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The Angular Overlap Model

How to use it and why

Virtually every chemist today is aware of the interpretability of the salient magnetic and spectral properties of transition metal ion complexes in terms of the configurations of the (primarily) d -electrons on the metal. The approach adopted by the majority of textbooks focuses either on the crystal field method or on a semi-empirical molecular orbital scheme.

The former method, which is the more common, considers only the effect of point charges or dipoles on the d -orbital energies. Although the model permits calculation of orbital energies, it is incapable of reflecting the covalent nature of the metal-ligand bond. In the ligand field model the orbital energies are parameterized, leaving the effective charge on the metal ion, the metal-ligand bond length, and the ligand point charge or dipole as undecided. However, the limited applicability of chemical intuition in parameterizing certain metal-ligand interactions, especially in complexes of low symmetry, undermines the general utility of this technique to chemists. In the semi-empirical MO calculation, interactions between metal and ligand orbitals are explicitly considered. However, although chemical intuition may be used to parameterize the input data, the final calculation is unlikely to yield spectral and/or bonding data which can be extrapolated to other related complexes.

Thus most textbooks make no attempt to allow MO theory to provide parameters for describing the orbital energies of a complex. We feel that the isolated stand of ligand field theory is an unnecessary pedagogical weakness. In this article the angular overlap model, AOM, will be discussed in some detail and its formulation as an empirical MO model will be emphasized. The general method for parameterizing the orbital energies in complexes of metal ions with a partly filled d (or f) shell will be demonstrated and several examples of the utility of this technique will be given.

Principles

There are two computational schemes generally used for obtaining the orbital energies for d -electrons: the weak and strong field approaches, respectively (1). In both cases matrix elements are of the form $\langle \Psi | \mathbf{H} | \Psi' \rangle$, where \mathbf{H} is a Hamiltonian describing the perturbation due to the complex formation and the inter-electronic repulsion: $\mathbf{H} = V_{LF} + \sum r_{ij}^{-1}$. Ψ and Ψ' are Slater determinants of the states constructed as a starting set. The weak field and the strong field schemes are different in the way these starting states are constructed.

The weak field method utilizes d -orbitals which are already eigenfunctions of $\sum 1/r_{ij}$ and are combinations of the complex functions d_0 , $d_{\pm 1}$, and $d_{\pm 2}$. Therefore, the diagonal elements in the secular determinant to be solved consist of inter-electronic repulsion parameters $\langle d_i d_j | \sum 1/$

$r_{ij} | d_i d_j \rangle$ and ligand field parameters ($\langle d | V_{LF} | d' \rangle$), whereas the non-diagonal elements are made up solely of ligand field parameters ($\langle d | V_{LF} | d' \rangle$, where $d \neq d'$).

When one proceeds according to the strong field scheme one starts out with d -functions which are already eigenfunctions to V_{LF} (or nearly so if the symmetry is low). These functions can be the real functions d_{z^2} , $d_{x^2 - y^2}$, d_{xy} , d_{yz} , d_{zx} . The pertinent secular determinant to be solved will now have both interelectronic repulsion parameters and ligand field parameters along the diagonal, as in the weak field treatment, while the non-diagonal elements most often contain only inter-electronic repulsion parameters. These two approaches will of course yield the same solutions.

As indicated above, the angular overlap model (2) is concerned with the parameterization of $\langle d | V_{LF} | d' \rangle$. In what follows we shall keep to the strong field treatment since this seems to offer some pedagogical advantages and seems generally more easy to apply on an introductory level. As mentioned above the off-diagonal elements ($\langle d | V_{LF} | d' \rangle$, $d \neq d'$) are equal to zero when the starting d -functions are eigenfunctions of V_{LF} and then the diagonal elements, $\langle d_i | V_{LF} | d_i \rangle$, represent the energy of an electron in the d_i orbital experiencing V_{LF} . Accordingly, this energy integral is called the one-electron orbital energy. For d^1 and d^9 electron systems the two electron integrals vanish and the one-electron orbital energies are the only ones to occur. The AOM thus directly gives the energy levels for d^1 and d^9 complexes.

Assumptions of the AOM

The formation of molecular orbitals between a d -orbital and a ligator orbital yields a bonding orbital (most often this consists essentially of the ligator orbital) with lower energy than the starting orbitals and an antibonding orbital (thus, most often it consists of mainly the d -orbital) which is raised in energy. Such energy changes of the d -orbitals are parameterized in the AOM. The two basic assumptions are

1) The energy change $\Delta E(d)$ of a given d -orbital on a metal ion caused by bond formation with orbitals of a ligator is given by the sum

$$(F(d, \sigma))^2 l_\sigma + (F(d, \pi_x))^2 l_{\pi_x} + (F(d, \pi_y))^2 l_{\pi_y}$$

where F stands for the fraction of the maximum overlap integral obtained at the particular geometry considered. The letter l with index σ , π_x or π_y symbolizes the unit energy change obtained when the geometry is ideal for bond formation, i.e., when the overlap integral in question is maximum and thus F is one. If desired the model is capable of handling δ bonding as well.

2) The energy change of a given d -orbital caused by coordination of several ligators is the sum of the effects from each of the ligators.

These basic assumptions can not be proven but can be justified by the successful application of the model. How-

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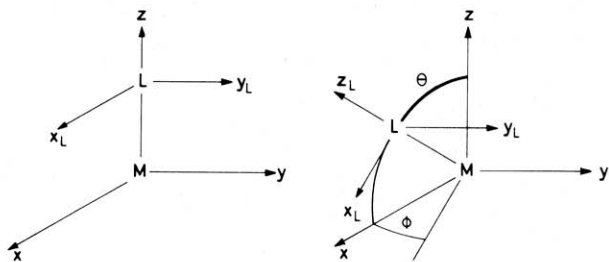


Figure 1. (left) Diatomic molecule with coordinate systems drawn in such a way that the overlap integrals $S_\sigma = \langle d_{z^2} | \sigma_L \rangle$, $S_{\pi^x} = \langle d_{xz} | p_x \rangle$ and $S_{\pi^y} = \langle d_{yz} | p_y \rangle$ are maximum for the M-L distance. This is the same as saying that the basis orbitals are diagonal.

Figure 2. (right) This illustrates how any position on a sphere around the metal ion M can be reached from the position on the positive z-axis by rotation around the y-axis an angle θ ($0 < \theta \leq 180^\circ$) and an angle φ ($0 \leq \varphi < 360^\circ$) around the z-axis. By rotating an angle Ψ around z_L the x_L and y_L coordinates can be brought parallel to a chosen coordinate system on the sphere.

ever, let us demonstrate that supposition (1) is a reasonable assumption which is already used widely. Without loss of generality we can consider as an example the formation of a sigma bond between $d(z^2)$ of a vanadium(IV) ion and a p_z^0 orbital of an oxygen(-2) ion arranged in a coordinate system as in Figure 1. Since only two orbitals are dealt with the secular determinant is simply

$$\begin{vmatrix} d_{z^2} \langle d_{z^2} | H | d_{z^2} \rangle - E & \langle d_{z^2} | H | p_z^0 \rangle - E \langle d_{z^2} | p_z^0 \rangle \\ p_z^0 \langle p_z^0 | H | d_{z^2} \rangle - E \langle p_z^0 | p_z^0 \rangle & \langle p_z^0 | H | p_z^0 \rangle - E \end{vmatrix} = 0$$

The solution of this secular determinant will give the energies of the two molecular orbitals. To ease the arithmetic it is convenient to use orthogonal basis functions. This is accomplished by the substitution of p_z^0 with $p_z' = (p_z^0 - S \times d_{z^2}) / \sqrt{1 - S^2}$. The consequence of this substitution is that the overlap integral $\langle d_{z^2} | p_z' \rangle$ vanishes. The elements in the new secular determinant

$$\begin{vmatrix} d_{z^2} \langle d_{z^2} | H | d_{z^2} \rangle - E & \langle d_{z^2} | H | p_z' \rangle \\ p_z' \langle p_z' | H | d_{z^2} \rangle & \langle p_z' | H | p_z' \rangle - E \end{vmatrix} = 0$$

can be expressed by the former

$$\langle d_{z^2} | H | p_z' \rangle = \frac{1}{\sqrt{1 - S^2}} (\langle d_{z^2} | H | p_z^0 \rangle - S \langle d_{z^2} | H | d_{z^2} \rangle)$$

$$\langle p_z' | H | p_z' \rangle = \frac{1}{1 - S^2} (\langle p_z^0 | H | p_z^0 \rangle + S^2 \langle d_{z^2} | H | d_{z^2} \rangle - 2S \langle d_{z^2} | H | p_z^0 \rangle)$$

Let us introduce the obvious short hand notations

$$\begin{vmatrix} H(z^2, z^2) - E & H(z^2, p_z') \\ H(p_z', z^2) & H(p_z', p_z') - E \end{vmatrix} = 0$$

and solve the second-order equation in E

$$E = \frac{1}{2} (H(z^2, z^2) + H(p_z', p_z')) \pm \left[\frac{1}{4} (H(z^2, z^2) + H(p_z', p_z'))^2 - H(z^2, z^2) H(p_z', p_z') + H(z^2, p_z')^2 \right]^{1/2}$$

$$E \sim \frac{1}{2} (H(z^2, z^2) + H(p_z', p_z')) \pm \frac{1}{2} (H(z^2, z^2) - H(p_z', p_z')) \times \left(1 + \frac{2H(z^2, p_z')^2}{(H(z^2, z^2) - H(p_z', p_z'))^2} \right)$$

For the molecular orbital with highest energy we find

$$E_+ \sim H(z^2, z^2) + \frac{H(z^2, p_z')^2}{H(z^2, z^2) - H(p_z', p_z')}$$

Thus the energy change in the (essentially) d_{z^2} orbital

caused by σ -bond formation with p_z' is proportional to $H(z^2, p_z')^2$

$$\Delta E(z^2) = H(z^2, p_z')^2 / (H(z^2, z^2) - H(p_z', p_z'))$$

Extensive experience with semi-empirical MO calculations supports the proportionality between $H(z^2, p_z')$ and the overlap integral $S(z^2, p_z^0)$. This assumption is basic to (extended) Hückel calculations in organic chemistry and Wolfberg-Helmholz calculations in inorganic chemistry. Hence ΔE becomes

$$\begin{aligned} \Delta E(z^2) &= c \cdot S(z^2, p_z^0)^2 / (H(z^2, z^2) - H(p_z', p_z')) \\ &= c' \cdot S(z^2, p_z^0)^2 \end{aligned}$$

and introducing the AOM language

$$\Delta E(z^2) = l_\sigma \cdot F(z^2, p_z^0)^2$$

For maximum overlap at the given metal-ligand distance $\Delta E(z^2) = l_\sigma \cdot 1 = l$.

One could equally well think of a σ -bond formed by d_{z^2} and a hybrid orbital of $2s^0$ and $2p_z^0$. It is equally feasible to include π bonds formed between d_{yz} , d_{xz} , and p_x^0 and p_y^0 , respectively. From the first assumption we can say that the energies of the five d -orbitals on V(IV) in VO^{2+} are

$$\begin{aligned} \Delta E(z^2) &= 1 \cdot l_\sigma \\ \Delta E(yz) = \Delta E(zx) &= 1 \cdot l_\pi \\ \Delta E(xy) = \Delta E(x^2 - y^2) &= 1 \cdot l_\delta \sim 0 \end{aligned}$$

This result is obtained so easily because the basis functions used are symmetry adapted, i.e., because the coordinate systems have been so arranged that for a given vanadium-oxygen distance the overlap integrals are already maximum. The l_σ and l_π parameters depend upon the metal and the ligand as well as on their distance. They are not calculated but determined empirically from spectral transitions. It is found ($2e$) that generally $l_\sigma > l_\pi$. In cases where δ bonds can form $l_\delta < l_\pi$.

Sample Calculations

At this time it may be worthwhile to review the angular dependence of overlap integrals from which the AOM derives its name. Let two atoms be arranged with coordinate systems as in Figure 1. We shall use as basis orbitals the angular functions

$\left. \begin{aligned} \text{for the central atom} \\ d_{z^2} = z^2 - \frac{1}{2}(x^2 + y^2) \\ d_{x^2 - y^2} = \frac{\sqrt{3}}{2}(x^2 - y^2) \\ d_{yz} = \sqrt{3}yz \\ d_{zx} = \sqrt{3}zx \\ d_{y^2 - z^2} = \sqrt{3}y^2 - 3z^2 \\ p_x, p_y, p_z = x, y, z \end{aligned} \right\}$	$\left. \begin{aligned} \text{for the ligand atom} \\ \sigma \text{ (may be thought of} \\ \text{as a hybrid)} \\ \pi_x, \pi_y = p_x, p_y \end{aligned} \right\}$
$\left. \begin{aligned} \text{All normalized to} \\ \frac{4\pi}{5} \end{aligned} \right\}$	

The two sets of atomic orbitals form overlap integrals of various types. For example

$$\begin{aligned} \langle s^{(1)} | \sigma^{(2)} \rangle &= S(s, \sigma) \\ \langle p_z^{(1)} | \sigma^{(2)} \rangle &= S(p_\sigma, \sigma) \\ \langle p_x^{(1)} | \pi_x^{(2)} \rangle &= S(p_\pi, p_\pi) \\ \langle p_x^{(1)} | \pi_y^{(2)} \rangle &= 0 \\ \langle d_{z^2}^{(1)} | \sigma^{(2)} \rangle &= S(d_\sigma, \sigma) \\ \langle d_{yz}^{(1)} | \pi_x^{(2)} \rangle &= S(d_\pi, p_\pi)_y \\ \langle d_{yz}^{(1)} | \pi_x^{(2)} \rangle &= 0 \\ \langle p_z^{(1)} | p_x^{(2)} \rangle &= 0 \\ \langle d_{z^2}^{(1)} | p_x^{(2)} \rangle &= 0 \end{aligned}$$

If one of the coordinate systems is "misdirected," the expressions for the overlap integrals are more complicated. Consider, for example, the case where the ligand atom with coordinate system has been rotated an angle θ around the y -axis as in Figure 2. Now the overlap integrals are

$$\begin{aligned} \langle s^{(1)} | \sigma^{(2)} \rangle &= S(s, \sigma) \\ \langle p_z^{(1)} | \sigma^{(2)} \rangle &= S(s, \sigma) \cos \theta \\ \langle p_x^{(1)} | \pi_x^{(2)} \rangle &= S(p_\pi, p_\pi)_x \cos \theta \\ \langle p_x^{(1)} | \pi_y^{(2)} \rangle &= 0 \\ \langle d_z^{(1)} | \sigma^{(2)} \rangle &= \left\langle z_1^2 - \frac{1}{2}(x_1^2 + y_1^2) \middle| \sigma^{(1)} \right\rangle = S(d_\sigma, \sigma) \left(\cos^2 \theta - \frac{1}{2} \sin^2 \theta \right) \\ \langle d_{yz}^{(1)} | \pi_y^{(2)} \rangle &= S(d_\pi, p_\pi)_y \cos \theta \\ \langle d_{yz}^{(1)} | \pi_x^{(2)} \rangle &= 0 \\ \langle p_z^{(1)} | \pi_x^{(2)} \rangle &= S(p_\pi, p_\pi)_x \sin \theta \\ \langle d_z^{(1)} | \pi_x^{(2)} \rangle &= \left\langle z_1^2 - \frac{1}{2}(x_1^2 - y_1^2) \middle| p_x^{(2)} \right\rangle \\ &= \left\langle \left[\frac{1}{2}(z_1^2 - x_1^2) + \frac{1}{2}(z_1^2 - y_1^2) \right] \middle| p_x^{(2)} \right\rangle \\ &= -\frac{\sqrt{3}}{2} S(d_\pi, p_\pi)_x \sin 2\theta \end{aligned}$$

The ligand atom may reach any position on a sphere around the central atom by rotation of an angle θ around the y -axis and then an angle φ around the z -axis. In case of a complex containing one or more conjugated organic molecules as chelate ligands it is possible to disentangle the π -bonding from the conjugated system to the metal from the (probably much weaker) π -bonding in the plane of chelate. This is done by rotating the coordinate system belonging to the ligator an angle ψ around z_1 until, e.g., the x_1 -axis coincides with the ligand π -orbitals. This aspect will be elaborated later. It is not surprising that with three coordinates to characterize each ligator position the factor by which any overlap integral is diminished from its possible maximum value is complicated. Schäffer (2c) has worked out a table of these factors for all five central ion d -functions and ligator orbitals characterized by θ , φ , and ψ (Fig. 2). These angular overlap factors $F_{\lambda\omega}(d, L(\theta, \varphi, \psi))$ are reproduced in Table 1. Here λ stands for σ or π interactions and ω specifies the two π interactions which are only different for non-linear ligating systems where ψ (vide infra) can not be chosen arbitrarily.

According to the suppositions the diagonal matrix element is

$$\langle d_i | V_{LF} | d_i \rangle = \sum_{\lambda\omega} \sum_{n=1}^N L_{\lambda n} F(d_i, L_n)^2$$

where the first summation is over σ , π_x , and π_y effects,

and the latter over the N ligators. It follows from the nature of the ligand field matrix that any off-diagonal element must have the form

$$\langle d_i | V_{LF} | d_j \rangle = \sum_{\lambda\omega} \sum_n^N L_{\lambda n} \cdot F_{\lambda\omega}(d_i, L_n) \cdot F_{\lambda\omega}(d_j, L_n)$$

This is thus the general form for the ligand field matrix element.

It is intuitively understandable in view of the trigonometric functions involved in the F values that a sum rule exists (2b) such that

$$\sum_n \sum_i^5 F_{\lambda\omega}(d_i, L_n)^2 = N$$

where N = the total number of ligators. This provides a desirable check on the obtained results.

Examples of the Use of the AOM

The foregoing part is not intended as a vigorous introduction to the AOM. For this we refer to the original papers on the subject (2). Instead we want to present some easily understandable examples of the use of the model.

First let us reconsider the VO^{2+} ion with O^{2-} on the position $(\theta, \varphi) = (45^\circ, 0^\circ)$. Notice that for the unidentate ligands or linearly ligating molecules in general, ψ may take an arbitrary value, e.g., 0° . From Table 1 the following values for F are

$$\begin{aligned} F_\sigma(z^2, \sigma) &= \frac{1}{4} \\ F_{\pi^x}(z^2, p_x) &= -\frac{\sqrt{3}}{2} \\ F_\sigma(zx, \sigma) &= \frac{\sqrt{3}}{2} \\ F_{\pi^y}(yz, p_z) &= \frac{\sqrt{2}}{2} \\ F_{\pi^y}(xy, p_y) &= \frac{\sqrt{2}}{2} \end{aligned}$$

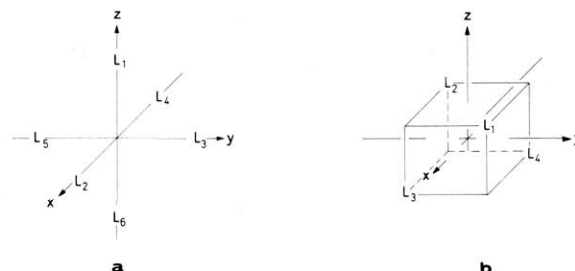


Figure 3. The numbering system used for (a) octahedral coordination (notice that the sum of numbers for trans ligands is always 7) and (b) for the tetrahedron.

Table 1. Schäffer's Angular Overlap Factors for Five Central Ion d Functions and Ligator Orbitals

	$F_\sigma(d, L(\theta, \varphi, \psi))$	$F_{\pi_y}(d, L(\theta, \varphi, \psi))$	$F_{\pi_x}(d, L(\theta, \varphi, \psi))$
d_{z^2}	$(1 + 3 \cos 2\theta)/4$	$\frac{\sqrt{3}}{2} \sin 2\theta \sin \psi$	$-\frac{\sqrt{3}}{2} \sin 2\theta \cos \psi$
d_{yz}	$\frac{\sqrt{3}}{2} \sin \varphi \sin 2\theta$	$\begin{pmatrix} \cos \varphi \cos \theta \cos \psi \\ -\cos \varphi \cos 2\theta \sin \psi \end{pmatrix}$	$\begin{pmatrix} \cos \varphi \cos \theta \sin \psi \\ +\sin \varphi \cos 2\theta \cos \psi \end{pmatrix}$
d_{zx}	$\frac{\sqrt{3}}{2} \cos \varphi \sin 2\theta$	$\begin{pmatrix} -\sin \varphi \cos \theta \cos \psi \\ -\cos \varphi \cos 2\theta \sin \psi \end{pmatrix}$	$\begin{pmatrix} -\sin \varphi \cos \theta \sin \psi \\ +\cos \varphi \cos 2\theta \cos \psi \end{pmatrix}$
d_{xy}	$\frac{\sqrt{3}}{3} \sin 2\varphi (1 - \cos 2\theta)$	$\begin{pmatrix} \cos 2\varphi \sin \theta \cos \psi \\ -\frac{1}{2} \sin 2\varphi \sin 2\theta \sin \psi \end{pmatrix}$	$\begin{pmatrix} \cos 2\varphi \sin \theta \sin \psi \\ +\frac{1}{2} \sin 2\varphi \sin 2\theta \cos \psi \end{pmatrix}$
$d_{x^2-y^2}$	$\frac{\sqrt{3}}{4} \cos 2\varphi (1 - \cos 2\theta)$	$\begin{pmatrix} -\sin 2\varphi \sin \theta \cos \psi \\ -\frac{1}{2} \cos 2\varphi \sin 2\theta \sin \psi \end{pmatrix}$	$\begin{pmatrix} -\sin 2\varphi \sin \theta \sin \psi \\ +\frac{1}{2} \cos 2\varphi \sin 2\theta \cos \psi \end{pmatrix}$

$F_{\lambda\omega}$ are listed to represent the fraction of the maximum overlap integral specified as σ , π_y (or π_s for sin) and π_x (or π_c for cos) obtained for the overlap between a d -orbital and the ligand orbitals σ , π_y and π_x when the ligator position (see Fig. 2) is (θ, φ) and the ligator coordinate system is rotated an angle ψ relative to the standard position on the $+z$ -axis.

$$F_{\sigma}(x^2 - y^2, \sigma) = \frac{\sqrt{3}}{4}$$

$$F_{\pi^x}(x^2 - y^2, \pi_x) = \frac{1}{2}$$

All other F values equal zero.

From these values the secular determinant for the ligand field perturbations is found to be

$$\begin{vmatrix} d_{z^2} & d_{zx} & d_{yz} & d_{xy} & d_{x^2-y^2} \\ d_{z^2} & \frac{1}{16}l_{\sigma} + \frac{3}{4}l_{\pi^x} - E & \frac{\sqrt{3}}{8}l_{\sigma} & 0 & \frac{\sqrt{3}}{16}l_{\sigma} - \frac{\sqrt{3}}{4}l_{\pi^x} \\ d_{zx} & & \frac{3}{4}l_{\sigma} - E & 0 & \frac{3}{8}l_{\sigma} \\ d_{yz} & & & \frac{1}{2}l_{\pi^y} - E & \frac{1}{2}l_{\pi^y} \\ d_{xy} & & & & \frac{1}{2}l_{\pi^y} - E \\ d_{x^2-y^2} & & & & \frac{3}{16}l_{\sigma} + \frac{1}{4}l_{\pi^x} - E \end{vmatrix} = 0$$

This determinant is easily broken up into one 3×3 l_{σ} , 2×2 l_{π^x} , and one 2×2 l_{π^y} determinant. The solutions are then found as $E = l_{\sigma}$, l_{π^x} , l_{π^y} , 0 (twice). The tediousness involved in this procedure compared to that used earlier shows clearly the advantage of using symmetry adapted d -functions, i.e., giving the orientation of the coordinate system relative to the ligands some thought.

Δ in Complexes of O_h Symmetry

In octahedral symmetry the five d -orbitals split up into three t_{2g} and two e_g orbitals. Their energy difference is normally called Δ or $10 Dq$. For Cr(III), Co(III), and Ni(II) complexes, for example, this energy difference is observed as the maximum absorption frequency for the first (lowest lying) spin allowed transition.

Taking the four-fold axis as the z -axis and placing ligands on the coordinate axes as in Figure 3a the basis d -orbitals are eigenfunctions. The ligands have the coordinates

	1	2	3	4	5	6
θ	0	$\frac{\pi}{2}$	$\frac{\pi}{2}$	$\frac{\pi}{2}$	$\frac{\pi}{2}$	π
φ	0	0	$\frac{\pi}{2}$	π	$\frac{3\pi}{2}$	0

A ligand such as NH_3 is known to have very little, if any, π -bonding to metal ions and we may set $l_{\pi} = 0$. Then the following F values are found from Table 1 to be

$$F_{\sigma}(z^2, \sigma_1) = F_{\sigma}(z^2, \sigma_6) = 1$$

$$F_{\sigma}(z^2, \sigma_2) = F_{\sigma}(z^2, \sigma_3) = F_{\sigma}(z^2, \sigma_4) = F_{\sigma}(z^2, \sigma_5) = -\frac{1}{2}$$

$$\langle z^2 | V_{LF} | z^2 \rangle = \sum_{n=1}^6 l_{\sigma} F(z^2, \sigma_n)^2 = e_{\sigma} \left(1 + 1 + 4 \cdot \frac{1}{4} \right) = 3e_{\sigma}$$

$$F_{\sigma}(x^2 - y^2, \sigma_1) = F_{\sigma}(x^2 - y^2, \sigma_6) = 0$$

$$F_{\sigma}(x^2 - y^2, \sigma_2) = -F_{\sigma}(x^2 - y^2, \sigma_3) = -F_{\sigma}(x^2 - y^2, \sigma_4) =$$

$$F_{\sigma}(x^2 - y^2, \sigma_5) = \frac{\sqrt{3}}{2}$$

$$\langle x^2 - y^2 | V_{LF} | x^2 - y^2 \rangle = l_{\sigma} 4 \cdot 3/4 = 3l_{\sigma}$$

$$\langle yz | V_{LF} | yz \rangle = \langle zx | V_{LF} | zx \rangle = \langle xy | V_{LF} | xy \rangle = 0$$

Thus the one-electron orbital energy difference $\Delta = \langle e_g | V_{LF} | e_g \rangle - \langle t_{2g} | V_{LF} | t_{2g} \rangle$ equals $3l_{\sigma\text{NH}_3}$ in hexamine complexes.

For ligands which are capable of π -bonding to the t_{2g} orbitals, we find using Table 1

$$F_{\pi}(xy, \pi_2^y) = -F_{\pi}(xy, \pi_3^y) = +F_{\pi}(xy, \pi_4^y) = -F_{\pi}(xy, \pi_5^y) = 1$$

$$\langle xy | V_{LF} | xy \rangle = \langle zx | V_{LF} | zx \rangle = \langle yz | V_{LF} | yz \rangle = 4l_{\pi}$$

when $l_{\pi^x} = l_{\pi^y} = l_{\pi}$. Therefore, the octahedral splitting of the d -orbitals is $\Delta = 3l_{\sigma} - 4l_{\pi}$ when π -bonding is included.

Δ in Complexes of T_d Symmetry

Again, it is favorable to choose as the z -axis the symmetry axis of highest order, here the S_4 axis as shown in Fig-

ure 3b. The coordinates for the four ligands are

	1	2	3	4
θ	$\text{Arccos} \frac{1}{\sqrt{3}}$	$\text{Arccos} \frac{1}{\sqrt{3}}$	$\pi - \text{Arccos} \frac{1}{\sqrt{3}}$	$\pi - \text{Arccos} \frac{1}{\sqrt{3}}$
φ	$\frac{\pi}{4}$	$\frac{5\pi}{4}$	$\frac{3\pi}{4}$	$\frac{7\pi}{4}$

With these coordinates we find

$$F(z^2, \sigma_1) = F(x^2 - y^2, \sigma_1) = 0$$

$$F(z^2, \pi_1^x) = -\sqrt{\frac{2}{3}}$$

$$\langle z^2 | V_{LF} | z^2 \rangle = \langle x^2 - y^2 | V_{LF} | x^2 - y^2 \rangle = 4 \cdot \frac{2}{3} l_{\pi} = \frac{8}{3} l_{\pi}$$

$$F(xy, \sigma_1) = \frac{1}{\sqrt{3}}$$

$$F(xy, \pi_1^y) = \frac{\sqrt{2}}{3}$$

$$\langle xy | V_{LF} | xy \rangle = 4 \cdot \frac{1}{3} l_{\sigma} + 4 \cdot \frac{2}{9} l_{\pi} = \langle zx | V_{LF} | zx \rangle = \langle yz | V_{LF} | yz \rangle$$

Again eigenfunctions have been chosen and ΔT_d is therefore

$$\Delta E(xy) - \Delta E(z^2) = \frac{4}{3} l_{\sigma} - \frac{16}{9} l_{\pi} = \frac{4}{9} (3l_{\sigma} - 4l_{\pi}) = -\frac{4}{9} \Delta O_h$$

This latter relation was commented upon a great deal in the beginning of the era of ligand field calculations (3). It should be emphasized that the relation

$$\Delta T_d = -\frac{4}{9} \Delta O_h$$

like all similar cases where AOM parameters or other ligand field parameters are transferred from one system to another, holds only when the metal-ligand distance is kept constant. This restriction is not fulfilled by nature as often as chemists would like. For example, the chromophore CuCl_4^{2-} in the crystalline state exists as a planar molecule in $\text{Pt}(\text{NH}_3)_4\text{CuCl}_4$ (4), it is believed (5) to be tetrahedral in a LiCl-KCl eutecticum at 400° , and in Cs_2CuCl_4 (6) and $(\text{C}_6\text{H}_5\text{CH}_2)_2\text{N}(\text{CH}_3)_2\text{CuCl}_4$ (7) it takes an intermediate configuration. However, in those cases where X-ray structure determinations have been carried through, significantly different Cu-Cl distances have been found. It is, therefore, not surprising that it is impossible to obtain one set of l_{σ} and l_{π} parameters which correctly predicts the one electron orbital differences in different CuCl_4 chromophores.

Chemical Applications

Cis-Trans Isomers of Tetragonal Cr(III) and Co(III) Complexes

The kinetically inertness—or robustness—of chromium(III) and cobalt(III) complexes has made possible the synthesis of a variety of cis and trans isomers of the general chromophore $[M(III)(NH_3)_4X_2]^{n+}$ and $[M(III)en_2X_2]^{n+}$ where X is a variable unidentate ligand and en is ethylenediamine. These complexes are well suited for comparative spectroscopic studies since the M-N distances are virtually independent of X. Thus the ligand field or AOM parameters should be transferable.

These cis and trans complexes exhibit the general property that the first spin allowed absorption band is split, with the splitting in the trans complexes approximately twice that found in the analogous cis isomer. This behavior first explained by Yamatera (8) can be simply reconciled by the AOM (vide infra). In addition, for these complexes, and especially those of Cr(III), it is possible to see a large enough number of *d-d* transitions so that the AOM parameters and the interelectronic repulsion parameter, *B*, can be determined. Schäffer (2e) has analyzed the spectra of such complexes and found the following series for l_σ and l_π in Cr(III) complexes.

$$l_\sigma \text{ Br}^- < \text{Cl}^- < \text{H}_2\text{O} < \text{NH}_3 < \text{F}^- < \text{OH}^-$$

$$l_\pi \text{ NH}_3 < \text{Br}^- < \text{Cl}^- \sim \text{H}_2\text{O} < \text{F}^- < \text{OH}^-$$

These series are more informative than the spectrochemical series which lists ligands effectively according to

$$\Delta_{O_h} = 3l_\sigma - 4l_\pi$$

The l_π series show the satisfactory feature that NH_3 is the least π -bonding ligand and it does follow an intuitively satisfactory pattern, e.g., in $l_\pi(\text{H}_2\text{O}) < l_\pi(\text{OH}^-)$.

AOM Parameters for trans and cis, $[M(\text{NH}_3)_4X_2]^{n+}$

The symmetry axis of highest order (C_4) is used as the *z*-axis and thus the coordinates are

	X(1)	N(2)	N(3)	N(4)	N(5)	X(6)
θ	0	$\frac{\pi}{2}$	$\frac{\pi}{2}$	$\frac{\pi}{2}$	$\frac{\pi}{2}$	π
φ	0	0	$\frac{\pi}{2}$	π	$\frac{3\pi}{2}$	0

The one electron orbital energies and their irreducible representations in D_{4h} are

$$\begin{array}{ll} x^2 - y^2 & : \frac{3}{4} \cdot 1 \cdot 1 \cdot 4l_\sigma^N = 3l_\sigma^N & b_{1g} \\ z^2 & : 2 \cdot \frac{1}{4} (1 \cdot 3 - 1)^2 l_\sigma^x + 4 \cdot \frac{1}{4} (3 \cdot 0 - 1)^2 l_\sigma^N = 2l_\sigma^x + l_\sigma^N & a_{1g} \\ \left. \begin{array}{l} yz \\ zx \end{array} \right\} & : 2l_\pi & e_g \\ yx & : 0 & b_{2g} \\ x^2 - y^2 - z^2 & = 2l_\sigma^N - 2l_\sigma^x & \end{array}$$

Notice that the transition $xy \rightarrow x^2 - y^2$ has the orbital energy difference $3e_\sigma^N$ which is Δ in the hexamine complex. The first spin-allowed absorption band in Co(III) complexes of O_h symmetry is caused by this transition (${}^1A_{1g} \rightarrow {}^1T_{1g}$). In D_{4h} symmetry the ${}^1T_{1g}$ state is split into ${}^1A_{2g}$ and 1E_g states. The 1E state can mix with the 1E state arising from the second excited singlet state, ${}^1T_{2g}$, whereas ${}^1A_{2g}$ does not interact with any other state. Since the ${}^1A_{1g} \rightarrow {}^1A_{2g}$ transition is the orbital jump $xy \rightarrow x^2 - y^2$, this explains why the trans complexes have an absorption component exactly where the hexamine absorbs. Ignoring electron repulsion effects, the splitting of the ${}^1A_{1g} \rightarrow {}^1T_{1g}$ band in Co(III) complexes is just $E(xz, yz) - E(xy) = 2l_\pi^x$.

For the cis complex let X occupy the 2 and 3 positions of Figure 3a. The energy integrals for the cis complex are then found to be

$$\begin{array}{ll} x^2 - y^2 & : \frac{3}{2} l_\sigma^N + \frac{3}{2} l_\sigma^x & a_1 \\ z^2 & : \frac{5}{2} l_\sigma^N + \frac{1}{2} l_\sigma^x & a_1 \\ xy & : 2l_\pi^x & a_2 \\ zx & : l_\pi^x & b_1 \\ yz & : l_\pi^x & b_2 \\ z^2 - x^2 - y^2 & : l_\sigma^N - l_\sigma^x & \end{array}$$

Notice the accidental degeneracy of the orbitals with b_1 and b_2 symmetry. This phenomenon we could have predicted with the use of the *holohedrized symmetry* (2e) of the molecule. The holohedrized symmetry is found from the true symmetry by averaging the interaction along each coordinate axis. Here, it means that the x , $-x$ and y , $-y$ axes become identical and the z -axis becomes a four-fold symmetry axis. For the cis complex, the splitting of the first spin allowed band is $E(xy) - E(xz \text{ or } yz) = l_\pi$, or half that predicted for the trans isomer.

Comparison of one-electron orbital energies in complexes of these and other symmetries have been made within the electrostatic schemes (see Yamatera (8) and McClure (9)).

Trigonal Complexes—Ground State Properties

The AOM seems to be useful in connection with complexes of conjugated ligands such as ox^{2-} , acac^- , *o*-phen, etc. The symmetry of tris bidentate like $\text{Co}(\text{acac})_3$ is D_3 . In this symmetry energy levels can only be doubly degenerate and thus the triply degenerate transitions in a hypothetical analogous complex of O_h symmetry (meaning that all M-L distances are identical and all $\angle \text{LML}' = \pi/2$) must split up. This must happen because of a difference in the in-plane and out-of-plane (of the conjugated chelate) π -bonding.

In the following, complexes of D_3 symmetry will be dealt with first to try to rationalize some geometric features, thus connecting crystallographic results with electronic structure. Thereafter trigonal complexes of C_2 symmetry will be treated with special reference to the further splitting of the *d*-orbitals as studied by nmr.

Let us find for a complex of D_3 symmetry the one-electron orbital energies expressed in l_σ , l_π^\perp , and l_π^\parallel , where the latter two parameters describe the effect from the chelate π -orbital system and from the in-plane orbitals of π -symmetry, respectively.

Geometric Restrictions on Coordinates. In chelate complexes there must exist relations between the bite angle (α), e.g., for a bidentate ligand and the θ , φ , and ψ values for the two ligators. From spherical geometry one may deduce the following relations for a tris complex of a planar bidentate (see Fig. 4)

$$\cos \frac{\alpha}{2} = \sin \theta_1 \cos \varphi_1 \quad \theta_1 = \theta_2 = \theta_3$$

$$\cos \psi_1 = \cos \theta_1 / \sin \frac{\alpha}{2} \quad \varphi_4 = \varphi_5 = \varphi_6$$

$$\theta = \pi - \theta_1; \varphi = -\varphi_1 \quad \varphi_3 = \varphi_2 + 120^\circ = \varphi_1 + 240^\circ \text{ etc.}$$

where θ_1 , φ_1 , and ψ_1 are the coordinates for L_1 bridged to L_4 through the chelate.

Experimentally one finds rather constant bite distances for a given chelate ligand. Thus for a complex like trispropionato cobalt(III) (CoT) it is possible from the known bite distance 2.5 Å and the normal Co(III)-oxygen distance, 2.0 Å, to postulate a bite angle of $\sim 77^\circ$. Using this value for α and varying φ_1 it is possible to compute θ_1 and ψ_1 . Using the three-fold symmetry and the above relations the other coordinates follow. These coordinates are then used and the angular overlap matrix can be constructed. Except for the situations where φ_1 equals 0° a non-diagonal

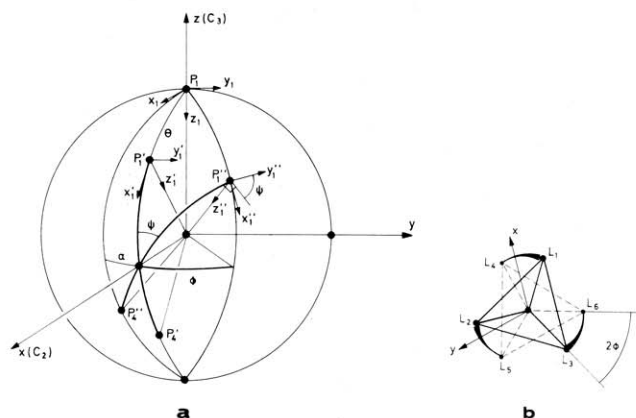


Figure 4. A planar chelate with ligands P_1' and P_4' span the chelate angle α . This position creates a complex with trigonal prismatic structure when the three-fold symmetry is introduced. By rotating an angle ψ around x the ligands are brought to P_1'' and P_4'' . This corresponds to a general trigonal structure when all three chelates are placed. The angle ψ is also the angle to rotate the ligand coordinate system x_1, y_1 around z_1 to bring y_1'' perpendicular to the plane $MP_1''P_4''$ and thus parallel to the ligand π -orbitals.

nal element occurs between the d -orbitals of e symmetry. The diagonalized energy matrix has been used in Figure 5 to construct correlation diagrams in which the orbital energies are plotted against the trigonal twist angle ($2\varphi_1$). The solid line is obtained when only σ -bonding is considered ($l_{\pi}^{\pm} = l_{\pi}^{\mp} = 0$). For the dotted lines the out-of-plane π -bonding is assumed to be 10% and -10%, respectively, of the σ -bonding ($l_{\sigma} = l, l_{\pi}^{\pm} = \pm 0.1 l, l_{\pi}^{\mp} = 0$). The latter two parameter choices are probable upper and lower limits for the π effects in such complexes and it is seen that these values do not drastically change the overall picture. Therefore, any reasonable parameter will produce the same trend. It is seen that somewhere near $\varphi_1 = 20$ - 25° there is a minimum in the sum of the orbital energies of the lowest lying three $3d$ -orbitals of CoT_3 . Thus, on this basis we may postulate that a complex like CoT_3 is most likely distorted towards a trigonal prismatic structure. This, of course, is without taking ligand-ligand repulsions into account and therefore the exact position found experimentally may well be somewhat different from the predicted value.

The degeneracy of the e -orbitals is lifted in trigonal complexes of mixed ligands ML_2L' or MLL_2' , where L and L' differ only in symmetrical substituents. The symmetry is lowered to C_2 raising the orbital degeneracy $e(D_3) \rightarrow a, b(C_2)$. For the case where the parent trigonal chelate, ML_3 , is paramagnetic and has an E ground state, it has been demonstrated that nuclear magnetic resonance may be used to determine whether the resulting ground state

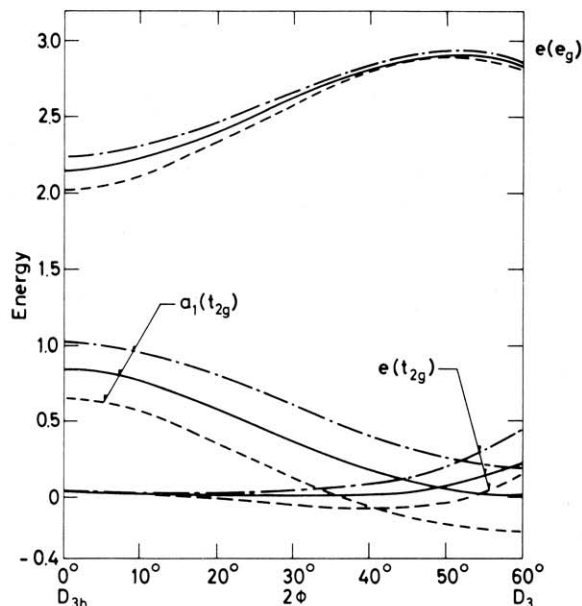


Figure 5. Diagonalized one-electron orbital energies plotted against the trigonal twist angle (2φ of Fig. 4) for a tris complex of a planar, conjugated ligand with a chelate angle of 77° . The energy is in units of l_{σ} . The full line is for $l_{\pi}^{\pm} = l_{\pi}^{\mp} = 0$, --- is for $l_{\pi}^{\pm} = -0.1 l_{\sigma}, l_{\pi}^{\mp} = 0$, and - . - . - is for $l_{\pi}^{\pm} = 0.1 l_{\sigma}$ and $l_{\pi}^{\mp} = 0$.

for a given mixed chelate complex is A or B (10). In particular it has been observed for a given pair of ligands L, L' , that if ML_2L' passes the A ground state, then MLL_2' exhibits the B ground state, or vice versa. This phenomenon can be simply predicted by the AOM and an example of such a calculation on orbital energies is shown in Table 2.

Antiferromagnetic Coupling

Recently, Glerup has applied the AOM to gain insight into antiferromagnetic coupling observed in the binuclear complex μ -oxobis[pentamminechromium(III)] (basic rhodo) (11). This complex has a linear arrangement $Cr-O-Cr$ with the symmetry D_{4h} (12), and in spite of the fact that it is built up of two $Cr(III)$ parts each having a quartet ground state, the ground state of the molecule is a singlet. Triplet, quintet, and septet states are placed only 450, 3×450 , and $6 \times 450 \text{ cm}^{-1}$, respectively, above the singlet state as found from magnetic susceptibility measurements. Antiferromagnetic coupling of this nature has long been a puzzle because Hund's rule so obviously is not obeyed. Experimental magnetic susceptibility measurements have been rationalized by means of a positive spin-spin coupling constant in the Heisenberg-Dirac-Van Vleck operator $J \cdot S_a \cdot S_b$. The eigenvalues of this operator take

Table 2. Calculated Energies of $t_{2g}(O_h)$ Orbitals in ML_2L' Complexes

input									
l_{σ}	1	1.1	1.0	1.0	1.1	1.0	1.0	1.1	1.0
l_{π}^{\perp} for ligand 1	0	0	0	0.1	0.11	0.10	-0.1	-0.11	-0.1
l_{σ}	1	1	1.1	1.0	1.0	1.1	1.0	1.0	1.0
l_{π}^{\perp} for ligand 2 and 3	0	0	0	0.1	0.1	0.11	-0.1	-0.1	-0.11
output									
$a(a)$	-1.116	-1.153	-1.190	-1.118	-1.157	-1.195	-1.113	-1.150	-1.187
$a(e)$	-1.151	-1.189	-1.229	-1.048	-1.074	-1.124	-1.124	-1.303	-1.332
$b(e)$		-1.190	-1.227		-1.090	-1.110	-1.254	-1.290	-1.344
$\Delta = a(e) - b(e)$		+0.001	-0.002		+0.016	-0.014		-0.013	+0.012

This table is concerned with the calculated energies of the $t_{2g}(O_h)$ orbitals in complexes as ML_2L' , where L and L' are different planar, conjugated, bidentate chelates. Such an example is $Cr(\text{phen})_2(4,7\text{-dimethylphen})^{2+}$ (10). The input l_{σ} and l_{π}^{\perp} parameters are chosen such that l^{\perp} is either 0 or 10% of l_{σ} for the ligand. For comparison, the results of some computations for D_3 symmetry are included. The geometry has been kept constant with a bite angle of 77° and a trigonal twist of 50° . The output in unit of l_{σ} shows in the second and third column how small the splitting is for the metal π -orbitals of e symmetry in D_3 when the descent in symmetry to C_2 is made only through the σ interaction. However, notice that the two complexes ML_2L' and MLL_2' have opposite ordering of the $e(D_3)$ orbitals. This effect is an order of magnitude larger when the lowering in symmetry is due to the π -interaction. It is at present not even known whether l_{π}^{\perp} for phenanthroline in a $Cr(II)$ complex is positive or negative and, therefore, computations for both situations are reported. If we have independent means to determine the relative π ligand field strengths for L and L' the sign of Δ as obtained by experiment may reveal the sign of l_{π}^{\perp} for phenanthrolines in $Cr(II)$ complexes.

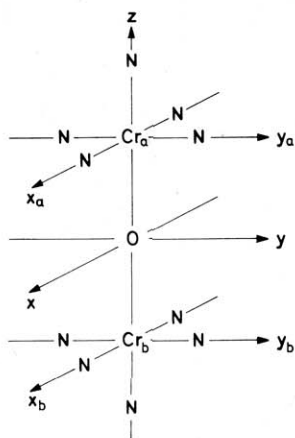


Figure 6. Basic rhodo.

the values 0, 1, 3, and 6. The same level distribution was found by Glerup by AOM considerations. Figure 6 shows the coordinate systems for the molecule. From the d -orbitals of Cr_a and Cr_b linear combinations are formed which transform as the irreducible representations of the group D_{4h} . Some of these are

$$\frac{1}{\sqrt{2}}(d_{yz^a} + d_{yz^b})$$

$$\text{transforming as } e_g \text{ and}$$

$$\frac{1}{\sqrt{2}}(d_{yz^a} - d_{yz^b})$$

transforming as e_u . The σ

bonds are formed by the antisymmetric combination of the two $d(z^2)$ orbitals and the oxygen p_z orbital. The chromium d_π combinations of e_u symmetry are able to form π -bonds to the oxygen p_x and p_y orbitals.

For each half part the orbital energies are found using the foregoing to be

$$d_{x^2-y^2} \quad 3l_\sigma^N \quad 3l_\sigma^N - \frac{2}{3}l_\pi^0$$

$$d_{z^2} \quad 2l_\sigma^N \quad 2l_\sigma^N - \frac{2}{3}l_\pi^0$$

$$d_{yz}, d_{zx} \quad l_\pi^0 \quad \frac{1}{3}l_\pi^0$$

$$d_{xy} \quad 0 \quad -\frac{2}{3}l_\pi^0$$

This would be the result for a hypothetical complex like oxopentamminechromium(III). The three unpaired electrons would be in the orbitals of t_{2g} octahedral parentage, i.e., d_{xy} , d_{yz} , and d_{zx} . The last column gives the energies in such a way that the baricenter of the t_{2g} levels is preserved. In the dinuclear complex the bonding must be through the a_{2u} σ -orbitals and the e_u π -orbitals. First-order perturbation due to bond formation on the metal e_u orbitals leads to the two identical secular determinants

$$(I) \begin{vmatrix} d_{yz^a} & d_{yz^b} & d_{xz^a} & d_{xz^b} \\ d_{yz^a} \left| \frac{1}{3}l_\pi^0 - E \right. & x & d_{xz^a} \left| \frac{1}{3}l_\pi^0 - E \right. & x \\ d_{yz^b} & x & d_{xz^b} & x \\ d_{yz^b} \left| \frac{1}{3}l_\pi^0 - E \right. & x & d_{xz^b} \left| \frac{1}{3}l_\pi^0 - E \right. & x \end{vmatrix} = 0$$

with the solutions $E = \frac{1}{3}l_\pi^0 \pm x$ with normalized eigenfunctions $(d_{yz^a} \pm d_{yz^b})/\sqrt{2}$ and $(d_{xz^a} \pm d_{xz^b})/\sqrt{2}$.

At the moment we see no way of calculating x directly. However, it is possible to use arguments based on baricenter rules as demonstrated so elegantly by Glerup. The e_g , b_{2g} , and b_{1u} combinations are not interacting with the oxygen orbitals and, therefore, have identical energies in the dinuclear complex

$$E(e_g) = E(b_{2g}) = E(b_{1u}) = E_n$$

$E(b_{1u})$ is of course unchanged from $E(d_{xy})$. Thus

$$E_n = -\frac{2}{3}l_\pi^0$$

Likewise, there is no difference in the energy of the metal e_u combinations

$$E(e_u) = E_i$$

The baricenter of the orbital energies is considered fixed and equal to zero with the result that

$$4E_n + 2E_i = 0 \quad E_i = -2E_n = \frac{4}{3}l_\pi^0$$

It is known that the two combinations in which the metal d_{xz} orbitals enter do not mix. The interaction ma-

trix between the two is therefore diagonal, for example

$$\frac{1}{\sqrt{2}}(d_{xz^a} - d_{xz^b}) \quad \frac{1}{\sqrt{2}}(d_{xz^a} + d_{xz^b})$$

$$\begin{vmatrix} \frac{1}{\sqrt{2}}(d_{xz^a} - d_{xz^b}) & H_- - E & 0 \\ \frac{1}{\sqrt{2}}(d_{xz^a} + d_{xz^b}) & 0 & H_+ - E \end{vmatrix} = 0$$

H_+ and H_- are the interaction integrals found above to be E_i and E_n , respectively. Thus the matrix reads

$$\frac{1}{\sqrt{2}}(d_{xz^a} - d_{xz^b}) \begin{vmatrix} E_i - E & 0 \\ 0 & -\frac{1}{2}E_i - E \end{vmatrix} = 0$$

$$\frac{1}{\sqrt{2}}(d_{xz^a} + d_{xz^b}) \begin{vmatrix} \frac{4}{3}l_\pi^0 - E & 0 \\ 0 & -\frac{2}{3}l_\pi^0 - E \end{vmatrix} = 0$$

This matrix is the diagonalized solution to the matrix (I) and therefore x can be found

$$\frac{1}{3}l_\pi^0 + x = \frac{4}{3}l_\pi^0 \rightarrow x = l_\pi^0$$

$$\frac{1}{3}l_\pi^0 - x = -\frac{2}{3}l_\pi^0 \rightarrow x = l_\pi^0$$

It is thus proved that a one-electron integral (of the form $\langle d^a | V_{LF} | d^b \rangle$) exists which mixes the d -orbitals on the metals A and B. Therefore, the Hamiltonian for the dinuclear complex takes the form

$$H = H_a + H_b + H_{ab} = V_{LF^a} + \sum_{i < j} \frac{1}{r_{ij}} + V_{LF^b} + \sum_{i < j} \frac{1}{r_{ij}} + V_{ab}$$

where V_{ab} is the parameter just derived.

The coupling of two quartet ground states (4B_1) of two $Cr(NH_3)_5O$ units gives rise to ${}^7A_{2u}$, ${}^5A_{1g}$, ${}^3A_{2u}$, and ${}^1A_{1g}$ states in which three electrons are localized on each chromium. Charge transfer states can be constructed from coupling of the two ground states of $Cr(NH_3)_5O$ units with two and four electrons, respectively. Among such states are ${}^5A_{1g}$, ${}^3A_{2u}$, and ${}^1A_{1g}$ states. Configuration interaction between the former and latter states can be calculated and it is found to occur with the non-diagonal elements always proportional to l_π^0 . Solving the secular equations for singlet, triplet, pentet, and septet follows the state ordering: singlet < triplet < pentet < septet, and both the temperature dependent magnetism and uv/vis absorption energies can be understood.

This model for anti-ferromagnetic coupling has so far only been used in a quantitative sense for basic rhodo. It seems directly applicable to many bioinorganic systems around which so much research is going on presently.

In fact the model is easily extended to many important systems. For linear σ -interaction through a bridging atom between two paramagnetic metal ions the non-diagonal element corresponding to x in (I) is e_σ . This would be useful in dealing with, e.g., oxygen bridged binuclear Fe(III) complexes. For binuclear complexes bridged by two atoms antiferromagnetic coupling may be thought of in the same way as in complexes with one bridging atom. Baricenter considerations again lead to one-electron off-diagonal interaction matrix elements. For ideal geometry with all angles equal to 90° off-diagonal elements are also in this case e_σ or e_π depending on the orbitals. Less ideal symmetry of course enhances the complexity but the one-electron scheme is still manageable using the angular dependences of the overlap integrals.

It is hoped that these examples demonstrate that the angular overlap model is pedagogically a very satisfactory means of obtaining ligand field parameters. The concepts

are very easy to learn and to use. The MO formulation of the model only presumes a small theoretical foundation on the part of the student and it seems possible to get far without a preceding course in group theory. In fact group theoretical arguments are illustrated by the model rather than just demanded in its use.

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