Is the Angular Overlap Model Chemically Significant?

By **Malcolm Gerloch**, University Chemical Laboratories, Lensfield Road, Cambridge CB2 1EW
R. Guy Woolley,* Cavendish Laboratory, Madingley Road, Cambridge CB3 0HE

Recent comments on the transferability of angular overlap parameters and a criticism of the practice of setting $e_\delta \approx 0$ are discussed, and arguments in favour of $e_\delta \approx 0$ are presented. It is emphasised that the angular overlap model is a sub-division of ligand-field theory, qualitatively distinct from molecular-orbital theory.

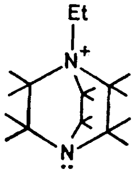
WHILE the angular overlap model (a.o.m.) [1-5] has enjoyed increasing attention and success of late, it has frequently been misunderstood. We must recognize at the outset the central promise of the a.o.m., which is to bring to ligand-field theory the notion of the functional group, a concept of obvious ubiquity and utility throughout chemistry in general. As argued recently,[6] we have little taste for the older, global parameterization of ligand fields in which quantities like Dq, Dt, Ds, $D\tau$, $D\sigma$ merely recast experimental data in a manner reflecting total molecular symmetry and fail to suggest and correlate with the features of chemical bonding which are central in chemical thinking. Further, any remaining advantages conferred by such parameterization schemes are lost in applications to molecules with little or no symmetry which are, after all, the norm. The a.o.m. has modest aims, however. It is no more than a scheme by which the global ligand field may be factored into spatially discrete regions of space so that local interactions relating to individual metal–ligand bonds may be identified and semi-quantitatively characterized with respect to ligand σ and π donor or acceptor function.

DISCUSSION

Some recent achievements in this area are illustrated by the data collected in the Table, showing a.o.m. parameters derived from various studies of the optical and e.s.r. spectroscopic and paramagnetic susceptibility properties of transition-metal complexes, frequently as single crystals. Sensible, although not invariably totally expected, trends in both a.o.m. and interelectron repulsion parameters are evident in these data, some of which we briefly review.

The first seven complexes in the Table involve nickel(II) and cobalt(II) approximately tetrahedrally co-ordinated by phosphine and halogen ligators. Each independently evidences a strong π-acceptor role for the phosphines and in those complexes with two phosphine ligands [(3)—(7)] electron drift from the metal to the π acids appears [7] to be compensated by a marked increase in π-donor strength of the halogens in line with the electroneutrality principle. Comparing (1) and (2), the lesser σ-donor strength of three iodines relative to three bromines is accompanied by a greater σ-donor role for the phosphine: [8] this is demonstrated not only by the a.o.m. e_σ(P) values but also by the Ni–P bond lengths (2.32 and 2.28 Å in the bromo-[9] and iodo-complexes,[10] respectively). The large nephelauxetic effects observed throughout the series of phosphine complexes have been interpreted [7] to reflect the extensive π-bond network in these species and the B values for the first two systems also evidence the softer nature of the iodine ligands.

Complexes (8)—(11) involve almost perfectly trigonally distorted tetrahedral co-ordination of nickel(II) and cobalt(II) by one tertiary amine (L^2) and three halogens. The single-crystal spectral and magnetic properties of these compounds are well reproduced [11] with a



L^2

a.o.m. Parameters derived from various studies [a]

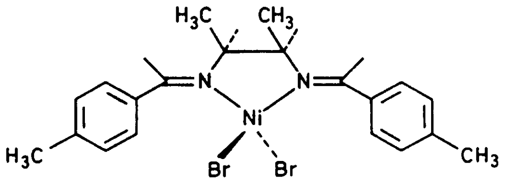
	Complex	e_σ(P)	e_π(P)	e_σ(Hal)	e_π(Hal)	e_σ(N)	$e_{\pi\perp}$(N)	B	Ref.
(1)	$[Ni(PPh_3)Br_3]^-$	5 000	−1 500	3 000	700			620	7, 8
(2)	$[Ni(PPh_3)I_3]^-$	6 000	−1 500	2 000	600			490	7, 8
(3)	$[Ni(PPh_3)_2Cl_2]$	(4 500)	(−2 500)	(4 500)	(2 000)			(550)	*b*
(4)	$[Ni(PPh_3)_2Br_2]$	(4 000)	(−1 500)	(4 000)	(1 500)			(550)	*b*
(5)	$[Co(PPh_3)_2Cl_2]$	(4 000)	(−1 000)	(3 500)	(2 000)			(575)	*b*
(6)	$[Co(PPh_3)_2Br_2]$	(3 500)	(−1 000)	(3 500)	(1 500)			(575)	*b*
(7)	$[NiL^1Cl_2]$ [c]	5 000	−1 500	3 600	1 500			550	7
(8)	$[NiL^2Cl_3]$			3 250	1 000	6 100	0	760	7, 11
(9)	$[NiL^2Br_3]$			3 000	850	5 900	0	720	7, 11
(10)	$[CoL^2Cl_3]$			3 500	1 100	4 250	0	740	11
(11)	$[CoL^2Br_3]$			3 500	1 000	4 000	0	700	11
(12)	$[NiL^3Br_3]^-$ [d]			3 600	500	3 600	−600	720	7, 13
(13)	$[CoL^3Br_3]^-$ [d]			3 000	450	3 500	−500	670	13
(14)	$[NiL^4Br_2]$ [e]			3 500	850	4 200	−1 000	790	7
(15)	$[NiL^5Br_2]$			3 500	800	5 200	(−250)	630	7
(16)	$[NiL^6{}_2]$					(4 000)	+900	(660)	7, 14

[a] Values in parentheses are less well determined. [b] J. E. Davies, M. Gerloch, and D. J. Phillips, *J. Chem. Soc., Dalton Trans.*, 1979, 1836. [c] $L^1 = Ph_2PCH_2CH_2{-}O{-}CH_2CH_2PPh_2$. [d] L^3 = Quinoline. [e] L^4 = Biquinoline.

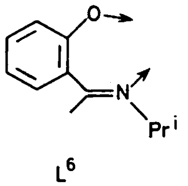
vanishing π interaction, although the point is not definitively proved. The relative behaviour of chlorine and bromine in these systems is as expected and the higher B values (relative to those in the phosphine complexes) are in line with the diminished π delocalization. The most notable feature of the a.o.m. parameters in this series, however, concerns the much larger e_σ(amine) values in the d^8 systems. Corresponding d^1 calculations with the values given in the Table show that the extra electron gained on replacing cobalt(II) by nickel(II) occupies the $d_{x^2-y^2}/d_{xy}$ orbital pair, where z is taken parallel to the metal–amine vector. It has been argued [11] that the ensuing attenuation in metal acceptor role associated with these functions tends to decrease the transfer of negative charge from the halogens in the nickel complex, approximately cancelling any increase due to the increased effective nuclear charge on the metal. In consequence, the tertiary amine interacts more strongly in the nickel species, so tending to maintain a more even distribution of charge, as required by the electroneutrality principle. Detailed bond lengths throughout this series of complexes again reflect these trends.[11,12]

Quinoline [13] and biquinoline [7] are shown to act as significant π acids in the complexes (12)—(14): the greater π-acceptor role of the biquinoline ligand is consistent with the common property of this group as tending to stabilize lower oxidation states in the transition-metal series.

The last pair of systems [7] [(15) and (16)] included in the Table illustrate the variability of the imine π function. Angular-overlap e parameters reflect the net influence of ligand donor and acceptor functions and the greater (that is, positive) $e_{\pi\perp}$ value [14] for the imine ligator (L^6) in the salicylaldiminato-complex, (16), is taken to indicate an enhanced role of the π function due to the presence of the electron-rich phenolic oxygen nearby, in contrast with a dominant π^* acceptor role for the simple imines (L^5) [7] in (15). The low Racah B values in both complexes appear to support the idea [7] of moderately extensive π-bonding roles for both ligands, but reflect the *gross* π network (involving both π and π^* ligand functions), while the a.o.m. e parameters reflect the *net* π bonding.



(15)

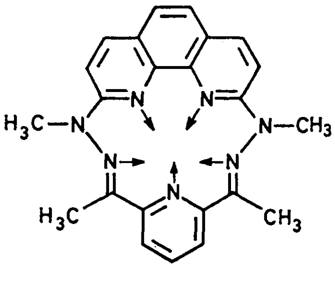


L^6

Altogether there can be little doubt of the empirical utility and overall relevance of the angular overlap model. The a.o.m. parameter values describe, *inter alia*, variations in charge distribution in these and other complexes studied so far, which correlate, albeit in a semi-quantitative fashion only, with ligand electrophilicity or nucleophilicity; with our preconceptions of the separate roles of σ and π bonding, especially with regard to the concept of 'synergic back-bonding'; generally with the electroneutrality principle; and with detailed bond-length variations within the co-ordination shell. Tennyson and Murrell [15] have argued recently, however, that a strength of the a.o.m. approach is the transferability of parameter values with ligand as a means of reducing the degree of parameterization engendered in low-symmetry systems.

First we must note that the number of degrees of freedom is often not excessive because, for example, ligands in essentially chemically equivalent environments may be assigned common parameters, or again because we may often work with complexes involving some linear ligators (so that $e_{\pi x} = e_{\pi y}$). Further, values are best determined for the resulting parameter set by reference to more than one ligand-field property: measurements of single-crystal magnetic susceptibilities and e.s.r. g values are especially valuable complements to optical spectroscopy in this respect. Part of the problem of overparameterization, it has been suggested,[15] arises from there being a maximum of 'only five d orbital energies to measure'.[15] This is not so, however, for in general within the global frame, the one-electron ligand-field potential is not a diagonal operator within a symmetry-defined d orbital basis so that with the combined use of spectroscopic and magnetic techniques we may hope to determine a maximum of 15 independent matrix elements. Empirically it is true that special problems of pseudo-symmetry, of holohedral symmetry,[4] for example, may prevent accurate (rarely better than 10%) estimates of all variables in the model being obtained, but these difficulties arise from practice rather than principle.

Secondly, however, the notion of transferability of a.o.m. parameters is only qualitatively helpful at best and can be totally misleading on occasion. This can be seen at an empirical level from the Table and discussions above. A further, and dramatic, example derives from a recent analysis [16] of the spectroscopic and magnetic properties of two seven-co-ordinate complexes $[ML(OH_2)_2]^{2+}$; M = Co^{II} or Ni^{II} and L is the, essentially planar, quinquedentate macrocycle (17). The a.o.m. parameters determined for the phenanthroline moiety in these complexes characterize a strong σ-donor role, which is not unexpected, but also a strong *π-donor* role, which is. There is little doubt that the π-bonding properties of this group have been greatly modified by the adjacent, electron-rich, non-co-ordinating amines in the macrocycle. None of this should occasion much surprise, of course, for while a given ligand may act in a ' typical ' way, other things being equal, there is no reason to suppose that its role should not be modified by the metal together with its other ligands. This is, after all, the stuff of chemistry, so that fixing a.o.m. parameter values from one system to another, as recently suggested,[15] effectively pre-empts the potential of the a.o.m. approach. Apart from this fundamental objection, we note that the procedure frequently fails in practice.



(17)

A further aspect of the a.o.m. arises out of the paper by Tennyson and Murrell.[15] These authors made a computational quantum chemistry study of the orbital energies in the complexes, octahedral $[\mathrm{MnF}_{6-i}\mathrm{Cl}_i]^{k-}$ (i = 1—6, $k = 2$ or 4), and distorted octahedral $[\mathrm{MnF}_6]^{k-}$ ($k = 2$ or 4), with a view to making an *ab initio* test of the angular overlap model in ligand-field theory. They performed SCF MO calculations on these complexes and then fitted the calculated orbital energies using a one-electron Hamiltonian of the a.o.m. type containing the usual parameters ($e_\lambda{}^n$, $\lambda = \sigma$, π, or δ) for each of the n ligands. They concluded that such a fit was quite satisfactory but obtained the disquieting result that the differences in their e_δ parameters for F^- and Cl^- ligands were comparable with the differences in the e_π parameters, and there was no reason for taking the e_δ values to be negligible. This is clearly an extremely important point since in the practical applications of the a.o.m. one can usually only obtain a reduced set of parameters $e_\sigma' = e_\sigma - e_\delta$, $e_\pi' = e_\pi - e_\delta$ for each ligand (the primes are conventionally omitted, as in the Table), and the utility of the a.o.m. depends on the chemical interpretation of the parameters e_σ', e_π' obtained by fitting electronic spectra and/or magnetic susceptibilities. There is for example the well established empirical finding [4] that ligands with no valence π orbitals (*e.g.* $\mathrm{NH_3}$) have $e_\pi' \approx 0$ [4] and this is hard to understand as the equation $e_\pi - e_\delta \approx 0$ *unless* both e_π and e_δ are separately ≈ 0. Our own recent investigations [17,18] of the theoretical foundations of the a.o.m. suggest an explanation of this discrepancy between usual practice and the computational results.

It is unfortunate that the a.o.m emerged historically as a form of molecular-orbital theory,[19] frequently illustrated as of the extended-Hückel or Wolfsberg–Helmholz type. This has begotten not only the name of the a.o.m. (which might be better called the ' localized potential model '), but also the notion that the ratio of e_π/e_σ for a given ligand might be expected to follow the ratio of squared overlap integrals, $(S_{\mathrm{ML}}{}^{\pi})^2/(S_{\mathrm{ML}}{}^{\sigma})^2$, for example.[20] Most important for the present discussion is that, despite the heuristically tempting molecular-orbital approach to the model, the a.o.m. e_λ parameters are *not* obtained in practice from fitting to one-electron orbital energies, as described in ref. 15. Rather, the a.o.m. e parameters, which can be given a sensible chemical interpretation, arise as parameterized matrix elements of a full configuration interaction calculation based on the many-electron states constructed in a pure d orbital basis for the metal ion in a definite oxidation state (d^n configuration): they must be obtained concurrently with the Condon–Shortley interelectron repulsion parameters for the complex.[19] This distinction is analogous to one that must be made in the older parameterizations of ligand-field theory. Thus, taking an octahedral complex for simplicity, one conventionally defines [21] $10Dq$ as the difference in energy of the one-electron orbitals in the e_g and t_{2g} sets: these orbitals may be pure d orbitals as in crystal-field theory, but they could also be molecular orbitals for the complex. Hence $10Dq$ is a purely theoretical quantity occurring in a one-electron (orbital) model. In fitting the ligand-field model to the experimental data, however, one parameterizes the matrix elements of the ligand-field potential in a basis of degenerate d orbitals using a global co-ordinate frame; in an octahedral complex one can use a cubic d-orbital basis and there is then the single ligand-field parameter $\Delta_{\mathrm{oct.}} = \langle d_{z^2}|V_{\mathrm{LF}}|d_{z^2}\rangle - \langle d_{xy}|V_{\mathrm{LF}}|d_{xy}\rangle$ which again must be obtained at the same time as the Condon–Shortley interelectron repulsion parameters. Thus, in general ' $10Dq$ ' and ' $\Delta_{\mathrm{oct.}}$ ' should not be identified, although these two kinds of parameters may coincide in numerical value in some cases.

The choice of a pure d (*i.e.* $l = 2$) orbital basis defines the form of the rotation matrices required in the a.o.m., is sensible as an approximation to a set of localized metal orbitals of a clearly defined configuration within which the Laporte rule is closely obeyed, both being characteristic of a ligand-field regime, but is otherwise a matter of exact but arbitrary definition. The physical meaning of the matrix elements of an effective, ligand-field, potential in this basis is, in part, determined by the basis. The process of fitting e_λ values to experimental ligand-field properties in no way determines orbitals or one-electron energies which are, of course, features of a molecular-orbital model rather than of the molecular complex. We have shown [17,18] that the operators in the ligand-field potential matrix elements which are parameterized by the ($e_\lambda{}^n$) arise from the nuclei and all the electrons in the metal complex *with the exception of the metal valence d electrons*, which are treated explicitly in the basis wavefunctions. Molecular-orbital calculations and X-ray crystallographic studies show that the charge density arising from the incomplete shell of d electrons is strongly angular dependent and consequently the Hartree and exchange-correlation potentials it gives rise to would also be expected to be strongly anisotropic.

Accordingly, one would expect significant π and δ components in an a.o.m. decomposition of a ' ligand-field potential ' which includes this anisotropic charge distribution. But since the *d* electrons are excluded from the ligand-field potential in the many-electron ligand-field theory, they must also be excluded if one wishes to make a one-electron model of the $(e_\lambda{}^n)$ parameters. When this is done one can reasonably argue [17,18] that the resulting static potential of a ligand has a negligible matrix element of δ symmetry in the local *d*-orbital basis. Only in this way is a theoretical description of the a.o.m. obtained that fully supports the usual chemical interpretation of the empirical parameters. In our view, the calculations of Tennyson and Murrell [15] do not generate ' a.o.m. parameters ' which are strictly comparable with those obtained from experimental data: the latter must be modelled as described above [17,18] since we see no way of separating out the (anisotropic) purely *d*-electron potential in an analysis based on one-electron orbital energies. An analysis based on one-electron orbital energies should not, therefore, cause us to doubt the chemical utility of the a.o.m. parameterization of the ligand-field potential in transition-metal complexes. We believe, therefore, that the empirical position of contemporary a.o.m. studies is adequately supported within quantum chemistry.

One of us (R. G. W.) acknowledges financial support under the S.R.C. Advanced Fellowship Programme.

[1/174 *Received*, 4*th February*, 1981]

REFERENCES

[1] C. E. Schäffer and C. K. Jørgensen, *J. Inorg. Nucl. Chem.*, 1958, **8**, 143.

[2] C. E. Schäffer and C. K. Jørgensen, *Mat. Fys. Medd. Kgl. Dan Vid Selsk.*, 1965, **34**, 13.

[3] C. E. Schäffer, *Struct. Bonding* (*Berlin*), 1968, **5**, 68.

[4] C. K. Jørgensen, ' Modern Aspects of Ligand Field Theory,' North Holland Publishers, Amsterdam, 1971.

[5] S. E. Harnung and C. E. Schäffer, *Struct. Bonding* (*Berlin*), 1972, **12**, 257.

[6] M. Gerloch, *Prog. Inorg. Chem.*, 1979, **26**, 1.

[7] M. Gerloch, L. R. Hanton, and M. R. Manning, *Inorg. Chim. Acta*, 1981, in the press.

[8] M. Gerloch and L. R. Hanton, *Inorg. Chem.*, 1981, in the press.

[9] L. R. Hanton and P. R. Raithby, *Acta Crystallogr.*, *Sect. B*, 1980, **36**, 2417.

[10] R. P. Taylor, D. H. Templeton, A. Zalkin, and W. Dew. Horrocks jun., *Inorg. Chem.*, 1968, **7**, 2629.

[11] M. Gerloch and M. R. Manning, *Inorg. Chem.*, 1981, in the press.

[12] M. Gerloch, M. R. Manning, and P. R. Raithby, in preparation.

[13] M. Gerloch and L. R. Hanton, *Inorg. Chem.*, 1980, **19**, 1692.

[14] D. A. Cruse and M. Gerloch, *J. Chem. Soc.*, *Dalton Trans.*, 1977, 1613.

[15] J. Tennyson and J. N. Murrell, *J. Chem. Soc.*, *Dalton Trans.*, 1980, 2395.

[16] M. Gerloch and L. R. Hanton, *Inorg. Chim. Acta*, 1981, in the press.

[17] R. G. Woolley, *Mol. Phys.*, 1981, **42**, 703.

[18] M. Gerloch, J. H. Harding, and R. G. Woolley, *Struct. Bonding* (*Berlin*), 1981, **46**, in the press.

[19] M. Gerloch and R. C. Slade, ' Ligand Field Parameters,' Cambridge University Press, London, 1973.

[20] M. A. Hitchman, *J. Chem. Soc.*, *Faraday Trans.* 2, 1972, 846.

[21] C. J. Ballhausen, ' Molecular Electronic Structures of Transition Metal Complexes,' McGraw-Hill, 1979, p. 57.