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# Articles

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## Ligand Field of Conjugated Bidentate Ligands Parametrized by the Angular Overlap Model

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The effect of the $\pi\perp$ perturbation of a symmetrical, conjugated bidentate ligand upon the central ion d orbital energies is described in a ligand-field framework. The method is based upon the symmetry-dictated orientation of the angular overlap model (AOM) toward a molecular orbital model. The result is, as far as geometry is concerned, that the bidentate moiety, LL, still can be represented by its two ligators, L. However, as far as the d-orbital perturbation energies are concerned, the usual reference to the symmetry $C_{\infty v}$ of M(L) must be replaced by reference to the symmetry $C_{2v}$ of M(LL). Thereby the single radial parameter $e_{\pi\perp}$, which the two ligators have in common in the conventional AOM and which is atomic in character, must be replaced by two independent parameters, $e_{\psi L}$ and $e_{\chi L}$, which are molecular in character. The new radial parameters $e_{\psi L}$ and $e_{\chi L}$ belong to our *ligator parametrization scheme*. These parameters are closely related to the eigenenergies of two of the central ion d orbitals in a system containing only one bidentate moiety of the kind mentioned. In this M(LL) system, $\psi$ and $\chi$ refer to the irreducible representations $b_2$ and $a_2$, respectively, of the group $C_{2v}$ where the subindex 2 in both cases means odd with respect to reflection in the molecular plane of the coordinated bidentate and thereby is synonymous with the symbol $\perp$ in $\pi\perp$. When the parameters mentioned are used, the bite angle of the bidentate moiety occurs in the $\pi\perp$ energy expressions. However, an alternative set of radial, molecular parameters $e_{\psi LL}$ and $e_{\chi LL}$ belong to our *ligand parametrization scheme*. These parameters are directly the two nonvanishing d-orbital eigenenergies of our M(LL) system. The coefficients to these parameters do not contain the bite angle. In this scheme a bidentate moiety behaves as a non linearly ligating unidentate ligand, situated on the $C_2$ axis of the bidentate ligand. With our results, a large number of metal complexes containing conjugated bidentate ligands reaching from the carbonate ion to 2,2′-bipyridine can now be subjected to a ligand-field description. The present problem, first addressed by Orgel, was recently examined by Ceulemans, Dendooven, and Vanquickenborne. They found that the problem could not be solved by using the AOM alone and that an extra, so-called phase-coupling term had to be introduced in connection with the $\psi/\chi$ separation of the ligand field. Our treatment does not involve any extra terms and is fully consistent with the AOM as it was originally formulated. The semiempirical AOM furthermore allows for gradual diminution of the delocalization or other ligator–ligator interactions within the bidentate ligand until the perturbations by the ligators are no longer correlated. At this point $e_{\psi L} = e_{\chi L} = (e_{\psi LL} + e_{\chi LL})/2 = e_{\pi\perp}$ and the conventional AOM may be used. Conversely, the concept of individual ligator $\pi\perp$ perturbations gradually loses its meaning as the ligator–ligator interaction sets in. This treatment also retains the AOM additivity and the associated sum rules for coefficients to the energy parameters $e_{\psi LL}$ and $e_{\chi LL}$. The analysis shows that the plus and minus combinations of these $\psi$ and $\chi$ ligand fields, associated with a single ligand LL, have effectively linear and orthorhombic symmetries, respectively. In the Appendix it is shown that the ligand-field approach is not likely to be useful for an unsymmetrical bidentate ligand, because this must involve yet another radial parameter.

### I. Introduction

The present paper was inspired by two contributions by Ceulemans, Dendooven, and Vanquickenborne[1,2] (CDV), concerned with a representation of the ligand field produced by the $\pi$-part of conjugated bidentate ligands. CDV aimed at adapting the angular overlap model (AOM) to treat the special interaction between central ions and ligands that occurs when these ligands contain a delocalized $\pi$-electron system. They concluded that it was necessary to introduce an extra term, a so-called phase-coupling term, and that the additive character of AOM had to be sacrificed in order to adapt the AOM to treat the ligand field of a conjugated bidentate ligand. Furthermore, in their conclusion, they used radial parameters, associated with the coordinating atoms (the ligators), in spite of the fact that their formalism is based upon a division of the conjugated ligands into classes defined by the symmetry of their frontier molecular orbitals rather than of orbitals localized on the ligators. We disagree with their treatment[1,2] in all these points.

The present paper is essentially limited to a discussion of symmetrical, conjugated bidentates LL for which the metal–bidentate ligand subsystem M(LL) has the symmetry $C_{2v}$. However, in the Appendix, we shall comment briefly on the problem of unsymmetrical ligands[1,2] for which the subsystem has only $C_{1h}$ symmetry.

We find that there is an inconsistency in the CDV formalism such that when this is corrected, no phase-coupling term arises and the additive character of the AOM is conserved, even if its form is slightly modified in one of our proposed parametrization schemes. Our radial AOM parameters are more directly conceived as being caused by a molecular perturber as opposed to a preponderantly atomic one. All our symmetrical bidentate ligands fall into one class rather than two classes depending on frontier-orbital symmetries.[1] Our approach is to go back to the LCAO–MO basis of the AOM through the LCAO description of the delocalized orbitals of the bidentate ligand and then to use the AOM in the way it was originally proposed.

The AOM embodies two kinds of additivity: ligator or ligand additivity on the one hand and additivity of $\sigma$- and $\pi$-perturbation contributions on the other. This paper is concerned with the first kind of additivity. The second kind of additivity in the AOM is not influenced by a reformulation of the effect of conjugation within the coordination sphere, and we therefore follow CDV in restricting ourselves to discussing $\pi\perp$ interactions and not including the stronger $\sigma$ interactions. We assume, at least for the purpose of the present paper, that these interactions can simply be added by using the AOM in the conventional way. [These interactions can be directly combined with other modifications

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(1) Ceulemans, A.; Dendooven, M.; Vanquickenborne, L. G. *Inorg. Chem.* **1985**, *24*, 1153–1158.

(2) Ceulemans, A.; Dendooven, M.; Vanquickenborne, L. G. *Inorg. Chem.* **1985**, *24*, 1159–1165.

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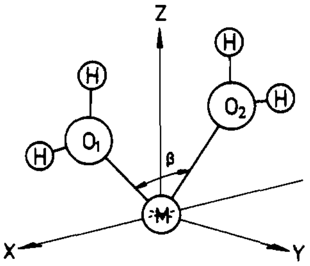
of the AOM that do not involve the $\pi\perp$ interaction itself. For example, intermixing of $\sigma$ and $\pi\|$ interactions,[3] which are symmetry-allowed for our present ligand perturbations, can immediately be accommodated into the present treatment. Similarly, s–d mixing can be accommodated. However, we decline from discussing these modifications of the AOM here as they will necessarily involve extra radial parameters, which probably will make them impractical. In quoting work of the Gerloch group,[4–6] we would like to point out that although we largely agree with the philosophy of the cellular ligand-field model of Gerloch and coworkers as this has recently been expressed,[7] our *formalism* for the AOM presented here is *different* from that of the cellular model (cf. Section IIC).]

Most of the results, which are described in detail in this paper, were communicated[8] at the XXIV ICCC in Greece (1986) and at that occasion also discussed with Ceulemans of CDV. Moreover, at the XXVII ICCC in Australia (1989), we attended Ceulemans' talk[9] on this very subject, and it is our impression that the controversies between CDV and us are by and large settled. However, the ligand field of bidentate ligands with ligator–ligator interactions,[10] and particularly conjugated ones,[11,12] is an old problem,[13,14] which recently has been reconsidered.[9,15–17] We present here our systematic solution within the formalism of the AOM.

Our paper is structured as follows. Section II gives an illustration of the two equivalent formulations of the AOM—that using the single ligator orbital overlap formulation and that using the group overlap formulation. Section III, which contains the main body of the paper, discusses one conjugated bidentate moiety, first as a molecule ready for chelation and second as a ligand providing a ligand field described by AOM parameters. Thereafter, discussion of the molecular orbital interpretation of these parameters is followed by an account of their semiempirical application. Finally, an analysis of the effective symmetries of the new $\pi\perp$ operators is provided. Section IV contains examples of the practical application of the AOM beginning with a short discussion of the additivity formalism. The concluding section, Section V, summarizes the main results for symmetrical bidentate moieties, and the paper finishes with an appendix concerned with the problem of the unsymmetrical bidentate. Here we are also at variance with CDV.[1,2]

## II. The Two Formulations of the Conventional Angular Overlap Model

**A. A Model-Illuminating Example.** In this section, we shall discuss a chemical system that, from an experimental point of view, is somewhat artificial, but from a model-theoretical point of view contains *everything* necessary to illuminate the symmetry features of this paper's problem and to allow performing of a preliminary comparison between the present approach and that of CDV. The system consists of two water molecules that act as two geometrically correlated non linearly ligating ligands.[18] We place the two water molecules with all their six atoms in the $ZX$ plane of a Cartesian coordinate system, the oxygen ligators being symmetrically disposed about the $Z$ axis and the central atom placed at the origin (**1**).



1

Planar seven-atom molecule

The system has the symmetry $C_{2v}$, and the coordinates of the ligating oxygen atoms $O_1$ and $O_2$ are (sin ($\beta/2$), 0, cos ($\beta/2$)) and (−sin ($\beta/2$), 0, cos ($\beta/2$)), respectively, so that the valence angle at M is equal to $\beta$. This valence angle is the geometrical prerequisite for the AOM calculation. We now consider the perturbation of the central-ion d orbitals associated with the $p_y$ ligator orbitals, $p_y^1$ and $p_y^2$, of $O_1$ and $O_2$. These orbitals are odd with respect to reflection in the $ZX$ plane, a property that must apply also to the central ion d orbitals that are to overlap with them and interact with them in an AOM sense. This symmetry requirement on the d orbitals reduces the five-dimensional d space to a two-dimensional subspace spanned by $(yz)$ and $(xy)$. Each of these perturbed d orbitals transforms irreducibly under $C_{2v}$ and spans $b_2$ and $a_2$, respectively, where the subindex 2 expresses the fact that they are $\pi\perp$ orbitals.

Independently of the way in which the AOM is applied, the relevant theoretical quantities are the geometry-dependent quantities called the diatomic angular overlap integrals.[18] Here we only need the following four diatomic angular overlap integrals:

$$\langle (yz)|p_y^1\rangle_{\text{ang}} = +\cos(\beta/2)$$

$$\langle (xy)|p_y^1\rangle_{\text{ang}} = +\sin(\beta/2)$$

$$\langle (yz)|p_y^2\rangle_{\text{ang}} = +\cos(\beta/2)$$

$$\langle (xy)|p_y^2\rangle_{\text{ang}} = -\sin(\beta/2) \qquad (1)$$

They will now be used to illustrate the two formulations,[13,18–20] which are equivalent in the conventional AOM algebra and which may be called the diatomic-overlap formulation and the group-overlap formulation,[21] respectively.

**B. The Formulation Based on Individual Ligator Orbitals or the Diatomic-Overlap Formulation.** We consider the perturbing effect upon the d orbitals of the central atom, which arises from the interaction with the two $p_y$ oxygen ligator orbitals. According to the individual ligator-orbital approach to the AOM, the energy matrix associated with each of these ligator orbitals must be set up in the same basis (and in this particular case the basis $(yz)(xy)$ is chosen, with the orbitals in the given order), and the total energy matrix is then the sum of these two matrices; i.e., the perturbation contributions from the two *ligators* are additive. Each energy

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(3) Deeth, R. J.; Duer, M. J.; Gerloch, M. *Inorg. Chem.* **1987**, *26*, 2573–2578.
(4) Gerloch, M.; Harding, J. H.; Woolley, R. G. *Struct. Bonding (Berlin)* **1981**, *46*, 1–46.
(5) Woolley, R. G. *Mol. Phys.* **1981**, *42*, 703–720.
(6) Gerloch, M.; Woolley, R. G. *Prog. Inorg. Chem.* **1983**, *31*, 371–446.
(7) Deeth, R. H.; Duer, M. J.; Gerloch, M. *Inorg. Chem.* **1987**, *26*, 2578–2582.
(8) Yamatera, H.; Schäffer, C. E. *Proceedings of the XXIV International Conference on Coordination Chemistry*, Athens, Greece, Aug 1986; Pergamon: Oxford, England; 1986; p 125.
(9) Ceulemans, A.; Vanquickenborne, L. G. *Pure Appl. Chem.* **1990**, *62*, 1081–1086.
(10) Jørgensen, C. K. *Mol. Phys.* **1962**, *5*, 485–492.
(11) Orgel, L. E. *J. Chem. Soc.* **1961**, 3683–3686.
(12) Lin, W. C.; Orgel, L. E. *Mol. Phys.* **1964**, *7*, 131–136.
(13) Schäffer, C. E. *Proc. R. Soc. London* **1967**, *A297*, 96–133.
(14) Larsen, E.; La Mar, G. N.; Wagner, B. E.; Parks, J. E.; Holm, R. H. *Inorg. Chem.* **1972**, *11*, 2652–2668.
(15) Atanasov, M. A.; Schönherr, T.; Schmidtke, H.-H. *Theor. Chim. Acta* **1987**, *71*, 59–73.
(16) Schönherr, T.; Atanasov, M. A.; Schmidtke, H.-H. *Inorg. Chim. Acta* **1988**, *141*, 27–32.
(17) Atanasov, M.; Schönherr, T. *Inorg. Chem.* **1990**, *29*, 4545–4550.
(18) Schäffer, C. E. *Struct. Bonding (Berlin)* **1968**, *5*, 68–95.
(19) Schäffer, C. E.; Jørgensen, C. K. *Mol. Phys.* **1965**, *9*, 401–412.
(20) Schäffer, C. E. *Pure Appl. Chem.* **1970**, *24*, 361–391.
(21) Yamatera, H. *Bull. Chem. Soc. Jpn.* **1958**, *31*, 95–108. This paper is the prototype illustration of how the geometrical overlap integrals can be found in special cases. Actually, for the special systems, later called orthoaxial systems,[22] this paper contains results which from almost every point of view are the same as those of AOM.
(22) Schäffer, C. E.; Jørgensen, C. K. *Mat. Fys. Medd. Dan. Vid. Selsk.* **1965**, No. 13, 1–20.

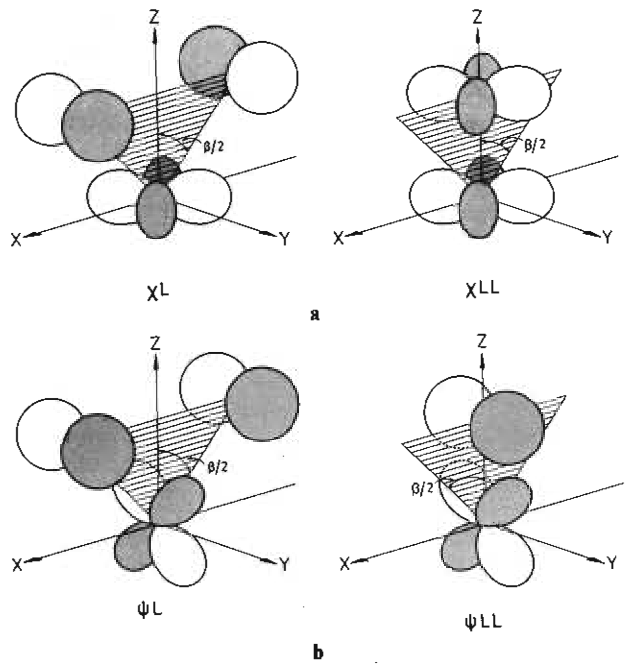


**Figure 1.** Orbitals associated with the ligand-field $\pi\perp$ perturbations from a symmetrical, conjugated bidentate ligand. Parts a and b illustrate ligand orbitals that are even ($\chi$) and odd ($\psi$), respectively, with regard to rotation about the $C_2$ axis of the bidentate moiety. The $\chi$ and $\psi$ orbitals belong to the symmetry species $a_2(C_{2v})$ and $b_2(C_{2v})$, respectively. The left-hand and right-hand sides illustrate the symmetry orbitals of the ligator (L) and the ligand (LL) parametrization schemes, respectively. The former scheme orbitals are out-of-phase ($\chi$L) and in-phase ($\psi$L) linear combinations of ligator orbitals, whereas the latter ($\chi$LL and $\psi$LL) are $\chi$ and $\psi$ atomic orbitals of a non linearly ligating, unidentate ligand, situated on the $C_2$ axis of the bidentate moiety.

matrix consists of the product of a matrix of angular elements (consisting of squares and cross-products of angular overlap integrals) and a radial energy parameter, $e_{\pi\perp}$. This parameter is the same for the two oxygen ligators.

The two matrices, as well as their sum, are given in eq 2 in units[13] of $e_{\pi\perp}$. Nonvanishing nondiagonal elements appear in

$$\begin{array}{c|cc} \hat{A}(O_1) & (yz) & (xy) \\ (yz) & \cos^2(\beta/2) & \cos(\beta/2)\sin(\beta/2) \\ (xy) & \cos(\beta/2)\sin(\beta/2) & \sin^2(\beta/2) \end{array} \; + \; \begin{array}{c|cc} \hat{A}(O_2) & (yz) & (xy) \\ (yz) & \cos^2(\beta/2) & -\cos(\beta/2)\sin(\beta/2) \\ (xy) & -\cos(\beta/2)\sin(\beta/2) & \sin^2(\beta/2) \end{array} \; =$$

$$\begin{array}{c|cc} \hat{A}(O_1) + \hat{A}(O_2) & (yz) & (xy) \\ (yz) & 2\cos^2(\beta/2) & 0 \\ (xy) & 0 & 2\sin^2(\beta/2) \end{array} \qquad (2)$$

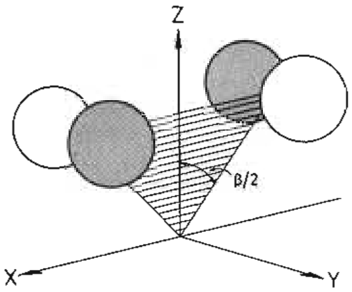
the matrices of the individual ligator operators, but these disappear in the matrix sum in agreement with the above symmetry result that $(yz)$ and $(xy)$ belong to different irreducible representations of the symmetry group $C_{2v}$ of the chemical system. One observes that the traces of the individual ligator matrices are equal to unity and hence that the trace of the sum matrix is equal to 2, i.e., the number of ligators. These sum rules[19] are associated with the magnitude specification of the radial AOM parameters.

In the following subsection, we reconsider the same chemical system using the alternative formulation.

**C. The Group-Overlap Formulation or the Formulation Based upon Linear Combinations of Ligator Orbitals. The $\psi$–$\chi$ Symmetry Classification of Ligator Group Orbitals.** In subsection B the central ion d orbitals were perturbed, according to the AOM, by their interaction with the two ligator orbitals $p_y^1$ and $p_y^2$ (**1**). The total perturbation was expressed as a sum of terms, each term being associated with one particular ligator orbital. We now form two linear combinations of $p_y^1$ and $p_y^2$, which are symmetry-adapted[13,20] to the point group $C_{2v}$ of the system. In eq 3, the $C_{2v}$

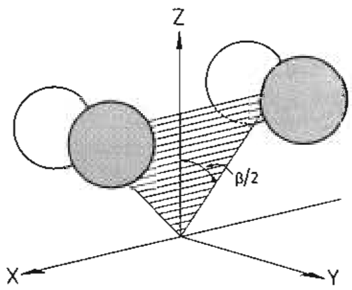
$$O_\psi = (p_y^1 + p_y^2)/2^{1/2} \quad b_2(C_{2v})$$
$$O_\chi = (p_y^1 - p_y^2)/2^{1/2} \quad a_2(C_{2v}) \qquad (3)$$

symmetry classification $b_2$ and $a_2$, mentioned in section IIA, has been associated with the symbols $\psi$ and $\chi$, thereby following Orgel,[11,12] who originally put forward the qualitative LCAO–MO idea that inspired CDV's papers[1,2,9] and through these the present paper. Note that the orbitals of symmetries $\psi$ and $\chi$ carry plus and minus signs, respectively, which means that the two constituent orbitals in these equations have the same and the opposite signs (*in-phase* and *out-of-phase*, respectively) on a given side of the plane of the seven-atom molecule (**2b,a**).



2a

$\chi$ symmetry = $a_2$ symmetry



2b

$\psi$ symmetry = $b_2$ symmetry

According to the symmetry-orbital formulation[13] of the AOM, the energy matrix associated with each of these ligator group orbitals must be set up in the same basis (and in this particular case we choose the same basis $\{(yz)(xy)\}$ with the same order of the functions as we did in section IIB), and the total energy matrix is again the sum of these individual energy matrices. The perturbation contributions are now additive in the operators associated with the ligator symmetry orbitals. Each of the individual energy matrices again consists of a matrix of angular elements (this time embodying squared group angular overlap integrals and their cross products) multiplied by the same radial energy parameter $e_{\pi\perp}$ for both individual matrices as for the individual matrices of eq 2. The results are given in eq 4 in units of $e_{\pi\perp}$. The individual

$$\begin{array}{c|cc} \hat{A}(O_\psi) & (yz) & (xy) \\ (yz) & 2\cos^2(\beta/2) & 0 \\ (xy) & 0 & 0 \end{array} \; + \; \begin{array}{c|cc} \hat{A}(O_\chi) & (yz) & (xy) \\ (yz) & 0 & 0 \\ (xy) & 0 & 2\sin^2(\beta/2) \end{array} \; =$$

$$\begin{array}{c|cc} \hat{A}(O_\psi) + \hat{A}(O_\chi) & (yz) & (xy) \\ (yz) & 2\cos^2(\beta/2) & 0 \\ (xy) & 0 & 2\sin^2(\beta/2) \end{array} \qquad (4)$$

operators $\hat{A}(O_\psi)$ and $\hat{A}(O_\chi)$ build the bridge toward the LCAO–MO model for central ion to ligand bonding. For example, $O_\psi$

of eq 3 is the ligator symmetry orbital that represents half of the $p\pi\perp$ orbitals of the two ligators. This means that the ligators are now conceived at one time together. However, they still perturb the central ion d orbitals independently. One may express this by saying that their perturbations are noncorrelated or noncoupled. These terms will be useful to refer back to when bidentate ligands with ligator–ligator interactions are considered in section III. $O_\psi$ is symmetry-compatible with the central ion orbital $(yz)$ with which it makes a bonding and an antibonding linear combination. The first matrix on the left-hand side of eq 4 expresses the associated antibonding energy.

In addition to this bridging to the LCAO–MO model, the information of the matrices of eq 4 may be put into words as follows: when the $\pi\perp$ perturbation from two ligators is analyzed into a $\psi$ part and a $\chi$ part, the total perturbation contains the fraction $\cos^2(\beta/2)$ of $\psi$ character and $\sin^2(\beta/2)$ of $\chi$ character.

The equality of the formulations of eqs 2 and 4 is an example of a quite general result, which has been proved in different contexts[18–20] for the conventional AOM.

It is seen that there are two equivalent main formulations of conventional AOM, one (section IIB) using the ligator orbitals directly and one using them indirectly by first forming in-phase and out-of-phase linear combinations of them. This has not been realized by CDV when they state[1] that phase relationships are as a matter of principle ignored in the AOM. [The situation is similar with Gerloch, Woolley and co-workers,[4–6] who in their cellular ligand-field model use our formulation based upon individual ligator orbitals (section IIB) but as a matter of principle reject the molecular orbital oriented formulation (section IIC).] The final results of eqs 2 and 4 involve two parameters, the valence angle $\beta$, which is of geometrical character, and the radial energy-parameter $e_{\pi\perp}$ of the AOM.

In conclusion, the additive character of the conventional AOM energy operator $\hat{A}$ of our present example may be expressed either through eq 5a or eq 5b as

$$\hat{A}(\pi\perp) = \hat{A}(O_1) + \hat{A}(O_2) \tag{5a}$$

$$\hat{A}(\pi\perp) = \hat{A}(O_\psi) + \hat{A}(O_\chi) \tag{5b}$$

by using either the direct (diatomic overlap) formulation (eq 5a) of subsection B or the indirect (group overlap) formulation (eq 5b) of this subsection.

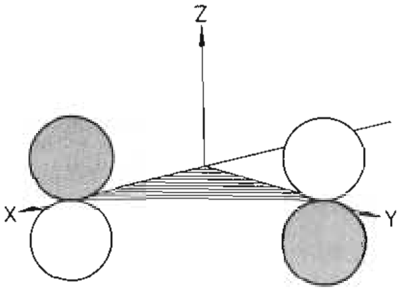
**D. Comparison between the Angular Factors of the Energy Operator. Discussion of the CDV Statements about the AOM.** In our example of a ligand system consisting of two coplanar water molecules, connected by a 2-fold axis, the symmetry is $C_{2v}$. This symmetry remains when the central atom is included. From a symmetry point of view, our system of metal and ligands is identical with a system containing a metal ion and one symmetrical, planar, bidentate ligand so that the $p\pi\perp$ orbitals of our oxygen ligators exactly correspond to the $p\pi\perp$ orbitals of the ligating atoms of a symmetrical, conjugated bidentate moiety. In fact our present example is from an AOM point of view *identical* with the model of the planar bidentate ligand used by CDV. This statement may be expressed formally by eq 6, where the left-hand

$$\hat{A}_{\text{ang}}(O_\psi) = \hat{A}^{\text{L}}_{\text{ang}}(\psi)$$

$$\hat{A}_{\text{ang}}(O_\chi) = \hat{A}^{\text{L}}_{\text{ang}}(\chi) \tag{6}$$

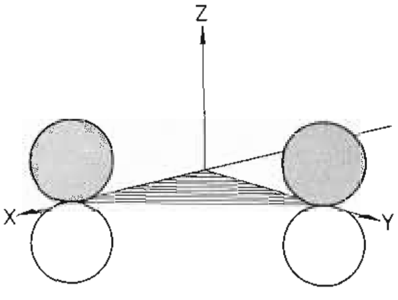
sides are the angular factors of the ligand-field operator for the two water molecules of subsection C and the right-hand sides are the corresponding expressions for a symmetrical, conjugated bidentate ligand with ligators L. The angular factors are the theoretical factors that are in fact symmetry-determined ($\psi$, $\chi$) and geometry-determined ($\beta$) (cf. eq 4).

In their introductory remarks to their work,[1] CDV apply the AOM by using the diatomic-overlap formulation as in our subsection B. They place their ligators on the positive $X$ and $Y$ axes so that their valence angle $\beta$ is equal to 90°. If we place the oxygen ligators of our $H_2O$ molecules in the same way (**3a,b**), our results



3a

$\chi$ symmetry



3b

$\psi$ symmetry

for the $\pi\perp$ perturbation are, in the diatomic-overlap formulation, given in eq 7 where the unit of energy is again the radial parameter $e_{\pi\perp}$.

$$\begin{array}{ccc} \hat{A}(O_1) & (zx) & (yz) \\ (zx) & 1 & 0 \\ (yz) & 0 & 0 \end{array} + \begin{array}{ccc} \hat{A}(O_2) & (zx) & (yz) \\ (zx) & 0 & 0 \\ (yz) & 0 & 1 \end{array} = \begin{array}{ccc} \hat{A}(O_1) + \hat{A}(O_2) & (zx) & (yz) \\ (zx) & 1 & 0 \\ (yz) & 0 & 1 \end{array} \tag{7}$$

Comparing our result of eq 7 with that of CDV (the relevant part of their eq 1), we observe that the angular factors are identical and this is true for the results altogether except that we denote our radial parameter $e_{\pi\perp}$ as is usual in the AOM while CDV call their parameter $\pi_\perp$. So we conclude that our $e_{\pi\perp}$ is identical with their $\pi_\perp$.

We now apply the group-overlap formulation using the setup of 3. Our results are given in eq 8, again in units of $e_{\pi\perp}$. In

$$\begin{array}{ccc} \hat{A}(O_\psi) & (zx) & (yz) \\ (zx) & 1/2 & 1/2 \\ (yz) & 1/2 & 1/2 \end{array} + \begin{array}{ccc} \hat{A}(O_\chi) & (zx) & (yz) \\ (zx) & 1/2 & -1/2 \\ (yz) & -1/2 & 1/2 \end{array} = \begin{array}{ccc} \hat{A}(O_\psi) + \hat{A}(O_\chi) & (zx) & (yz) \\ (zx) & 1 & 0 \\ (yz) & 0 & 1 \end{array} \tag{8}$$

agreement with the conclusion of the preceding subsection (expressed by eq 5a,b) the two different formulations, eqs 7 and 8, provide identical angular matrices (the right-hand sides of eqs 7 and 8).

If the two terms on the left-hand side of eq 8 are compared with eqs 3a and 4 of CDV, respectively, it is immediate that the angular factors of CDV are twice as large as ours. This observation may be expressed by eq 9, where $\mathcal{V}(\psi)$ and $\mathcal{V}(\chi)$ are the

$$\mathcal{V}_{\text{ang}}(\psi) = 2\hat{A}_{\text{ang}}(\psi)$$

$$\mathcal{V}_{\text{ang}}(\chi) = 2\hat{A}_{\text{ang}}(\chi) \tag{9}$$

CDV expressions for the $\psi$ and $\chi$ operator terms when the radial parameters are included.

Since CDV's eq 1 agrees with the AOM while CDV's eqs 3a and 4 do not and since the basis of the statements made by CDV about the AOM is a comparison of their three equations, (1), (3a), and (4), all the CDV statements about the AOM should be examined most carefully. We shall return to a further comparison with CDV in section IIIE.

In section IVB, we shall refer back to eq 8, which represents the situation of 3. If $O_1$ is left on the positive $X$ axis but $O_2$ is moved to the negative $Y$ axis, then the only consequence is that the coefficient matrices on the left-hand side of eq 8 become permuted.

## III. An Example of a Symmetrical, Conjugated Bidentate as a Central-Ion Perturber

**A. The Ligand Ready for Chelation. Ligand $\psi$ and $\chi$ Orbitals.** The following discussion will reveal that, for the understanding of the fundamental concepts, it is useful to think about an example of a symmetrical, conjugated bidentate moiety before it is actually coordinated. We discuss in detail the CDV example of the diimine *N,N'*-dimethylglyoxaldiimine (see 4) and add some brief comments on the acetylacetonate ion. The following symmetry characterization is common to all symmetrical, conjugated bidentate moieties.

The set of $p\pi\perp$ orbitals of the ligand-backbone atoms in the planar conformation (where the ligand is ready for chelation) span a reducible representation of the point group $C_{2v}$ of the system which invariably contains irreducible species of only $b_2$ and $a_2$ types. These irreducible types are called for short $\psi$ and $\chi$, respectively (cf. eq 3 and 2).

We here add subindex numbers on the linear combinations of atomic $p\pi\perp$ backbone orbitals of $\psi$ and $\chi$ types so that the subindices equal the number of nodal planes perpendicular to the backbone. We note that the number of nodes of this type is even for $\psi$ orbitals and odd for $\chi$ orbitals. Within a given ligand the orbital energies are expected to increase with the number of nodes.

A simple notation is obtained by first pairing the symmetry related atomic $p\pi\perp$ orbitals. With an obvious notation exemplified by the diimine orbitals (4), we obtain

$$\psi^{N} = (N_1 + N_2)/2^{1/2}$$

$$\psi^{C} = (C_1 + C_2)/2^{1/2}$$

$$\chi^{N} = (N_1 - N_2)/2^{1/2}$$

$$\chi^{C} = (C_1 - C_2)/2^{1/2} \qquad (10)$$

In terms of these symmetry orbitals, the ligand eigenorbitals can quite generally be written as in eq 11 within the $\pi$-only LCAO model (leaving out the renormalization factors, which arise from the overlap of the atomic orbitals). 4 gives an illustration of these orbitals when $u$ and $v$ are both in the interval $[0; (\pi/2)]$.

$$\chi_3 = \chi^{N} \sin u - \chi^{C} \cos u$$

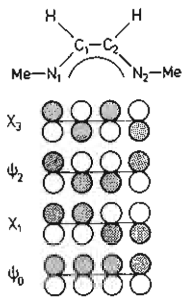
$$\psi_2 = \psi^{N} \sin v - \psi^{C} \cos v$$

$$\chi_1 = \chi^{N} \cos u + \chi^{C} \sin u$$

$$\psi_0 = \psi^{N} \cos v + \psi^{C} \sin v \qquad (11)$$

The diimine is in the $\pi$-only model a four-electron–four-orbital ligand, and if the energies increase with the number of nodes, $\chi_1$ of 4 is therefore its HOMO and $\psi_2$ its LUMO so that the diimine may be classified as a $\chi$(HOMO)$\psi$(LUMO) ligand.

The discussion of the four-electron–four-orbital ligand can be generalized to other cases. For example, acetylacetonate, or a $\beta$-diketonate in general, has a six-electron–five-orbital conjugated system, which by symmetry contains three $\psi$-type and two $\chi$-type orbitals. Under the assumption that the energy increases with the number of nodes, $\psi_2$ is the HOMO and $\chi_3$ is the LUMO, so that the $\beta$-diketonate may be classified as a $\psi$(HOMO)$\chi$(LUMO) ligand.



4

**B. Interaction between Central Ion d Orbitals and Ligand $\psi$ and $\chi$ Orbitals. Adaptation of the Angular Overlap Model.** We now apply the AOM using the group-overlap formulation of section IIC. In the present case, the number of ligand orbitals that may interact with the central ion orbitals exceeds the number of ligators. This is a *new feature* that we have to *accommodate* into the AOM. For the diimine case there is a set of four orbitals (eq 11 and 4) to consider, two of which replace the interaction from $O_\psi$ and two others which replace that from $O_\chi$ of section IIC (cf. also eq 6).

It is instructive to begin this discussion under the unrealistic restriction that the ligand orbitals all have the same energies. In this event, the energetic effect upon a metal d orbital arising from the interaction with each of the ligand orbitals will be proportional to the square of its group angular overlap integral with the same constant of proportionality. Let us use the coordinate system of 2 and exemplify the situation by considering the interaction energy between the central ion orbital $(yz)$ and the ligand orbital $\psi_2$ of 4. One only has to consider the overlap between $(yz)$ and the ligator orbitals contained in $\psi_2$. Using eq 11, one has

$$\langle (yz)|\psi_2\rangle = \langle (yz)|\psi^{N} \sin v\rangle = \langle (yz)|\psi^{N}\rangle \sin v \qquad (12)$$

This means that the overlap $\langle (yz)|\psi_2\rangle$ obtains an *extra*-AOM factor of $\sin v$ and the squared overlap accordingly a factor of $\sin^2 v$, but otherwise the situation is the same as in the first matrix of eq 4; i.e., the interaction energy is $2 \cos^2 (\beta/2) \sin^2 v\, e_{\pi\perp}$. $\psi_0$ behaves analogously, except that its *extra*-AOM factor is $\cos v$ in overlap and $\cos^2 v$ in interaction energy. Each one of these squared factors represents in this restricted model a fraction of the total $\psi$ perturbation.

The analysis of the $\chi$ perturbation is analogous, $\chi_1$ contributing the fraction $\cos^2 u$ and $\chi_3$ the fraction $\sin^2 u$ to the total $\chi$ perturbation. In this unrealistically restricted model, which is a model of a nonconjugated yet planar bidentate ligand, the same radial parameter applies to all four perturbations, two of $\psi$ type and two of $\chi$ type (4).

In conclusion, in the particular example, *N,N'*-dimethylglyoxaldiimine has two orbitals within each of the classes $\psi$ and $\chi$, where the important point is that the members within each orbital class have the same symmetry. According to the AOM additivity principle (square and add), the different orbitals, for example, $\psi_0$ and $\psi_2$ of 4, give perturbation energy contributions proportional to their percentage content of $\psi^{N}$ and likewise $\chi_1$ and $\chi_3$ give contributions proportional to their percentage content of $\chi^{N}$, where $\psi^{N}$ and $\chi^{N}$ are defined in eq 10.

We now remove the restrictive assumption that the ligand orbitals all have the same energy; i.e., we allow for conjugation or other kinds of ligator–ligator interactions.[10] This has no symmetry consequences and therefore—as we shall see—for our discussion of the semiempirical model no consequences at all. However, conceptually, different radial parameters now have to be used for different ligand group orbitals. Reconsidering the interaction between $(yz)$ and the $\psi$ orbitals, we may now combine the trigonometric, *always positive*, squared *extra*-AOM factors, discussed just above, with the radial factors $e(\psi_2)$ and $e(\psi_0)$, which now are different. The AOM factor $2 \cos^2 (\beta/2)$ will still be common to $\psi_2$ and $\psi_0$, and we may for the diimine rewrite eq 12 as

$$\begin{aligned}\langle (yz)|\hat{A}(\psi)|(yz)\rangle &= 2\cos^2(\beta/2)\,(\sin^2 v\; e(\psi_2) + \cos^2 v\; e(\psi_0)) \\ &= 2\cos^2(\beta/2)\; e_{\psi L} = e_{\psi LL}\end{aligned} \tag{13}$$

In this equation and in the following we have replaced N by L in order to emphasize the generality. With reference to the discussion immediately after eq 11, $e(\psi_2) < 0$ and $e(\psi_0) > 0$. Analogously, we obtain

$$\begin{aligned}\langle (xy)|\hat{A}(\chi)|(xy)\rangle &= 2\sin^2(\beta/2)\,(\sin^2 u\; e(\chi_3) + \cos^2 u\; e(\chi_1)) \\ &= 2\sin^2(\beta/2)\; e_{\chi L} = e_{\chi LL}\end{aligned} \tag{14}$$

where $e(\chi_3) < 0$ and $e(\chi_1) > 0$.

The results of eqs 13 and 14 are the final results of our adaptation of the AOM to treat a symmetrical, conjugated bidentate LL as a ligand. The results are formally identical with those for the two water molecules of eq 4, apart from the fact that the perturbations of $\psi$ and $\chi$ types have their *own radial parameters* $e_{\psi L}$ and $e_{\chi L}$ in eqs 13 and 14 whereas in eq 4 they have the same radial parameter $e_{\pi\perp}$. The ligator radial parameter $e_{\pi\perp}$ of the $M(OH_2)_2$ case is, in the AOM, associated with the *preponderantly atomic* orbital $p_y$ of the ligator O as discussed in section IIC, and we therefore call it an *atomic radial parameter*. As opposed to this situation, each of the ligator parameters $e_{\psi L}$ and $e_{\chi L}$ is associated with molecular orbitals, and we therefore call these parameters *molecular radial parameters* even though they are indexed by the ligating atoms. Moreover, the parameters $e_{\psi L}$ and $e_{\chi L}$ are accumulative in being associated with several molecular orbitals of the ligand. If the $\pi$-delocalization and other ligator–ligator interactions could be gradually made to vanish, then the molecular radial parameters $e_{\psi L}$ and $e_{\chi L}$ would, independently of their original signs, converge toward having the same sign and magnitude and thereby become the atomic radial parameters $e_{\pi\perp}$ of the conventional AOM.[13]

Equations 13 and 14 define not only the radial parameters $e_{\psi L}$ and $e_{\chi L}$ of what we would like to call our *ligator* parametrization scheme but also the two additional radial parameters $e_{\psi LL}$ and $e_{\chi LL}$ of our *ligand* parametrization scheme. These parameters are purely symmetry-based and, of course, also molecular in character. In addition, they have the property of individually referring to the whole ligand in the special sense that the trace of the angular factor of the energy operator representing a whole bidentate ligand over d space is unity for both of them. The concepts of *ligator* and *ligand* parametrization schemes are based upon the origin of the coefficients to the associated parameters, which make up the theoretical part of the semiempirical AOM. $e_{\psi L}$ and $e_{\chi L}$ of the ligator scheme have coefficients that are based upon group angular overlap integrals, which are linear combinations of *ligator* angular overlap integrals. As will be further discussed in the following sections (see, for example, Figure 1) $e_{\psi LL}$ and $e_{\chi LL}$, conversely, have coefficients that are based upon diatomic angular overlap integrals of a non linearly ligating, unidentate ligand whose perturbation within the model is identical with that of the whole bidentate ligand. These coefficients will turn out to depend on the position and rotational orientation of the bidentate moiety but not on the positions of its ligators. In a semiempirical use of the AOM, $e_{\psi LL}$ and $e_{\chi LL}$ are the most relevant $\pi\perp$ radial parameters, as discussed in subsection D.

The AOM formalism leads to the result that the perturbation associated with all ligand eigenorbitals in which the ligator orbitals are *in phase* must be described by one accumulative parameter $e_{\psi L}$ (or $e_{\psi LL}$) and the perturbation associated with eigenorbitals in which the ligator orbitals are *out of phase* by another parameter $e_{\chi L}$ (or $e_{\chi LL}$). This fact suggests retaining the CDV model wording of *phase coupling* of *ligators* in order to express the consequence of conjugation or other ligator–ligator interactions on the AOM ligand-field description. This concept of phase coupling was also adopted by Atanasov, Schönherr, and Schmidtke.[15-17]

**C. Interpretation of the Radial Parameters in the Molecular-Orbital-Oriented Version of the Angular Overlap Model.** The discussion of the preceding subsection revealed that the usual molecular-orbital orientation of the AOM, illustrated in section IIC as the group-overlap formulation, could be extended quite naturally to apply also to symmetrical, conjugated bidentate ligands. The number of perturbing orbitals increases from two, which is the number of ligators, up to the number of atomic $p\pi\perp$ orbitals of the ligand, but the effective AOM perturbation falls invariably into only two symmetry types $\psi$ and $\chi$ (eq 3). It is the total perturbation within each symmetry type that counts in an AOM sense. Now, the angular factors of the AOM, i.e. the coefficient matrices, whose elements consist of squares and cross-products of group angular overlap integrals, are the same for all contributions within each symmetry type, but different for the two symmetry types. These coefficient matrices are those of the conventional AOM, provided that this is expressed by using the group overlap formalism (section IIC, eq 4).

We now discuss by way of examples the expected signs of the radial parameters associated with the individual orbitals of the conjugated ligands and include qualitative remarks about their expected relative magnitudes.

In the diimine case (eq 11 and 4), we expect the two occupied orbitals $\psi_0$ and $\chi_1$ to be lower in energy than the central ion d orbitals while the empty orbitals $\psi_2$ and $\chi_3$ have higher energies. Under this assumption the radial parameters $e(\psi_0)$ and $e(\chi_1)$ are positive while $e(\psi_2)$ and $e(\chi_3)$ are negative. Since $\chi_1$ is the HOMO and $\psi_2$ the LUMO, the radial parameters associated with these two orbitals are expected to dominate the issue so that the diimine—in a net energetic sense within each of the two symmetry classes $\psi$ and $\chi$—becomes a $\chi$ donor and a $\psi$ acceptor.

In a $\pi$-only LCAO–MO model of a conjugated bidentate ligand, situations with an even and an odd number $n$ of atomic $\pi\perp$ orbitals often differ energetically in an essential way. It is instructive to compare two systems of this kind for which $n = 2m$ and $2m + 1$ and the number of electrons is $2m$ and $2m + 2$, respectively. The diimine and the $\beta$-diketonate, respectively, exemplify the two possibilities for $m = 2$. In the diimine case, two orbitals are stabilized to accommodate the four electrons and two orbitals are destabilized. In the $\beta$-diketonate case, there are also two orbitals that are stabilized to accommodate four electrons and two empty orbitals of higher energy. However, in this case, we are still left with one orbital to accommodate two electrons. This orbital is nearly nonbonding and this is what makes the essential difference, because this filled orbital may come close to the central ion d orbitals in energy. Even though this model is crude, it may still qualitatively account for the empirical indication that the $\beta$-diketonate is a net $\pi$ donor (the nonbonding orbital $\psi_2$ is slightly lower in energy than the d orbitals, while $\chi_3$ is much higher in energy than the d orbitals because of its conjugation destabilization). On the other hand, the diimine could from this point of view be either a net $\pi$ donor or a net $\pi$ acceptor (see the next paragraph though).

It will be interesting to see to what extent these predictions of the present model will be borne out by experiment in the future. Here, we only point to the fact that the ligand cyanide has an unusually high value of $\Delta = \Delta_\sigma - \Delta_\pi$ in octahedral $d^6$ systems.[23] A possible explanation for this is that the $\Delta_\pi$ parameter for $CN^-$ is negative in spite of the fact that other evidence would classify $CN^-$ as only a weak $\pi$-acid. If this explanation of the high $\Delta$ value for $CN^-$ nevertheless is right, then $CN^-$ may exhibit an illustration of a large energetic effect upon central atom d orbitals caused by even a weak $\pi$-acceptor interaction. This could well be a general phenomenon that would turn up also in the case of conjugated bidentates and perhaps cause the diimine ligands to become net $\pi$ acids in this particular energetic sense (though not necessarily also in a net electron population sense). In this connection, we would like to point out also that the unidentate non linearly ligating ligand pyridine has been found[24] to have an $e_{\pi\perp}$ parameter which is slightly negative when the central ion is chromium(III). This result has given rise to some discussion.[25,26]

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(23) Josephsen, J.; Schäffer, C. E. *Acta Chem. Scand.* **1977**, *A31*, 813–824.

(24) Glerup, J.; Mønsted, O.; Schäffer, C. E. *Inorg. Chem.* **1976**, *15*, 1399–1407.

(25) Smith, D. W. *Inorg. Chem.* **1978**, *17*, 3153–3156.

**D. Use of a Semiempirical Angular Overlap Model To Represent the Ligand Field of a Conjugated Bidentate Ligand.** In the preceding subsection, the interpretation of the individual parameters of the ligator parametrization scheme of eqs 13 and 14 was discussed qualitatively by using the molecular orbital orientation of the AOM, referring to the parameters $e_{\psi L}$ and $e_{\chi L}$. In the most common application of the AOM, however, the model is used quantitatively as a semiempirical model, i.e. by taking its coefficient matrices as the theoretical part of the model and using its radial parameters to express its empirical part.[27]

The AOM operator, representing a symmetrical, conjugated bidentate moiety, is given by replacing $\hat{A}(O_\psi)$ and $\hat{A}(O_\chi)$ in eqs 4 and 5b by $\hat{A}(\psi)$ and $\hat{A}(\chi)$ of eqs 12 and 13 (see also eq 6). Comparison of these two terms with the two terms on the left-hand side of eq 4 reveals that they are formally identical apart from the fact that eqs 13 and 14 contain the two *different* radial parameters, $e_{\psi L}$ and $e_{\chi L}$. The geometrical prerequisite for the use of the parameters $e_{\psi L}$ and $e_{\chi L}$ is the polar coordinates of the two ligators. These coordinates, of course, imply the bite angle $\beta$. When the bidentate moiety is in a general position relative to the coordinate frame defining the d basis, the sum rule for the coefficients to each of the parameters $e_{\psi L}$ and $e_{\chi L}$ is that the coefficient sum is $2\cos^2(\beta/2)$ for $e_{\psi L}$ and $2\sin^2(\beta/2)$ for $e_{\chi L}$ so that the sum of the coefficients to the parameters describing the total $\pi\perp$ perturbation from the bidentate LL is 2, i.e. equal to the number of ligators of this bidentate.

The interpretation of eqs 13 and 14 in terms of the ligand parametrization scheme has special importance for the use of the model semiempirically since the model in this scheme requires one fewer geometrical parameters (the three Euler angles of the $C_2$ axis of the bidentate moiety as compared with the four polar coordinates or its two ligators) and still only two radial parameters ($e_{\psi LL}$ and $e_{\chi LL}$). The reason is that in this scheme the knowledge of the bite angle $\beta$ is no longer a geometrical requirement. [The discussion about whether or not the bite angle $\beta$ is an AOM prerequisite is somewhat academic. It is certainly true that knowledge of $\beta$ is unnecessary for setting up the energy matrix in the radial parameters $e_{\psi LL}$ and $e_{\chi LL}$. However, in the practical use of the AOM, it will be necessary to account for $\hat{A}(\sigma)$ in the first place; then the coordinates of the ligators are necessary.]

In order to calculate the AOM angular factors of the parameters $e_{\psi LL}$ and $e_{\chi LL}$ for a bidentate ligand LL, in a general position, the angular coordinates of the $C_2$ axis of the ligand and the orientation of the ligand about this axis make up the geometrical knowledge required. This is the same as knowing the Euler angles[18] of the $C_2$ axis. If the planar ligand is placed in the $ZX$ plane with its $C_2$ axis coinciding with the $Z$ axis of the Cartesian coordinate system according to which the d basis is defined, then its $\psi$ orbitals only overlap with the d$\pi$s (=$(yz)$) orbital, while its $\chi$ orbitals only overlap with the d$\delta$s (=$(xy)$) orbital. Thus a $\psi$ orbital of the bidentate behaves as a particular one of the $\pi$ orbitals of a non linearly ligating ligand, while a $\chi$ orbital behaves as a particular $\delta$ orbital.

The symmetries of the perturbing and the perturbed orbitals may be seen in Figure 1, where the molecular character of the perturbing orbitals is also illustrated.

Although in a semiempirical model, one is bound to accept the parameter values determined from experimental data, it is still allowed, and hopefully chemically useful, to ponder about the values of such parameters both before and after they have been obtained from the data reduction of the experimental results. For a general symmetrical bidentate LL, we would like to comment on the magnitudes and signs of the radial parameters. First, since the radial parameters $e_{\psi LL}$ and $e_{\chi LL}$ are molecular, it is not correct to make the usual and probably usually justified conclusion for atomic parameters that $|e_\pi| > |e_\delta|$. The signs may also vary for $e_{\psi LL}$ and $e_{\chi LL}$ types of parameters and an individual sign may be changed by varying only the central ion, for example from a reducing one to an oxidizing one as in the case of the two d$^6$ systems manganese(I) and cobalt(III). Second, $e_{\psi LL}$ and $e_{\chi LL}$ need not resemble the $e_{\pi\perp}$ values found for the ligating atoms L in other chemical surroundings. For a series of ligands, all containing nitrogen ligators, it is likely that both positive and negative values of $e_{\psi NN}$ and $e_{\chi NN}$ type parameters will be found to occur.

Unfortunately, it is rather much to have to determine two empirical $\pi\perp$ parameters for one bidentate ligand, whose contributions to the ligand field are already dominated by a large value for its $\sigma$ parameter. There is, however, no way out of this dilemma, which is a common one when ligand-field theory is applied to interpret experiments on low-symmetry systems. There is a special feature here: when the parameters $e_{\psi LL}$ and $e_{\chi LL}$ have been obtained from experiment, $e_{\psi L}$ and $e_{\chi L}$ will not immediately be known. However, if the additional geometrical knowledge of the bite angle $\beta$ is available, eqs 13 and 14 allow the determination of $e_{\psi L}$ and $e_{\chi L}$. In the special case where $\beta = 90°$ we have the following two identities.

$$e_{\psi LL} = e_{\psi L} \qquad e_{\chi LL} = e_{\chi L} \quad \text{for } \beta = 90° \tag{15}$$

For the parameters $e_{\psi LL}$ and $e_{\chi LL}$ the sum rules of the conventional AOM apply, when it is remembered that a bidentate ligand behaves as *one* non linearly ligating ligator. Thus, for example, the sum of the coefficients to $e_{\chi LL}$ over the five d orbital energies is equal to the number of bidentate LL moieties present in the coordination sphere rather than the number of ligators.

We now discuss the case of a planar, bidentate ligand without ligator–ligator interactions using eqs 13 and 14. This case includes, of course, the planar bidentate ligand without conjugation. In this case, $e_{\psi LL}$ and $e_{\chi LL}$ could in principle be determined experimentally from spectral data, where they invariably should be found to have the same sign and to obey eq 16, as derived from

$$\tan^2(\beta/2) = e_{\chi LL}/e_{\psi LL} \quad e_{\psi L} = e_{\chi L} \tag{16}$$

combining eqs 13 and 14 under the condition $e_{\psi L} = e_{\chi L}$. From eq 16, the bite angle $\beta$ might be determined from spectral data by using the AOM. However, the most characteristic feature here is the condition itself, which allows $e_{\psi L}$ and $e_{\chi L}$ to be denoted by the common symbol $e_{\pi\perp L}$ as in the conventional[13] AOM. For independently perturbing ligators we therefore have the equalities

$$e_{\psi L} = e_{\chi L} = e_{\pi\perp L} = (e_{\psi LL} + e_{\chi LL})/2 \tag{17}$$

where the last one was derived by addition of eqs 13 and 14. For the special case of $\beta = 90°$, one has for the ligand without ligator–ligator interactions the combined results of eqs 15 and 17:

$$e_{\pi\perp L} = e_{\psi LL} = e_{\chi LL} = e_{\psi L} = e_{\chi L} \quad \text{for } \beta = 90° \tag{18}$$

In section IV examples will be given to illustrate the additivity of perturbations when more bidentate moieties are present in a coordination sphere and to exemplify the AOM calculational approaches to conjugated, bidentate ligands when the two different formulations of eqs 13 and 14 are used.

**E. A Second Comparison between Our Approach and That of Ceulemans, Dendooven, and Vanquickenborne.** In the previous subsections the AOM was adapted to discuss the problem of a ligand-field representation of the interaction between a metal ion and a symmetrical, conjugated bidentate ligand. The result was that the formulation of the AOM of eq 5a, based upon independent, individual ligators, no longer applies and in this point we agree with the conclusion of the CDV paper.[1] We also agree with Orgel[11,12] and CDV[1,2] that subdivision of ligand orbitals into a $\psi$ type and a $\chi$ type (cf. eq 3) is now the important issue, but while we use this classification to introduce the concepts of $\psi$ and $\chi$ perturbations through the use of the AOM, CDV[1,2] consider the classification alien to the AOM (cf. section IIC). Ceulemans, and Vanquickenborne in ref 9 do not seem to retain this view, however.

In formulating the basis of their model, CDV assume that a ligand can be considered as *either* of $\psi$ type *or* of $\chi$ type depending on the symmetry of a particular one of its frontier orbitals. Once this either/or idea has been introduced, CDV make the assumption

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(26) Glerup, J.; Mønsted, O.; Schäffer, C. E. *Inorg. Chem.* **1980**, *19*, 2855–2857.

(27) Schäffer, C. E. *Struct. Bonding (Berlin)* **1973**, *14*, 69–110.

that the trace of the $\pi\perp$ perturbation energy matrix, corresponding to one bidentate ligand (i.e. two ligators) and being set up in a d basis, is equal to $2\pi_\perp$ where $\pi_\perp$ is their notation for the usual AOM radial parameter $e_{\pi\perp}$ referring to one ligator. This means that the angular factor of their $\pi\perp$ perturbation operator has a trace of 2, and this is plausible because it means on their premises that one bidentate perturbs as much as two ligators. However, this is still where the CDV treatment is at variance with the AOM because of the above-mentioned either/or situation (see also the discussion in section IID and eq 9). While in the CDV model the ligands are *either* $\psi$ type *or* $\chi$ type perturbers so that one bidentate ligand gives only one of these contributions, in our model they are fundamentally *both* $\psi$ *and* $\chi$ perturbers so that one bidentate moiety must give both a $\psi$ and a $\chi$ contribution (even though one of these contributions might incidentally turn out to be small). [This is the situation that is advocated by Schönherr, Atanasov, and Schmidtke[16] in connection with their analysis of tris(acetylacetonate) complexes. For these systems they put $e_\chi$ (their $e'_{\pi s}$) equal to zero (see our discussion in section IIIC). In this connection we want to make two points, both regarding the concept of a non-additive ligand field: (1) Atanasov et al. characterize their phase-coupling formalism, which is equivalent to our formalism (cf. Section IIIB), as their nonadditive model, thereby taking over this term from CDV. The term is only valid as far as individual ligator perturbation contributions are concerned. However, the $\pi$ conjugation imaged by the phase-coupling prevents these individual contributions from being identifiable and thereby additive. (2) The use of the concept nonadditive is moreover unfortunate because the concept of nonadditive ligand fields[28,29] already has been used in the literature as referring to the situation in which the total ligand field of a chemical species is parametrized by using parameters based alone upon the symmetry of this species.] Therefore the $\pi\perp$ perturbation operator of our bidentate (given by eqs 5b and 6) has angular factors whose traces add up to 2.

Moreover, while the radial parameters in the CDV model[1,2,9] have a character that we call preponderantly atomic, which means related to the properties of the ligating atom, just as in the conventional AOM, those in our model are molecular in character. It is important in this connection to note that this molecular characterization applies independent of whether the radial parameters are of the ligand parametrization scheme (e.g. $e_{\psi LL}$) or of the ligator scheme type (e.g. $e_{\psi L}$). The values of our parameters are expected to depend on the *whole ligand backbone* including the *ligators* and on the *central ion*. This is evident from the way they were derived (subsection B).

With regard to the semiempirical application of the CDV model and our model, a further important difference appears. While in the CDV model each symmetrical bidentate moiety has one $\pi\perp$ parameter either of $e_{\psi N}$ type or of $e_{\chi N}$ type, in our model such a perturber has to have two $\pi\perp$ parameters, $e_{\psi N}$ and $e_{\chi N}$, which have to be considered as independent empirical parameters.

In illustrating their model by applying it to various ligand systems, CDV later in their paper[1] gave a discussion that we have appreciated, and our previous discussion of the present section is indebted to them. At this stage of the CDV paper,[1] the ligands appear, however, no longer to be *either* $\psi$ *or* $\chi$ perturbers, but rather to be *both* $\psi$ *and* $\chi$ perturbers, which is just the way we find it necessary to conceive them. Thereby, this conceptual discrepancy between CDV and us vanishes even though the associated, numerical discrepancy[1,2] consisting of the factor of 2 in the formalisms remains (cf. eq 9).

Because of this discrepancy in the formalisms, the two modifications of the AOM, that of CDV and ours, give completely different comparisons with the conventional AOM. CDV are able to write

$$\mathcal{V}^{\mathrm{AOM}} = (\mathcal{V}(\psi) + \mathcal{V}(\chi))/2 \tag{19}$$

so that $\mathcal{V}^{\mathrm{AOM}}$ is the arithmetic mean of their $\psi$ and $\chi$ perturbation operators. However, the condition for eq 19 (i.e. eq 5 of CDV[1] compared with our eqs 6 and 5b, where $\hat{A}(\pi\perp)$ is our $\hat{A}^{\mathrm{AOM}}$) is that the radial ligator parameter of the AOM is also the parameter of both $\mathcal{V}(\psi)$ and $\mathcal{V}(\chi)$. CDV put emphasis on the consequence of eq 19 that the factor of $^1/_2$ breaks down the additivity of AOM and makes it necessary to introduce an *extra*-AOM term, a so-called phase-coupling term, denoted by $\mathcal{V}^{\mathrm{cping}}$, which does not appear in our formalism.

In conclusion, the CDV[1,2] model for symmetrical bidentate moieties is in itself, i.e., without regard to its relationship with the AOM, mathematically equivalent to our model, provided independent radial parameters are used for $\mathcal{V}(\psi)$ and $\mathcal{V}(\chi)$. However, the relationship between the CDV model and the AOM is unnecessarily complicated, and moreover, since the CDV model was presented as a modification of the AOM that had to be drastic, we have found it useful to pinpoint the lack of logic in the way the CDV modification of the AOM was made and at the same time, more constructively, show how simply the AOM can be adapted to become a consistent model for the $\pi\perp$ perturbation of general, planar symmetrical bidentate moieties. As a final remark here, we need to mention that the discrepancy of the factor of 2, mentioned above, has been removed in ref 9.

In the next subsection, we shall discuss the formal relationship between our model for $\pi$-conjugated systems and the conventional AOM. In this discussion the question about additivity within the AOM will also be answered.

**F. The Angular Overlap Model for a Symmetrical, Bidentate Ligand with Ligator–Ligator Interactions.** It is *not* possible to give an explicit relationship between the conventional AOM operator for the present systems and the operator developed in this paper.

The reason for this impossibility is that the conventional AOM involves only one $\pi\perp$ parameter while our present model involves two radial parameters. However, since the theory part of the semiempirical AOM is concerned with coefficients to the parameters rather than the parameters themselves, it is possible to write for a symmetrical, bidentate ligand

$$\hat{A}^{\mathrm{AOM}}_{\mathrm{ang}}(\pi\perp) = \hat{A}^{\mathrm{L}}_{\mathrm{ang}}(\psi) + \hat{A}^{\mathrm{L}}_{\mathrm{ang}}(\chi) \tag{20}$$

and refer to eqs 4 and 6, as well as to the angular parts of eqs 13 and 14. The use of the subindex ang on all the perturbation operators corresponds to its use in eq 1 and means that we are concerned *only* with the angular factor in the operators. Equation 20 needs to be qualified by the remark that our total $\pi\perp$ operator, i.e., the operator including its radial dependence, is no longer separable into a product of an angular and a radial factor but has to be written as the linear combination

$$\begin{aligned}\hat{A}(\pi\perp) &= \hat{A}(\psi) + \hat{A}(\chi)\\ &= e_{\psi\mathrm{L}}\hat{A}^{\mathrm{L}}_{\mathrm{ang}}(\psi) + e_{\chi\mathrm{L}}\hat{A}^{\mathrm{L}}_{\mathrm{ang}}(\chi)\end{aligned} \tag{21}$$

This expression is in its formalism not at all alien to the AOM since it is analogous to, for example, the expression[18,19]

$$\hat{A} = e_\sigma\hat{A}_{\mathrm{ang}}(\sigma) + e_{\pi s}\hat{A}_{\mathrm{ang}}(\pi \mathrm{s}) + e_{\pi c}\hat{A}_{\mathrm{ang}}(\pi \mathrm{c}) + e_{\delta s}\hat{A}_{\mathrm{ang}}(\delta \mathrm{s}) + e_{\delta c}\hat{A}_{\mathrm{ang}}(\delta \mathrm{c}) \tag{22}$$

or, for a linear M–L system

$$\hat{A} = e_\sigma\hat{A}_{\mathrm{ang}}(\sigma) + e_\pi[\hat{A}_{\mathrm{ang}}(\pi \mathrm{s}) + \hat{A}_{\mathrm{ang}}(\pi \mathrm{c})] + e_\delta[\hat{A}_{\mathrm{ang}}(\delta \mathrm{s}) + \hat{A}_{\mathrm{ang}}(\delta \mathrm{c})] \tag{23}$$

However, the symmetry-required necessity for two radial parameters in eq 21 increases the requirement for information content of the experiment from which values of the radial parameters are to be obtained.

The general values of the traces as well as of the lengths[30-32] of the two operators of eq 20 are $2\cos^2(\beta/2)$ and $2\sin^2(\beta/2)$,

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(28) Schäffer, C. E. *Wave-Mechanic—The First Fifty Years*; Price, William C., Chissick, Seymour S., Ravensdale, Tom, Eds.; Butterworths: London, 1973; Chapter XII, pp 174–192.

(29) Schäffer, C. E. *Theor. Chim. Acta (Berlin)* **1974**, *34*, 237–243.

(30) Schäffer, C. E. *Physica* **1982**, *114A*, 28–49.

(31) Schäffer, C. E. *Understanding Molecular Properties*; Avery, J., et al., Eds.; D. Reidel Publishing Company: Dordrecht, The Netherlands, 1987; pp 143–175.

(32) Bendix, J.; Schäffer, C. E.; Brorson, M. *Coord. Chem. Rev.* **1989**, *94*, 181–241.

respectively, so that only the sum of their traces makes up the invariant, which is equal to the number of ligators of the system under consideration (cf. eq 4). So the *intra*ligand sum rule associated with eq 21, which represents our adapted AOM, is to a certain extent analogous with those of eq 22, which represents the conventional AOM. These sum rules are closely connected with the question of additivity. In our adapted AOM, there is no longer the concept of the perturbation from the individual ligators of the conjugated bidentate moiety, and the question of the additivity of these perturbations is therefore not appropriate. However, the *two* ligators of this bidentate moiety are together represented by the operator $\hat{A}(\pi\perp)$ of eq 21, and $\hat{A}^{\mathrm{AOM}}_{\mathrm{ang}}(\pi\perp)$ of eq 20 has a trace of *2* when acting on a set of d functions. Only when the ligator–ligator interactions become vanishingly small and eq 17 applies, do the conventional AOM and the adapted AOM become indistinguishable.

The analogy with eq 22 is complete when $\hat{A}(\pi\perp)$ is written out in terms of our radial parameters $e_{\psi\mathrm{LL}}$ and $e_{\chi\mathrm{LL}}$ as in eq 24

$$\hat{A}(\pi\perp) = e_{\psi\mathrm{LL}}\,\hat{A}^{\mathrm{LL}}_{\mathrm{ang}}(\psi) + e_{\chi\mathrm{LL}}\,\hat{A}^{\mathrm{LL}}_{\mathrm{ang}}(\chi) \tag{24}$$

since both angular operators on the right-hand side of eq 24 have a trace and a length[30–32] of unity.

In the following subsection we shall analyze the symmetry properties of the operator of eqs 21 and 24.

**G. A Symmetry Analysis of the $\pi\perp$ Perturbation Operator.** In the last 20 years, symmetry-hierarchic studies of additive[13] as well as nonadditive[30–32] ligand fields have perhaps made up the main progress in ligand-field theory and in the use of symmetry in chemistry. We shall now give a symmetry-hierarchic analysis of the operators describing the $\pi\perp$ perturbation of the planar, symmetrical bidentate.

We consider the *ligand* parametrization scheme first. We rewrite eq 24 as

$$\begin{aligned}\hat{A}(\pi\perp) &= \hat{A}^{\mathrm{LL}}_{\mathrm{ang}}(\psi)\,e_{\psi\mathrm{LL}} + \hat{A}^{\mathrm{LL}}_{\mathrm{ang}}(\chi)\,e_{\chi\mathrm{LL}} = \\ &[(\hat{A}^{\mathrm{LL}}_{\mathrm{ang}}(\psi) + \hat{A}^{\mathrm{LL}}_{\mathrm{ang}}(\chi))/2^{1/2}][(e_{\psi\mathrm{LL}} + e_{\chi\mathrm{LL}})/2^{1/2}] + [(\hat{A}^{\mathrm{LL}}_{\mathrm{ang}}(\psi) \\ &- \hat{A}^{\mathrm{LL}}_{\mathrm{ang}}(\chi))/2^{1/2}][(e_{\psi\mathrm{LL}} - e_{\chi\mathrm{LL}})/2^{1/2}] = \hat{A}^{\mathrm{LL}+}_{\mathrm{ang}}e^{+}_{\mathrm{LL}} + \hat{A}^{\mathrm{LL}-}_{\mathrm{ang}}e^{-}_{\mathrm{LL}}\end{aligned} \tag{25}$$

whose last expression is an abbreviated notation for the operators and parameters given in square brackets earlier in eq 25.

The matrix analogue of eq 25 using the function basis $\{(yz)(xy)\}$ and referring to the bidentate moiety spanning the $Z$ axis as in Figure 1 is

$$\mathbf{A}(\pi\perp) = \mathbf{A}^{\mathrm{LL}+}_{\mathrm{ang}}e^{+}_{\mathrm{LL}} + \mathbf{A}^{\mathrm{LL}-}_{\mathrm{ang}}e^{-}_{\mathrm{LL}} = \begin{bmatrix} 1/2^{1/2} & 0 \\ 0 & 1/2^{1/2} \end{bmatrix} e^{+}_{\mathrm{LL}} + \begin{bmatrix} 1/2^{1/2} & 0 \\ 0 & -1/2^{1/2} \end{bmatrix} e^{-}_{\mathrm{LL}} \tag{26}$$

where eqs 13 and 14 have provided the numerical results. Equation 26 contains the following symmetry analysis of the *ligand* parametrization scheme: the basis functions are eigenfunctions of $\hat{A}(\pi\perp)$ and the operator $\hat{A}^{\mathrm{LL}+}$ produces an equal energy shift of (yz) and (xy) just as an operator of linear symmetry about the Y axis would do. So, effectively, the model operator $\hat{A}^{\mathrm{LL}+}$ behaves as if it had $D_{\infty h}$ symmetry with the Y axis—i.e. the axis perpendicular to the plane of the bidentate moiety—as the $C_\infty$ axis. On the other hand, $\hat{A}^{\mathrm{LL}-}$ produces a barycentered splitting of $(yz)$ and $(xy)$ and behaves as an operator of $D_{2h}$ symmetry with the Cartesian axes as $C_2$ axes.

For the symmetry comparison between the conventional AOM ($e_{\psi\mathrm{L}} = e_{\chi\mathrm{L}} = e_{\pi\perp}$) and the AOM adapted to account for ligator–ligator interactions, one has, however, to use the *ligator* parametrization scheme.

This can be done by defining the new radial parameters $e^{+}_{\mathrm{L}}$ and $e^{-}_{\mathrm{L}}$ of eq 27, by letting them refer to angular operators of $D_{\infty h}$ and

$$\mathbf{A}(\pi\perp) = \mathbf{A}^{\mathrm{L}+}_{\mathrm{ang}}e^{+}_{\mathrm{L}} + \mathbf{A}^{\mathrm{L}-}_{\mathrm{ang}}e^{-}_{\mathrm{L}} \tag{27}$$

$D_{2h}$ symmetry, respectively. Because of these symmetry restrictions, the new angular operators must be proportional to the angular operators $\hat{A}^{\mathrm{LL}+}_{\mathrm{ang}}$ and $\hat{A}^{\mathrm{LL}-}_{\mathrm{ang}}$, respectively, and we take them to be identical. Equation 27 will thereby be rewritten as

$$\mathbf{A}(\pi\perp) = \mathbf{A}^{\mathrm{LL}+}_{\mathrm{ang}}e^{+}_{\mathrm{L}} + \mathbf{A}^{\mathrm{LL}-}_{\mathrm{ang}}e^{-}_{\mathrm{L}} \tag{28}$$

Combining now eqs 25, 26, and 28 and using again eqs 13 and 14, one obtains

$$\begin{aligned} e^{+}_{\mathrm{L}} = e^{+}_{\mathrm{LL}} &= (e_{\psi\mathrm{LL}} + e_{\chi\mathrm{LL}})/2^{1/2} \\ &= 2^{1/2}\cos^2(\beta/2)\,e_{\psi\mathrm{L}} + 2^{1/2}\sin^2(\beta/2)\,e_{\chi\mathrm{L}} \\ e^{-}_{\mathrm{L}} = e^{-}_{\mathrm{LL}} &= (e_{\psi\mathrm{LL}} - e_{\chi\mathrm{LL}})/2^{1/2} \\ &= 2^{1/2}\cos^2(\beta/2)\,e_{\psi\mathrm{L}} - 2^{1/2}\sin^2(\beta/2)\,e_{\chi\mathrm{L}} \end{aligned} \tag{29}$$

Held together with eq 26, eq 29 shows that $\hat{A}(\pi\perp)$ can be analysed as consisting of the sum of an energy shift of the set $\{(yz)(xy)\}$ of $\cos^2(\beta/2)\,e_{\psi\mathrm{L}} + \sin^2(\beta/2)\,e_{\chi\mathrm{L}}$ and a baricentered energy splitting contributing $\cos^2(\beta/2)\,e_{\psi\mathrm{L}} - \sin^2(\beta/2)\,e_{\chi\mathrm{L}}$ to $(yz)$ and the same quantity with opposite sign to $(xy)$. For the special case of $\beta = 90°$, the shift is $(e_{\psi\mathrm{L}} + e_{\chi\mathrm{L}})/2$ and the splitting is $e_{\psi\mathrm{L}} - e_{\chi\mathrm{L}}$ as also found by Ceulemans and Vanquickenborne.[9] When the ligator–ligator interactions become vanishingly small so that eq 17 is valid, the shift will be equal to the single ligator parameter $e_{\pi\perp}$ and the splitting equal to $2\cos\beta\,e_{\pi\perp}$ in agreement with eqs 4 and 6. If, moreover, $\beta = 90°$, the splitting will vanish and the holohedrized symmetry[20,22] of $\hat{A}(\pi\perp)$ for one planar ligand will be $D_{4h}$ (or, effectively $D_{\infty h}$). This is in agreement with the Ceulemans and Vanquickenborne[9] statement.

The conclusion therefore is that in the general case (i.e. when $\beta \neq 90°$) both the effectively linear and the orthorhombic terms (with radial parameters of $e^{+}$ and $e^{-}$ type, respectively) are linear combinations of $e_{\psi\mathrm{L}}$ and $e_{\chi\mathrm{L}}$ with $\beta$-dependent coefficients.

## IV. The Additive Model for $\pi\perp$ Perturbations from Two or More Conjugated Bidentates. Examples of Bis(bidentate) Square Planar, Tris(bidentate) Octahedral, and Bis(bidentate) Tetrahedral Complexes

**A. Application of the Additive Model.** In the following we present a short illustration of our model by considering certain simple systems consisting of combinations of identical bidentates LL. These systems have high symmetries and occur frequently in chemistry.

In the preceding part of this paper, we have only included explicitly those d orbitals of the central ion that are perturbed by the interaction with the $\pi\perp$ orbitals of the conjugated bidentate. If the rest of the d orbitals are included, the energy matrix $\mathbf{A}_{\mathrm{LL}}(\pi\perp)$ of the ligand field of a bidentate LL moiety, whose $C_2$ axis is along the $Z$ axis and whose molecular plane (including the central ion) is in the $ZX$ plane, has the following expression

$$\begin{array}{llccccc} & A_{\mathrm{LL}}(\pi\perp) & (z^2) & (yz) & (zx) & (xy) & (x^2-y^2) \\ \mathrm{d}\sigma & (z^2) & 0 & 0 & 0 & 0 & 0 \\ \mathrm{d}\pi & (yz) & 0 & e_{\psi\mathrm{LL}} & 0 & 0 & 0 \\ & (zx) & 0 & 0 & 0 & 0 & 0 \\ \mathrm{d}\delta & (xy) & 0 & 0 & 0 & e_{\chi\mathrm{LL}} & 0 \\ & (x^2-y^2) & 0 & 0 & 0 & 0 & 0 \end{array} \tag{30}$$

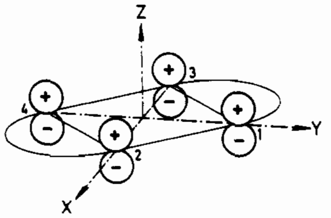
In the *ligand parametrization scheme* (eqs 13, 14, and 24), which uses the ligand radial parameters $e_{\psi\mathrm{LL}}$ and $e_{\chi\mathrm{LL}}$, the geometrical prerequisite is the direction of the $C_2$ axis of the bidentate moiety and the orientation of its molecular plane referred to the coordinate system defining the d orbital basis. In the *ligator parametrization scheme*, which uses the ligator radial parameters $e_{\psi\mathrm{L}}$ and $e_{\chi\mathrm{L}}$ of eqs 13, 14, and 21, the geometrical prerequisites are the ligator polar coordinates, which also imply a knowledge of the bite angle $\beta$. The main parametrical difference between the two schemes is that this bite angle occurs explicitly in the energy matrices when the ligator parametrization scheme is used (see eq 4).

The $\hat{A}(\sigma)$ perturbation is not the subject of the present paper. It can be handled by using the conventional AOM. Two closely related points should be noted, however. The coordinates of the ligators are the geometrical prerequisites of the conventional $\hat{A}(\sigma)$ calculation and for the present $\hat{A}(\pi\perp)$ calculation when the ligator parametrization scheme is used, while the coordinate system having the $Z$ axis as the $C_2$ axis of the bidentate and the $ZX$ plane as its molecular plane must be chosen as the frame when the ligand parametrization scheme is used.

Once all these matters concerning the individual bidentates have been clarified, it has to be borne in mind that the $XYZ$ coordinate system referred to is a local one from the point of view of the metal complex to be handled by the model. The ligand field arising from each bidentate moiety will thus at this stage be represented by its energy matrices of $\hat{A}(\sigma)$ and $\hat{A}(\pi\perp)$ in their own particular local d bases. Therefore, in order to obtain the expression for the total additive field, i.e., the field representing the sum of all the contributions from bidentate moieties plus any monodentate moieties present, one has to transform all these matrices into some common basis, which one might call the global basis.[32] In order to do this, the conventional formalism[18,19] is completely adequate. This will now be illustrated for a few systems containing only bidentate moieties.

**B. A Bis(bidentate) Square-Planar Complex.** In this and the following subsection, we assume that the bite angle $\beta$ of our bidentate moieties is equal to 90°. Thereby eqs 13 and 14 imply that both angular and radial factors of the perturbation operators are the same for the ligator and the ligand parametrization schemes (cf. also eq 15).

We start out from the ligator scheme in the present example. The p$\pi$ orbitals are numbered and given with signs in **5** and will be denoted by $\pi_1$, $\pi_2$, $\pi_3$, and $\pi_4$ where $\pi_2$ is connected with $\pi_4$ by the backbone of one of the bidentate moieties $L_2L_4$ and $\pi_1$ with $\pi_3$ by that of the other moiety $L_1L_3$.



5

We consider the perturbation from $L_2L_4$ first. It is immediate on inspection that the following equations are valid:

$$\langle (zx)|\pi_2\rangle_{\text{ang}} = 1 \tag{31}$$

$$\langle (zx)|\pi_4\rangle_{\text{ang}} = 0 \tag{32}$$

$$\langle (yz)|\pi_4\rangle_{\text{ang}} = -1 \tag{33}$$

$$\langle (yz)|\pi_2\rangle_{\text{ang}} = 0 \tag{34}$$

$$\langle (zx)|\psi\rangle_{\text{ang}} = \langle (zx)|(\pi_2 + \pi_4)/2^{1/2}\rangle_{\text{ang}} = 1/2^{1/2} \tag{35}$$

$$\langle (yz)|\psi\rangle_{\text{ang}} = \langle (yz)|(\pi_2 + \pi_4)/2^{1/2}\rangle_{\text{ang}} = -1/2^{1/2} \tag{36}$$

and the matrix of $\hat{A}(\psi)$ in the basis $\{(zx)(yz)\}$ is

$$\mathbf{A}(\psi) = \mathbf{A}_{\text{ang}}(\psi)\, e_{\psi L} = \begin{bmatrix} {}^1/_2 & -{}^1/_2 \\ -{}^1/_2 & {}^1/_2 \end{bmatrix} e_{\psi L} \tag{37}$$

Similarly, the matrix of $\hat{A}(\chi)$ is found to be

$$\mathbf{A}(\chi) = \mathbf{A}_{\text{ang}}(\chi)\, e_{\chi L} = \begin{bmatrix} {}^1/_2 & {}^1/_2 \\ {}^1/_2 & {}^1/_2 \end{bmatrix} e_{\chi L} \tag{38}$$

As was already mentioned in the last paragraph of section IID, $\mathbf{A}_{\text{ang}}(\psi)$ and $\mathbf{A}_{\text{ang}}(\chi)$ of eqs 37 and 38 are permuted relative to the situation of **3** and eq 8 where the bidentate moiety spans the positive $X$ and $Y$ axes.

In the ligator parametrization scheme, we obtain from eqs 37 and 38 directly our present AOM expression for the $\pi\perp$ perturbation energy matrix of the bidentate $L_2L_4$ moiety. Equation 39 is equivalent to eq 7 of Atanasov et al.,[15] who see it as a consequence of a three-center interaction.

$$\mathbf{A}(L_2L_4) = \mathbf{A}(\psi) + \mathbf{A}(\chi) = \begin{bmatrix} {}^1/_2(e_{\chi L}) + e_{\psi L}) & {}^1/_2(e_{\chi L} - e_{\psi L}) \\ {}^1/_2(e_{\chi L}) - e_{\psi L}) & {}^1/_2(e_{\chi L} - e_{\psi L}) \end{bmatrix} \tag{39}$$

These authors use the notation $e_{\pi s}$ and $e_{\pi s'}$ for the parameters $e_{\psi L}$ and $e_{\chi L}$, respectively, of our ligator parametrization scheme. Equation 39 is also equivalent to eq 2 of ref 9.

In conventional AOM, where $e_{\psi L} = e_{\chi L}$, i.e., for independent ligators $L_2$ and $L_4$, the matrix of eq 39 is diagonal. The new feature of the AOM, adapted to the bidentate situation, may in the particular case, $\beta$ = 90°, considered by Ceulemans and Vanquickenborne,[9] be conceived as the nondiagonal element of eq 39, which is nonvanishing when ligator–ligator interactions are present and which mixes $(zx)$ and $(yz)$. The removal of degeneracy associated with this mixing may be thought of as being due to a phase coupling of the ligators through the backbone of the bidentate moiety or due to direct bonding/antibonding ligator–ligator interaction causing the $\psi$ and $\chi$ linear combinations of ligator orbitals (cf. eq 3) to interact to different extents with the central ion d orbitals. This view matched the intuitive background of previous papers.[1,2,9,15] The analysis of sections IIIF and IIIG shows, however, that the consequence of ligator–ligator interactions for $\beta \neq 90°$ cannot in a natural way be separated out.

For use in the following section, we note that the eigenfunctions of $\hat{A}(L_2L_4)$ of eq 39 and their associated eigenvalues are as given in eqs 40 and 41.

$$[(zx) + (yz)]/2^{1/2} = e_{\chi L} \tag{40}$$

$$[(zx) - (yz)]/2^{1/2} = e_{\psi L} \tag{41}$$

In order to use the ligand parametrization scheme, we need to view the central ion from the 2-fold axis of $L_2L_4$, i.e. from $x = -y$ and $z = 0$, and to replace the bidentate ligand by a nonlinearly ligating, unidentate ligand as described in section IIID and illustrated by Figure 1, where a different coordinate frame is used. The eigenvalues for the eigenfunctions of eqs 40 and 41 are $e_{\chi LL}$ and $e_{\psi LL}$, respectively.

The coefficients to corresponding ligator and ligand radial parameters, e.g., $e_{\psi L}$ and $e_{\psi LL}$, are the same when $\beta$ = 90° (cf. eqs 13–15).

We are left with the problem of adding the perturbation contribution from the ligand $L_1L_3$ (**5**). However, by the inversion symmetry of the central ion d orbitals, the eigenfunctions of the perturbation from $L_1L_3$ and their associated eigenvalues are the same as for $L_2L_4$. Therefore, we only need to change the coefficients to $e_{\chi L}$ and $e_{\psi L}$ of eqs 40 and 41 to 2 instead of 1 in order to obtain the final result for the bis(bidentate) complex.

It is too early at the stage of this paper to discuss the actual values of our present empirical parameters since comparison of the model with experiments is a major effort in itself. However, we believe it is useful to consider the consequences of some relative values of the parameters $e_{\psi L}$ and $e_{\chi L}$ that are qualitatively in agreement with our theoretical discussion of section IIIC. We choose for the diimine ligands

$$e_{\psi NN} = -5 \qquad e_{\chi NN} = -2 \tag{42}$$

and for the $\beta$-diketonate ligands

$$e_{\psi OO} = 5 \qquad e_{\chi OO} = -2 \tag{43}$$

both choices illustrating the prospect of having negative radial parameters corresponding to the d orbitals becoming bonding rather than antibonding. Furthermore, the $\beta$-diketonate choice illustrates the possibility of having the two new parameters of $e_{\pi\perp}$ type appear with different signs.

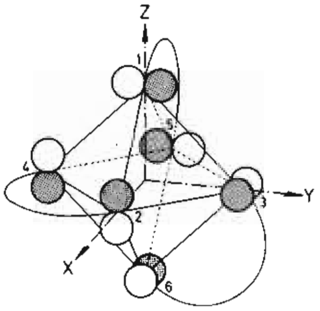
The important energy quantity, which is the experimental consequence of the $\pi\perp$ perturbation in the bis(bidentate) case, is the splitting of the orbital set $\{(zx)(yz)\}$. For this splitting $\Delta h$, we have according to eqs 40 and 41 and including the factor of

2 because of the two bidentate moieties

$$\Delta h = 2e_{\psi\mathrm{L}} - 2e_{\chi\mathrm{L}} \tag{44}$$

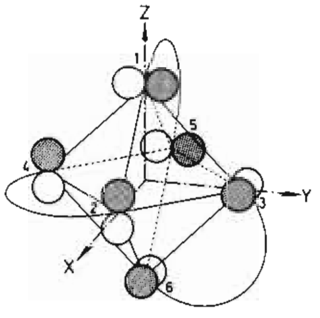
which shows that the most pronounced experimental effects of the $\pi\perp$ perturbation from conjugated ligands in the present planar complexes are expected when opposite signs of the $\pi\perp$ parameters occur, as possibly happens in the case when the bidentate moiety is a $\beta$-diketonate (eq 43).

**C. A Tris(bidentate) Octahedral Complex.** We assume again that the bite angle $\beta$ of the bidentate is 90°. We use the setup of **6a** and **6b**, which illustrate the symmetries $\chi$ and $\psi$, respectively, of the $\pi\perp$ orbitals of the three bidentate moieties $L_2L_4$, $L_3L_6$, and $L_1L_5$, which lie in the *XY*, *YZ*, and *ZX* planes, respectively. Our problem can be formulated as follows



6a

$\chi$ orbitals



6b

$\psi$ orbitals

$$\begin{aligned}\hat{A}(\pi\perp) &= \hat{A}^{L_2L_4}(\pi\perp) + \hat{A}^{L_3L_6}(\pi\perp) + \hat{A}^{L_1L_5}(\pi\perp) \\ &= \hat{A}^{L_2L_4}(\psi) + \hat{A}^{L_2L_4}(\chi) + \hat{A}^{L_3L_6}(\psi) + \hat{A}^{L_3L_6}(\chi) + \\ &\qquad \hat{A}^{L_1L_5}(\psi) + \hat{A}^{L_1L_5}(\chi) \\ &= \hat{A}(\psi) + \hat{A}(\chi)\end{aligned} \tag{45}$$

Equation 45 shows in algebraic language what **6a** and **6b** depict: the total $\pi\perp$ perturbation from the three bidentate moieties can be conceived as a sum of a $\psi$ and a $\chi$ contribution, each of these contributions consisting of three terms corresponding to the three bidentate moieties. This result is analogous to the general result of the AOM that the perturbation from a whole coordination sphere can be written as a sum of a $\sigma$ perturbation, a $\pi$ perturbation, and perhaps more terms.[13]

Before considering the $\pi\perp$ perturbation, we note that the six $\pi\perp$ ligator orbitals by holohedrization[20,22] comprise all of the 12 possible ligator $\pi$ orbitals of the octahedron, which span $t_{1g} \oplus t_{2g} \oplus t_{1u} \oplus t_{2u}$. Since $e_g$ is not among these irreducible representations, we conclude at the outset that the space of d orbitals that may be perturbed by the $\pi\perp$ orbitals of a tris(bidentate) ligand system with $\beta = 90°$ is limited to $dt_{2g}$ or, in other words, to the orbitals ($yz$), ($zx$), and ($xy$), referred to a global coordinate system with the axes coinciding with the $C_4$ axes of $O_h$.

Knowing this, we now begin by considering the $\psi$ perturbations and, in particular, that from the bidentate moiety $L_2L_4$. The coefficient matrix is already given in eq 37, but it is repeated here—with the orbitals in the natural order for the present purpose[13]—as (46) in order to associate it with the ligand $L_2L_4$.

$$\begin{array}{ccc} \hat{A}_{\mathrm{ang}}^{L_2L_4}(\psi) & (yz) & (zx) \\ (yz) & {}^1/_2 & -{}^1/_2 \\ (zx) & -{}^1/_2 & {}^1/_2 \end{array} \tag{46}$$

The corresponding d basis for the two other bidentates can be obtained by cyclic permutation[13] of $x$, $y$, and $z$. Thus we obtain the following expressions:

$$\begin{array}{ccc} \hat{A}_{\mathrm{ang}}^{L_3L_6}(\psi) & (zx) & (xy) \\ (zx) & {}^1/_2 & -{}^1/_2 \\ (xy) & -{}^1/_2 & {}^1/_2 \end{array} \tag{47}$$

$$\begin{array}{ccc} \hat{A}_{\mathrm{ang}}^{L_1L_5}(\psi) & (xy) & (yz) \\ (xy) & {}^1/_2 & -{}^1/_2 \\ (yz) & -{}^1/_2 & {}^1/_2 \end{array} \tag{48}$$

The matrices (46)–(48) consist of coefficients to the same radial parameter $e_{\psi\mathrm{L}} = e_{\psi\mathrm{LL}}$, where the equality is valid because $\beta = 90°$ (cf. eqs 12–14), and this parameter will be denoted by $e_\psi$.

By the use of eq 45, the combined information of (46)–(48) may be written

$$\begin{aligned}\langle(yz)|\hat{A}(\psi)|(yz)\rangle = \langle(zx)|\hat{A}(\psi)|(zx)\rangle &= \\ \langle(xy)|\hat{A}(\psi)|(xy)\rangle &= e_\psi \\ \langle(yz)|\hat{A}(\psi)|(zx)\rangle = \langle(zx)|\hat{A}(\psi)|(xy)\rangle &= \\ \langle(xy)|\hat{A}(\psi)|(yz)\rangle &= -(1/2)e_\psi\end{aligned} \tag{49}$$

The three single-ligand matrices of $\hat{A}_{\mathrm{ang}}(\chi)$ are identical with those of (46)–(48) apart from the fact that the nondiagonal elements have opposite signs (cf. eqs 37 and 38). Therefore for $\hat{A}(\chi)$, we have

$$\begin{aligned}\langle(yz)|\hat{A}(\chi)|(yz)\rangle = \langle(zx)|\hat{A}(\chi)|(zx)\rangle &= \\ \langle(xy)|\hat{A}(\chi)|(xy)\rangle &= e_\chi \\ \langle(yz)|\hat{A}(\chi)|(zx)\rangle = \langle(zx)|\hat{A}(\chi)|(xy)\rangle &= \\ \langle(xy)|\hat{A}(\chi)|(yz)\rangle &= (1/2)e_\chi\end{aligned} \tag{50}$$

Our eqs 49 and 50 are equivalent to eq 8 of Atanasov et al.[15] apart from their inclusion of the so-called $\pi\|$ perturbation.[13]

Since the eigenfunctions of $\hat{A}(\psi)$ and $\hat{A}(\chi)$ must be $t_{2g}(O_h)$ functions, they are completely determined by symmetry[13] in our present tris(bidentate) system of symmetry $D_3$, apart from the freedom associated with the degeneracy $t_{2g}(O_h)e(D_3)$ and the free choice of sign (phase).

If the group hierarchy $O_h \supset D_3 \supset C_2$ is used to break the degeneracy freedom for the eigenfunctions, the following functions are the fully specified ones, including a convention for choosing the phases:[31]

$$\begin{aligned} t_{2g}^{\alpha} &= t_{2g}(O_h)e(D_3)a(C_2) = [(yz) + (zx) - 2(xy)]/6^{1/2} \\ t_{2g}^{\beta} &= t_{2g}(O_h)e(D_3)b(C_2) = [(zx) - (yz)]/2^{1/2} \\ t_{2g}^{\gamma} &= t_{2g}(O_h)a_1(D_3)a(C_2) = [(yz) + (zx) + (xy)]/3^{1/2} \end{aligned} \tag{51}$$

From these eigenfunctions together with eqs 49 and 50, the $\pi\perp$ perturbation energies $h$ may be found to be

$$\begin{aligned} h(t_{2g}^{\alpha}) = h(t_{2g}^{\beta}) &= (3/2)e_\psi + (1/2)e_\chi \\ h(t_{2g}^{\gamma}) &= 0e_\psi + 2e_\chi \end{aligned} \tag{52}$$

The quantitative result of eq 52 needs some further comments: the average perturbation energy of the three $t_{2g}$ orbitals, the energy shift, is $e_\psi + e_\chi$. This is the cubic part[8] of the perturbation $\hat{A}(\pi\perp)$ of eq 45. The sum of the coefficients in each energy expression of eq 52 is 2 and this number, multiplied by 3 (because of the three orbitals), equals the number of ligators. The energy differences between the $e(D_3)$ and $a_1(D_3)$ split components are $(3/2)e_\psi$ and $-(3/2)e_\chi$ for the $\psi$ and the $\chi$ terms. The total trigonal splitting is

$$h(\mathrm{e}) - h(\mathrm{a}_1) = (3/2)(e_\psi - e_\chi) \qquad (53)$$

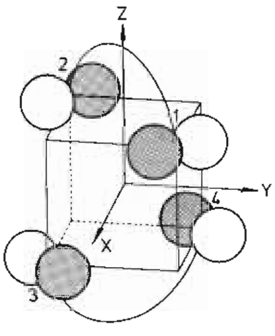
showing that the splitting is zero in the conventional[13] AOM (cf. eqs 17 and 18), in which case the total perturbation gives rise to the energy shift $2e_{\pi\perp}$ (eq 52). Equation 53 shows that especially large splitting effects are expected when $e_\psi$ and $e_\chi$ have opposite signs. For Schönherr et al.[15] it was enough to put $e_\chi$ equal to zero in order to explain the large trigonal splitting of ${}^4\mathrm{T}_{2g}(O_h)$ in the tris(acetylacetonato)chromium(III) complex, which is found in spite of the fact that the ligators of this complex are almost octahedrally disposed about their central ion (cf. also eq 44).

**D. A Bis(bidentate) Tetrahedral Complex.** As our last example, we study a system where two bidentate moieties bite over the edges of a regular tetrahedron, which means that the bite angles $\beta$ are equal to the tetrahedral valence angle $\beta(T_d) = 109.47°$, or cos $[\beta(T_d)] = -(1/3)$. According to eqs 13 and 14, we therefore have

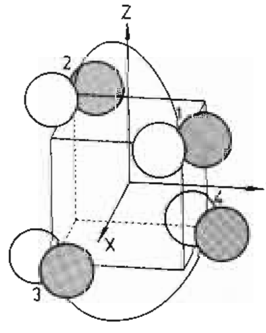
$$e_{\psi\mathrm{LL}} = (2/3)e_{\psi\mathrm{L}}$$

$$e_{\chi\mathrm{LL}} = (4/3)e_{\chi\mathrm{L}} \qquad (54)$$

In **7a** and **7b** are seen the $\chi$ and $\psi$ ligand symmetry orbitals, respectively and also the Cartesian coordinate system (the global system) that is used to define the set of real central ion d functions. In this example the local coordinate systems for the ligand parametrization scheme may be chosen to have their axes coinciding with those of the global system (cf. also Figure 2).



7a
χ orbitals



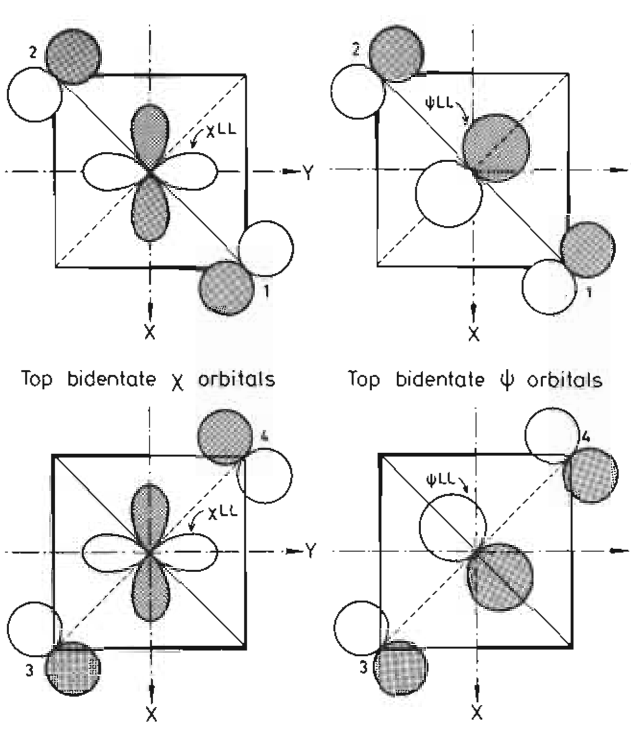
7b
ψ orbitals

We consider this parametrization scheme first since it is particularly simple here. Since the $Z$ axis is the 2-fold axis of both bidentate moieties, these will, when acting as non linearly ligating unidentate ligands LL, perturb d$\pi$ and d$\delta$ orbitals referred to this axis. We shall in fact be able to obtain all our results in this scheme by inspection rather than algebra.

The $\chi$ perturbations will be considered first. For each bidentate acting as a unidentate ligand, the $\chi$ perturbation is associated with the $\chi$LL orbital, which is odd with respect to reflection in both planes of symmetry of the bidentate moiety. The situation is illustrated for the top bidentate on the upper left of Figure 2, so that the $Z$ axis is the $C_2$ axis of the bidentate moiety and comes up through the centroid of the tetrahedron with its direction perpendicular to the plane of the paper. The $\chi$LL orbital is thus centered on the positive $Z$ axis. This $\chi$LL orbital matches the central ion d$(x^2 - y^2)$ orbital (not shown) perfectly so as to give an angular overlap integral of unity between the two orbitals and a perturbation of $e_{\chi\mathrm{LL}}$ on d$(x^2 - y^2)$. The lower left of the figure shows that the bottom bidentate moiety also produces a $\chi$ perturbation of $e_{\chi\mathrm{LL}}$ on d$(x^2 - y^2)$. We thus have

$$h(x^2 - y^2) = h(\mathrm{b}_1) = 2e_{\chi\mathrm{LL}} = (8/3)e_{\chi\mathrm{L}} \qquad (55)$$

where a notation of the fact that the irreducible representation $\mathrm{b}_1$ is spanned by d$(x^2 - y^2)$ in $D_{2d}$ is contained.



Top bidentate χ orbitals Top bidentate ψ orbitals

Bottom bidentate χ orbitals Bottom bidentate ψ orbitals

**Figure 2.** Orbital perturbers of the bis(bidentate) tetrahedral complex, seen from the $S_4$ axis. The two upper parts refer to the top bidentate moiety and the two lower ones to the bottom bidentate moiety. The left-hand side illustrates $\chi$ orbitals; the right-hand side illustrates $\psi$ orbitals. In all of the parts, the orbitals associated with both ligator and ligand parametrization schemes of the AOM have been drawn. The former orbitals are linear combinations of the ligator orbitals of **8** whose coefficient signs are given by the shading. The latter orbitals are $\chi$ and $\psi$ atomic orbitals of a non linearly ligating, unidentate ligand, situated on the $C_2$ axis common to the two bidentates. They have been denoted by $\chi$LL and $\psi$LL.

Next we consider the $\psi$ perturbations. For each bidentate moiety the $\psi$ perturbation can be regarded as associated with a non linearly ligating unidentate ligand $\psi$LL orbital that is even with respect to reflection in the plane perpendicular to the molecular plane of the particular bidentate. The $\psi$LL orbital for the top bidentate (the upper right part of Figure 2) matches the central ion d orbital $[(yz) - (zx)]/2^{1/2}$ perfectly to contribute the perturbation energy $e_{\psi\mathrm{LL}}$ by its interaction with this orbital. Similarly, the $\psi$LL orbital of the bottom bidentate moiety matches $[(zx) + (yz)]/2^{1/2}$ perfectly to give it also the energy $e_{\psi\mathrm{LL}}$. The final result by using also eq 54 is then

$$h(\mathrm{zx}) = h(\mathrm{yz}) = h(\mathrm{e}) = e_{\psi\mathrm{LL}} = (2/3)e_{\psi\mathrm{L}} \qquad (56)$$

since $(zx)$ and $(yz)$ span $\mathrm{e}(D_{2d})$.

The energies of eqs 55 and 56 are the splitting energies of the central ion orbital sets de$(T_d)$ and dt$_2(T_d)$, respectively. Therefore, in this case of a "tetrahedral bisphenoide" system, the two independent $\pi\perp$ perturbation parameters, $e_{\chi\mathrm{LL}}$ and $e_{\psi\mathrm{LL}}$, can in principle be determined on the basis of spectral splittings. Unfortunately, the interpretation of d–d spectra of tetrahedral complexes has not been so successful as that of octahedral ones.[33]

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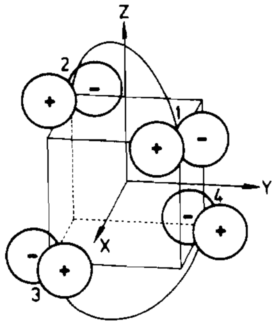
(33) Reisfeld, R.; Cherniak, V.; Eyal, M.; Jørgensen, C. K. *Chem. Phys. Lett.* **1989**, *164*, 307–312.

We now outline the results of using the ligator parametrization scheme on our bis(bidentate) system. Placing the ligating atoms of the top bidentate in the directions $L_1(1,1,1)$ and $L_2(-1,-1,1)$ and with the positive lobe of their $p\pi\perp$ orbitals in the direction (1,–1,0), and the ligators of the bottom bidentate in the directions $L_3(1,-1,-1)$ and $L_4(-1,1,-1)$ and $p\pi\perp$ direction (1,1,0) (**8**), one



**8**

has a $T_d$ system of ligators. The four ligator $p\pi\perp$ orbitals transform under $D_{2d}$ as $a_2 \oplus b_1 \oplus e$ among which only the two latter symmetry species are also represented by the central ion d orbitals, and in fact $b_1$ is represented by $(x^2 - y^2)$ and e by the set $\{(zx)(yz)\}$ (cf. also eqs 55 and 56). The linear combination of ligator $\pi\perp$ orbitals of $b_1$ symmetry is here of $\chi$ type while those of e symmetry are of $\psi$ type. The two kinds of linear combinations are illustrated in Figure 2. The relevant group angular overlap integrals are given in eq 57.

$$\begin{aligned} &b_1(D_{2d}) \quad \langle (x^2 - y^2)|\tfrac{1}{2}[(\pi_1 - \pi_2) + (\pi_3 - \pi_4)]\rangle_{\text{ang}} = (8/3)^{1/2} \\ &e_{zx}(D_{2d}) \quad \langle (zx)|-\tfrac{1}{2}[(\pi_1 + \pi_2) + (\pi_3 + \pi_4)]\rangle_{\text{ang}} = (2/3)^{1/2} \\ &e_{yz}(D_{2d}) \quad \langle (yz)|\tfrac{1}{2}[(\pi_1 + \pi_2) - (\pi_3 + \pi_4)]\rangle_{\text{ang}} = (2/3)^{1/2} \end{aligned} \tag{57}$$

The results of eq 57 are in agreement with eqs 55 and 56. This example of a "tetrahedral" bis(bidentate) system has thus illustrated our general result that one may use either the ligand or the ligator parametrization scheme.

We finish this example of a "tetrahedral" complex with a symmetry analysis and note again that $\hat{A}(\psi)$ acts only on part of the $t_2(T_d)$ subshell and $\hat{A}(\chi)$ only on part of the $e(T_d)$ subshell. In fact the two operators are responsible for the splittings of the subshells as we have already seen in eqs 56 and 55. What we still need to discuss is that the total $\pi\perp$ perturbation has a term of tetrahedral symmetry.

The usual definition of the parameter $\Delta$ for a regularly tetrahedral complex is

$$\Delta \equiv h(t_2) - h(e) \tag{58}$$

This definition can be carried over to our present complex of symmetry $D_{2d}$ by writing as follows:

$$h(t_2) \equiv \bar{h}(t_2) \qquad h(e) \equiv \bar{h}(e) \tag{59}$$

Here the bars mean averaging within the orbital sets in parentheses so that

$$\bar{h}(t_2) = [h(xy) + h(yz) + h(zx)]/3 \tag{60}$$

$$\bar{h}(e) = [h(z^2) + h(x^2 - y^2)]/2 \tag{61}$$

In the present paper only the $\pi\perp$ perturbation is under consideration, and we may therefore use the second kind of additivity of the AOM to define the parameter $\Delta_{\pi\perp}$, which describes the part of the $\pi\perp$ perturbation that has regular tetrahedral symmetry. The definition has to be

$$\Delta_{\pi\perp} \equiv h_{\pi\perp}(e) - h_{\pi\perp}(t_2) \tag{62}$$

where the sign is based upon the usual definition

$$\Delta \equiv \Delta_\sigma - \Delta_\pi \tag{63}$$

Using eqs 55 and 61, one obtains

$$h_{\pi\perp}(e) = e_{\chi LL} \tag{64}$$

and using eqs 56 and 60, one obtains

$$h_{\pi\perp}(t_2) = (2/3)e_{\psi LL} \tag{65}$$

so that eqs 62, 64, and 65 provide our expression for the $\pi\perp$ part of the tetrahedral field

$$\Delta_{\pi\perp} = e_{\chi LL} - (2/3)e_{\psi LL} \tag{66}$$

Equation 66 shows that the synergistic influence of the $\psi$ and $\chi$ perturbations affect the tetrahedral part of the ligand field rather than the part that splits the tetrahedrally based subshells (cf. eqs 55 and 56). As usual, this synergism happens when $e_{\psi LL}$ and $e_{\chi LL}$ have opposite signs (cf. eqs 39, 44, and 53).

## V. Conclusion

The $\pi\perp$ perturbation of a symmetrical bidentate is in conventional AOM parametrized[13] by the radial parameter $e_{\pi\perp}$, which refers to the *individual* ligating atoms. This parameter may therefore be said to be preponderantly atomic in character even though the values of $e_{\pi\perp}$ are found to be somewhat different for different ligands containing the same ligators.

Conjugated bidentate moieties, for which this conventional AOM is known from comparison with experiments not to work, were treated here by using the usual molecular orbital orientation of the AOM. Since the ligators of conjugated bidentates interact with each other through the backbone of the ligand, the values of the AOM parameters depend on the extent of the interaction or, rather, on its energetic consequences on the central ion d shell. In this sense, the present radial parameters are essentially molecular in character. The analysis concludes that the $e_{\pi\perp}$ parameter of the conventional AOM has to be replaced by two independent parameters in the adapted AOM. These parameters, $e_\psi$ and $e_\chi$, correspond to *in-phase* and *out-of-phase* combinations of ligator $\pi\perp$ orbitals, respectively. This division is symmetry-based and the ligator–orbital linear combinations fall into a $\psi$ and a $\chi$ class also in conventional AOM. The new issue here is that the ligator–ligator interactions are accounted for by associating *different* parameters with each of the two classes.

Two equivalent parametrization schemes, a ligand scheme and a ligator scheme, have been devised. In the ligand scheme a symmetrical, conjugated bidentate moiety behaves as a non linearly ligating unidentate ligand, located on the 2-fold axis of this bidentate and perturbing one $d\pi$ orbital of the $d\pi$ set (the $\psi$ perturbation) and one $d\delta$ orbital of the $d\delta$ set (the $\chi$ perturbation), where the $\pi$ and $\delta$ symmetry designations refer to this 2-fold axis as if it were a $C_\infty$ axis (cf. section IIID). Both of the perturbed d orbitals have the plane of the bidentate as a plane of antisymmetry. In the ligator parametrization scheme, the perturbations are associated with ligator group orbitals of symmetries $\psi$ and $\chi$. The AOM formalism is retained unchanged, provided its group overlap formulation is used (section IIC).

Since the present AOM formalism for symmetrical bidentate moieties is symmetry-based, it applies also to situations where the ligator–ligator interactions of the model are caused by direct antibonding–bonding interactions between the two ligators of the bidentate ligand. This type of interaction was qualitatively considered by Jørgensen[10] many years ago.

If two or more bidentates, conjugated or nonconjugated, are present in a coordination sphere, their perturbation contributions are additive as is usual in the AOM. Moreover, for extra unidentate ligands, the usual additive character of the AOM is retained.

The ligand fields of many ligands in the forefront of science at this time[34-36] are embodied in the present adapted AOM.

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(34) Meyer, T. J. *Acc. Chem. Res.* **1989**, *22*, 163–170.

(35) Krausz, E.; Ferguson, J. *Prog. Inorg. Chem.* **1989**, *37*, 293–390.

(36) De Armond, M. K.; Myrick, M. L. *Acc. Chem. Res.* **1989**, *22*, 364–370.

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### Appendix. Note on the Ligand Field Arising from Coordination of an Unsymmetrical, Planar, Conjugated Bidentate Moiety

The $\pi\perp$ perturbation from an unsymmetrical, planar, conjugated bidentate moiety LL′ can be treated analogously to that of a symmetrical one by using the methods of the present paper. If the plane of the ligand is chosen to be the *ZX* plane, then again the $\pi\perp$ orbitals of the bidentate overlap only with the d orbitals ($yz$) and ($xy$). However, because of the loss of the 2-fold axis of the bidentate moiety, a phase-based classification of the ligand $\pi\perp$ orbitals into $\psi$ and $\chi$ no longer coincides with different symmetry species. In other words, both $\psi$ and $\chi$ orbitals are $A''(C_{1h})$, where $C_{1h}$ is the point group defined by the central ion and the planar unsymmetrical bidentate ligand. Therefore, ($yz$) and ($xy$) will in general no longer be eigenfunctions in an AOM sense, and the matrix of $\hat{A}(\pi\perp)$ will contain a nonvanishing, nondiagonal element so that its form will be

$$\begin{array}{ccc} \hat{A}(\pi\perp) & (yz) & (xy) \\ (yz) & e_{\psi LL'} & e_{\psi\chi LL'} \\ (xy) & e_{\psi\chi LL'} & e_{\chi LL'} \end{array} \qquad (67)$$

where $e_{\psi LL'}$, $e_{\chi LL'}$, and $e_{\psi\chi LL'}$ are independent, radial parameters to be found empirically.

We have already mentioned that the numerical values of the independent parameters $e_{\psi LL}$ and $e_{\chi LL}$, required in the case of a symmetrical bidentate moiety, will not be easy to obtain from spectral and magnetic data. This, of course, will be even more true when yet another parameter has to be extracted from experiment.

We want to further comment on the three independent parameters in the energy matrix (67). The sum of the squares of the elements of a matrix is invariant to a unitary transformation. Therefore, this sum is for the matrix (67) independent of the way in which LL′ is placed within the *ZX* plane. However, this is not true for the individual parameter values. There will certainly be a placement of LL′ for which the nondiagonal element $e_{\psi\chi LL'}$ will be zero, but this placement is not determined by symmetry and therefore will remain unknown until a full parametrical analysis of experimental results has been made on the basis of an arbitrarily chosen placement. Therefore, there will always remain three independent empirical parameters even if one of them may be chosen as an angle[1] instead of an energy parameter.

Our conclusion is that there is little hope that an AOM treatment of an unsymmetrical conjugated bidentate will be useful. Therefore, regarding this type of ligands, the implications of the CDV work[1,2] and especially that regarding parametrization of their perturbation by only two parameters, should be reexamined carefully.

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# Steric Constraints inside the Metal-Coordination Sphere As Revealed by Diastereotopic Splitting of Methylene Protons

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A solution NMR study performed on [PtCl$_2$(ethambutol)] [ethambutol = *N*,*N*′-bis(1-hydroxy-2-butyl)ethylenediamine] has shown that the nitrogen substituents [$-CH(CH_2OH)(CH_2CH_3)$] conform themselves so as to direct the least bulky side (the tertiary hydrogen atom) toward the cis chlorine ligand, and this appears to be the most compelling steric requirement. As a consequence, the hydroxymethyl and ethyl radicals (R) are directed one inward and the other outward with respect to the chelating moiety. The radical directed toward the chelate ring deeply interacts with it, and as a consequence, the methylene protons of this radical exhibit, in the NMR spectrum, a diastereotopic splitting the average value of which is 0.45 ppm in the case of hydroxymethyl and 0.80 ppm in the case of ethyl.

## Introduction

The stereochemistry of complexes with chelate ligands has been widely investigated in the past. As far as the chelate ring of ethylenediamines is concerned, it has been found that this is markedly puckered in an essentially strain-free structure.[1] In solution, by internal rotation, the skew conformation of the N–C–C–N chain can change to another skew form, which is a reflection of the original; as a result of this process axial bonds are transformed into equatorial bonds and vice versa so that, on the average, the chelate ring is coplanar with the coordination plane and the substituents on the chelating moiety are equally displaced above and below this plane.

Another feature of the complexes with N-substituted ethylenediamines is that, in the solid state, the N substituents are rotated in such a way as to direct the least bulky side toward the cis metal ligand, and this appears to be the most compelling steric requirement.[2] The present investigation has shown that the same situation occurs also in solution and it brings about very peculiar and noticeable features.

## Results and Discussion

Ethambutol is a symmetrically substituted ethylenediamine [*N*,*N*′-bis(1-hydroxy-2-butyl)ethylenediamine] and can be synthesized in three isomeric forms having absolute configurations *R*,*R*, *S*,*S*, and *R*,*S* at the asymmetric carbons. It has a tuberculostatic activity and has been in clinical use since the mid-1960s.[3]

Optically pure isomers of the diamine were prepared by the method of ref 3, and by reaction with [PtCl$_2$(DMSO)$_2$], in methanol, the complexes [PtCl$_2$(ethambutol)] were obtained in

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(1) Corey, E. J.; Bailar, J. C., Jr. *J. Am. Chem. Soc.* **1959**, *81*, 2520–2529. Hawkins, C. J. *Absolute Configurations of Metal Complexes*; Wiley-Interscience: New York, 1971; Chapter 6. Beattie, J. K. *Acc. Chem. Res.* **1971**, *4*, 253–259. Erickson, L. E.; McDonald, J. M.; Howie, J. K.; Clow, R. P. *J. Am. Chem. Soc.* **1968**, *90*, 6371–6382. Appleton, T. G.; Hall, J. R. *Inorg. Chem.* **1970**, *9*, 1800–1806, 1807–1814; **1971**, *10*, 1717–1725. Erickson, L. E.; Erickson, M. D.; Smith, B. L. *Inorg. Chem.* **1973**, *12*, 412–422. Erickson, L. E.; Sarneski, J. E.; Reilley, C. N. *Inorg. Chem.* **1975**, *14*, 3007–3017.

(2) Fanizzi, F. P.; Maresca, L.; Natile, G.; Lanfranchi, M.; Manotti-Lanfredi, A. M.; Tiripicchio, A. *Inorg. Chem.* **1988**, *27*, 2422–2431. Fanizzi, F. P.; Intini, F. P.; Maresca, L.; Natile, G.; Uccello-Barretta, G. *Inorg. Chem.* **1990**, *29*, 29–33.

(3) Wilkinson, R. G.; Shepherd, R. G.; Thomas, I. R.; Baughn, C. *J. Am. Chem. Soc.* **1961**, *83*, 2212–2214. Wilkinson, R. G.; Cantrall, M. B.; Shepherd, R. G. *J. Med. Pharm. Chem.* **1962**, *5*, 835–845. Pitrè, D.; Grandi, M. *Farmaco* **1969**, *24*, 490–495.

0020-1669/91/1330-2853$02.50/0