A Non-empirical Appraisal of the Angular-overlap Model for Transition-metal Complexes

By **Jonathan Tennyson** and **John N. Murell**,* School of Molecular Sciences, University of Sussex, Brighton BN1 9QJ

Non-empirical SCF molecular-orbital calculations of the *d*-orbital energies in the complexes $[MnF_{6-i}Cl_i]^{k-}$ (i = 1—6) and distorted $[MnF_6]^{k-}$ (k = 2 or 4) have been made within a valence-electron approximation. These energies have been shown to be accurately modelled by a one-electron angular-overlap Hamiltonian. The angular-overlap parameters for Cl and F have a relationship which is similar to that determined from experiment for some chromium(III) complexes.

DESPITE the success of ligand-field theory in correlating the properties, particularly spectroscopic, of transition-metal complexes the theory has largely been confined to high-symmetry structures: octahedral, tetrahedral, and to a smaller extent tetragonal and square planar. Notwithstanding the importance of these structures they often have less interesting physical properties, particularly magnetic, than those of lower symmetry.

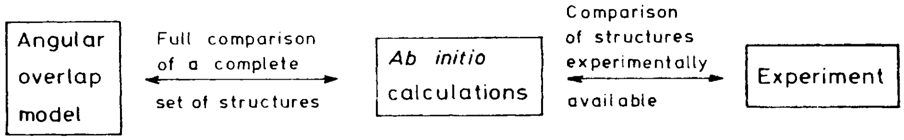
Ligand-field theory itself is not well suited for extension to low-symmetry complexes. The number of parameters required to express the full spherical harmonic components of the ligand field is greater than the number of determinable energy differences amongst the *d* orbitals. For example, C_{2v} symmetry requires nine parameters to represent those components of the ligand field which have non-zero *d*–*d* matrix elements, whereas there are only five *d*-orbital energies to measure.

An alternative approach is to identify the perturbing potential with individual ligands rather than as components of the collective potential of the whole ligand structure. Although this approach might appear to require more parameters it has the advantage that these may be transferred between complexes within restricted classes, thus increasing the data from which they may be evaluated. This is essentially the approach introduced first by Yamatera [1,2] and McClure [3] which has evolved into the so-called angular-overlap model (a.o.m.). The method has been frequently reviewed.[4–6]

Unfortunately, the analysis of low-symmetry structures is still difficult in the a.o.m. because one generally has insufficient data for full parameterisation. This insufficiency arises, for example, from the imperfect resolution of electronic spectra and the failure to synthesise and isolate key complexes.

Ab initio calculations provide, in principle, a basis for deciding that a spectral observation is consistent with an assumed structure but give little in the way of physical explanation of spectral patterns. In practice such calculations cannot generally be done within the current limits of computer time with sufficient accuracy to reproduce experimental results.

An advantage of *ab initio* calculations is that structures are not restricted by experimental availability. Moreover, the resulting energies obtained from such calculations may always be completely assigned on the basis of their orbital wavefunctions and not guessed from the nature of spectral appearance or correlation within families. This suggests an alternative way to evaluate the a.o.m. which is with a series of *ab initio* calculations, some but not all of which could be compared with experiment. This procedure is summarised in the Scheme.



SCHEME

Although we can at present make only crude *ab initio* calculations on transition-metal complexes compared to what is currently possible on light-atom molecules, it is not unreasonable to assume that if crude *ab initio* calculations confirm the general principles of the a.o.m. then accurate *ab initio* calculations would do likewise. The precise values of the angular-overlap parameters deduced by such comparisons would of course depend on the quality of the calculations.

In this paper we compare angular-overlap and *ab initio* calculations on two series of complexes. The first is the series $[MnF_{6-i}Cl_i]^{k-}$ ($k = 2$ or 4, $i = 1$—6). The complexes are assumed to have octahedrally directed bonds (are orthoaxial). The second is the series $[MnF_6]^{k-}$ ($k = 2$ or 4), in which the metal–ligand bond directions are displaced from octahedral.

CALCULATIONS ON ORTHOAXIAL COMPLEXES

$[MnX_6]^{2-}$ is a d^3 system and in an octahedral field the ground state is $^4A_{2g}$. Excited doublet states are sufficiently high in energy that the ground state is also a quartet in all lower-symmetry structures that we examined. $[MnX_6]^{4-}$ is d^5 and in a weak octahedral field the ground state is $^6A_{1g}$. The ground states of both $[MnF_6]^{4-}$ and $[MnCl_6]^{4-}$ are known to have this designation and it is reasonable to assume that all systems we considered of lower symmetry are sextet states.

To make the calculation computationally inexpensive we have chosen a non-empirical valence-electron model[7] rather than full *ab initio* calculations. The model has been fully described in previous papers and used for predictive purposes.[8,9] Because all the complexes have the same number of valence orbitals the convergence of the SCF procedure for the whole series can be started from the converged vectors of a high-symmetry member of the series, and this gave a significant saving in computer time.

Metal–halogen bond lengths were taken from the experimental values of $[MnF_6]^{2-}$ and $[MnCl_6]^{2-}$ in $K_2[MnX_6]$:[10,11] Mn–F 1.74, Mn–Cl 2.28 Å. They were assumed constant for all compounds including the d^5 complexes; this assumption enabled us to use a common set of integrals for d^3 and d^5 calculations.

To further limit the computational requirements we restricted the orbital basis to a minimal description of the halogen ligands. It is not too expensive to take a larger basis for the metal, for example, choosing *d* orbitals at the double-zeta level, but such an unbalanced basis set may lead to a charge distribution which is far from the correct value. Preliminary calculations showed that with a double-zeta *d* basis the diffuse component of the 3*d* orbital was compensating for a relatively poor description of the ligands. The basis used is described in Table 1. We are making no claim that this is optimal for its size for the systems studied but we believe it has a reasonable compromise between balance and accuracy for our purposes.

TABLE 1

Summary of the basis *

Atom type	Core orbitals		Valence orbitals	
Mn	1*s*, 2*s*, 2*p*	STO–3G	3*s*, 3*p*	STO–3G
			3*d*	5G
			4*s*, 4*p*	1G
F	1*s*	STO–3G	2*s*	STO–3G
			2*p*	4G
Cl	1*s*, 2*s*, 2*p*	STO–3G	3*s*, 3*p*	STO–3G

* STO–3G using exponents of E. Clementi and D. L. Raimondi, *J. Chem. Phys.*, 1963, **38**, 2686; 5G, compact part of the double-zeta basis of P. J. Hay, *J. Chem. Phys.*, 1977, **66**, 4377; 1G, single Gaussian with exponent 0.32 after J. Demuynck, A. Veillard, and V. Waulgren, *J. Amer. Chem. Soc.*, 1973, **95**,5563, 4G, four-Gaussian fit to the Hartree–Fock 2*p* atomic orbital (R. F. Stewart, *J. Chem. Phys.*, 1969, **50**, 2485.

Examination of the orbital wavefunctions showed that the singly occupied orbitals for d^5 systems were 95% composed of *d* functions and the same was true of the singly occupied orbitals and two lowest virtual orbitals in the d^3 systems.

Figure 1 shows the orbital energies calculated for the series $[MnF_{6-i}Cl_i]^{k-}$ in a way that brings out the orbital correlations in the series. The occupied-virtual splitting in the d^3 ions is much larger than the corresponding splitting in d^5 and this is a property of the SCF Hamiltonian. To obtain a t_{2g}—e_g splitting for the d^3 case that can be directly compared to experiment it would be necessary to make a

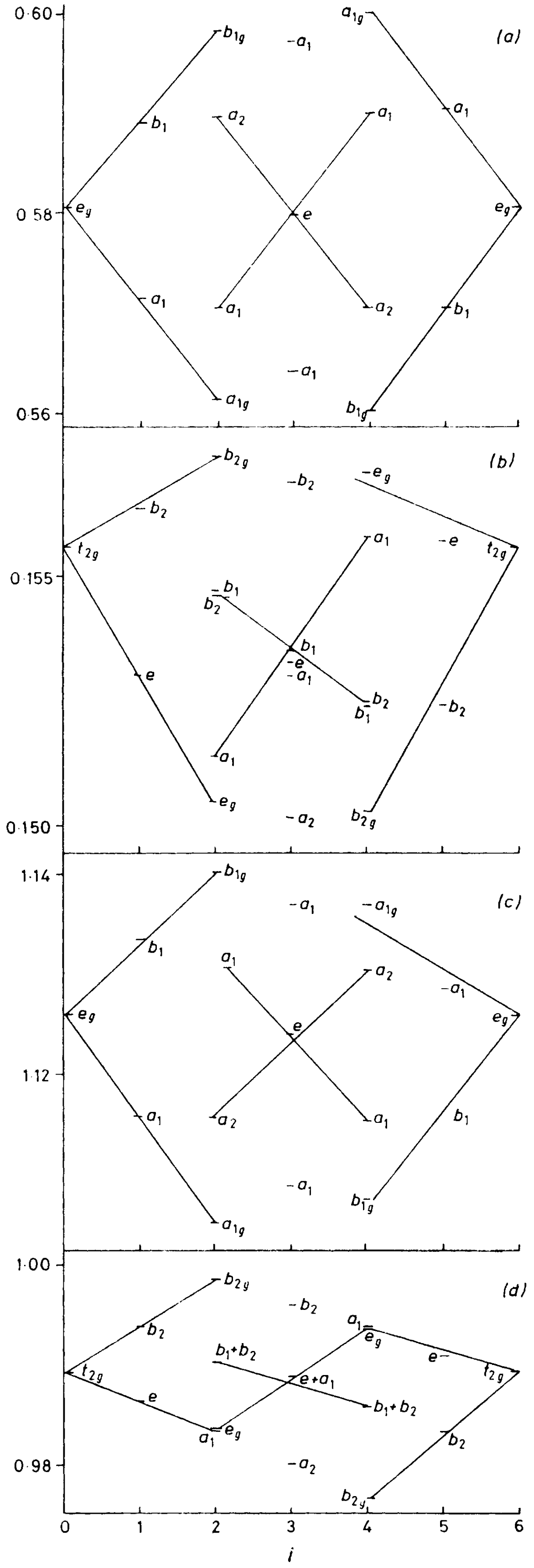


FIGURE 1 Calculated orbital energies for the series $[MnF_{6-i}Cl_i]^{k-}$ transformed according to equation (1): $k = 2$ (*a*, *b*) or 4 (*c*, *d*); $E(6) - E(0) = 0.0067$ (*a*), -0.0352 (*b*), -0.1275 (*c*), or -0.2037 E_h (*d*). The lines which pass through or close to calculated points have been inserted to bring out more clearly the pattern between the calculated orbital energies

separate calculation on a configuration with the e_g orbital occupied.

We shall separately consider the behaviour of the e_g and t_{2g} sets of both ion types. A t_{2g} set is defined as the orbitals that originate as t_{2g} in octahedral symmetry and which are split in lower symmetries. Within each set we make a linear transformation such that the orbital energies of the two octahedral ions are equal. This can be achieved by defining an energy E' as in equation (1) where $E(i)$ is an

$$E'(i) = E(i) + [(3 - i)/6][E(6) - E(0)] \qquad (1)$$

orbital energy of a complex with i chlorine ligands. There will be one such transformation for each of the four sets. Energy differences for isomers within a set are unaffected by the transformation. The calculated values of $E'(i)$ are shown in Figure 1.

The symmetry apparent in Figure 1 leads one to expect that the orbital energies can be represented by an empirical Hamiltonian of simple form, possibly a one-electron Hamiltonian. Points to be noted are: (*a*) the symmetry centre shown by each t_{2g} and e_g orbital set at the degenerate (*e*) orbital for the *fac*-$[\mathrm{MnF_3Cl_3}]^{k-}$ structure; (*b*) the existence of near degeneracies such as those in the t_{2g} orbital set between b_1 and b_2 orbitals for *cis*-$[\mathrm{MnX_4Y_2}]^{k-}$, and a_1 and e_g orbitals of *cis*- and *trans*-$[\mathrm{MnX_4Y_2}]^{k-}$; (*c*) the splittings of both the t_{2g} and e_g are twice as large for *trans*-$[\mathrm{MnX_4Y_2}]^{k-}$ as for $[\mathrm{MnX_5Y}]^{k-}$; (*d*) that the t_{2g} orbital set forms a parallelogram grid [shown particularly in Figure 1(*d*)]; and (*e*) the mirror planes in the horizontal and vertical axes through the symmetry centre of the e_g sets.

MODEL HAMILTONIANS

Before turning to the angularly distorted structures, we establish a model one-electron Hamiltonian whose eigen-

$$\mathscr{H} = \Sigma_{k=1}^{6} \mathrm{A}^k \qquad (2)$$

$$A_{11}^1 = \langle d_{z^2}|\mathrm{A}^1|d_{z^2}\rangle = \mathrm{e}_\sigma \qquad (3)$$

$$A_{22}^1 = \langle d_{xz}|\mathrm{A}^1|d_{xz}\rangle = \mathrm{e}_\pi \qquad (4)$$

$$A_{33}^1 = \langle d_{yz}|\mathrm{A}^1|d_{yz}\rangle = \mathrm{e}_\pi \qquad (5)$$

$$A_{44}^1 = \langle d_{xy}|\mathrm{A}^1|d_{xy}\rangle = \mathrm{e}_\delta \qquad (6)$$

$$A_{55}^1 = \langle d_{x^2-y^2}|\mathrm{A}^1|d_{x^2-y^2}\rangle = \mathrm{e}_\delta \qquad (7)$$

$$A^k = \tilde{F}^{(d)}(\theta_k,\phi_k)A^1F^{(d)}(\theta_k,\phi_k) \qquad (8)$$

values simulate the calculated orbital energies of the last section and which is consistent with the basic tenets of the angular-overlap model. We assume that the Hamiltonian is the sum of separate operators A^k for each ligand (k) [equation (2)] and that A^k is invariant to rotation about the M–X^k bond (we only consider linearly ligating ligands). Thus the 5 × 5 d orbital matrix of any A^k can be diagonalised to σ, $\pi(2)$, and $\delta(2)$ components. This allows the effect of an individual ligand to be parameterised by three matrix elements.

Taking M–X^1 to define the z direction, the matrix of A^1 is diagonal with elements (3)—(7).* The matrix A^k will therefore be obtained from A^1 by the matrix transformation (8) where $F^{(d)}$ is the orthogonal matrix known as the angular-overlap matrix [equation (9)]. For example, for a ligand on the x axis [ligand 2 with polar co-ordinates $(\pi/2, 0)$], application of (9) gives (10), and for ligand 3 on the y axis we obtain (11). As the d-orbital basis is of even inversion symmetry, elements of A^k are the same for ligands along the positive and negative directions of a Cartesian axis.

$$A^2 = \begin{bmatrix} \frac{1}{4}(\mathrm{e}_\sigma + 3\mathrm{e}_\delta) & 0 & 0 & 0 & -(3^{\frac{1}{2}}/4)(\mathrm{e}_\sigma - \mathrm{e}_\delta) \\ 0 & \mathrm{e}_\delta & 0 & 0 & 0 \\ 0 & 0 & \mathrm{e}_\pi & 0 & 0 \\ 0 & 0 & 0 & \mathrm{e}_\pi & 0 \\ -(3^{\frac{1}{2}}/4)(\mathrm{e}_\sigma - \mathrm{e}_\delta) & 0 & 0 & 0 & \frac{1}{4}(3\mathrm{e}_\sigma + \mathrm{e}_\delta) \end{bmatrix} \qquad (10)$$

$$A^3 = \begin{bmatrix} \frac{1}{4}(\mathrm{e}_\sigma + 3\mathrm{e}_\delta) & 0 & 0 & 0 & (3^{\frac{1}{2}}/4)(\mathrm{e}_\sigma - \mathrm{e}_\delta) \\ 0 & \mathrm{e}_\pi & 0 & 0 & 0 \\ 0 & 0 & \mathrm{e}_\delta & 0 & 0 \\ 0 & 0 & 0 & \mathrm{e}_\pi & 0 \\ (3^{\frac{1}{2}}/4)(\mathrm{e}_\sigma - \mathrm{e}_\delta) & 0 & 0 & 0 & \frac{1}{4}(3\mathrm{e}_\sigma + \mathrm{e}_\delta) \end{bmatrix} \qquad (11)$$

If the matrix H is constructed for an octahedral complex

$$E(t_{2g}) = 4\mathrm{e}_\pi + 2\mathrm{e}_\delta \qquad (12)$$

$$E(e_g) = 3\mathrm{e}_\sigma + 3\mathrm{e}_\delta \qquad (13)$$

from the A^k matrices defined above, then its eigenvalues are as in (12) and (13). The splitting between the two levels is as in (14).

$$\Delta_{\mathrm{oct}} = 3\mathrm{e}_\sigma - 4\mathrm{e}_\pi + \mathrm{e}_\delta \qquad (14)$$

For a mixed-ligand complex $[\mathrm{MnF}_{6-i}\mathrm{Cl}_i]^{k-}$ the eigenvalues can be expressed in terms of e_λ for Cl and F ligands or the difference between them if any two members of the series are compared. We thus define a set of parameters (15) in

$$\mathrm{f}_\lambda = \mathrm{e}_\lambda(\mathrm{Cl}) - \mathrm{e}_\lambda(\mathrm{F}) \text{ where } \lambda = \sigma, \pi, \text{ or } \delta \qquad (15)$$

terms of which we can represent all such differences. If however we scale our energies according to the same formula as (1) then the eigenvalues of H' [equation (16)] can be

$$H'(i) = H(i) + [(3 - i)/6][H(6) - H(0)] \qquad (16)$$

expressed in terms of two parameters: $\mathrm{f}'_\sigma = \mathrm{f}_\sigma - \mathrm{f}_\delta$ for the e_g set and $\mathrm{f}'_\pi = \mathrm{f}_\pi - \mathrm{f}_\delta$ for the t_{2g} set. The splittings expressed in these units are relative to mean values of $i(2\mathrm{f}_\pi + \mathrm{f}_\delta)$ and $(3i/2)(\mathrm{f}_\sigma + \mathrm{f}_\delta)$ for the t_{2g} and e_g orbital sets respectively and are given in Table 2.

$$^{(d)} = \begin{bmatrix} \frac{1}{4}(1 + 3\cos2\theta) & 0 & -(3^{\frac{1}{2}}/2)\sin2\theta & 0 & (3^{\frac{1}{2}}/4)(1 - \cos2\theta) \\ (3^{\frac{1}{2}}/2)\sin\phi\sin2\theta & \cos\phi\cos\theta & \sin\phi\cos2\theta & -\cos\phi\sin\theta & -\frac{1}{2}\sin\phi\sin2\theta \\ (3^{\frac{1}{2}}/2)\cos\phi\sin2\theta & -\sin\phi\cos\theta & \cos\phi\cos2\theta & \sin\phi\sin\theta & -\frac{1}{2}\cos\phi\sin2\theta \\ (3^{\frac{1}{2}}/4)\sin2\phi(1 - \cos2\theta) & \cos2\phi\sin\theta & \frac{1}{2}\sin2\phi\sin2\theta & \cos2\phi\cos\theta & \frac{1}{4}\sin2\phi(3 + \cos2\theta) \\ (3^{\frac{1}{2}}/4)\cos2\phi(1 - \cos2\theta) & -\sin2\phi\sin\theta & \frac{1}{2}\cos2\phi\sin2\theta & -\sin2\phi\cos\theta & \frac{1}{4}\cos2\phi(3 + \cos2\theta) \end{bmatrix} \qquad (9)$$

We note that as we have the absolute values for the orbital energies it is possible to determine all three f_λ parameters whereas only information about the splittings is required to get the two f'_λ parameters. Experimentally it is usually only possible to obtain information about the splittings and not the absolute energies. Thus e'_λ parameters [equation (17)] are generally deduced from experiment.

$$\mathrm{e}'_\lambda = \mathrm{e}_\lambda - \mathrm{e}_\delta \text{ where } \lambda = \sigma \text{ or } \pi \qquad (17)$$

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* To conform with convention these are given the symbol e, which we trust will not be confused with the group-theory symbol.

PARAMETER FITTING

In contrast to the usual experimental situation, from calculation we have more data than parameters: 38 distinct orbital energies for each $[MnF_{6-i}Cl_i]^{k-}$ series to fit three f_λ parameters. We can thus adopt a least-squares fit using suitable differences between members of the series. Since the equations relating parameters and energies are linear this fitting can be accomplished analytically.

TABLE 2

Coefficients of the f'_λ parameters for all complexes considered: $\lambda = \sigma$ for the e_g set and $\lambda = \pi$ for the t_{2g} set. The eigenvalues have been identified by the *d*-orbital Cartesian equivalent, although for *cis* and *mer* complexes there is mixing of these

i	0	1	2	2	3	3	4	4	5	6
Isomer			*cis*	*trans*	*fac*	*mer*	*cis*	*trans*		
z^2	0	$\frac{1}{2}$	$-\frac{1}{2}$	1	0	$(3^{\frac{1}{2}}/2)$	$\frac{1}{2}$	-1	$-\frac{1}{2}$	0
$x^2 - y^2$	0	$-\frac{1}{2}$	$\frac{1}{2}$	-1	0	$-(3^{\frac{1}{2}}/2)$	$-\frac{1}{2}$	1	$\frac{1}{2}$	0
xy	0	$-\frac{2}{3}$	$-\frac{1}{3}$	$-\frac{4}{3}$	0	1	$\frac{1}{3}$	$\frac{4}{3}$	$\frac{2}{3}$	0
xz	0	$\frac{1}{3}$	$-\frac{1}{3}$	$\frac{2}{3}$	0	0	$\frac{1}{3}$	$-\frac{2}{3}$	$-\frac{1}{3}$	0
yz	0	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{2}{3}$	0	-1	$-\frac{2}{3}$	$-\frac{2}{3}$	$-\frac{1}{3}$	0

From the transformed energies (11) optimum values of f'_σ and f'_π are calculated and each of the means provides a separate fitting to f_δ. In fact the separate fittings give almost the same value for f_δ (0.003 4E_h and 0.003 6E_h for the dinegative ions and −0.026 0E_h and −0.025 8E_h for the tetranegative ions). We have therefore used an average in each case; the optimum f_λ parameters are given in Table 3.

A comparison of the calculated and model orbital energies is shown in Figure 2. The poorest fitting is for the t_{2g} set of the dinegative complexes [Figure 2(*b*)] and this is to be expected from Figure 1(*b*) which has a less perfect symmetry than the others; however, we note the greatly expanded energy scale of Figure 2(*b*) compared to the others.

TABLE 3

Optimised f_λ parameters (in E_h) * for the series $[MnF_{6-i}Cl_i]^{k-}$ (i = 1—6)

	f_σ	f_π	f_δ
$k = 2$	−0.0156	−0.0001	0.0035
$k = 4$	−0.0425	−0.0339	−0.0259

* Throughout this paper: 1E_h = 2 626 kJ mol^{-1}.

From Table 3, f_σ is much larger than f_π and f_δ as is expected. It must be remembered that these parameters represent the difference between Cl and F ligands and we are

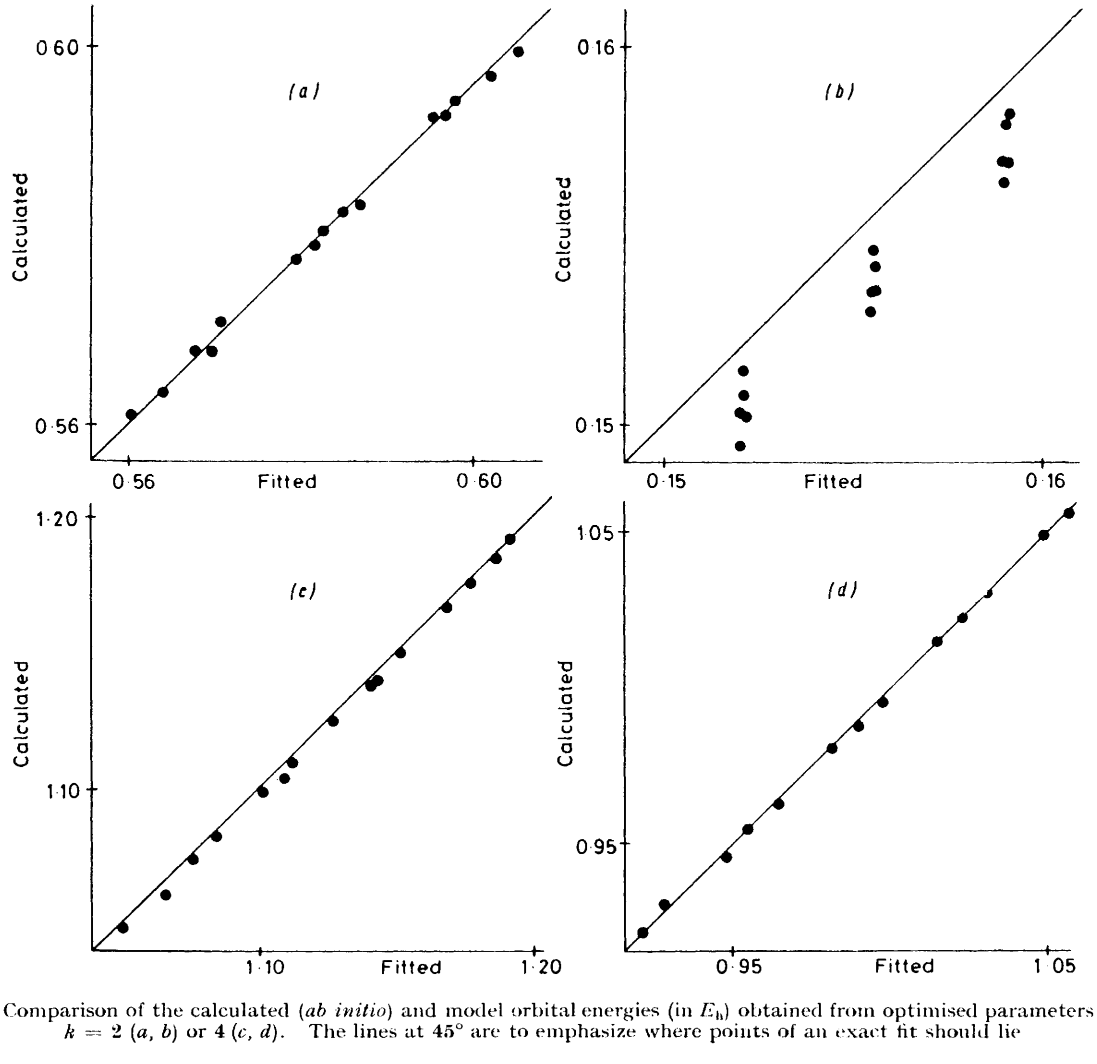

FIGURE 2 Comparison of the calculated (*ab initio*) and model orbital energies (in E_h) obtained from optimised parameters (Table 3): k = 2 (*a, b*) or 4 (*c, d*). The lines at 45° are to emphasize where points of an exact fit should lie

led to conclude that there is a larger difference in σ metal–ligand interaction between these ligands than there is between π and δ interaction. Whether the term ' interaction ' can be replaced by ' bonding ' is arguable. Since there are no *d* orbitals on the ligands there is no δ bonding in the normal sense, but a δ electrostatic effect is present.

THE EFFECT OF ANGULAR DISTORTIONS

To examine the predictions of the angular-overlap model for bond-angle distortion we have studied the change in orbital energies of $[MnF_6]^{k-}$ ($k = 2$ or 4) when the two *z*-axis ligands are displaced to polar angles (θ, ϕ) and $(\pi - \theta, \phi)$ respectively. All Mn–F bond lengths were kept constant. The lowest symmetry of the distorted complex is C_s. Calculations were made for $\theta = 5$ and 10° with $\phi = 0$, 15, 30, and 45° (values of ϕ outside this range are related by symmetry).

For all values of ϕ the orbital energies in the e_g and t_{2g} sets were found to vary as $\sin^2\theta$ over the range of θ examined. We therefore show in Table 4 the energies relative to the undistorted structure for $\theta = 10°$ only. The most striking feature of these results is that the dependence on ϕ is very weak.

TABLE 4

Calculated orbital-energy differences (in E_h) between distorted (with $\theta = 10°$) and undistorted $[MnF_6]^{k-}$. The eigenvalues are the Cartesian components of the dominant *d* orbital; for $\phi = 45°$ the t_{2g} components are $yz - xz$, xy, and $yz + xz$ respectively

		$\phi/°$	0	15	30	45
(*a*)	$k = 2$	z^2	−0.0042	−0.0042	−0.0041	−0.0041
		$x^2 - y^2$	0.0052	0.0051	0.0050	0.0049
(*b*)	$k = 2$	yz	0.0032	0.0031	0.0028	0.0027
		xy	0.0050	0.0049	0.0049	0.0049
		xz	0.0119	0.0120	0.0122	0.0123
(*c*)	$k = 4$	z^2	−0.0080	−0.0080	−0.0080	−0.0080
		$x^2 - y^2$	0.0005	0.0003	0.0002	0.0002
(*d*)	$k = 4$	yz	−0.0012	−0.0013	−0.0014	−0.0015
		xy	0.0003	0.0003	0.0003	0.0003
		xz	0.0045	0.0046	0.0047	0.0048

Looking at the results in the spirit of the a.o.m. described in Model Hamiltonians, the perturbation Hamiltonian (*i.e.* the difference between *H* for the distorted and undistorted structures) for the displaced structure is, from (8), given by equation (18). From (9) the matrix $H'(\theta, \phi)$ can be shown to have the non-zero elements (19)—(24) which

$$H'(\theta, \phi) = \tilde{F}^{(d)}(\theta, \phi)A^1F^{(d)}(\theta, \phi) + \tilde{F}^{(d)}(\pi - \theta, \phi)A^1F^{(d)}(\pi - \theta, \phi) - 2A^1 \quad (18)$$

$$H'_{11} = -\tfrac{3}{8}(5 + 3\cos2\theta)(1 - \cos2\theta)e'_\sigma + \tfrac{3}{2}\sin^2 2\theta\ e'_\pi \quad (19)$$

$$H'_{15} = H'_{51} = (3^{\frac{1}{2}}/8)(1 - \cos2\theta)(1 + 3\cos2\theta) - (3^{\frac{1}{2}}/2)\sin^2 2\theta\ e'_\pi \quad (20)$$

$$H'_{22} = -2\sin^2\theta\ e'_\pi \quad (21)$$

$$H'_{33} = \tfrac{3}{2}\sin^2 2\theta\ e'_\sigma - 2\sin^2 2\theta\ e'_\pi \quad (22)$$

$$H'_{44} = 2\sin^2\theta\ e'_\pi \quad (23)$$

$$H'_{55} = \tfrac{3}{8}(1 - \cos2\theta)^2\ e'_\sigma + \tfrac{1}{2}\sin^2 2\theta\ e'_\pi \quad (24)$$

depend on the e'_λ parameters defined by (17). The only non-zero off-diagonal element is $H'_{15} = \langle z^2|H'|x^2 - y^2\rangle$ which is at first sight surprising because for a general angle ϕ the matrix should be symmetry factorised into 3 × 3 (symmetry *A'*) and 2 × 2 (*A''*) blocks. The angular-overlap Hamiltonian (for linearly ligating ligands) therefore has a higher symmetry within a *d*-orbital basis than the full Hamiltonian.

We note the following properties of *H'*. (*i*) The elements have no dependence on ϕ. (*ii*) The orbital energies can be shown to have a $\sin^2\theta$ dependence for small values of θ. The diagonal t_{2g} block of *H'* depends on $\sin^2\theta$ or $\sin^2 2\theta$ (which is approximately $4\sin^2\theta$ for small θ). For the e_g block the trace of the 2 × 2 matrix is as in equation (25) and the determinant is as in (26). It follows that the eigenvalues which obey equation (27) will depend on $\sin^2\theta$.

$$T = (2e'_\pi - \tfrac{3}{2}e'_\sigma)\sin^2 2\theta \quad (25)$$

$$D = -3\sin^4\theta(e'_\sigma)^2 \quad (26)$$

$$\lambda^2 - T\lambda + D = 0 \quad (27)$$

(*iii*) The trace of *H'* (the average energy of the *d* orbitals) is independent of (θ, ϕ).

Points (*i*) and (*ii*) are consistent with the calculated results shown in Table 4, but point (*iii*) is not. The net shift of the orbital energies is not predicted by the a.o.m. and we deduce that it arises from a charge redistribution on the complexes as they are distorted. A Mulliken population analysis of the orbitals confirms this and shows an electron shift from the ligands to the metal which is proportional to $\sin^2\theta$.

In order to fit the changes in calculated orbital energies with angular-overlap parameters it is therefore necessary to introduce a further parameter $\eta\sin^2\theta$ to accommodate the shift in the sum of orbital energies discussed above. This transforms [*cf.* (19)—(24)] as in equation (28). Fitting

$$K'_{ij} = H'_{ij} + \delta_{ij}\ \eta\sin^2\theta \quad (28)$$

can then be achieved using the diagonal t_{2g} block of *K'* and checked against the e_g block. Table 5 gives the values for e'_σ, e'_π, and η. These parameters obey (27) for the e_g orbital set in a satisfactory manner.

TABLE 5

e'_λ (F) and η parameters (in E_h) as fitted for the t_{2g} orbital set of distorted $[MnF_6]^{k-}$, and comparison between calculated and fitted levels for the e_g orbital set using these values; λ_1 and λ_2 are the roots of expression (27)

	e'_σ	e'_π	η
$k = 2$	0.0663	0.0158	0.1380
$k = 4$	0.0498	0.0141	−0.0279

	$\lambda_1 + \lambda_2$		$(-\lambda_1\lambda_2)^{\frac{1}{2}}$	
	Calc.	Fitted	Calc.	Fitted
$k = 2$	−0.0060	−0.0054	0.0028	0.0026
$k = 4$	−0.0075	−0.0079	0.0026	0.0034

COMPARISON WITH EXPERIMENT

By adding e'_λ(F) [equation (17)] and f'_λ [$= e'_\lambda$(Cl) − e'_λ(F)] it is possible to obtain values for e'_λ(Cl) as well as e'_λ(F); these may be compared with experimental results where available. Glerup *et al.*[12] have determined these parameters using the spectra of *trans*-$[Cr(amine)_4A(B)]^{n+}$ (amine = NH_3 or pyridine; A, B = F^-, Cl^-, Br^-, OH_2, OH^-, *etc.*) complexes. Although our parameters for manganese complexes are not directly transferable to chromium(III) complexes a comparison is nevertheless interesting as one would expect ratios between parameters to be similar. Table 6 gives such a comparison. Although our parameters are approximately double those obtained for Cr^{III} the ordering and relative magnitude are in good agreement.

TABLE 6

Angular-overlap parameters in E_h ($1E_h = 2.159 \times 10^5$ cm^{-1}) from this work and derived experimentally [12] for Cr^{III}

	Mn^{IV}	Mn^{II}	Cr^{III}
e'_σ(Cl)	0.0472	0.0332	0.0252
e'_π(Cl)	0.0122	0.0061	0.0040
e'_σ(F)	0.0663	0.0498	0.0336
e'_π(F)	0.0158	0.0141	0.0077

Glerup *et al.*[12] also consider a scheme similar to ours for analysing the experimental spectra of the series $[Cr(OH_2)_{6-i}(NH_3)_i]^{3+}$ (i = 1—6) because spectral data for ten isomers were available. However, they concluded that their fitting was unreliable as the water ligand appears to change its mode of ligation between members of the series.

CONCLUSION

Contrary to our expectation when starting this project we have found that the *d*-orbital energies obtained from non-empirical SCF molecular orbital calculations can be modelled accurately by the angular-overlap model. The only modification that we have found necessary to achieve a fit between the two sets of energies was to add a parameter representing charge redistribution for the distorted $[MnF_6]^{k-}$ structures.

The SCF calculations allow one to make a more detailed analysis of the a.o.m. than does experiment because absolute values of the parameters $e_\lambda(\lambda = \sigma, \pi,$ or $\delta)$ can be obtained; from experiment one normally has only sufficient information to obtain the differences $e'_\sigma = e_\sigma - e_\delta$ and $e'_\pi = e_\pi - e_\delta$. Our calculations show that there is no justification in equating e_λ with e'_λ, *i.e.* in neglecting e_δ. We found that the difference in e_δ between F and Cl is of similar magnitude to the difference in e_π values.

Finally we recognize that our calculations have provided a test for the a.o.m. only for complexes in which their is little metal–ligand covalent bonding. Unfortunately covalent bonding ligands are computationally more demanding because they are necessarily polyatomic and at the present time a series of calculations of the type we have made using CN^- ligands, say, would be difficult to justify.

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