^{l-2} \vartheta \sin^2 \vartheta + \frac{l(l-1)(l-2)(l-3)}{2 \times 4 \times 2 \times 4} \cos^{l-4} \vartheta \sin^4 \vartheta - \dots \right] \tag{8a}$$

with an analogous expression for the corresponding solid harmonic

$$(rl\sigma) \equiv r^l(l\sigma) = \left[z^l - \frac{l(l-1)}{2 \times 2} z^{l-2}(x^2 + y^2) + \frac{l(l-1)(l-2)(l-3)}{2 \times 4 \times 2 \times 4} z^{l-4}(x^2 + y^2)^2 - \dots \right] \tag{8b}$$

The first five of these axial harmonics are given in Table 2. We note the property that $(l\sigma) = 1$ when $\vartheta = 0$. This property of the σ -functions is of particular importance for the angular overlap model.

Table 2. σ -Functions for $l = 0$ to $l = 4$ given as surface harmonics and as solid harmonics

l	$(l\sigma)$	$(rl\sigma)$
0	1	1
1	$\cos \vartheta$	z
2	$\cos^2 \vartheta - \frac{1}{2} \sin^2 \vartheta$	$\frac{3}{2}z^2 - \frac{1}{2}r^2$
3	$\cos^3 \vartheta - \frac{3}{2} \cos \vartheta \sin^2 \vartheta$	$\frac{5}{2}z^3 - \frac{3}{2}zr^2$
4	$\cos^4 \vartheta - 3 \cos^2 \vartheta \sin^2 \vartheta + \frac{3}{8} \sin^4 \vartheta$	$\frac{35}{8}z^4 - \frac{15}{4}z^2r^2 + \frac{3}{8}r^4$

The functions further have cylindrical symmetry about the Z-axis and are therefore basis functions for the totally symmetrical representation of C_{∞} , and as such are called σ -functions. The locus

$$(l\sigma) = 0 \tag{9}$$

consists of l parallels of latitude symmetrically spaced about the equator $\vartheta = \pi/2$, which itself is a node line for l uneven. The locus thus divides the surface of the sphere into zones (zonal harmonics). The nodes of $(rl\sigma)$ form circular cones having Z as their axis.

(e) $(\lambda\sigma)$ -Functions or tesseral and sectorial harmonics

The functions Y_l^λ and $Y_l^{-\lambda}$ ($\lambda > 0$) (Table 1) form the standard complex basis functions for the pseudo two-dimensional reps of C_{∞} , characterized by their value of λ . These can be expressed with the phase choice of Condon and Shortley as:

$$Y_l^\lambda = \sqrt{\{(2l + 1)/4\pi\}} \{(-1)^\lambda/\sqrt{2}\} [(l\lambda c) + i(l\lambda s)] \tag{10a}$$

$$Y_l^{-\lambda} = \sqrt{\{(2l + 1)/4\pi\}} \{1/\sqrt{2}\} [(l\lambda c) - i(l\lambda s)] \tag{10b}$$

where $(l\lambda c)$ and $(l\lambda s)$ making up the real basis, normalized to $4\pi(2l + 1)^{-1}$, are given by:

$$(l\lambda s) = \sqrt{2\{\sqrt{[(l - \lambda)!/(l + \lambda)!]}\}} P_l^\lambda(\cos \vartheta) \sin \lambda\varphi \tag{11a}$$

$$(l\lambda c) = \sqrt{2\{\sqrt{[(l - \lambda)!/(l + \lambda)!]}\}} P_l^\lambda(\cos \vartheta) \cos \lambda\varphi \tag{11b}$$

or, by using an extension of a proposal by Kuse and Jørgensen⁴⁰, in the common form

$$(l\lambda\sigma) = \sqrt{2\{\sqrt{[(l - \lambda)!/(l + \lambda)!]}\}} P_l^\lambda(\cos \vartheta) \varrho(\lambda\varphi) \tag{11c}$$

where ϱ represents either a sine function or a cosine function.

In equations 11 $P_l^\lambda(\cos \vartheta)$ is the associated Legendre function of degree l and order λ which can be written

$$P_l^\lambda(\cos \vartheta) = \{(l + \lambda)!/2^\lambda \lambda!(l - \lambda)!\} P_{l,\lambda}(\cos \vartheta) \sin^\lambda \vartheta \tag{12}$$

where

$$P_{l,\lambda}(\cos \vartheta) = [\cos^{l-\lambda} \vartheta - \{(l-\lambda)(l-\lambda-1)/2(2\lambda+2)\} \cos^{l-\lambda-2} \vartheta \sin^2 \vartheta + \frac{(l-\lambda)(l-\lambda-1)(l-\lambda-2)(l-\lambda-3)}{2 \times 4(2\lambda+2)(2\lambda+4)} \cos^{l-\lambda-4} \vartheta \sin^4 \vartheta - \dots] \quad (13)$$

By combining equations 11, 12 and 13, the following explicit expression* for $(l\lambda\zeta)$ is obtained

$$(l\lambda\zeta) = \left(\frac{2(l+\lambda)!}{(l-\lambda)!}\right)^{\frac{1}{2}} \frac{1}{2^{\lambda}\lambda!} \left[\cos^{l-\lambda} \vartheta - \frac{(l-\lambda)(l-\lambda-1)}{2(2\lambda+2)} \cos^{l-\lambda-2} \vartheta \sin^2 \vartheta + \frac{(l-\lambda)(l-\lambda-1)(l-\lambda-2)(l-\lambda-3)}{2 \times 4(2\lambda+2)(2\lambda+4)} \cos^{l-\lambda-4} \vartheta \sin^4 \vartheta - \dots \right] \times \sin^{\lambda} \vartheta \zeta(\lambda\varphi) \quad (14a)$$

and the expression for the corresponding solid harmonic

$$(r^l l\lambda\zeta) \equiv r^l (l\lambda\zeta) = \left(\frac{2(l+\lambda)!}{(l-\lambda)!}\right)^{\frac{1}{2}} \frac{1}{2^{\lambda}\lambda!} \left[z^{l-\lambda} - \frac{(l-\lambda)(l-\lambda-1)}{2(2\lambda+2)} \times z^{l-\lambda-2}(x^2+y^2) + \frac{(l-\lambda)(l-\lambda-1)(l-\lambda-2)(l-\lambda-3)}{2 \times 4(2\lambda+2)(2\lambda+4)} \times z^{l-\lambda-4}(x^2+y^2)^2 - \dots \right] r^{\lambda} \sin^{\lambda} \vartheta \zeta(\lambda\varphi) \quad (14b)$$

where for ζ representing sine we have

$$r^{\lambda} \sin^{\lambda} \vartheta \sin(\lambda\varphi) = \left[\binom{\lambda}{1} x^{\lambda-1} y - \binom{\lambda}{3} x^{\lambda-3} y^3 + \dots \right] = s(\lambda) \quad (15a)$$

* $P_{l,\lambda}$ of equation 13 can be written in the alternative form

$$P_{l,\lambda} = \frac{2^{\lambda}\lambda!(2l)!}{2^l l!(l+\lambda)!} \left[\cos^{l-\lambda} \vartheta - \frac{(l-\lambda)(l-\lambda-1)}{2(2l-1)} \cos^{l-\lambda-2} \vartheta + \frac{(l-\lambda)(l-\lambda-1)(l-\lambda-2)(l-\lambda-3)}{2 \times 4(2l-1)(2l-3)} \cos^{l-\lambda-4} \vartheta - \dots \right]$$

which on being applied to equations 10, 11 and 12 and on multiplication by r^l gives the general expression for the solid complex harmonics

$$r^l Y_l^m = \left(\frac{2l+1}{4\pi}\right)^{\frac{1}{2}} (-1)^{\lambda} ((l-\lambda)!(l+\lambda)!)^{-\frac{1}{2}} \frac{(2l)!}{2^l l!} \times \left[z^{l-\lambda} - \frac{(l-\lambda)(l-\lambda-1)}{2(2l-1)} z^{l-\lambda-2} r^2 + \frac{(l-\lambda)(l-\lambda-1)(l-\lambda-2)(l-\lambda-3)}{2 \times 4(2l-1)(2l-3)} z^{l-\lambda-4} r^4 - \dots \right] [x+iy]^{\lambda}$$

where $m = \lambda \geq 0$. The expression for Y_l^{-m} is obtained by changing the sign of the imaginary unit and leaving out the factor $(-1)^{\lambda}$. By leaving out the factor $((2l+1)/4\pi)^{\frac{1}{2}}$ the solid harmonic $r^l Y_l^m$, which is normalized to unity in the closed interval $-1 \leq \vartheta \leq +1$ of the three Cartesian variables, becomes normalized to $4\pi/(2l+1)$ like the functions $(l\lambda\zeta)$. It is worth noting that the expression for $r^l Y_l^m$ is valid also for $m = \lambda = 0$. However, this is not true of expressions 14, which for $\lambda = 0$, equal $\sqrt{2}(\sigma)$ and $\sqrt{2}(r\lambda\sigma)$. The reason for this apparent absurdity is that for $\lambda = 0$ the φ dependence of $(l\sigma)$ is unity $[\cos(\lambda\varphi) = 1]$ so that its square integrates over the interval $0 \leq \varphi < 2\pi$ to 2π , whereas $[\zeta(\lambda\varphi)]^2$ integrates only to π .

and cosine,

$$r^\lambda \sin^\lambda \vartheta \cos(\lambda\varphi) = [x^\lambda - \binom{\lambda}{2} x^{\lambda-2} y^2 + \binom{\lambda}{4} x^{\lambda-4} y^4 - \dots] = c(\lambda) \quad (15b)$$

The expressions 14 represent for $\lambda < l$ the so-called tesseral harmonics as mentioned below. For $\lambda = l$ the expressions 14 degenerate to

$$(ll\zeta) = [2(2l)!]^\frac{1}{2} 2^{-l}(l!)^{-1} \sin^l \vartheta \zeta(l\varphi) \quad (16a)$$

and

$$(rll\zeta) \equiv r^l(ll\zeta) = [2(2l)!]^\frac{1}{2} 2^{-l}(l!)^{-1} r^l \sin^l \vartheta \zeta(l\varphi) \quad (16b)$$

representing the so-called sectorial harmonics. It is seen that the solid sectorial harmonics are given explicitly in equations 15, apart from their normalization constant.

The functions $P_{l,\lambda}(\cos \vartheta)$ of equation 13 with cylindrical symmetry (σ -symmetry) resemble $P_{l-\lambda}$, but they are not spherical harmonics, except for $l - \lambda = 1$ when $P_{l,l-1} = P_1$. Also $P_{l,\lambda} = 1$ when $\vartheta = 0$, the same relation as for $P_{l-\lambda}$. Further, parallel to the case of $P_{l-\lambda}$, the locus

$$P_{l,\lambda}(\cos \vartheta) = 0 \quad (17)$$

consists of $l - \lambda$ parallels of latitude symmetrically spaced about the equator ($\vartheta = \pi/2$). The locus

$$\zeta(\lambda\varphi) = 0 \quad (18)$$

consists of λ great circles through $z = 1$ and $z = -1$, inclined at an angle π/λ to one another. For ζ representing sine one such great circle passes through the origin of longitude $\varphi = 0$, or $x = 1$; for the cosine function one passes through $\varphi = \pi/2\lambda$, or $\lambda\varphi = \pi/2$. Since $\sin^\lambda \vartheta = 0$ for $\vartheta = 0$ and π , i.e. $z = 1$ and $z = -1$, this factor in equation 14 does not contribute anything extra to the locus

$$(ll\zeta) = 0 \quad (19)$$

which is the sum of that for $P_{l,\lambda}$ and that for $\zeta(\lambda\varphi)$, thus giving rise to a division of the sphere into quadrilaterals or tessera (tesseral harmonics), except when $\lambda = l$.

In this case $P_{l,l} = 1$ and the locus

$$(ll\zeta) = 0 \quad (20)$$

gives a division of the sphere into sectors (sectorial harmonics).

We note the important property of the real as well as of the complex standard basis sets that for $\lambda > 0$ the functions vanish on the Z -axis and for $\lambda = 0$ they are equal to unity (section 5b).

In conclusion the $(2l + 1)$ standard* real spherical surface harmonics consist of one zonal harmonic ($l\sigma$) (8), pairs† of tesseral harmonics (lls),

* The word standard here means that the coordinate system XYZ has been chosen and the real harmonics have been referred to this coordinate system. A rotation of the coordinate system (equation 24) will mean that linear combinations of the $2l + 1$ standard functions will be formed (equation 27), but the functions make up for each l -value a closed space for themselves.

† The tesseral harmonics only exist for $l \geq 2$. For $l = 2$ there is only one such pair. In general there are $l - 1$ such pairs.

$(l\lambda c)$ ($l > \lambda > 0$) (equations 14) and one pair* of sectorial harmonics ($l\lambda s$), $(l\lambda c)$ ($l = \lambda$) (equations 16). The zonal harmonic is equal to unity when $\vartheta = 0$, whereas all the other harmonics vanish for $\vartheta = 0$. As it will appear, the zonal and sectorial harmonics are of particular importance for the angular overlap model.

4. THE ANGULAR OVERLAP MODEL, AOM

(a) Situation and assumptions of AOM

The idea for the angular overlap model was originally based upon considerations concerning the approximate consequences of molecular orbital models of the linear-combination-of-atomic-orbitals type. We cite again the work of Yamatera^{18,19} and refer to Jørgensen's illuminating discussions^{34,35 p 95,36} of the problems of such models in general.

The Wolfsberg-Helmholz³² version of a molecular orbital model was considered under two main assumptions³⁴⁻³⁶, when applied to a complex consisting of a central ion surrounded by ligands. First it was assumed that the molecule had central ion to ligand bonds of heteropolar character with the diagonal elements of energy, representing the ligand orbitals, being much more negative than those representing the central atom orbitals with which the ligand orbitals interact. Secondly it was assumed that overlap integrals between the interacting central atom and ligand orbitals were small. Under these assumptions the formalism of the Wolfsberg-Helmholz model leads to the consequence that the energies of interaction become proportional to the squares of these small overlap integrals.

This was the basis for the development of the angular overlap model. However, it must be realized that this business of basing one model upon a restricted previous one does not imply that the second model is less general, or less good, if you wish, than the first one.

The development of any model is essentially a matter of having a good idea for a starting point and then judging by its consequences. As Professor Hartmann said at the ICCG in Vienna⁴¹, with a German pun: *Modelle werden erfunden und nicht gefunden*. 'Models cannot be discovered, they must be invented.'

After this introduction the angular overlap model may be characterized briefly as follows. The model is expected to apply to systems containing heteropolar bonds. With the conceptual pre-requisite of the one-electron approximation the ligand field $V(x, y, z)$ may with Jørgensen³⁶ be defined as the difference between the core field $U(x, y, z)$ of the molecule and the central field of the central ion $U(r)$, so that

$$V(x, y, z) \equiv U(x, y, z) - U(r) \quad (21)$$

Further the ligand field may be expanded as a sum of terms transforming as the components of the irreducible representations of the three-dimensional rotation group. We shall write the ligand field here as a sum of $V(r)$ representing the term of the expansion corresponding to the unit representation and

* The sectorial harmonics only exist for $l > 0$, and for $l \geq 1$ there always exists one such pair.

$A(x, y, z)$ representing the sum of the terms corresponding to all the rest of the representations.

$$V(x, y, z) = V(r) + A(x, y, z) \quad (22)$$

The angular overlap model endeavours to represent the potential energy term $A(x, y, z)$.

Combining equations 21 and 22 we obtain the expression

$$U(x, y, z) = U(r) + V(r) + A(x, y, z) \quad (23)$$

which shows that the core field $U(x, y, z)$ is equal to the sum of a spherically symmetrical or central field term $U(r) + V(r)$, whose eigenfunctions are also eigenfunctions of l^2 , i.e. have a well-defined l -value, and a lower symmetry term $A(x, y, z)$.

The ligand field part of the spherically symmetrical term corresponds to the central field covalency of Jørgensen⁴² and gives a plausible explanation of a nephelauxetic effect (i.e. an apparent l -orbital expansion) caused by the ligand electrons entering the region between the l -electrons and the central atom core.

With this background it is possible to describe the angular overlap model which can be defined by quoting its three additional assumptions.

I $A(x, y, z)$ can be accounted for by a first order perturbation either upon a d -basis or upon an f -basis.

II If the l -basis is defined relative to a coordinate system XYZ , then the perturbation matrix due to a ligand placed on the Z -axis is diagonal.

III Perturbation contributions from different ligands are additive.

It is immediately apparent that the angular overlap model, based upon the above assumptions, is equivalent, in a formalistic sense, to a generalized electrostatic model.

The restricted angular overlap model is in this context of particular interest. In this model assumption II is replaced by the assumption that each central ion to ligand bond has the linear symmetry $C_{\infty v}$. It is now a symmetry property which allows the following reformulation of assumption II.

Assumption II for the restricted angular overlap model:

If the l -orbital basis is defined relative to a coordinate system XYZ , then the perturbation matrix due to a ligand placed on the Z -axis is diagonal and the energy of an orbital ($l\lambda\zeta$) is independent of whether ζ represents the sine or the cosine function.

The restricted angular overlap model is equivalent to the point charge or point dipole electrostatic model in the sense that a linear relationship exists between the parameters of the two models^{17, 22, 29}.

(b) The AOM rotation matrix

We want to prepare a formalization of the assumptions made in the previous sub-section. We consider, for example, the d -basis set given in Table 3. The functions occur in Table 3 as surface harmonics as well as solid harmonics and the common notation, usually used for the surface harmonics, has been included.

When a coordinate system XYZ is given, the d -basis set is, for our purpose, completely specified as functions of x , y and z , by equations 8b and 14b

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because we do not, as stated in section 3a, concern ourselves about the radial part of the functions. We choose a space-fixed coordinate system XYZ with the origin at the nucleus of the central ion and completely defining a d -set of basis functions, and we shall have this system for all the time to follow. We shall also need to consider a movable or floating coordinate system $X'Y'Z'$, with a primed d -set of basis functions, obtained by a rotation of a coordinate system, originally coinciding with XYZ , by the operator R , which may be further specified in different ways.

Table 3. s , p , and d -Functions, normalized to $4\pi/(2l + 1)$, given in standard order as surface harmonics and as solid harmonics. Columns I and VI give our standard notation and standard numbering.

I	II	III	IV	V	VI
(σ)	s	(s)	1	1	1
(σ)	p_z	(z)	$\cos \vartheta$	z	1
(πs)	p_y	(y)	$\sin \vartheta \sin \varphi$	y	2
(πc)	p_x	(x)	$\sin \vartheta \cos \varphi$	x	3
(σ)	d_{z^2}	(z^2)	$\cos^2 \vartheta - \frac{1}{2} \sin^2 \vartheta$	$z^2 - \frac{1}{2}x^2 - \frac{1}{2}y^2$	1
(πs)	d_{yz}	(yz)	$\sqrt{3} \cos \vartheta \sin \vartheta \sin \varphi$	$\sqrt{3}yz$	2
(πc)	d_{zx}	(zx)	$\sqrt{3} \cos \vartheta \sin \vartheta \cos \varphi$	$\sqrt{3}zx$	3
(δs)	d_{xy}	(xy)	$\frac{1}{2}\sqrt{3} \sin^2 \vartheta \sin 2\varphi$	$\sqrt{3}xy$	4
(δc)	$d_{x^2-y^2}$	$(x^2 - y^2)$	$\frac{1}{2}\sqrt{3} \sin^2 \vartheta \cos 2\varphi$	$\frac{1}{2}\sqrt{3}(x^2 - y^2)$	5

We specify the rotation operator of the AOM as

$$R(\varphi, \vartheta) = R_z(\varphi) R_y(\vartheta) \tag{24}$$

which reads as follows (Figure 1). Take the $X'Y'Z'$ coordinate system with its set of primed d -functions, place it so that it coincides with the space-fixed system XYZ and rotate it first by the angle ϑ about the Y -axis and then, after the first rotation has taken place, rotate it by the angle φ about the Z -axis (of the XYZ -system!). In this way the direction of the positive Z' -axis becomes (ϑ, φ) , where ϑ and φ are the usual angular polar coordinates relative to the XYZ coordinate system*. By our rotation the axes of the primed right-handed coordinate system $Z'X'Y'$ coincide with the respective infinitesimal direction vectors for the right-handed polar coordinate system $r\vartheta\varphi$.

We now have two different coordinate systems, an unprimed one and a primed one, and with them two different d -function standard basis sets which span the same space, or in other words are related to each other by a linear transformation which may be written

$$f' = Rf = fF \tag{25}$$

* The rotation $R(\varphi, \vartheta)$ that we have considered does not contain enough parameters to specify a general rotation of the original coordinate system. A general rotation operator²⁷ is

$$R = R_z(\varphi) R_y(\vartheta) R_z(\psi) = R_z(\psi) R_z(\varphi) R_y(\vartheta)$$

where the ψ rotation either precedes the other rotations and then takes place about the Z -axis, or may be performed at any time during the other rotations and then takes place about the Z' -axis. R_z commutes with R_z as well as with R_y (see dashed coordinate axes on Figure 1.)

where \mathbf{f}' and \mathbf{f} represent the primed and the unprimed set of d -functions set up in a row matrix in the standard order of Table 3. \mathbf{F} is the orthogonal matrix which has been called the angular overlap matrix (see also later, equation 43).

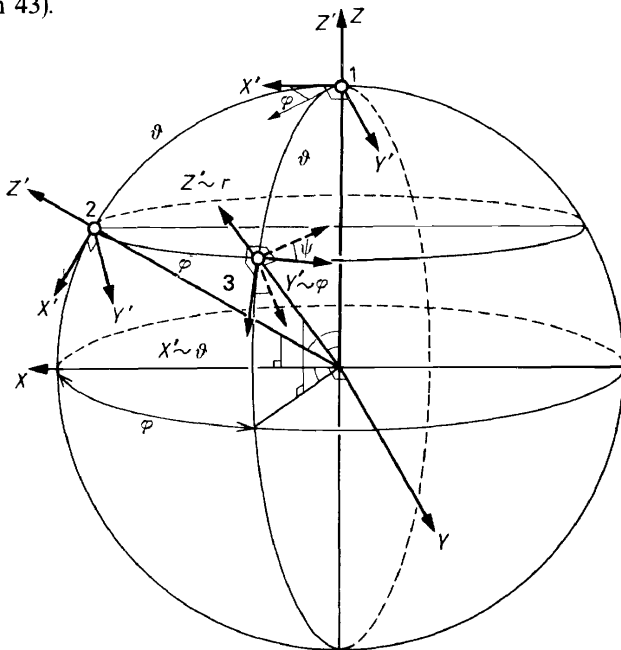


Figure 1. Illustration of standard rotation operator of AOM

$$R(\varphi, \vartheta) = R_Z(\varphi)R_Y(\vartheta)$$

The XYZ coordinate system has its origin at the central ion nucleus. The rotation $R_Y(\vartheta)$ moves a point upon the unit sphere from position 1, $(\vartheta, \varphi) = (0, 0)$, to position 2, $(\vartheta, 0)$, and $R_Z(\varphi)$ moves it on to position 3, (ϑ, φ) . The primed central ion coordinate systems which arise have not been shown in the figure, but the ligand coordinate systems corresponding to each of the three positions and having their coordinate axes parallel to the primed central ion coordinate systems are shown. The final primed coordinate system (position 3) has its axes coinciding with the infinitesimal direction vectors of the usual polar coordinate axes.

Equation 25 has a reciprocal relation

$$\mathbf{f} = \mathbf{R}^{-1}\mathbf{f}' = \mathbf{f}'\mathbf{F}^{-1} = \mathbf{f}'\tilde{\mathbf{F}} \tag{26}$$

where the orthogonality of the \mathbf{F} matrix causes its reciprocal \mathbf{F}^{-1} to be equal to its transpose $\tilde{\mathbf{F}}$. Let us pick out one of the functions of the unprimed basis set, (t) say, where (t) may be specified either by one of the symbols (σ) , (π_s) , (π_c) , (δ_s) , or (δ_c) or, alternatively, by its number in the standard order given here, as well as in Table 3. We shall need an expression for (t) as a linear combination of the functions of the primed basis set. By using equation 26 we obtain

$$(t) = \sum_{w'=1}^{w'=5} (w)' \tilde{\mathbf{F}}_{w't} = \sum_{w=1}^{w=5} (w) \mathbf{F}_{tw'} \tag{27}$$

where we have placed the primes outside the parentheses specifying the functions. This is unimportant, but will simplify the notation later.

(c) AOM as a perturbation model

We are now in a position to return to the angular overlap model and we consider a ligand $L(k)$ placed on the positive Z' -axis. k refers to the polar coordinates of Z' , (ϑ_k, φ_k) , say. The functional dependence of the expansion coefficients \mathbf{F} of equation 27 on k may be written \mathbf{F}^k so that $\mathbf{F}^k = \mathbf{F}(\varphi_k, \vartheta_k)$. According to assumption I we are only concerned with matrix elements of the type $(t' | \mathbf{A}^k | w')$. According to assumption II this perturbation is diagonal, or,

$$(t' | \mathbf{A}^k | w') = \delta_{t'w'} e_{t'L(k)} = (t' | \mathbf{A}^k | t') = e_{t'L(k)} = e_{tL(k)} \quad (28)$$

where the Kronecker δ vanishes when (w') is different from (t') and equals unity when $(w') = (t')$. $e_{tL(k)}$ is the radial parameter, the semiempirical parameter of the AOM. When $t = 1$, for example, we have the parameter representing the σ -perturbation of the ligand L in position k .

We require the general matrix element of \mathbf{A}^k , $(u | \mathbf{A}^k | v)$, taken with respect to our space-fixed unprimed basis set. Introducing equations 27 and 28 consecutively we obtain:

$$\begin{aligned} (u | \mathbf{A}^k | v) &= (\{ \mathbf{F}_{u1}^k(\sigma)' + \mathbf{F}_{u2}^k(\pi s)' + \mathbf{F}_{u3}^k(\pi c)' + \mathbf{F}_{u4}^k(\delta s)' \\ &+ \mathbf{F}_{u5}^k(\delta c)' \} | \mathbf{A}^k | \{ \mathbf{F}_{v1}^k(\sigma)' + \mathbf{F}_{v2}^k(\pi s)' + \mathbf{F}_{v3}^k(\pi c)' + \mathbf{F}_{v4}^k(\delta s)' + \mathbf{F}_{v5}^k(\delta c)' \}) \\ &= \sum_{t'=1}^{t'=5} \mathbf{F}_{ut'}^k \mathbf{F}_{vt'}^k (t' | \mathbf{A}^k | t') = \sum_{t'=1}^{t'=5} \mathbf{F}_{ut'}^k \mathbf{F}_{vt'}^k e_{t'L(k)} \end{aligned} \quad (29)$$

with the special case of the diagonal element when $v = u$

$$(u | \mathbf{A}^k | u) = \sum_{t'=1}^{t'=5} (\mathbf{F}_{ut'}^k)^2 e_{t'L(k)} \quad (30)$$

We see that the matrix elements have become expressed as a sum of (σ) , (πs) , (πc) , (δs) and (δc) contributions. Since \mathbf{F} is an orthogonal matrix

$$\sum_u (\mathbf{F}_{ut'}^k)^2 = \sum_{t'} (\mathbf{F}_{ut'}^k)^2 = 1 \quad (31)$$

and we see that the coefficients of $e_{t'L(k)}$ for a given t' summed over the unprimed basis set are equal to unity and that, for a given matrix element $(u | \mathbf{A}^k | u)$, say, the sum of the coefficients to the five different $e_{t'L(k)}$ parameters also equals unity.

Finally we use assumption III which states that the perturbation contributions are additive. This means that we have to sum over k in equations 29 and 30, and the general matrix element becomes

$$(u | \mathbf{A} | v) = \sum_{k=1}^{k=N} \sum_{t'=1}^{t'=5} \mathbf{F}_{ut'}^k \mathbf{F}_{vt'}^k e_{tL(k)} \quad (32)$$

where the prime has been removed from the dummy index. N is the number of ligands, whose positions are indicated by the upper index k , and whose possibly different radial parameters are indicated by the sub-index to e_t . $L(k)$ may refer to different ligands when k varies, so that k is used to refer to the position of ligand as well as to the kind of ligand.

The relation 31 now becomes

$$\sum_{k=1}^{k=N} \sum_{u=1}^{u=5} (\mathbf{F}_{ur}^k)^2 = \sum_{k=1}^{k=N} \sum_{r'=1}^{r'=5} (\mathbf{F}_{ur'}^k)^2 = N \quad (33)$$

which are the sum rules of the angular overlap model. Since the spur of a matrix is equal to the sum of the eigenvalues of the corresponding secular determinant the rules can be expressed as follows:

(1) For the sum of the eigenvalues of an angular overlap model calculation the coefficient to each of the radial parameters e_i is equal to the number of ligands, N .

(2) Each eigenvalue as well as each diagonal element is expressed as a linear combination of e_i -terms whose coefficients add up to the number of ligands, N .

We finish this sub-section by two examples.

Example 1(a). One linearly ligating ligand placed on the Z' -axis, whose coordinates are (ϑ, φ) , as obtained by operation 24. We recall that for a ligand of this type the central ion to ligand bond has cylindrical symmetry so that the pairs of λ orbitals remain degenerate. We are then able to write down the perturbation energies immediately. They are:

$$\begin{aligned} (\sigma' | A | \sigma') &= e_\sigma; & (\sigma') &= z'^2 - 1/2x'^2 - 1/2y'^2; \\ (\pi' | A | \pi') &= e_\pi; & (\pi s)' &= \sqrt{3}y'z'; & (\pi c)' &= \sqrt{3}z'x'; \\ (\delta' | A | \delta') &= e_\delta; & (\delta s)' &= \sqrt{3}x'y'; & (\delta c)' &= \sqrt{3/2}(x'^2 - y'^2); \end{aligned} \quad (34)$$

and the eigenfunctions are (σ') , corresponding to the non-degenerate eigenvalue e_σ , (πs) and (πc) corresponding to the doubly degenerate eigenvalue e_π and so on.

If we wanted to have the eigenfunctions written in terms of our space-fixed set of basis functions we would have to use the \mathbf{F} -matrix (Table 4) of equations 25 and 26 whose matrix elements are the coefficients of equation 27.

In this way, for example,

$$\begin{aligned} (\sigma') &= (\cos^2 \vartheta - \frac{1}{2} \sin^2 \vartheta) (\sigma) + (\sqrt{3} \cos \vartheta \sin \vartheta \sin \varphi) (\pi s) \\ &+ (\sqrt{3} \cos \vartheta \sin \vartheta \cos \varphi) (\pi c) + (\sqrt{3/2} \sin^2 \vartheta \sin 2\varphi) (\delta s) \\ &+ (\sqrt{3/2} \sin^2 \vartheta \cos 2\varphi) (\delta c) \end{aligned} \quad (35)$$

Example 2(a). Two equal linearly ligating ligands, one placed on the X -axis, the other one on the Y -axis. Let us consider the ligand on the X -axis first. The results for a Z -axis ligand can here be applied by performing the following transformation 24 of coordinates (Figure 1) $Z \rightarrow Z' = X$, $Y \rightarrow Y' = Y$; $X \rightarrow X' = -Z$. This leads to the following eigenvalues and eigenfunctions:

$$\begin{aligned} e_\sigma \quad (\sigma') &= x^2 - 1/2y^2 - 1/2z^2 = -1/2(\sigma) + \sqrt{3/2}(\delta c); \\ e_\pi \quad (\pi s)' &= \sqrt{3}xy = (\delta s); & (\pi c)' &= -\sqrt{3}zx = -(\pi c); \\ e_\delta \quad (\delta s)' &= -\sqrt{3}yz = -(\pi s); & (\delta c)' &= -\sqrt{3/2}(y^2 - z^2) = \sqrt{3/2}(\sigma) + 1/2(\delta c); \end{aligned} \quad (36)$$

The next stage is, according to equation 29, the reverse relation

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$$\begin{aligned}
 (\sigma) &= -1/2(\sigma)' + \sqrt{3}/2(\delta c)' \\
 e_\delta (\pi s) &= -(\delta s)' \\
 e_\pi (\pi c) &= -(\pi c)' \\
 e_\pi (\delta s) &= (\pi s)' \\
 (\delta c) &= \sqrt{3}/2(\sigma)' + 1/2(\delta c)'
 \end{aligned}
 \tag{37}$$

which can be obtained either by using the **F**-matrix (Table 4) for $(\vartheta_k, \varphi_k) = (\frac{1}{2}\pi, 0)$ or by direct algebra using equation 36. The functions (πs) , (πc) and (δs) are seen to be eigenfunctions already and their eigenvalues have been given to the left. We further have to calculate the matrix elements

$$\begin{aligned}
 (\sigma | A^X | \sigma) &= \frac{1}{4} e_\sigma + \frac{3}{4} e_\delta \\
 (\sigma | A^X | \delta c) &= -\frac{\sqrt{3}}{4} e_\sigma + \frac{\sqrt{3}}{4} e_\delta \\
 (\delta c | A^X | \delta c) &= \frac{3}{4} e_\sigma + \frac{1}{4} e_\delta
 \end{aligned}
 \tag{38}$$

so that the 2×2 energy matrix becomes

$$\begin{array}{l}
 (\sigma) \left[\begin{array}{cc} \frac{1}{4} e_\sigma + \frac{3}{4} e_\delta & -\frac{\sqrt{3}}{4} e_\sigma + \frac{\sqrt{3}}{4} e_\delta \\ -\frac{\sqrt{3}}{4} e_\sigma + \frac{\sqrt{3}}{4} e_\delta & \frac{3}{4} e_\sigma + \frac{1}{4} e_\delta \end{array} \right] \\
 (\delta c)
 \end{array}
 \tag{39}$$

For the Y-axis ligand, $(\vartheta_k, \varphi_k) = (\frac{1}{2}\pi, \frac{1}{2}\pi)$, the perturbation contributions, referred to the unprimed basis and corresponding to equations 37 and 39, can be obtained analogously:

$$\begin{aligned}
 e_\pi (\pi s) &= -(\pi c)' \\
 e_\delta (\pi c) &= (\delta s)' \\
 e_\pi (\delta s) &= -(\pi s)' \\
 (\sigma) \left[\begin{array}{cc} \frac{1}{4} e_\sigma + \frac{3}{4} e_\delta & \frac{\sqrt{3}}{4} e_\sigma - \frac{\sqrt{3}}{4} e_\delta \\ \frac{\sqrt{3}}{4} e_\sigma - \frac{\sqrt{3}}{4} e_\delta & \frac{3}{4} e_\sigma + \frac{1}{4} e_\delta \end{array} \right] \\
 (\delta c)
 \end{aligned}
 \tag{40}$$

On adding the contributions from the two ligands taken from equations 37, 39 and 40, the non-diagonal elements of the 2×2 matrix disappear and we obtain:

$$\begin{aligned}
 (\sigma | A | \sigma) &= \frac{1}{2} e_\sigma + \frac{3}{2} e_\delta \\
 (\pi s | A | \pi s) &= (\pi c | A | \pi c) = e_\pi + e_\delta \\
 (\delta s | A | \delta s) &= 2e_\pi \\
 (\delta c | A | \delta c) &= \frac{3}{2} e_\sigma + \frac{1}{2} e_\delta
 \end{aligned}
 \tag{41}$$

We note that the sum of the coefficients to e_σ equals two, the number of ligands. For e_π and e_δ the sum is four, because the sine and cosine contributions have been added for the linearly ligating ligands. Also the sum of the coefficients to all the e_l for each eigenstate adds up to two.

(d) AOM oriented towards a molecular orbital model

We shall now reconsider the assumptions of the angular overlap model in the light of its intuitive basis. As mentioned in section 4a it was the original assumption that the bonding interaction between a central ion and a ligand orbital was proportional to the square of the overlap integral between the two orbitals. This assumption is equivalent to the assumption I that the model is a first order perturbation model. Further this assumption serves to clarify the assumption II that the perturbation matrix of a ligand on the Z-axis with respect to our standard basis is diagonal.

Let us consider a central ion orbital (Mu) which is the product of a radial factor normalized to $(2l + 1)/4\pi$ and an angular factor which is our standard basis (lu), normalized to $4\pi/(2l + 1)$, so that $(Mu|Mu) = \delta_{uv}$. For our primed basis we consider functions (Mu') defined analogously. We now place a new primed coordinate system $X'Y'Z'$, we can call it the primed ligand coordinate system, with the origin at the ligand nucleus, with the Z' -axis coinciding with that of the primed central ion coordinate system, and with the X' - and Y' -axes parallel to those of this system (Figure 1). In exactly the same way as the primed central ion system defines a basis set (Mu'), the primed ligand system defines a basis set of ligand orbitals (Lt'). Because both standard functions (Mu') and (Lt') form standard bases for the irreducible representations of $C_{\infty v}$ with Z' as the axis of symmetry, we have the relation

$$(Mu'|Lt') = \delta_{u't'} S_{MLt'} = (Mt'|Lt') = 1 \cdot S_{MLt'}^* = S_{MLt'}^* \quad (42)$$

We think of the overlap integral $S_{MLt'}$ as consisting of an angular factor, which we define as being equal to unity, and a radial factor $S_{MLt'}^*$. This is justified by considering the integral

$$(Mu|Lt') = \sum_{Mv'} (Mu|Mv')(Mv'|Lt') = (Mu|Mt')(Mt'|Lt') \\ = \mathbf{F}_{u't'} \cdot S_{MLt'}^* \quad (43)$$

where the unprimed central ion orbitals have been expressed in terms of the primed ones according to equation 27, and equation 42 introduced. It is seen that the overlap integral $(Mu|Lt')$ consists of the coefficient $\mathbf{F}_{u't'}$, which only depends on the angular coordinates, and the previously mentioned radial part of the overlap integral. We call $\mathbf{F}_{u't'}$ the angular overlap integral between the central ion orbital (Mu) and the ligand orbital (Lt'). By this definition it is equal to the overlap integral between the two central ion orbitals of the two different standard basis sets.

We are now able to consider a general matrix element of our primed central ion basis and express it by its proportionality to a squared overlap integral. In order to have an example which illustrates the generality of the procedure we think of a ligand which is able to provide a bonding function of (lt')-type with more than one l -value, (pt') and (dt'), say. We then have for the

part of the perturbation $A_{t'}$ which comes from the bond formation with a ligand orbital of symmetry t' :

$$\begin{aligned}
 (Mu' | A_{t'} | Mv) &= \sum_{Ll} c(M, Ll, t') (Mu' | Llt') (Llt' | Mv) \\
 &= \sum_{Ll} c(M, Ll, t') (Mt' | Llt') (Llt' | Mt') \quad (44) \\
 &= \sum_{Ll} c(M, Ll, t') (S_{MLlt'}^*)^2 = (Mt' | A_{t'} | Mt') \equiv e_{t'} = e_t
 \end{aligned}$$

It is seen that the radial parameter of the perturbation model e_t is expressed here as a sum of terms containing a squared overlap integral multiplied by a factor of proportionality. The interesting thing about it, as can be seen from equation 44, is how assumption II (p 370) of the perturbation model comes in as a consequence of the assumption about the proportionality of the bonding interaction with the squared overlap. Also the resolution of the perturbation A into $A_{t'}$ components is a consequence of this assumption.

We check the formalism by evaluating the matrix element of $A_{t'}$ with respect to our unprimed basis

$$\begin{aligned}
 (Mu | A_{t'} | Mv) &= \sum_{Ll} c(M, Ll, t') (Mu | Llt') (Llt' | Mv) \\
 &= \sum_{Ll} \sum_{p'} \sum_{q'} c(M, Ll, t') (Mu | Mp') (Mp' | Llt') (Llt' | Mq') (Mq' | Mv) \\
 &= \mathbf{F}_{ut'} \mathbf{F}_{vt'} \sum_{Ll} c(M, Ll, t') (Mt' | Llt') (Llt' | Mt') = \mathbf{F}_{ut'} \mathbf{F}_{vt'} e_{t'} \quad (45)
 \end{aligned}$$

It is seen that if we add the indices to specify the ligand and its position and sum over the different symmetry types of overlap t' , and thereby the different bonding possibilities for our central ion l -shell, we obtain an expression identical to equation 29.

In the following we drop the summation over Ll , since, as we have seen, for a given ligand it is always the sum of the bonding effects over all the ligand orbitals of symmetry type t' (pt' and dt' , say) which makes up our semi-empirical parameter $e_{t'}$. Such a ligand orbital of t' type may therefore also be a hybrid type of orbital. For example, for $(t') = (\pi c)$, it could be a linear combination of an $(Lp\pi c)$ and an $(Ld\pi c)$ orbital⁴³. For the AOM it is only its (t') -character, in this case (πc) -character, which counts.

The general form of equation 45 can then be expressed:

$$\begin{aligned}
 (Mu | A | Mv) &= \sum_k \sum_{t'} (Mu | A_{t'}^k | Mv) \\
 &= \sum_k \sum_{t'} \mathbf{F}_{ut'}^k \mathbf{F}_{vt'}^k c(M, L(k), t') (M(k)t' | L(k)t')^2 \\
 &= \sum_k \sum_{t'} \mathbf{F}_{ut}^k \mathbf{F}_{vt}^k e_{tL(k)} \quad (46)
 \end{aligned}$$

where the association between the position k and the primed basis functions t' has been emphasized both for central ion and ligand orbitals. Equation 46 expresses the same result as equation 32. We note that in deriving equation 46 from equation 45 we have used the assumption III (p 370) that the single ligand perturbation contributions are additive.

We now want to investigate the AOM as an overlap model in terms of linear combinations of ligand orbitals ($\chi(\kappa)t'$). In order to do this we introduce ($\chi(\kappa)t'$) as an orthonormal set of linear combinations of the N single ligand orbitals ($L(k)t'$), and we assume that these for different k are mutually orthogonal, an assumption which corresponds to the assumption III (p 370). We can then write

$$(\chi(\kappa)t') = \sum_k (L(k)t' | \chi(\kappa)t') (L(k)t') = \sum_k \mathbf{U}_{k\kappa} (L(k)t') \quad (47)$$

where \mathbf{U} is an orthogonal matrix so that

$$\sum_x \mathbf{U}_{ix} \mathbf{U}_{jx} = \delta_{ij} \quad (48)$$

The overlap integral between a central ion orbital (Mu) and the ligand linear combination ($\chi(\kappa)t'$)

$$(Mu | \chi(\kappa)t') = \sum_k \mathbf{U}_{k\kappa} (Mu | L(k)t') = \sum_k \mathbf{U}_{k\kappa} \mathbf{F}_{ut'}^k S_{ML(k)t'}^* \quad (49)$$

can be written as a product of a radial factor and an angular factor provided $S_{ML(k)t'}^*$ can be put outside the summation sign. This can be done if all the ligands $L(k)$ are identical. Then

$$(Mu | \chi(\kappa)t') = S_{MLt'}^* \sum_k \mathbf{U}_{k\kappa} \mathbf{F}_{ut'}^k = \mathbf{F}_{ut'}^\kappa S_{MLt'}^* \quad (50)$$

where $\mathbf{F}_{ut'}^\kappa$ is called the angular group overlap integral[†].

The assumption that the ligands $L(k)$, making up the linear combination $\chi(\kappa)$, must be identical is no restriction, since symmetry cannot ever bring non-identical ligands into coincidence. Therefore this assumption only means that the matrix \mathbf{U} of equation 47 has a block form, each block corresponding to one kind of ligand. It would be quite reasonable, for these cases of identical ligands, just for the sake of symmetry in the notation, to write

$$S_{MLt'}^* = S_{M\chi t'}^* \quad (51)$$

or correspondingly

$$e_{t'L(k)} = e_{t'\chi(\kappa)} \quad (52)$$

Doing this we obtain an alternative formula to equation 46:

$$\begin{aligned} (Mu | \mathbf{A} | Mv) &= \sum_x \sum_{t'} \mathbf{F}_{ut'}^\kappa \mathbf{F}_{vt'}^\kappa e_{t'\chi(\kappa)} \\ &= \sum_x \sum_i \sum_j \sum_{t'} \mathbf{U}_{ix} \mathbf{U}_{jx} \mathbf{F}_{ut'}^i \mathbf{F}_{vt'}^j e_{t'L(k)} \\ &= \sum_i \sum_j \sum_{t'} \delta_{ij} \mathbf{F}_{ut'}^i \mathbf{F}_{vt'}^j e_{t'L(k)} \\ &= \sum_k \sum_{t'} \mathbf{F}_{ut'}^k \mathbf{F}_{vt'}^k e_{t'L(k)} \end{aligned} \quad (53)$$

[†] $\mathbf{F}_{ut'}^\kappa$ is usually called the group overlap coefficient, i.e. the ratio between the group overlap integral and the appropriate diatomic overlap integral. While the absolute value of $\mathbf{F}_{ut'}^\kappa$ is always less than unity, that of $\mathbf{F}_{ut'}^\kappa$ is bound by an upper limit of \sqrt{N} , where N is the number of ligands of the k type.

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where the first expression of equation 53 applies within each group of identical ligands. However, k as well as κ in equation 53 might represent more such groups of identical ligands.

We now reconsider the examples of section 4(c) on the basis of the overlap description.

Example 1(b). The central ion orbitals (Mt') and the ligand orbitals (Llt') are symmetry adapted here so as to be basis functions for reps of $C_{\infty v}$ having Z' as the axis. We simply have the situation of equation 44 and are therefore able to write down the results of equation 34 immediately.

Example 2(b). In order to apply equation 46 we need the individual angular overlap matrices for $L(X)$ and $L(Y)$.

For $L(X)$ the angular overlap matrix elements can be read directly from equation 37:

$$\begin{array}{l}
 F^X \\
 (\sigma) \\
 (\pi s) \\
 (\pi c) \\
 (\delta s) \\
 (\delta c)
 \end{array}
 \begin{array}{l}
 (\sigma)_x \\
 (\sigma)' \\
 -1/2 \\
 0 \\
 0 \\
 0 \\
 \sqrt{3}/2
 \end{array}
 \begin{array}{l}
 (\pi s)_x \\
 (\pi s)' \\
 0 \\
 0 \\
 +1 \\
 0
 \end{array}
 \begin{array}{l}
 (\pi c)_x \\
 (\pi c)' \\
 0 \\
 -1 \\
 0 \\
 0
 \end{array}
 \begin{array}{l}
 (\delta s)_x \\
 (\delta s)' \\
 0 \\
 -1 \\
 0 \\
 0
 \end{array}
 \begin{array}{l}
 (\delta c)_x \\
 (\delta c)' \\
 \sqrt{3}/2 \\
 0 \\
 0 \\
 1/2
 \end{array}
 \quad (54)$$

and for $L(Y)$ one obtains analogously:

$$\begin{array}{l}
 F^Y \\
 (\sigma) \\
 (\pi s) \\
 (\pi c) \\
 (\delta s) \\
 (\delta c)
 \end{array}
 \begin{array}{l}
 (\sigma)_y \\
 (\sigma)' \\
 -1/2 \\
 0 \\
 0 \\
 -\sqrt{3}/2
 \end{array}
 \begin{array}{l}
 (\pi s)_y \\
 (\pi s)' \\
 0 \\
 0 \\
 -1 \\
 0
 \end{array}
 \begin{array}{l}
 (\pi c)_y \\
 (\pi c)' \\
 0 \\
 -1 \\
 0 \\
 0
 \end{array}
 \begin{array}{l}
 (\delta s)_y \\
 (\delta s)' \\
 0 \\
 0 \\
 1 \\
 0
 \end{array}
 \begin{array}{l}
 (\delta c)_y \\
 (\delta c)' \\
 \sqrt{3}/2 \\
 0 \\
 0 \\
 -1/2
 \end{array}
 \quad (55)$$

where it must be remembered that the primed functions of the F^X - and the F^Y -matrices belong to two different basis sets. This has been indicated by the two different sets of sub-indices.

We are now in a position to use equation 46 and we obtain, for example

$$\begin{aligned}
 (M\sigma|A|M\delta c) &= (M\sigma|A_\sigma|M\delta c) + (M\sigma|A_{\delta c}|M\delta c) \\
 &= (M\sigma|A_\sigma^X|M\delta c) + (M\sigma|A_\sigma^Y|M\delta c) \\
 &+ (M\sigma|A_{\delta c}^X|M\delta c) + (M\sigma|A_{\delta c}^Y|M\delta c) \\
 &= (-1/2)(\sqrt{3}/2)e_\sigma + (-1/2)(-\sqrt{3}/2)e_\sigma \\
 &+ (\sqrt{3}/2)(1/2)e_{\delta c} + (\sqrt{3}/2)(-1/2)e_{\delta c} = 0
 \end{aligned}
 \quad (56)$$

In a similar way the results of equation 41 can be obtained.

Let us now instead of adding the individual ligand squared overlap

contributions use the orthonormalized linear combinations of mutually orthogonal ligand orbitals

$$t^{\pm} = (\sqrt{2}/2)(t_x \pm t_y) \quad (57)$$

Let us, for example, calculate $(M\sigma | A_{\sigma} | M\sigma)$. It is now clear that only t^+ will be able to contribute here since only t^+ belongs to the symmetry type a_1 of the molecular point group C_{2v} , as do $M\sigma$.

$$(M\sigma | A_{\sigma} | M\sigma) = [\sqrt{2}/2(-1/2 - 1/2)]^2 e_{\sigma} = 1/2 e_{\sigma} \quad (58)$$

in agreement with equation 41. For the standard $(M\pi)$ -orbitals that are not symmetry-adapted to C_{2v} there is no particular advantage in using the linear combinations of ligand-orbitals although, of course, it is quite permissible.

5. EVALUATION OF ANGULAR OVERLAP INTEGRALS

(a) The angular overlap matrix

We shall show how the individual columns of the angular overlap matrix can be obtained. We refer to the definition of the matrix by equation 25 and to the justification for its name in equation 43. Using the definition of the unprimed and the primed sets of p 371, equation 25 can be written out for a single one of the rotated functions as

$$t(x', y', z') = (Rt)(x, y, z) = \sum_{w=1}^{w=5} w(x, y, z) \mathbf{F}_{wt'} = t'(x, y, z) \quad (59)$$

where it is seen that it is a matter of taste whether the matrix elements of \mathbf{F} are called \mathbf{F}_{wt} or $\mathbf{F}_{wt'}$ (see also, for example, equations 32 and 46). (x, y, z) and (x', y', z') refer in equation 59 to the same point in space and from the definition of the rotation operator $R(\vartheta, \varphi)$ of equation 24 the coordinate interrelations are:

$$\begin{aligned} z' &= z \cos \vartheta + y \sin \vartheta \sin \varphi + x \sin \vartheta \cos \varphi \\ y' &= \quad \quad \quad y \cos \varphi \quad - x \sin \varphi \\ x' &= -z \sin \vartheta + y \cos \vartheta \sin \varphi + x \cos \vartheta \cos \varphi \end{aligned} \quad (60)$$

Using equations 59 and 60 we illustrate by two examples how the columns of the $\mathbf{F}^{(l)}$ -matrices in general can be obtained.

Example 3. The $(\pi c)'$ -column (Table 3) of the $\mathbf{F}^{(p)}$ -matrix (Table 5), $t' = (p\pi c)'$. We obtain

$$\begin{aligned} (p\pi c)' = x' &= z \mathbf{F}_{13} + y \mathbf{F}_{23} + x \mathbf{F}_{33} \\ &= z(-\sin \vartheta) + y(\cos \vartheta \sin \varphi) + x(\cos \vartheta \cos \varphi) \end{aligned} \quad (61)$$

giving

$$\mathbf{F}_{13} = -\sin \vartheta; \quad \mathbf{F}_{23} = \cos \vartheta \sin \varphi; \quad \mathbf{F}_{33} = \cos \vartheta \cos \varphi \quad (62)$$

with the full $\mathbf{F}^{(p)}$ -matrix given in Table 5.

Table 4. The angular overlap matrix $\mathbf{F}^{(4)}(\varphi, \vartheta)$.

	(z^2) (σ)	(yz) (πs)	(z^2) (πc)	(y^2z) (πs)	(z^2x^2) (πc)	(x^2y^2) (δc)	$(x^2y^2 - y^4)$ (δc)
	$3/2(\cos^2 \vartheta - 1/3)$	0	$-\sqrt{3} \cos \vartheta \sin \vartheta$	$2 \cos^2 \vartheta - 1$	$2 \cos^2 \vartheta - 1$	$2 \cos^2 \vartheta - 1$	0
	$\sqrt{3} \cos \vartheta \sin \vartheta \sin \varphi$	$\cos \vartheta \cos \varphi$	$(2 \cos^2 \vartheta - 1) \sin \varphi$	$2 \cos^2 \vartheta - 1$	$2 \cos^2 \vartheta - 1$	$2 \cos^2 \vartheta - 1$	$-\sin \vartheta \cos \varphi$
	$\sqrt{3} \cos \vartheta \sin \vartheta \cos \varphi$	$-\cos \vartheta \sin \varphi$	$(2 \cos^2 \vartheta - 1) \cos \varphi$	$2 \cos^2 \vartheta - 1$	$2 \cos^2 \vartheta - 1$	$2 \cos^2 \vartheta - 1$	$\sin \vartheta \sin \varphi$
	$\sqrt{3/2} \sin^2 \vartheta \sin 2\varphi$	$\sin \vartheta \cos 2\varphi$	$\cos \vartheta \sin \vartheta \sin 2\varphi$	$\cos \vartheta \sin \vartheta \sin 2\varphi$	$\cos \vartheta \sin \vartheta \sin 2\varphi$	$\cos \vartheta \sin \vartheta \sin 2\varphi$	$\cos \vartheta \cos 2\varphi$
	$\sqrt{3/2} \sin^2 \vartheta \cos 2\varphi$	$-\sin \vartheta \sin 2\varphi$	$\cos \vartheta \sin \vartheta \cos 2\varphi$	$\cos \vartheta \sin \vartheta \cos 2\varphi$	$\cos \vartheta \sin \vartheta \cos 2\varphi$	$\cos \vartheta \sin \vartheta \cos 2\varphi$	$-\cos \vartheta \sin 2\varphi$
							$-\cos \vartheta \sin 2\varphi$
							$1/2(\cos^2 \vartheta + 1) \sin 2\varphi$
							$1/2(\cos^2 \vartheta + 1) \cos 2\varphi$
							$\sqrt{3/2} \sin^2 \vartheta$
							$-\cos \vartheta \sin \vartheta \sin \varphi$
							$-\cos \vartheta \sin \vartheta \cos \varphi$
							$1/2(\cos^2 \vartheta + 1) \sin 2\varphi$
							$1/2(\cos^2 \vartheta + 1) \cos 2\varphi$

Table 5. The angular overlap matrix $\mathbf{F}^{(6)}(\varphi, \vartheta)$.

	(z) (σ)	(y) (πs)	(x) (πc)
(z)	$\cos \vartheta$	0	$-\sin \vartheta$
(y)	$\sin \vartheta \sin \varphi$	$\cos \varphi$	$\cos \vartheta \sin \varphi$
(x)	$\sin \vartheta \cos \varphi$	$-\sin \varphi$	$\cos \vartheta \cos \varphi$

Example 4(a). The $(d\delta c)'$ -column of the $\mathbf{F}^{(d)}$ -matrix (Table 4), $t' = (d\delta c)'$.

$$\begin{aligned}
 (d\delta c)' &= \sqrt{3/2}(x'^2 - y'^2) = (d\sigma) \mathbf{F}_{15} + (d\pi s) \mathbf{F}_{25} + (d\pi c) \mathbf{F}_{35} \\
 &\quad + (d\delta s) \mathbf{F}_{45} + (d\delta c) \mathbf{F}_{55} \\
 &= (\sqrt{3/2})(-z \sin \vartheta + y \cos \vartheta \sin \varphi + x \cos \vartheta \cos \varphi)^2 \\
 &\quad - (\sqrt{3/2})(y \cos \varphi - x \sin \varphi)^2 \quad (63) \\
 &= (z^2 - 1/2x^2 - 1/2y^2) \sqrt{3/2} \sin^2 \vartheta + (\sqrt{3}yz) (-\sin \vartheta \cos \vartheta \sin \varphi) \\
 &\quad + (\sqrt{3}zx) (-\sin \vartheta \cos \vartheta \cos \varphi) + (\sqrt{3}xy) (1/2(\cos^2 \vartheta + 1) \sin 2\varphi) \\
 &\quad + (\sqrt{3/2}(x^2 - y^2))(1/2(\cos^2 \vartheta + 1) \cos 2\varphi)
 \end{aligned}$$

where, as in example 3, the coefficients to the unprimed functions make up the $\mathbf{F}^{(d)}$ -matrix elements of the $(\delta c)'$ -column. The full $\mathbf{F}^{(d)}$ -matrix is given in Table 4.

It may be recognized that the first column of the \mathbf{F} -matrices expresses the addition theorem for spherical harmonics.

(b) Transformation properties of standard l -functions. Angular overlap operators

The σ -functions, which are basis functions for the unit representation of the two-dimensional rotation group C_{∞} , transform into themselves by any rotation about the Z -axis, so that one may write

$$R_Z(\varphi)(l\sigma) = (l\sigma) [1] \quad (64)$$

where a form has been chosen analogous to that which describes the transformation properties²⁷ of the doubly degenerate sets $(l\lambda\zeta)$ (see Table 1).

$$R_Z(\varphi) [(l\lambda s)(l\lambda c)] = [(l\lambda s)(l\lambda c)] \begin{bmatrix} \cos(\lambda\varphi) & \sin(\lambda\varphi) \\ -\sin(\lambda\varphi) & \cos(\lambda\varphi) \end{bmatrix} \quad (65)$$

For these we note some characteristics of importance for the following discussion about operators.

We have noted previously (p 369) that our standard primed l -orbitals, referred to a given coordinate system $X'Y'Z'$, have the properties that all the orbitals with $\lambda \neq 0$ vanish on the Z' -axis while the σ -orbital has the functional value of unity when $(x', y', z') = (0, 0, 1)$. This distinguishing property of the σ -functions, the zonal harmonics, can be applied directly for finding angular overlap integrals of σ -type.

As discussed in connection with equations 43 and 45 the general problem may be characterized as that of finding the angular overlap integral between the standard unprimed central ion l -orbitals of our space-fixed coordinate system and standard primed ligand orbitals referred to an $X'Y'Z'$ coordinate system with origin at the ligator nucleus. The primed ligand coordinate system has the directions of its axes completely specified by the condition that they are parallel to a corresponding primed central ion coordinate system which itself is connected to the space-fixed XYZ system by the rotation $R(\varphi, \vartheta)$ of equation 24 (see also Figure 1).

Using equation 27 we are always able to write down a standard unprimed orbital as a linear combination of primed central ion orbitals.

$$t = \sum_{w'=1}^{w'=5} w' \mathbf{F}_{tw'} \quad (66)$$

If we take the functional value at $(x', y', z') = (0, 0, 1)$ on both sides of this equation we obtain the result

$$[t(x, y, z)]_{(x, y, z) = (r \sin \vartheta \cos \varphi, r \sin \vartheta \sin \varphi, r \cos \vartheta)} = \mathbf{F}_{(t)(\sigma)'} \quad (r = 1) \quad (67)$$

We see that for a given orbital the angular overlap integral of σ -type along a given direction Z' , say, can be found simply as the functional value of the orbital at $(x', y', z') = (0, 0, 1)$. We have considered in equation 67 the solid harmonic form of the l -orbital on the unit sphere. We could as well have used the surface harmonic form and then specified the direction of Z' by the polar coordinates (ϑ, φ) , referred to XYZ .

The angular overlap integrals of more general type cannot, of course, be found by quite the same method. However, by the introduction of certain operators they can be found along somewhat similar lines. In order to understand this it is necessary first to consider the transformation properties of our standard functions by rotation about the Z -axis.

We first consider the spur of the representation matrix, i.e. the character χ of the representation (Table 1). $\chi = 2 \cos(\lambda\varphi)$. From this character we see that the direct product for two reps λ_1 and λ_2 gives a reducible representation whose character is $4 \cos(\lambda_1\varphi) \cos(\lambda_2\varphi)$ where

$$4 \cos(\lambda_1\varphi) \cos(\lambda_2\varphi) = 2 \cos[(\lambda_1 + \lambda_2)\varphi] + 2 \cos[(\lambda_1 - \lambda_2)\varphi] \quad (68)$$

showing the well known result that the reduction leads to the two reps $\lambda_1 + \lambda_2$ and $|\lambda_1 - \lambda_2|$.

A reduction of the reducible matrix representation so as to refer to standard $(\lambda_1 + \lambda_2)_c$ - and $(\lambda_1 - \lambda_2)_c$ -functions gives the following beautiful results, written in analogy to the right hand side of equation 65

$$\begin{aligned} (\lambda_1 - \lambda_2)_s &= [(\lambda_1)_s(\lambda_2)_c - (\lambda_1)_c(\lambda_2)_s] \begin{bmatrix} \cos[(\lambda_1 - \lambda_2)\varphi] & \sin[(\lambda_1 - \lambda_2)\varphi] \end{bmatrix} \\ (\lambda_1 - \lambda_2)_c &= [(\lambda_1)_c(\lambda_2)_c + (\lambda_1)_s(\lambda_2)_s] \begin{bmatrix} -\sin[(\lambda_1 - \lambda_2)\varphi] & \cos[(\lambda_1 - \lambda_2)\varphi] \end{bmatrix} \end{aligned} \quad (69)$$

$$\begin{aligned} (\lambda_1 + \lambda_2)_s &= [(\lambda_1)_s(\lambda_2)_c + (\lambda_1)_c(\lambda_2)_s] \begin{bmatrix} \cos[(\lambda_1 + \lambda_2)\varphi] & \sin[(\lambda_1 + \lambda_2)\varphi] \end{bmatrix} \\ (\lambda_1 + \lambda_2)_c &= [(\lambda_1)_c(\lambda_2)_c - (\lambda_1)_s(\lambda_2)_s] \begin{bmatrix} -\sin[(\lambda_1 + \lambda_2)\varphi] & \cos[(\lambda_1 + \lambda_2)\varphi] \end{bmatrix} \end{aligned} \quad (70)$$

showing that functions of the types $(c)(c)$ and $(s)(s)$ transform as cosine functions in product space as opposed to functions of $(s)(c)$ or $(c)(s)$ types which transform as sine functions in product space. We note that when $\lambda_1 = \lambda_2$ equation 69 becomes a unit matrix and the corresponding functions become σ -functions. We further note that equations 69 and 70 are based solely upon the transformation properties of the functions under the rotation $R_Z(\varphi)$, which characterize the functions as real standard basis functions for the two-dimensional rotation group C_∞ (Table 1).

Our next stage is to observe that the Cartesian differential operators of the same form as the sectorial harmonics transform as real standard representations of C_∞ (Table 1). These are formed by replacing the Cartesian coordinates x, y and z , by $\partial/\partial x, \partial/\partial y$ and $\partial/\partial z$ in the expressions for the sectorial harmonics. We now define the unnormalized angular overlap operators as the operators corresponding to the sectorial harmonics, as given in equations 15a and 15b. We use the expressions $s(\lambda)$ and $c(\lambda)$ for these operators with the common designation $\varphi(\lambda)$ as for the functions. The operators up to $\lambda = 3$ are given in Table 6. It can be shown that

$$\varphi(\lambda)\varphi(\lambda) = \lambda! 2^{\lambda-1} \tag{71}$$

is generally valid provided φ and φ represent either both sine or both cosine functions.

Table 6. The unnormalized angular overlap operators, $\varphi(\lambda)$. The normalization constant is $(2(l - \lambda)!/(l + \lambda)!)^{1/2}$. l is the degree of the solid harmonic upon which $\varphi(\lambda)$ is to operate. λ specifies the type of angular overlap integral which is obtained by equation 74.

λ	$\varphi = s$	$\varphi = c$
1	$\partial/\partial y$	$\partial/\partial x$
2	$2 \partial^2/\partial x \partial y$	$\partial^2/\partial x^2 - \partial^2/\partial y^2$
3	$3 \partial^3/\partial x^2 \partial y - \partial^3/\partial y^3$	$\partial^3/\partial x^3 - 3 \partial^3/\partial x \partial y^2$

We now rewrite the expression 14b for our general solid harmonic with $\lambda \neq 0$

$$(rl\lambda\varphi) = \left(\frac{2(l + \lambda)!}{(l - \lambda)!}\right)^{\frac{1}{2}} \frac{1}{2^\lambda \lambda!} r^{l-\lambda} P_{l,\lambda}(\cos \vartheta) \varphi(\lambda) \tag{14c}$$

and recall that $r^{l-\lambda} P_{l,\lambda}(\cos \vartheta)$ (equation 13 and p 368) has σ -symmetry and a functional value of unity at $(x, y, z) = (0, 0, 1)$. If we now operate on both sides of equation 14c with the operator $\varphi(\lambda)$ and take the functional value at $(x, y, z) = (0, 0, 1)$ we obtain, using equation 71

$$[\varphi(\lambda)(rl\lambda\varphi)]_{(x,y,z)=(0,0,1)} = \left(\frac{2(l + \lambda)!}{(l - \lambda)!}\right)^{\frac{1}{2}} \frac{1}{2^\lambda \lambda!} \lambda! 2^{\lambda-1} = \left(\frac{(l + \lambda)!}{2(l - \lambda)!}\right)^{\frac{1}{2}} \tag{72}$$

or

$$\left(\frac{2(l - \lambda)!}{(l + \lambda)!}\right)^{\frac{1}{2}} [\varphi(\lambda)(rl\lambda\varphi)]_{(x,y,z)=(0,0,1)} = 1 \tag{73}$$

The reason for the short form of equation 72 is the following. On operating with the differential operator $\varphi(\lambda)$ on equation 14c we observe that only the term in which $r^{l-\lambda} P_{l,\lambda}(\cos \vartheta)$ is not operated upon will remain non-vanishing at $(x, y, z) = (0, 0, 1)$. This is because a σ -function, as a consequence of the transformation properties of the operators, on being operated upon by a simple or composite operator containing $\partial/\partial x$ and $\partial/\partial y$ and transforming as a cosine or a sine function, will go over into a function which in general is a

linear combination of functions of either cosine or sine type, and which therefore will vanish at (0, 0, 1).

The normalized angular overlap operator

$$\left(\frac{2(l - \lambda_i)!}{(l + \lambda_i)!}\right)^{\frac{1}{2}} \varphi(\lambda_i) \tag{74}$$

when acting on a linear combination of $(rl\lambda\varphi)$ -functions (l fixed) will only be able to produce a σ -function out of the $(rl\lambda_i\varphi)$ -term so that all the rest of the functions that are created will vanish on putting $(x, y, z) = (0, 0, 1)$.

The reason that no σ -functions can occur when $\varphi(\lambda_i)$ operates on $\varphi(\lambda_j)$ ($\lambda_i \neq \lambda_j$) is that according to equation 68 only functions of the types $\lambda_i - \lambda_j$ and $\lambda_i + \lambda_j$ will be formed. Further for $\lambda_i = \lambda_j$ the second function of equation 69 will be the only non-vanishing function (one-electron σ -function) remaining, which means that $c(\lambda_i) s(\lambda_i)$ and $s(\lambda_i) c(\lambda_i)$ will vanish.

We have thus obtained an operator method for evaluating angular overlap integrals. This method can be used to develop the surface angular overlap operators of Table 7. These directly transform an unprimed standard surface harmonic (lt) into the general expression \mathbf{F}_{rw} for its angular overlap integral with a (w') function.

Table 7. Normalized surface angular overlap operators, equal to the constant $[2(l - \lambda)!/(l + \lambda)!]^{1/2}$ multiplied by the operator given in the table. l is the degree of the surface harmonic to be operated upon. λ characterizes the operator itself. The primed coordinates of the table refer to a coordinate system rotated according to equation 24. $s(\lambda)$ and $c(\lambda)$ correspond to the operators of equation 74, but are based upon the primed function system.

$r^\lambda s(\lambda) = r \frac{\partial}{\partial y'}$ ($\lambda = 1$)	$= \frac{1}{\sin \vartheta} \frac{\partial}{\partial \varphi}$
$r^\lambda c(\lambda) = r \frac{\partial}{\partial x'}$ ($\lambda = 1$)	$= \frac{\partial}{\partial \vartheta}$
$r^\lambda s(\lambda) = 2r^2 \frac{\partial^2}{\partial x' \partial y'}$ ($\lambda = 2$)	$= \frac{2\partial \left(\frac{1}{\sin \vartheta} \frac{\partial}{\partial \varphi} \right)}{\partial \vartheta}$
$r^\lambda c(\lambda) = r^2 \left[\frac{\partial^2}{\partial x'^2} - \frac{\partial^2}{\partial y'^2} \right]$ ($\lambda = 2$)	$= \frac{\partial \left(\frac{1}{\sin \vartheta} \frac{\partial}{\partial \vartheta} \right)}{\frac{1}{\sin \vartheta} \partial \vartheta} - \left[\frac{1}{\sin \vartheta} \frac{\partial}{\partial \varphi} \right]^2$

Since the σ -column of the $\mathbf{F}^{(l)}$ matrix consists of the (lt) functions themselves, we may also characterize the surface angular overlap operators as operators which transform the σ -columns of \mathbf{F} -matrices into the other columns.

We finish this section with a couple of examples.

Example 2(c). We want to show how the operator of the expression 74 can be used to obtain, for example, $\mathbf{F}_{(\sigma)(\delta c)}$ and $\mathbf{F}_{(\pi s)(\pi c)}$ of equations 54 and 55. The constant $(2(l - \lambda)!/(l + \lambda)!)^{\frac{1}{2}}$ of equation 74 takes for the two cases the values $1/(2\sqrt{3})$ ($l = 2, \lambda = 2$) and $1/\sqrt{3}$ ($l = 2, \lambda = 1$), respectively.

We then obtain [example 2(a)], using the relations between the unprimed and primed coordinates (see also *Figure 1*),

$$\begin{aligned} \mathbf{F}^X_{(\sigma)(\delta c)'} &= [1/(2\sqrt{3})] \left[\frac{\partial^2}{\partial x'^2} - \frac{\partial^2}{\partial y'^2} \right] (z^2 - 1/2x^2 - 1/2y^2) \\ &= [1/(2\sqrt{3})] \left[\frac{\partial^2}{\partial z^2} - \frac{\partial^2}{\partial y^2} \right] (z^2 - 1/2x^2 - 1/2y^2) \\ &= [1/(2\sqrt{3})] [2 + 1] = \sqrt{3}/2 \end{aligned}$$

in agreement with equation 54 and

$$\begin{aligned} \mathbf{F}^Y_{(\pi s)(\pi c)'} &= (1/\sqrt{3}) \left[\frac{\partial}{\partial x'} [\sqrt{3}yz] \right]_{(x,y,z) = (0,1,0)} \\ &= 1/\sqrt{3} \left[\left(-\frac{\partial}{\partial z} \right) [\sqrt{3}yz] \right]_{(x,y,z) = (0,1,0)} = -1 \end{aligned}$$

in agreement with equation 55.

Example 4(b). Let us calculate the general matrix element $\mathbf{F}_{(\sigma)(\delta c)'} = \mathbf{F}_{15}$ as a function of the polar coordinates ϑ and φ (*Table 4*). The constant here is $1/(2\sqrt{3})$ as in example 2(c).

$$\mathbf{F}_{15} = \frac{1}{2\sqrt{3}} \sin \vartheta \frac{\partial \left[\frac{1}{\sin \vartheta} \frac{\partial (\cos^2 \vartheta - 1/2 \sin^2 \vartheta)}{\partial \vartheta} \right]}{\partial \vartheta} = \frac{\sqrt{3}}{2} \sin^2 \vartheta$$

in agreement with *Table 4*.

6. SOME APPLICATIONS OF THE ANGULAR OVERLAP MODEL

(a) The expanded radial function model and the field strength series of ligands

The AOM meets with the same major problem as do all one-electron models when their results are to be applied to actual systems containing more than one electron in the outer shell. The one-electron model is itself able to account for the energies of the sub-configurations into which the l^q -configurations break up when the l -orbital set is split by the core field.

However, although the energy levels which arise from a given sub-configuration are completely determined by symmetry alone, their relative energy depends on the interelectronic repulsion between the electrons which (in atomic units) is accounted for by the two-electron operator $\sum_{i < j} 1/r_{ij}$.

In view of the assumption I (p 370) that the AOM is a first order perturbation model on an l -electron basis it seems natural also to calculate the interelectronic repulsion contributions on this basis. By doing this we have the so-called expanded radial function model⁴² which parametrizes the repulsion energies by the Racah parameters A , B and C . These parameters can be formally expressed as linear combinations of matrix elements of the two-electron operator $\sum_{i < j} 1/r_{ij}$ over the radial factors of our central ion l -functions,

but in the same way as the one-electron energy parameters are taken by the AOM as semiempirical parameters, the Racah parameters B and C are likewise taken as semiempirical. The coefficients to the Racah parameters are linear combinations of integrals of the angular part of $\sum_{i<j} 1/r_{ij}$ over the angular part of the l -functions and as such are completely determined by symmetry.

We see that apart from the choice of semiempirical parameters, one-electron parameters and two-electron parameters, the combination of the AOM and the expanded radial function model provides a completely quantitative description of ligand field systems.

There is a problem of some importance which cannot be discussed here in much detail, but only be pointed out, i.e. the question of the physical basis for the freedom in choice of Racah parameters and, in particular, in the choice of the ratio between them, i.e. C/B .

Even when using Hartree-Fock functions for atoms the Racah parameters calculated are from 20 to 40 per cent higher^{34, 36} than those found by taking them as semiempirical parameters obtained by fitting them to the atomic spectra. One may conclude that the correlation effects cause a kind of nephelauxetism even in atoms. It is now a question whether or not it is possible under these circumstances to obtain on a theoretical basis knowledge about the relative sizes of the Racah parameters.

It has been customary to make a definite choice of this ratio, for example, $C/B = 4$, thereby choosing the ratio as a constant having a value much the same as that found in atoms. However, thereby the freedom of choice of Racah parameters has been reduced and it turns out that the expanded radial function model breaks down in the sense that, for example, internal spin-forbidden transitions within a t_2 -subshell of an octahedral d -group complex show a smaller nephelauxetic reduction of the Racah parameters than do the usual spin-allowed transitions which involve also the e -subshell⁴³.

The semiempirical phenomenon of nephelauxetism has been of interest, more because of its regularity in occurrence and its support to chemical intuition about covalency, than because of the theoretical foundation for its interpretation. In the same way one may say that the kind of breakdown of the expanded radial function model mentioned above is chemically so satisfactory, that a completely free choice of C/B ratio, i.e. a choice of ratio very different from that of the gaseous ion, hardly seems justified at the present stage of understanding of these matters.

Finally we want to mention that within the expanded radial function model the mixing of sub-configurations, as already pointed out by Tanabe and

Table 8. Ligands arranged in the field strength series. The numbers given are the ratios $\Sigma = A/B$ which are dimensionless

	F^-	H_2O	Cl^-	$-NCS^-$	NH_3	CN^-
Cr(III)	17.1	22.0	23.4	28.7	30.4	46.0
Co(III)		29.8			40.7	79
Rh(III)		38.0	42.1		56.5	

Sugano, depends on the ratio between one-electron parameters and two-electron parameters; i.e. on pure numbers without the dimension of energy. We may say that we have a kind of natural unit of energy in the Racah parameters within each chromophore system²⁹.

It is possible with the assumption of $C/B = 4$ to establish for octahedral chromophores a field strength series²⁹ of ligands which, although not quite constant for different metal ions, corresponds to the spectrochemical and the nephelauxetic series. The field strength series (Table 8) arranges the ligands in order of increasing purity of cubic sub-configurations, for each central metal ion.

(b) Application of the AOM to orthoaxial chromophores

There is a class of six coordinated complexes based upon the octahedron whose ligands are, at least effectively, linearly ligating and whose ligators are placed on the axes of a Cartesian coordinate system with the central ion at the origin. This class is called orthoaxial.

Since for an orthoaxial chromophore it is a symmetry property that the d -orbitals fall into a σ -class, consisting of $(z^2) = (\sigma)$, $(x^2 - y^2) = (\delta c)$, and a π -class consisting of $(xy) = (\delta s)$, $(zx) = (\pi c)$, $(yz) = (\pi s)$ (Table 3), the results of the AOM can be obtained in a particularly simple way without using its formal techniques.

Each ligand gives a perturbation contribution of e_σ distributed upon the σ -bonding orbitals, so that the sum of the coefficients equals the number of ligands, i.e. six. Since for an orthoaxial chromophore the standard orbitals (δs) , (πc) and (πs) cannot form σ -bonds, and since for a regularly octahedral chromophore for which the (σ) and (δc) standard orbitals form bases for the e_g rep of O_h , the total σ -perturbation, $6e_\sigma$ must be distributed equally between these two orbitals so that the sum of the coefficients to e_σ for each one must be equal to three. The (δc) -orbital has a node including the Z -axis, and C_4 symmetry as far as its square, and thereby as far as its bonding is concerned, and therefore the coefficient to e_σ for each of the four ligands in the XY -plane is $3/4$, so that the perturbation energy h of this orbital is

$$h(x^2 - y^2) = h(\delta c) = \frac{3}{4}[e_{\sigma L(X)} + e_{\sigma L(Y)} + e_{\sigma L(-X)} + e_{\sigma L(-Y)}] \quad (75)$$

The rest of the perturbation contribution from these four ligands makes up the whole of their part to the perturbation energy of (σ) , which in order to obtain a sum of its coefficients equal to three, recalling that it has a horizontal plane of symmetry, gives the expression

$$h(z^2) = h(\sigma) = e_{\sigma L(Z)} + e_{\sigma L(-Z)} + \frac{1}{4}e_{\sigma L(X)} + \frac{1}{4}e_{\sigma L(-X)} + \frac{1}{4}e_{\sigma L(Y)} + \frac{1}{4}e_{\sigma L(-Y)} \quad (76)$$

For the π -orbitals of the octahedral coordination, (δs) , (πc) and (πs) , which cannot form σ -bonding, the sum of the coefficients of e_π from each ligand must be two and because of the C_4 symmetry properties, in analogy to the (δc) -case, we obtain the following expression

$$h(xy) = h(\delta s) = e_{\pi L(X)} + e_{\pi L(-X)} + e_{\pi L(Y)} + e_{\pi L(-Y)} \quad (77)$$

with analogous expressions for $h(yz)$ and $h(zx)$ to be obtained by cyclic permutations of the Cartesian labels.

In the equations 75 to 77 we have ignored the δ -contributions. If the model has any physical meaning these contributions are small anyhow, but it has been shown¹⁷ that formally to ignore δ -contributions only means to use the energy of the (δ)-orbitals of each ligand as a zero point for this ligand's perturbation contribution.

We have obtained in the equations 75 to 77 results which are equivalent to those of Yamatera¹⁹ and those of McClure²⁰, and which, as stated in section 2, made the first example of the application of the AOM.

We finally note that for a regularly octahedral chromophore the equations 75, 76 and 77 degenerate to

$$\begin{aligned} h(e_g) &= h(\sigma) = h(\delta c) = 3e_\sigma \equiv \Delta_\sigma \\ h(t_{2g}) &= h(\delta s) = h(\pi c) = h(\pi s) = 4e_\pi \equiv \Delta_\pi \end{aligned} \quad (78)$$

so that we have the splitting of Δ into a σ and a π part (equation 2) expressed in terms of the angular overlap parameters e_σ and e_π .

(c) The two-dimensional spectrochemical series

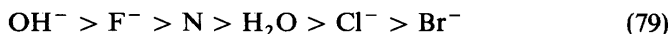
On the basis of the expanded radial function model [section 6(a)] and of the equations 75, 76 and 77 it is possible from the absorption spectra of chromium (III) complexes of the type *trans*-[CrN₄L₂] to obtain the components $\Delta_{\sigma L}$ and $\Delta_{\pi L}$ of the spectrochemical parameter Δ_L (see equation 2). Here L may represent any linearly ligating ligand, but results have at present only been obtained with a few simple ligands, OH⁻, F⁻, H₂O, Cl⁻ and Br⁻, where OH⁻ and H₂O have been included even though they may be assumed not to behave as linearly ligating. N represents a nitrogen ligator either belonging to an ammonia molecule or to an aliphatic monoamine or diamine.

Table 9. Some of the numbers (in kK units) which form the basis for the establishment of the Δ_σ - and Δ_π -series (equations 79 and 80). The values have been obtained from the absorption spectra of *trans*-L₂ tetramminechromium(III) complexes²¹, but should at the present stage be considered as tentative. Δ_π for ammonia has been put equal to zero, but if it had a value, $\Delta_{\pi N}$ this number would have to be added to all the numbers of the table referring to Δ_σ and Δ_π , thus leaving their relative values and the Δ -values unchanged. Values²¹ for L = H₂O are considered more uncertain and have therefore not been included in the table.

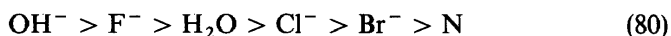
L	OH ⁻	F ⁻	Cl ⁻	Br ⁻	NH ₃
Δ	17.0	15.3	13.2	12.3	21.6
Δ_σ	25.6	22.4	16.6	14.3	21.6
Δ_π	8.6	7.1	3.4	1.9	(0)

In Table 9 where a few tentative results have been collected²¹ it has been assumed that $\Delta_{\pi N}$ is equal to zero. Since only three independent one-electron parameters can be determined from the experiments, such an assumption is necessary in order to obtain explicit numbers for the rest of the parameters, i.e. $\Delta_{\sigma N}$, $\Delta_{\sigma L}$ and $\Delta_{\pi L}$. However, the relative positions of the ligands in the two spectrochemical series, the Δ_σ -series and the Δ_π -series, are independent of the assumption of $\Delta_{\pi N} = 0$.

The Δ_σ -series has the appearance



and the Δ_π -series



The two series are seen to be identical apart from the position of N which is an exception among the ligands because of its lack of π -orbitals available for bonding to the central ion.

(d) The concept of holohedrized symmetry

In the equations 75 and 76 the different energy parameters e_σ may be all different and the same is true of the e_π parameters of equation 77. However, as may be seen from the equations, it is a general property that whenever a contribution $e_{\lambda L(Q)}$ ($\lambda = \sigma, \pi$; $Q = X, Y, Z$) occurs in the energy expression for a given orbital, $e_{\lambda L(-Q)}$ occurs also, and with the same coefficient. This means that we cannot observe the individual contributions from the two ends of a coordinate axis, but only their sum. This is caused by the well defined parity of the l -basis orbitals and leads to a general consideration of the concept of holohedrized symmetry^{22, 29, 33, 45}.

A formulation of the concept can be given by considering the ligand field A , which may have tensorial properties and defining \bar{A} by the relation

$$\bar{A} = IA \quad (81)$$

where I is the inversion operator. A may then be written

$$A = 1/2A + 1/2A + 1/2\bar{A} - 1/2\bar{A} = 1/2[A + \bar{A}] + 1/2[A - \bar{A}] = A_g + A_u \quad (82)$$

so as to split up A into a gerade and an ungerade part. Now the angular overlap model is a first order perturbation model with a basis set of pure l -functions, i.e. functions of well-defined parity. Therefore the effect of A_u will vanish and that of A will be identical to that of A_g . This means that the ligand field contribution from a given ligand may be accounted for by dividing its perturbing potential into two parts of half the size of that for the single ligand and related to each other by an inversion operation. In other words, the well defined inversion symmetry of the basis orbitals (gerade or ungerade) introduces an apparent inversion centre into the chromophore. This has been called a holohedrization. In general a hemihedric point group will by the holohedrization at least behave as the corresponding holohedric one (example 5). However, in certain cases the holohedrized symmetry will be even higher [example 2(d)].

Example 5. We think of a chromophore system of symmetry D_{3h} consisting of a central ion and three ligands in a plane. The d -functions will fall into the symmetry types $a'_1 (D_{3h})$, $e'' (D_{3h})$ and $e' (D_{3h})$ or characterized in terms of the holohedrized symmetry $a_1 (D_{6h})$, $e_1 (D_{6h})$ and $e_2 (D_{6h})$. We now introduce a fourth linearly ligating ligand on the trigonal axis so that the symmetry becomes C_{3v} and the d -functions fall into the symmetry types $a_1 (C_{3v})$, $e (C_{3v})$ and $e (C_{3v})$. We would expect *a priori* that a non-diagonal element would come into being. However, since the holohedrized symmetry remains D_{6h} ,

we are able to foresee that this matrix element within the AOM will vanish identically²⁵.

Example 2(d) (see p 374, p 379 and p 385). The true symmetry of our chromophore system with the two linearly ligating ligands on the X and Y axes is C_{2v} with the twofold axis falling at $x = y$. However, because the angle $L^X M L^Y$ is equal to 90° , the holohedrized symmetry is D_{4h} with the Z -axis as the fourfold axis. As a consequence of this the standard basis functions remain eigenfunctions of this chromophore system, and the functions of equation 41 may be characterized by their symmetry types under D_{4h} as a_1 , e , b_2 and b_1 (D_{4h}), respectively.

7. CONCLUSION

Find a modern text of inorganic chemistry and you will see that most of the discussion about chemical bonding is based upon the concepts of the molecular orbital description. But not only that. You will also find that the qualitative ideas about bonding, its division into σ -bonding and π -bonding and its dependence on the relative positions of the ligands around the central ions, are essentially based upon considerations of the angular properties of the central ion orbitals, and also of the ligand orbitals.

The concept of angular overlap makes these considerations quantitative, independent of whether the angular overlap model as such is applicable to the systems under consideration or not. The concept of the angular overlap can also be used as a simple means of forming central ion hybrid orbitals⁴⁴, of σ -type or of π -type, directed or oriented optimally towards any system of ligators.

In textbooks, the introduction of ligand field theory is usually based upon the electrostatic model. Then, after the whole structure has been discussed, the qualitative arguments of MO-theory are discussed and used to justify the fact that ligand field theory works so well when it comes to comparisons with experiment. The angular overlap model, in addition to its unsophisticated approach, has the pedagogic advantage that it introduces the final concepts from the very beginning and it may be characterized as a zeroth order molecular orbital model.

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