Paramagnetic Properties of Unsymmetrical Transition-metal Complexes

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A model and procedures are described which permit the calculation of optical and e.s.r. spectra and magnetic susceptibilities of p^n, d^n, or f^n electron systems for any basis chosen as free-ion terms and/or states relating to a molecule of any geometry. Ligand fields are parameterized within the angular-overlap model. Methods are described for calculating magnetic susceptibilities and g values in molecules whose symmetries do not predetermine the orientation of their principal molecular properties.

PAULING'S spin-only formula for the magnetic moments of transition-metal complexes and subsequent general refinements incorporating orbital contributions have been very useful for qualitative enquiries into co-ordination number, formal oxidation state, and bond type. More limited success, however, for much greater theoretical and experimental effort, has been achieved in quantitative interpretation of paramagnetism. Ligand-field theory in its various forms still appears to offer the only viable theoretical basis for calculation of susceptibilities and g values. Two main requirements of models in this area may be identified: first the models must be capable of reproducing observed properties virtually exactly, and secondly a chemical appreciation of the parameters the models employ must be apparent. The models almost invariably involve too many parameters to be used validly with average powder magnetic moments alone and so single-crystal paramagnetic anisotropies must surely constitute a minimum susceptibility data set; e.s.r. and electronic-absorption spectra are obviously desirable measurements too. Interelectronic repulsion, spin–orbit coupling, and orbital-reduction factors are common variables in many electron calculations, but ligand-field parameters frequently furnish most degrees of freedom in the models and are most subject to obscurity in their chemical significance.

Many studies of magnetic anisotropies have been concerned with magnetically axial systems; for example, tetragonally or trigonally distorted octahedra or tetrahedra or C_{4v} and D_{3h} five-co-ordinate molecules. Molecular symmetries leading to parallel and perpendicular susceptibilities are often presumed, based on idealized descriptions of the metal co-ordination sphere. It is desirable that the number of parameters such approximations involve is small and the hope, sometimes expressed but more often implicit, is that the errors of the idealizations will affect parameter values in some small and average way. While it is likely that such hopes are not in vain for spectral studies where eigenvalues are of predominant concern, the situation for magnetism is much less certain, calculations requiring knowledge of eigenvectors also. In any case such models have hardly been studied and idealizations to higher symmetry are most often made because of the computational difficulties associated with the more general case. We are concerned here, then, with the paramagnetism of molecules possessing any symmetry or, indeed, none whatever.

Conventional crystal-field parameterization schemes [1] may be subdivided into two types. Symmetry-defined parameters merely reflect the degrees of freedom required by symmetry, the conventional Dq, Ds, and Dt of D_{4h} systems being typical. An alternative approach, which attempts separation of the radial parameters from ligand orientation, is exemplified by the use of Dq, Cp, and θ, for example, in a trigonally distorted (D_{3d}) octahedron. Here θ is the angle subtended by the three-fold axis and any M–L bond in a point-charge calculation.

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

Representation of a ligand's influence on the metal as that of a point charge is a well known limitation of this approach and the frequent non-cylindrical nature of the field of any one ligand necessitates the view that θ must be taken as a parameter, its variation in any calculation hopefully accommodating the inadequacies of the point-charge representation. Some success has been achieved with this approach and has been recently been discussed in detail.[1]

Corresponding treatments of molecules without symmetry could be made. In the first case, definition of parameters corresponding to the degrees of freedom is equivalent to paramaterizing the expansion coefficients of a general crystal-field potential in terms of spherical harmonics and, in general, these coefficients are complex. Even where the number of such parameters may not be too large, little or no clear relation between them and the bonding or geometry can be obtained. Another possibility is to assign Dq and Cp values as radial parameters to each ligand or ligand type and to parameterize all bond angles subtended by the metal. As all these angles must be treated as variables, following the discussion above and elsewhere,[1] the situation rapidly becomes cumbersome if not actually useless. For these reasons we prefer to use the angular-overlap model (a.o.m.) of Schäffer and Jørgensen.[2-4]

The a.o.m. assigns the origin of the crystal field to weak covalency in which the central assumption is proportionality of antibonding energies of pure metal wavefunctions to the squares of the appropriate metal–ligand overlap integrals. In common with conventional crystal-field models, the a.o.m. assumes knowledge of the angular forms of the metal wavefunctions but not their radial parts and also presumes nothing of the radial or angular parts of the ligand functions. The precise geometrical arrangement of the ligands is taken as data and bonding between the ligand and metal is characterized into σ, π and, if necessary, δ types. The model involves one-electron operators and is thus fundamentally a ligand-field model. It has been reviewed in varying degrees of sophistication.[1,4,5]

We describe now a system for the calculation of ligand-field optical and e.s.r. spectra and of paramagnetic susceptibilities built from established theories in narrower contexts. We believe this is the first general approach applicable to molecules possessing little or no symmetry.

RESULTS AND DISCUSSION

The Angular-overlap Model.—The a.o.m. shares with other ligand-field models the aim of calculating metal-orbital energy differences in a complex within the general restriction to one-electron operators. A central assumption of the model is that the antibonding-orbital energies are determined by covalent perturbation weak enough to be proportional to the squares of appropriate overlap integrals. Contributions to these antibonding energies from different ligands and from metal–ligand bonding modes of different symmetry classification (*e.g.* σ and π) are deemed additive. Alternative descriptions of the axioms in the a.o.m. have been formalized[4] and shown to correspond very closely with those of electrostatically based crystal-field theory, in their consequences if not in their conceptual origins.

Specifically, we consider a group of ligands which may bond to a transition-metal atom using σ, π_x, and π_y bonds as defined by the local M–L moieties. For each ligand and each bonding symmetry type the a.o.m. assumes that the energy shift E^* of any one metal d orbital is given by equation (1), where $S_{\mathrm{ML}}{}^{td}$ is the diatomic overlap

$$E^* \propto (S_{\mathrm{ML}}{}^{td}A_t{}^d)^2 \qquad (1)$$

integral between the metal d orbital and the ligand orbital of symmetry t (σ, π_x, *etc.*) and $A_t{}^d$ is an angular factor expressing the fact that the chosen global co-ordinate frame of the metal atom is not generally coincident with the local frame to which the symmetry of the ligand functions are referred. Within the a.o.m. the diatomic overlap integrals are sequestered into the proportionality constants of (1) and we write (2). In

$$E^* = (A_t{}^d)^2 e_t \qquad (2)$$

general, we define one e_t parameter for each ligand type and for each bonding mode. For the exact octahedron involving σ and π ($\pi_x \equiv \pi_y$ here) bonding the relation (3)

$$10Dq = 3e_\sigma - 4e_\pi \qquad (3)$$

has been established.[3] The extra parameterization of the a.o.m. compared with the single degree of freedom required by O_h symmetry is clearly undesirable in this case. However, for a trigonally distorted octahedron with D_{3d} symmetry, for example, the familiar D_q, $D\sigma$, and $D\tau$ (or Dq, Cp, and θ) parameters in symmetry-defined or point-charge models may be replaced by e_σ and e_π. Generally, the degrees of parameterization involved by the electrostatic and a.o.m. approaches are similar but may not be related on a one-to-one basis. As discussed above and elsewhere[1] the a.o.m. has the particular advantage of relating ligand-field parameters to identifiable features of structure and bonding.

Schäffer[4] presented a general expression for one-electron matrix elements within the a.o.m. model as (4) in which V represents the total ligand-field (a.o.m.)

$$\langle lu|V|lv\rangle = \sum_{j}^{\textit{ligands}} \sum_{t}^{\textit{modes}} \mathscr{D}_{ut}{}^{l}(j)\, \mathscr{D}_{vt}{}^{l}(j) e_t(j) \qquad (4)$$

operator, $\mathscr{D}$ are matrices transforming the real metal orbitals into each ligand co-ordinate frame, u and v label real orbitals formed from complex orbitals with orbital quantum number l, and t designates the symmetry of bonding with respect to the local M–L axis. In general we wish to evaluate a.o.m. matrix elements in the

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

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

[4] C. E. Schäffer, *Structure and Bonding*, 1968, **5**, 68.

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

many electron bases conventionally described by terms or configurations. Harnung and Schäffer[6] constructed an appropriate equation within a real-orbital basis set, as is convenient in the a.o.m. approach, using tensor-operator techniques. However, as we also need to evaluate matrix elements of the spin–orbit coupling operator within the same basis, it was convenient to use the better known equations relating to $|J, M_J\rangle$ quantization.

Application to the Many-electron Problem.—A general ligand-field potential may be expressed as a superposition of spherical harmonics and many-electron matrix elements in a $|J, M_J\rangle$ basis under each term in this expansion are given by tensor-operator theory as in (5)

$$\langle \alpha lLSJM_J|Y_k^q|\alpha' lL'SJ'M_J'\rangle = (-1)^{J+J'+L+l+M_J-k-S} \left(\frac{2k+1}{4\pi}\right)^{\frac{1}{2}}[(2J+1)(2J'+1)]^{\frac{1}{2}}\begin{pmatrix} J & k & J' \\ -M_J & q & M_J' \end{pmatrix}\begin{Bmatrix} L & L' & k \\ J' & J & S \end{Bmatrix} (2l+1)\begin{pmatrix} l & k & l \\ 0 & 0 & 0 \end{pmatrix} \langle \alpha lLS||U^k||\alpha' lL'S\rangle \quad (5)$$

following the nomenclature and conventions of Brink and Satchler.[7] Application of this equation is straightforward and so the main ligand-field problem then devolves into establishing relations between the expansion coefficients of the crystal-field potential and the molecular structure and bonding characteristics. This must be done at the one-electron level, most conveniently by comparing the e parameters of (4) with the c parameters in the one-electron tensor-operator equation (6). The

$$\langle l,m_l|V|l,m_l'\rangle = \sum_j c_j \langle l,m_l|Y_k^q(j)|l,m_l'\rangle \quad (6)$$

assumption that the many-electron functions $|lLSJM_J\rangle$ are compounded solely from pure $|l, m_l\rangle$ functions or, equivalently, that they share common radial parts, allows us to write (7), so that the relation between c of

$$\langle \alpha lLSJM_J|V|\alpha' lL'SJ'M_J'\rangle = \sum_j c_j \langle \alpha lLSJM_J|Y_k^q(j)|\alpha' lL'SJ'M_J'\rangle \quad (7)$$

(6) and e of (4) at the one-electron level carries over to the many-electron problem. We present two routes for establishing this relation.

$$\begin{bmatrix} Z^2 \\ XZ \\ YZ \\ XY \\ X^2-Y^2 \end{bmatrix} \begin{bmatrix} (3\gamma_3^2-1)/2 & 3^{\frac{1}{2}}\alpha_3\gamma_3 & 3^{\frac{1}{2}}\beta_3\gamma_3 & 3^{\frac{1}{2}}\alpha_3\beta_3 & 3^{\frac{1}{2}}(\alpha_3^2-\beta_3^2)/2 \\ 3^{\frac{1}{2}}\gamma_1\gamma_3 & \alpha_1\gamma_3+\alpha_3\gamma_1 & \beta_1\gamma_3+\beta_3\gamma_1 & \alpha_1\beta_3+\alpha_3\beta_1 & \alpha_1\alpha_3-\beta_1\beta_3 \\ 3^{\frac{1}{2}}\gamma_2\gamma_3 & \alpha_2\gamma_3+\alpha_3\gamma_2 & \beta_2\gamma_3+\beta_3\gamma_2 & \alpha_2\beta_2+\alpha_3\beta_2 & \alpha_2\alpha_3-\beta_2\beta_3 \\ 3^{\frac{1}{2}}\gamma_1\gamma_2 & \alpha_1\gamma_2+\alpha_2\gamma_1 & \beta_1\gamma_2+\beta_2\gamma_1 & \alpha_1\beta_2+\alpha_2\beta_1 & \alpha_1\alpha_2-\beta_1\beta_2 \\ 3^{\frac{1}{2}}(\gamma_1^2-\gamma_2^2)/2 & \alpha_1\gamma_1-\alpha_2\gamma_2 & \beta_1\gamma_1-\beta_2\gamma_2 & \alpha_1\beta_1-\alpha_2\beta_2 & (\alpha_1^2-\alpha_2^2+\beta_2^2-\beta_1^2)/2 \end{bmatrix} \begin{bmatrix} z^2 \\ xz \\ yz \\ xy \\ x^2-y^2 \end{bmatrix} \quad (9)$$

Method A. Let there be a global cartesian frame X,Y,Z centred on the metal and a local frame x,y,z centred on any one ligand. We adopted the convention that the ligand z axis is directed from the metal towards the donor atom. The x and y directions were chosen parallel and perpendicular to local symmetry elements where possible: for example, parallel and perpendicular to the plane of a pyridine ligand. A co-ordinate transformation matrix may be established from crystallographic data in terms either of direction cosines or Eulerian rotations. Using direction cosines, we write (8). The angles α, β, γ* of the equivalent Eulerian

$$\begin{array}{c|ccc} & x & y & z \\ \hline X & \alpha_1 & \beta_1 & \gamma_1 \\ Y & \alpha_2 & \beta_2 & \gamma_2 \\ Z & \alpha_3 & \beta_3 & \gamma_3 \end{array} \quad (8)$$

rotation can be derived from (8) using a standard transformation[8] if desired.

The $\mathscr{D}$ matrices of (4) transform the real metal orbitals in the global frame into the ligand frame. Schäffer and Jørgensen[3] gave such a matrix for the transformation of d orbitals in terms of Eulerian rotations. An equivalent transformation matrix in terms of the direction cosines of (8) is given in (9). One such matrix must be constructed for each ligand in the complex. [For matrix elements within a pure orbital basis, *i.e.* pure d or f but not d and f, for example, any ligand-field operator is of even parity. Contributions from ligands related by a centre of inversion at the metal are identical. Accordingly, no new matrices need be constructed, a multiplicative factor of two being all that is required in centrosymmetric molecules.] As each ligand co-ordinate frame reflects the local symmetry with respect to the M–L bond (*i.e.* σ, π_x, *etc.*), quantities in the columns of the matrix in (9) refer respectively to σ, π_x π_y, δ_{xy}, and $\delta_{x^2-y^2}$ bonding modes [labelled t in (4)].

Single-electron a.o.m. matrix elements in the real-orbital basis may now be computed using (4). Specifically, for a d-orbital basis in a complex involving three centrically independent ligands with consideration of σ, π_x, and π_y bonding modes only, we may construct equation (10) in which the 15 independent matrix elements (*e.g.* $\langle d_{xy}|V|d_{yz}\rangle$) are related to nine a.o.m. parameters (e_σ, $e_{\pi x}$, and $e_{\pi y}$ for each ligand) by the quantities A_{ij} which are appropriate products of the elements of (9). These same matrix elements may be evaluated in terms of the general expansion of the ligand field for spherical harmonics as follows. The matrix elements in (6) may be evaluated by tensor-operator

$$M_i = A_{ij}e_j \quad (10)$$

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* We use α, β, γ without suffices for Eulerian angles, with suffices for direction cosines.

[6] S. E. Harnung and C. E. Schäffer, *Structure and Bonding*, 1972, **12**, 257.

[7] D. M. Brink and G. R. Satchler, 'Angular Momentum,' Oxford, 1968.

[8] H. Watanabe, 'Operator Methods in Ligand Field Theory,' Prentice-Hall, New Jersey, 1966, p. 148.

theory[7] using (11). For example, within a d-orbital

$$\langle l,m_l|Y_k^q|l,m_l'\rangle = (-1)^{m_l}\left(\frac{2k+1}{4\pi}\right)^{\frac{1}{2}}(2l+1)\begin{pmatrix} l & k & l \\ -m_l & q & m_l' \end{pmatrix}\begin{pmatrix} l & k & l \\ 0 & 0 & 0 \end{pmatrix} \qquad (11)$$

basis the harmonics Y_2^1 and Y_4^1 are effective only in the matrix elements $\langle m_l = 2|V|m_l = 1\rangle$ and $\langle 1|V|0\rangle$, *viz.* equations (12) and (13) where, for example, c_{21} is the

$$\langle 2|V|1\rangle = W_{21}{}^{21}c_{21} + W_{41}{}^{21}c_{41} \qquad (12)$$

$$\langle 1|V|0\rangle = W_{21}{}^{10}c_{21} + W_{41}{}^{10}c_{41} \qquad (13)$$

expansion coefficient of Y_2^1 in (6) and $W_{21}{}^{10}$ is determined from (11) as (14). Equations (12) and (13) thus furnish a

$$W_{21}{}^{10} = (-1)^1\left(\frac{5}{4\pi}\right)^{\frac{1}{2}}(5)\begin{pmatrix} 2 & 2 & 2 \\ -1 & 1 & 0 \end{pmatrix}\begin{pmatrix} 2 & 2 & 2 \\ 0 & 0 & 0 \end{pmatrix} = -\left(\frac{5}{4\pi}\right)^{\frac{1}{2}} 5\left(\frac{1}{70}\right)^{\frac{1}{2}}\cdot -\left(\frac{2}{35}\right)^{\frac{1}{2}} \qquad (14)$$

simultaneous pair for the evaluation of c_{21} and c_{41} in terms of $\langle 2|V|1\rangle$ and $\langle 1|V|0\rangle$.

Proceeding in a similar fashion for all c_{kq} involves the solution of up to three simultaneous equations and yields Table 1. Equivalent expressions for terms with q negative may be constructed using the relation (15),[7]

$$c_{qk} = (-1)^q\, c_{k,-q}{}^* \qquad (15)$$

a reminder that the matrix elements in the complex basis are generally complex. The relations in Table 1 are, of course, quite general, being applicable to molecules of any, or no, symmetry.

The real and complex d orbitals are related within the Condon–Shortley phase convention by (16)—(20) from

$$|z^2\rangle = |Y_2^0\rangle \qquad (16)$$

$$|xz\rangle = 2^{-\frac{1}{2}}|Y_2^{-1} - Y_2^1\rangle \qquad (17)$$

$$|yz\rangle = i2^{-\frac{1}{2}}|Y_2^{-1} + Y_2^1\rangle \qquad (18)$$

$$|xy\rangle = i2^{-\frac{1}{2}}|Y_2^{-2} - Y_2^2\rangle \qquad (19)$$

$$|x^2 - y^2\rangle = 2^{-\frac{1}{2}}|Y_2^{-2} + Y_2^2\rangle \qquad (20)$$

which the expansion coefficients c of (6) may be expressed in terms of the real crystal-field matrix elements by transformation of Table 1 to 2. Writing the expressions in Table 2 as the matrix equation (21) for the

$$c_i = B_{ij}M_j \qquad (21)$$

15 independent matrix elements M, then from (10) we have the required relations between the parameters of the a.o.m. and those of the general ligand-field expansion, *viz.* (22). In this way we may construct the

$$c_i = B_{ij}A_{jk}e_k \qquad (22)$$

crystal-field expansion in terms of spherical harmonics equivalent to a given molecular geometry parameterized by the a.o.m. technique.

It is clear that there are a number of parallels between the method just described and that outlined by Horrocks.[9] As he pointed out, one is not restricted to the a.o.m. in the calculation of one-electron matrix elements within the real-orbital basis set. One could equally well use a generalized point-charge model or an LCAO–MO scheme with eigenvectors truncated to a pure d-orbital form. It is not clear from his paper how these calculations might readily be made, especially in low-symmetry situations. Also at the time of publication the problems associated with complex potentials had apparently not been solved. Horrocks also suggested that the real-orbital one-electron matrix elements themselves might provide an improved form of ligand-field parameterization. However, in the case of molecules of low symmetry it is not clear that these parameters are related to features of chemical bonding in any more obvious a manner than the more usual crystal-field type parameters.

TABLE 1

General relations between c_{kq} and complex matrix elements for d functions

$$c_{00} = \tfrac{2}{5}\pi^{\frac{1}{2}}(2\langle 2|V|2\rangle + 2\langle 1|V|1\rangle + \langle 0|V|0\rangle)$$

$$c_{20} = -\left(\frac{4\pi}{5}\right)^{\frac{1}{2}}(2\langle 2|V|2\rangle - \langle 1|V|1\rangle - \langle 0|V|0\rangle)$$

$$c_{21} = \left(\frac{4\pi}{5}\right)^{\frac{1}{2}}(6^{\frac{1}{2}}\langle 2|V|1\rangle + \langle 1|V|0\rangle)$$

$$c_{22} = -\left(\frac{4\pi}{5}\right)^{\frac{1}{2}}[2\langle 2|V|0\rangle + (\tfrac{3}{2})^{\frac{1}{2}}\langle 1|V|-1\rangle]$$

$$c_{40} = \tfrac{2}{5}(\pi)^{\frac{1}{2}}(\langle 2|V|2\rangle - 4\langle 1|V|1\rangle + 3\langle 0|V|0\rangle)$$

$$c_{41} = 2\left(\frac{2\pi}{5}\right)^{\frac{1}{2}}(3^{\frac{1}{2}}\langle 1|V|0\rangle - 2^{-\frac{1}{2}}\langle 2|V|1\rangle)$$

$$c_{42} = 2\left(\frac{2\pi}{5}\right)^{\frac{1}{2}}[(\tfrac{3}{2})^{\frac{1}{2}}\langle 2|V|0\rangle - \langle 1|V|-1\rangle]$$

$$c_{43} = -\left(\frac{28\pi}{5}\right)^{\frac{1}{2}}\langle 2|V|-1\rangle$$

$$c_{44} = \left(\frac{14\pi}{5}\right)^{\frac{1}{2}}\langle 2|V|-2\rangle$$

Method B. The process described above involved comparison of matrix elements of the a.o.m. and of a general harmonic-expansion potential for a complete molecular complex. An alternative approach is to make this comparison for each M–L interaction followed by superposition. Let x',y',z' be a cartesian frame centred on the metal, in parallel orientation and of identical handedness to that on the ligand x,y,z. Assuming it is possible, and we return to this point later, to orient the ligand axes parallel to 'symmetry-classified' directions in the ligand while retaining z parallel to the M–L axis, the matrix of $V_{\text{a.o.m.}}$ is diagonal. For example, $\langle z^2|V|z^2\rangle = e_\sigma$, $\langle xz|V|xz\rangle = e_{\pi x}$, *etc.* Substitution of these identities into Table 2 then yields, quite generally for d orbitals, Table 3. Thus Table 3 lists the relations between c of (6) and e of (4) for an individual M–L perturbation.

Superposition of similar expressions for all the ligands in a complex is straightforward after their transformation

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[9] W. DeW. Horrocks, jun., *Inorg. Chem.*, 1974, **13**, 2775.

into the common global frame X,Y,Z. The c_{kq} of (6) are associated with spherical harmonics $Y_k{}^q$ in the crystal-field potential, which latter transform[7] according to (23),

$$Y_k{}^q(\text{global}) = \sum_{q'=-k}^{k} \mathscr{D}_{q'q}{}^k(\alpha\beta\gamma)\; Y_k{}^q(\text{ligand}) \qquad (23)$$

where

$$\mathscr{D}_{q'q}{}^k(\alpha\beta\gamma) = e^{-i(q'\alpha+q\gamma)} d_{q'q}{}^k(\beta) \qquad (24)$$

standard $d(\beta)$ matrices being tabulated by several authors.[7,10] Application * of (23) to c_{kq} (ligand) yields the desired relation between the c and e parameters for the given ligand in the global frame; superposition of contributions from all ligands may then be made.

TABLE 2

General relations between c_{kq} and real matrix elements for d functions

(a) Real parts of c_{kq}.

$$c_{00} = \tfrac{2}{5}(\pi)^{\frac{1}{2}}(\langle x^2-y^2|V|x^2-y^2\rangle + \langle xy|V|xy\rangle + \langle xz|V|xz\rangle + \langle yz|V|yz\rangle + \langle z^2|V|z^2\rangle)$$

$$c_{20} = -\left(\frac{\pi}{5}\right)^{\frac{1}{2}}(2\langle x^2-y^2|V|x^2-y^2\rangle + 2\langle xy|V|xy\rangle - \langle xz|V|xz\rangle - \langle yz|V|yz\rangle - 2\langle z^2|V|z^2\rangle)$$

$$c_{21} = -\left(\frac{4\pi}{5}\right)^{\frac{1}{2}}(\tfrac{6}{2}^{\frac{1}{2}}\langle yz|V|xy\rangle + \tfrac{6}{2}^{\frac{1}{2}}\langle xz|V|x^2-y^2\rangle + 2^{-\frac{1}{2}}\langle xz|V|z^2\rangle)$$

$$c_{22} = -\left(\frac{4\pi}{5}\right)^{\frac{1}{2}}[2^{\frac{1}{2}}\langle x^2-y^2|V|z^2\rangle + (\tfrac{3}{8})^{\frac{1}{2}}\langle yz|V|yz\rangle - (\tfrac{3}{8})^{\frac{1}{2}}\langle xz|V|xz\rangle]$$

$$c_{40} = \frac{\pi^{\frac{1}{2}}}{5}(\langle x^2-y^2|V|x^2-y^2\rangle + \langle xy|V|xy\rangle - 4\langle xz|V|xz\rangle - 4\langle yz|V|yz\rangle + 6\langle z^2|V|z^2\rangle)$$

$$c_{41} = 2\left(\frac{2\pi}{5}\right)^{\frac{1}{2}}[-(\tfrac{3}{2})^{\frac{1}{2}}\langle xz|V|z^2\rangle + 2^{-\frac{3}{2}}\langle yz|V|xy\rangle + 2^{-\frac{3}{2}}\langle xz|V|x^2-y^2\rangle]$$

$$c_{42} = 2\left(\frac{2\pi}{5}\right)^{\frac{1}{2}}(\tfrac{3}{2}^{\frac{1}{2}}\langle x^2-y^2|V|z^2\rangle + \tfrac{1}{2}\langle xz|V|xz\rangle - \tfrac{1}{2}\langle yz|V|yz\rangle)$$

$$c_{43} = \left(\frac{7\pi}{5}\right)^{\frac{1}{2}}(\langle yz|V|xy\rangle - \langle xz|V|x^2-y^2\rangle)$$

$$c_{44} = \left(\frac{7\pi}{10}\right)^{\frac{1}{2}}(\langle x^2-y^2|V|x^2-y^2\rangle - \langle xy|V|xy\rangle)$$

(b) Imaginary parts of c_{kq}

$$c_{00} = c_{20} = c_{40} = 0$$

$$c_{21} = \left(\frac{4\pi}{5}\right)^{\frac{1}{2}}[-(\tfrac{3}{2})^{\frac{1}{2}}\langle yz|V|x^2-y^2\rangle + (\tfrac{3}{2})^{\frac{1}{2}}\langle xz|V|xy\rangle + 2^{-\frac{1}{2}}\langle yz|V|z^2\rangle]$$

$$c_{22} = -\left(\frac{4\pi}{5}\right)^{\frac{1}{2}}[-2^{\frac{1}{2}}\langle xy|V|z^2\rangle + (\tfrac{3}{2})^{\frac{1}{2}}\langle xz|V|yz\rangle]$$

$$c_{41} = 2\left(\frac{2\pi}{5}\right)^{\frac{1}{2}}[(\tfrac{3}{2})^{\frac{1}{2}}\langle yz|V|z^2\rangle + 2^{-\frac{3}{2}}\langle yz|V|x^2-y^2\rangle - 2^{-\frac{3}{2}}\langle xz|V|xy\rangle]$$

$$c_{42} = 2\left(\frac{2\pi}{5}\right)^{\frac{1}{2}}[-(\tfrac{3}{4})^{\frac{1}{2}}\langle xy|V|z^2\rangle - \langle xz|V|yz\rangle]$$

$$c_{43} = \left(\frac{7\pi}{5}\right)^{\frac{1}{2}}(\langle xz|V|xy\rangle + \langle yz|V|x^2-y^2\rangle)$$

$$c_{44} = -\left(\frac{14\pi}{5}\right)^{\frac{1}{2}}(\langle x^2-y^2|V|xy\rangle)$$

TABLE 3

General relations between c_{kq} and e parameters for σ, π_x, and π_y bonding to d orbitals in ligand reference frame. All c_{kq} are real; remainder are zero

$$c_{00} = \tfrac{2}{5}\pi^{\frac{1}{2}}(e_\sigma + e_{\pi_x} + e_{\pi_y})$$

$$c_{20} = \left(\frac{\pi}{5}\right)^{\frac{1}{2}}(2e_\sigma + e_{\pi_x} + e_{\pi_y})$$

$$c_{22} = c_{2-2} = \left(\frac{3\pi}{10}\right)^{\frac{1}{2}}(e_{\pi_x} - e_{\pi_y})$$

$$c_{40} = \left(\frac{\pi}{5}\right)^{\frac{1}{2}}(6e_\sigma - 4e_{\pi_x} - 4e_{\pi_y})$$

$$c_{42} = c_{4-2} = \left(\frac{2\pi}{5}\right)^{\frac{1}{2}}(e_{\pi_x} - e_{\pi_y})$$

There are three ways in which this method is more convenient than A. (i) It may be desirable to investigate the effects on spectra and magnetism of rotating any ligand about its M–L axis. In method B this may be achieved by replacing $\mathscr{D}$ ($\alpha\beta\gamma$) in (23) by, say, $\mathscr{D}$ ($\alpha + \theta$, β, γ). Even more simply, the same result may be obtained by multiplying the right-hand sides of the expressions in Table 3 by $e^{-iq\theta}$, retaining the original $\mathscr{D}$ matrix. Method A is much less direct. (ii) Extension of the computational system to f-electron systems is also simple in method B. A table, equivalent to Table 2, relating c of (6) to complex matrix elements for f orbitals may be constructed using (11), as above. The equivalent of Table 3 is then derived using the transformation for σ and π bonding, expressions (25 and (26) being

$$|l,\sigma\rangle = (-1)^l\,|l,0\rangle \qquad (25)$$

$$(|l,\pi_y\rangle\ |l,\pi_x\rangle) = (|l,1\rangle\ |l,-1\rangle)\begin{pmatrix}(-1)^l i/2^{\frac{1}{2}} & (-1)^{l+1}/2^{\frac{1}{2}}\\ (-1)^l i/2^{\frac{1}{2}} & (-1)^l/2^{\frac{1}{2}}\end{pmatrix} \qquad (26)$$

derived from a more general one by Harnung and Schaffer,[6] recast into the phase convention of Condon and

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* It must be remembered that we are comparing matrix elements rather than transforming a potential operator explicitly.

[10] H. A. Buckmaster, *Canad. J. Phys.*, 1964, **42**, 386; 1966, **44**, 2525.

Shortley.[9] This procedure is, of course, common to both methods A and B. No more algebra is required for method B, however, while A requires the construction of an f-orbital transformation matrix equivalent to (9), a tedium we prefer to avoid. (iii) The consequences of 'misdirected valency' are most readily seen in method B. In the case of a chelating ligand, for example, it may be suitable to regard the donor-atom σ orbital as not directed exactly towards the metal. In such circumstances the chosen ligand axes with z directed from metal to donor atom may preclude rigorous classification of M–L overlap with respect to symmetry. The ligand σ orbital may overlap, say, with both the metal d_{z^2} and d_{xz} orbitals and the resulting $V_{\text{a.o.m.}}$ matrix is no longer diagonal. Not only do further harmonics, and hence c_{kq}, enter into the list of expressions in Table 3, but also extra e parameters describing 'cross σ–π' bonding become necessary. We do not pursue the matter further, however, merely noting that the appearance of the additional harmonics is particularly clear in method B.

The Complete Ligand-field Problem.—The total ligand-field calculation requires diagonalization of a given $|J,M_J\rangle$ basis under the Hamiltonian (27). The system

$$\mathscr{H} = \sum_{i<j} \frac{e^2}{r_{ij}} + \sum_i \xi_i l_i s_i + V_{\text{a.o.m.}} \quad (27)$$

we adopted permits definition of the basis functions as any combination of free-ion spectroscopic terms and/or states. The two-electron electrostatic perturbation-matrix elements were computed directly from appropriate reduced-matrix elements listed by Neilson and Koster [equation (28)].[11] The spin–orbit coupling

$$\langle \alpha LSJM_J | \sum_{i<j} \frac{e^2}{r_{ij}} | \alpha' L'S'J'M_J' \rangle = \sum_k \langle \alpha LS || F^k || \alpha' L'S' \rangle \, \delta_{LL'} \delta_{SS'} \delta_{JJ'} \delta_{M_J M_J'} \quad (28)$$

matrix was evaluated using relation (29). Reduced-matrix elements for this operator as for the crystal-field

$$\langle \alpha l LSJM_J | \sum_i \xi_i l_i s_i | \alpha' l L'S'J'M_J' \rangle = \zeta (-1)^{-J-L'-S} [l(l+1)(2l+1)]^{\frac{1}{2}} \begin{Bmatrix} S & L & J \\ L' & S' & 1 \end{Bmatrix} \langle \alpha l LS || V^{11} || \alpha' l L'S' \rangle \quad (29)$$

expression (5) were from the same source.[11] In common with usual practice in ligand-field calculation, both interelectron repulsion and spin–orbit matrices were calculated within a spherically symmetric approximation appropriate to free ions; this is necessary in the interests of minimal parameterization.

Matrices for the interelectron repulsion operator (two for d orbitals), one spin–orbit matrix, and one matrix for each harmonic [and hence c of (6)] in the ligand-field potential were constructed once only for the given basis and stored. Calculations were then made for many combinations of the F_k, ζ, and e parameters in which the first step is computation of the associated c parameters. Copies of the stored matrices were multiplied by the appropriate F_k, ζ, and c parameters and summed to yield a, generally complex, matrix for the complete perturbation (27). Diagonalization furnishes eigenvalues and eigenvectors for comparison with optical spectra and for the calculation of magnetic susceptibilities and e.s.r. g values, where appropriate.

Paramagnetic Susceptibility.—The usual expression for calculation of magnetic susceptibilities, first derived by Van Vleck,[12] presupposes knowledge of the orientation of the principal molecular susceptibilities. For molecules lacking the symmetry necessary to predetermine these directions, we require a more general susceptibility expression which we now derive.

We generally write a second-rank tensorial relation between the magnetic field H, applied to an assemblage of molecules, and the resulting magnetization M; the susceptibility tensor χ is a function of temperature [equation (30)]. Here we use the standard tensor

$$M_\alpha = \chi_{\alpha\beta} H_\beta \quad (30)$$

notation in which Greek letters used as non-repeating suffices refer to elements of the set (x,y,z), but when repeated imply summation over the entire set. The magnetization M_α, in direction α, for a system of identical molecules is given by (31). The perturbation

$$M_\alpha = -N_A \sum_i \frac{\partial E_i}{\partial H_\alpha} e^{-E_i/kT} \Big/ \sum_i e^{-E_i/kT} \quad (31)$$

expansion of E_i, the energy of the ith level, in a generally oriented magnetic field is, to second order, as in (32) in

$$E_i = E_i^0 + \langle i|\mu_\alpha|i\rangle H_\alpha + \sum_j \frac{[\langle i|\mu_\alpha|j\rangle \langle j|\mu_\beta|i\rangle H_\alpha H_\beta]}{E_i^0 - E_j^0} \quad (32)$$

which the basis set has been chosen such that all groups of levels degenerate before the perturbation are diagonal with respect to μH, and j sums over all levels where $E_j^0 \neq E_i^0$. Differentiating (32) with respect to components of the magnetic field yields (33). An expression for

$$\frac{\partial E_i}{\partial H_\alpha} = \langle i|\mu_\alpha|i\rangle + \sum_j \frac{[\langle i|\mu_\alpha|j\rangle \langle j|\mu_\beta|i\rangle H_\beta + \langle i|\mu_\beta|j\rangle \langle j|\mu_\alpha|i\rangle H_\beta}{E_i^0 - E_j^0} \quad (33)$$

magnetization valid to second order can be obtained by substitution of (32) and (33) into (31). Much simplification is possible if we follow the treatment of Van Vleck[12] in that we consider small magnetic fields only and write (34) and after substitution consider only terms linear in

$$e^{-E_i/kT} \sim e^{-E_i^0/kT}[1 - (\langle i|\mu_\alpha|i\rangle H_\alpha/kT)] \quad (34)$$

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[11] C. W. Neilson and G. F. Koster, 'Spectroscopic Coefficients for the p^n, d^n, and f^n Configurations,' MIT Press, Cambridge, Massachusetts, 1963.

[12] J. H. Van Vleck, 'Theory of Electric and Magnetic Susceptibilities,' Oxford University Press, 1932.

field. This is done because residual magnetization disappears at zero field and because coefficients of higher powers of field in (34) are negligibly small except at very low temperatures. On substitution we obtain (35).

$$M_\alpha = N_A \sum_i \left[(\langle i|\mu_\alpha|i\rangle \langle i|\mu_\beta|i\rangle H_\beta/\boldsymbol{k}T) - \sum_j \frac{(\langle i|\mu_\alpha|j\rangle \langle j|\mu_\beta|i\rangle + \langle i|\mu_\beta|j\rangle \langle j|\mu_\alpha|i\rangle)H_\beta}{E_i^0 - E_j^0} \right] e^{-E_i^0/\boldsymbol{k}T} \Big/ \sum_i e^{-E_i^0/\boldsymbol{k}T} \quad (35)$$

Since the choice of basis set is a function of field direction ω, we must write (36). If the magnetization can be

$$M_\alpha = A_{\alpha\beta}\omega H_\beta \quad (36)$$

related to the magnetic field by a second-rank susceptibility tensor as in (30), expression (37) must hold for all field directions. It follows, therefore, that a general

$$A_{\alpha\beta}\omega H_\beta = \chi_{\alpha\beta} H_\beta \quad (37)$$

element of the susceptibility χ is given by (38) where ω′

$$\chi_{\alpha\beta} = A_{\alpha\beta}(\omega') \quad (38)$$

is along the direction β, say. Accordingly, we obtain (39) where the basis set is diagonal with respect to μ_β.

$$\chi_{\alpha\beta} = N_A \sum_i \left[(\langle i|\mu_\alpha|i\rangle \langle i|\mu_\beta|i\rangle/\boldsymbol{k}T) - \sum_j \frac{(\langle i|\mu_\alpha|j\rangle \langle j|\mu_\beta|i\rangle + \langle i|\mu_\beta|j\rangle \langle j|\mu_\alpha|i\rangle)}{E_i^0 - E_j^0} \right] e^{-E_i^0/\boldsymbol{k}T} \Big/ \sum_i e^{-E_i^0/\boldsymbol{k}T} \quad (39)$$

We note that (39) reduces to Van Vleck's expression when applied to a diagonal element of the susceptibility tensor.

Only the temperature-dependent part of the susceptibility in (39) is affected by the choice of basis set, of course. However, it is possible to replace (40) in (39)

$$\sum_i \langle i|\mu_\alpha|i\rangle \langle i|\mu_\beta|i\rangle \quad (40)$$

where we use a diagonalized basis set by the more general expression (41) where i' sums over all elements of

$$\sum_{i'} \sum_{k'} \langle i'|\mu_\alpha|k'\rangle \langle k'|\mu_\beta|i'\rangle \quad (41)$$

a completely general basis and k' all elements where $E_{k'}^0 = E_{i'}^0$. The equality between (40) and (41) may be proved by considering all matrix elements within a degenerate set. Matrices A' ($a'_{ik} = \langle i'|\mu_\alpha|k'\rangle$) and B' ($b'_{ik} = \langle i'|\mu_\beta|k'\rangle$) are not, in general, diagonal. There exists, however, a unitary transformation (42)

$$B = U^{-1}B'U \quad (42)$$

relating the general matrix B' to the diagonal form B. The same unitary transformation when applied to A', (43), may not, however, yield a diagonal matrix. Defining expressions (44) and (45) gives (46). As the trace of a

$$A = U^{-1}A'U \quad (43)$$

$$C' = A'B' \quad (44)$$

$$C = U^{-1}C'U \quad (45)$$

$$C = AB \quad (46)$$

matrix is invariant under a unitary transformation, we have (47). Matrix B is diagonal and so the left-hand

$$\sum_i \sum_k a_{ik} b_{ki} = \sum_i \sum_k a_{ik}' b_{ki}' \quad (47)$$

side of (47) reduces to (40), while the right-hand side retains the more general form (41).

Moreover, verification of (37) reduces to proving relation (48) within a degenerate set where the basis is

$$\sum_i \langle i|\mu_\alpha|i\rangle \langle i|\mu_\beta|i\rangle H_\beta = \sum_i \sum_k \langle i|\mu_\alpha|k\rangle \langle k|\mu_\beta|i\rangle H_\beta \quad (48)$$

diagonal with respect to μH, recalling that the left-hand side of (48) derives from (35) and the right-hand side from (39). This reduces to showing that expression (49) is applicable, which is self evident when we recall our

$$\sum_i \sum_{k \neq i} \langle i|\mu_\alpha|k\rangle \langle k|\mu_\beta|i\rangle H_\beta = 0 \quad (49)$$

definition of the basis set such that (50) is obtained. We

$$\langle k|\mu_\beta|i\rangle H_\beta = 0,\ i \neq k \quad (50)$$

also note the symmetric nature of (47) and hence the proof that $\chi_{\alpha\beta} = \chi_{\beta\alpha}$; the symmetry of χ was not obvious from (39).

Application of the general susceptibility equation (39), using the equality of (40) and (41), to the eigenvectors of (27) for the six independent components of χ and subsequent diagonalization gave the principal molecular susceptibilities and their orientations with respect to the global molecular co-ordinate frame X,Y,Z. While the process is straightforward in principle, the lengthy nature of the calculation requires optimization of programming techniques if the whole investigation of low-symmetry systems is to be practicable. In addition to conventional computing tactics, there are two main ways in which computation may be reduced.

Writing a matrix element of (41) more fully as (51),

$$\langle i|\mu_\alpha|j\rangle = \langle \sum_p^{\text{basis}} a_p\phi_p|\mu_\alpha| \sum_q^{\text{basis}} a_q\phi_q\rangle = \sum_p \sum_q a_p{}^* a_q \langle \phi_p|\mu_\alpha|\phi_q\rangle \quad (51)$$

we note that matrix elements of μ within the original basis ϕ need be calculated once only, subsequently being multiplied by the coefficients $\boldsymbol{a}$ defining the vectors of (27). Accordingly, at the stage where the matrices of interelectron repulsion, spin–orbit coupling, and crystal field are constructed in the original basis, matrices of L_z, $L_\pm$, S_z, and $S_\pm$ are also set up and retained. They are calculated using the relations (52)—(59).[13] The second

$$\langle \alpha lLSJM_J|L_z|\alpha lLSJ'M_J\rangle = PQ \qquad (52)$$

$$\langle \alpha lLSJM_J|S_z|\alpha lLSJ'M_J\rangle = PR \qquad (53)$$

$$\langle \alpha lLSJM_J|L_\pm|\alpha lLSJ'M_J'\rangle = T_\pm Q \qquad (54)$$

$$\langle \alpha lLSJM_J|S_\pm|\alpha lLSJ'M_J'\rangle = T_\pm R \qquad (55)$$

$$P = (-1)^{J-M_J}\begin{pmatrix} J & 1 & J' \\ -M_J & 0 & M_J \end{pmatrix} \qquad (56)$$

$$T_\pm = \pm(-1)^{J-M_J}\begin{pmatrix} J & 1 & J' \\ -M_J & \mp 1 & M_J \end{pmatrix} \qquad (57)$$

$$Q = (-1)^{L+S+J'+1}[(2J+1)(2J'+1)]^{\frac{1}{2}} [L(L+1)(2L+1)]^{\frac{1}{2}}\begin{Bmatrix} J & 1 & J' \\ L & S & L \end{Bmatrix} \qquad (58)$$

$$R = (-1)^{L+S+J+1}[(2J+1)(2J'+1)]^{\frac{1}{2}} [S(S+1)(2S+1)]^{\frac{1}{2}}\begin{Bmatrix} J & 1 & J' \\ S & L & S \end{Bmatrix} \qquad (59)$$

technique for efficient calculation is to note that matrix elements in (39) always occur in products of two and that the magnetic-moment operator (60) involves multiplic-

$$\mu_\alpha = \beta_0(kL_\alpha + 2S_\alpha) \qquad (60)$$

ation of the orbital operator by Stevens' orbital-reduction factor [14,15] k, but not the spin operator. As we restricted our system to isotropic orbital-reduction factors in the interests of reducing the degree of parameterization, we may separately accumulate, over all relevant levels in (39), components in χ to be multiplied by k^2, by k, and by unity, corresponding to parts involving L^2, LS, or S^2, respectively. This has the considerable advantage that repeat calculations for various k values are extremely fast. Similarly, components of first- and second-order Zeeman effects to be divided by T, or not, in (39) were reserved separately. In this way repeat calculations for various temperatures require the minimum of further computation.

Comparison of experimental and theoretical susceptibilities in our earlier work was made at the molecular level.[16] This seemed natural when comparing what are fundamentally molecular properties and was possible in the axially distorted molecules then studied. The transformation from the observed crystal-susceptibility tensor to the corresponding molecular property is simple when the orientations of the principal molecular susceptibilities may be inferred from molecular symmetry. In molecules with little or no symmetry such information is not available and no significant transformation of experimental data to the molecular level is possible. Accordingly, the final step in the theoretical-susceptibility calculation is to transform from the molecule to the crystal, taking due note of the given molecular orientation in the lattice (*i.e.* the orientation of the global frame X,Y,Z, with respect to the crystallographic axes a,b,c) and of the crystal class. Comparison with experiment then takes place at the experimental level of crystal susceptibilities and anisotropies. In the case of monoclinic crystals, of course, the angle ϕ subtended by χ_1 and a (as defined in ref. 16) is a further element for comparison between theory and experiment. Generally, the lower the crystal symmetry class the more independent data for comparison. The triclinic system thus allows calculation and observation of three principal susceptibilities and three orientations or, equivalently, all six independent components of the χ tensor in (30). As measurements on triclinic crystals have been rather difficult in the past, the monoclinic system offers an acceptable compromise in the desire to maximize experimental information. The advent of the present system for susceptibility computation in unsymmetrical molecules, however, stresses the benefits that improved experimental techniques would bring to the study of triclinic crystals.

Electron Spin Resonance g *Values*.—Let us define an e.s.r. g value by the first-order Zeeman splitting of a degenerate manifold as $g\beta_0H$ between adjacent levels. We write D as the sum of the squares of the matrix elements diagonal in μH, from which we note that for a

$$D = \sum_i (\langle i|\mu_\alpha|i\rangle H_\alpha)^2 \qquad (61)$$

doublet level in the absence of the magnetic field, $H^2g^2 = 2D$, and for an equally split triplet, $H^2g^2 = D/2$, *etc.* Expanding (61) gives (62). Now the form of

$$D = d_\beta H_\beta \qquad (62)$$

$$d_\beta = \sum_i \langle i|\mu_\alpha|i\rangle \langle i|\mu_\beta|i\rangle H_\alpha \qquad (63)$$

d_β is exactly the same as that on the left-hand side of (48). So we may write (64) where, retaining the nomenclature of the earlier section, expression (65) is

$$d_\beta = T_{\alpha\beta}H_\alpha \qquad (64)$$

$$T_{\alpha\beta} = \sum_{i'}\sum_{k'} \langle i'|\mu_\alpha|k'\rangle \langle k'|\mu_\beta|i'\rangle \qquad (65)$$

applicable. Thus (66) is obtained. We have already

$$D = T_{\alpha\beta}H_\alpha H_\beta \qquad (66)$$

demonstrated that T is a symmetrical second-rank tensor which can always be diagonalized by a suitable choice of axis frame. Thus, from the intermediate parameters calculated during the susceptibility calculation, we have all the information required to calculate principal g values of isolated multiplets and their directions. This assumes, of course, exactly equal splitting under a magnetic field, which may not be the case for high multiplicities but is trivially true for the most important case of isolated doublets. It should

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[13] M. Gerloch and D. J. Mackay, *J. Chem. Soc.* (*A*), 1971, 2605 and refs. therein.

[14] K. W. H. Stevens, *Proc. Roy. Soc.*, 1953, **A219**, 542.

[15] M. Gerloch and J. R. Miller, *Progr. Inorg. Chem.*, 1968, **10**, 1.

[16] See, for example, M. Gerloch and P. N. Quested, *J. Chem. Soc.* (*A*), 1971, 2308.

be noted that the procedure described does not allow calculation of the signs of the principal g values. In fact, in molecules of low symmetry $g_{\alpha\beta} \neq g_{\beta\alpha}$ and it is impossible to diagonalize the g property. We calculated g^2 values which permit computation only of the magnitudes of splittings, but for magnetic fields in quite general directions.

Summary.—Calculations of spectral, e.s.r., and particularly susceptibility properties of transition-metal complexes have hitherto been generally limited to molecules possessing a fairly high degree of symmetry. Frequently small deviations from high symmetry have been ignored in approximations whose reasonableness has been based on a view of the geometric structure rather than on the consequent electronic properties. There have long been suspicions that anomalies in the parameters derived within a given compound or in relations within a series might be due to (unspecified) second-co-ordination-sphere effects or to a general, if partial, breakdown of ligand-field theory. After so much theoretical and calculational effort has been devoted to these systems, such ambiguities, anomalies, or simple ignorance are embarrassing. It has been clear for some time that a system for the calculation of electronic properties of these molecules, unhampered by suspect approximations regarding symmetry, defined an urgent need in this area. The present paper describes such a system.

Two main problems have had to be solved. The first was the choice of a ligand-field model capable of treating molecules with any co-ordination number and geometry but without an undue degree of parameterization and in which the relations between the parameters and chemical bonding might be reasonable and apparent. The angular-overlap model appears to satisfy these requirements far better than the older point-charge approach used with molecules of higher symmetry. We have described how the formation of the a.o.m. may be linked to that of a general expansion of the ligand-field Hamiltonian in spherical harmonics in such a way that the well established techniques of tensor-operator calculus may be exploited in many-electron problems. The second major point of concern was the calculation of magnetic tensors and e.s.r. g values for molecules in which the directions of principal susceptibilities are not defined by symmetry and hence are unknown *a priori.* A generalized form of Van Vleck's equation for susceptibility has been derived and several techniques have been described which reduce the amount of necessary computation to a level of practicability.

The procedures described here permit calculation of optical and e.s.r. spectra and of magnetic susceptibilities of any p^n, d^n, or f^n electron system for any basis chosen as free-ion terms and/or states relating to a molecule of any geometry. We mention just two examples of systems which were not previously capable of the proper study now afforded. The principal g values [17] and susceptibilities [16] of the nominally octahedral $[Co(OH_2)_6]^{2+}$ ion in Tutton salt are known to lie in unexpected and seemingly arbitrary directions with respect to the co-ordination geometry. Earlier theoretical treatments were not capable of making explicit recognition of the orientation of the water molecules with respect to the Co–O bonds and of calculating the magnetic properties in the consequently very low-symmetry molecule. Similarly, calculation of molecular susceptibilities from the measured crystal properties [18,19] of *trans*-$[Fe(py)_4(NCS)_2]$ on the assumption of D_4 symmetry or, at least, of one principal moment lying parallel to the $SC\underline{N}-Fe-\underline{N}CS$ axis produces inconsistent results using established methods described elsewhere.[16] The 'reasonable' structural assumption of a special role for the $SC\underline{N}-Fe-\underline{N}CS$ direction neglected the low symmetry to be noted when the orientation of the pyridine groups is recognized. Without the techniques described in this paper the problem could not have been solved. The studies of this and analogous systems we describe elsewhere [19] emphasize very strongly that structural details which may be negligible in some contexts must never be ignored if a significant understanding of magnetic and e.s.r. properties is desired.

[5/465 *Received,* 10*th March,* 1975]

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[17] B. Bleaney and D. J. E. Ingram, *Proc. Roy. Soc.*, 1951, **A208**, 143.

[18] A. M. White, Ph.D. Thesis, Cambridge University, 1974.

[19] M. Gerloch, R. F. McMeeking, and A. M. White, following paper.