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QUANTITATIVE FORMULATION OF LIGAND FIELD THEORY BY THE USE OF ORTHONORMAL OPERATORS. EXEMPLIFICATION BY MEANS OF p^q SYSTEMS

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A. INTRODUCTION

Ligand field theory's forerunner was crystal field theory which was developed by physicists around 1930. Physicists used the theory with success to interpret magnetic data. However, chemists wanted knowledge about the spectrum of energies of complexes in general, complexes with various metal ions in different oxidation states and with various ligands coordinated in different polyhedra. Seen in that perspective, the results of the physicists were small waves on a big ocean. Even though the chemists did not revolutionize the theory when they approached the subject in the fifties, they did bring the theory into a more suitable form from a chemical point of view. The main contribution from chemists was the realization that results of optical spectroscopy could be interpreted by the theory. Moreover, it was mainly the chemists who realized the limits of the theory and took interest in its relationship to molecular orbital theory.

In spite of its limitations, ligand field theory revolutionized transition metal chemistry. In order to exemplify this, one may just refer to the chemical concept of a d^3 system. While this concept at most had a quite formal meaning to the chemist of 1950, it images for the chemist of today a series of chemical systems, usually octahedral and kinetically inert, with a spin-quartet ground level, a maximum of ligand field stabilization energy, two or occasionally three cubic spin-allowed ligand field absorption bands and a spin-doublet level making it an emitter etc.

At the beginning the term ligand field was used to focus on the ligands as the immediate neighbours of the central ion, as opposed to the crystal field which consisted of a summation of contributions from nearest neighbours, next-nearest neighbours etc. Later, however, the concept of ligand field theory came to be used also for a qualitative molecular-orbital-oriented theory which might or might not include interelectronic repulsion. Quantitative ligand field theory is more well defined. It is a method of transforming spectroscopic data, g values and magnetic susceptibilities into energy parameters.

The energy parameters are empirical, while the rest of quantitative ligand field theory is based upon symmetry in combination with a limited function space of l orbitals, i.e. p, d or f orbitals [1]. The ligand field parameters, which reflect the splitting energies [2,3] within the l set, are, together with

the interelectronic repulsion parameters [4] and sometimes also with the spin–orbit coupling parameter [4], required to describe the experimental results.

In existing schemes of ligand field theory, the three kinds of energy parameters are not mutually comparable for a given chemical system. This review is concerned with some recent developments which not only allow a quantitative comparison of the terms of the ligand field with each other but also a comparison of the ligand field terms, individually or collectively, with those of the interelectronic repulsion and the spin–orbit coupling.

The main objective of the review is to illustrate the orthonormal operators' method of ligand field theory [1–4]. Its strategy is to work from simple examples, found among p electron systems. The molecule XeF_2, which in this context is a p^4 system, together with the p^2 systems BrF_2^+, BrF_3 and XeF_4 have been found to be almost sufficient to illustrate all the essentials of the method. It is essential that the concept of an operator and certain operator properties are discussed [1]. We have done this also by adhering to an extensive use of examples.

The review is mainly concerned with systems of high symmetry, cubic and tetragonal, treated using a holistic view of the ligand field, previously called the non-additive or the purely symmetry-determined ligand field. As opposed to the holistic view, we take the partitioned view of the ligand field, previously called the additive field. Here the total ligand field is written as a sum of terms arising from different parts of the ligand system. The partitioned view is, for example, that of the Angular Overlap Model [5–10], but this is not the main subject of the present review. The effect of interelectronic repulsion in p electron systems is also discussed, and the essential subject of the review is what we like to call the parametrical l^q model; we shall restrict ourselves to discussing mainly the case where $l = 1$, i.e. the p^q model.

The structure of the paper is the following. In Section B, operators on a p-orbital space are discussed. This section is also concerned with concepts such as orthonormality of operators [1], holohedral symmetry [11–13] and a point group hierarchy [9,14–15] or chain [16–18]. Furthermore, the ligand field is written as a sum of terms corresponding to the point groups of a hierarchy [2,3,9,14,17,18]. In Section C the function space is extended to that of a p^q configuration [19]. In Section D the interelectronic repulsion within a p^q configuration is discussed in terms of the spin-pairing energy parameter D [20]. Section E is concerned with the sum of the ligand field and the interelectronic repulsion, and in Section F the results are summarized and discussed as part of a historical development.

B. LIGAND FIELDS ON p ORBITALS

This section exemplifies most of the concepts that may be associated with the class of one-electron operators called ligand fields. As already mentioned, we shall restrict ourselves to discussing almost exclusively operators acting on p orbitals, or in other words, ligand fields of p electron systems.

In Section B(i) the usual standard set of p and d functions is given and their symmetry properties mentioned. The symmetry of the d functions turns out (Section B(v)) to be identical with that of the most general observable ligand field on p orbitals. In Section B(ii), ligand field observables are introduced and it is shown that a non-cubic field with a symmetry axis of an order higher than two is effectively axial when acting on p orbitals. In Section B(iii) the results of the action of a tetragonal ligand field are communicated in a multitude of ways. We hope in this fashion to diminish some of the less mathematical readers' worry about the fact that a ligand field has to be an operator in a quantum mechanical model. In Section B(iv) the similarity between functions and operators is demonstrated and operator orthogonality and operator magnitude defined, concepts that are essential for the whole paper. Section B(v) continues this demonstration of similarity by surveying all operators on p orbitals, and in particular, by discussing two different yet both useful ways of choosing them. One way leads to the basic operators that are either projection operators or shift operators. These shift operators have the property of transforming real p functions into one another as opposed to the step-up and step-down operators of angular momentum theory. The other way uses ligand field symmetry arguments to obtain a set of operators which directly represents the observables of the ligand field. These operators are found on the basis of character tables for a series of groups of decreasing symmetry (a group hierarchy or group chain). The concept of the holohedral rotation group is defined in Section B(vi), and in the last sections the holistic and the partitioned descriptions of ligand fields are briefly compared and the present chemical systems are discussed using the Angular Overlap Model.

(i) Standard real functions

For our discussion of functions as well as operators, a prerequisite is the usual real $(2l + 1)$-dimensional sets of l functions, where $l = 1$ and $l = 2$ refer to the p sets and d sets of functions which may be made bases for the ungerade three-dimensional and the gerade five-dimensional irreducible representations respectively of the three-dimensional rotation–reflection group R_{3i}. These usual real functions, whose p and d sets are given in eqns. (1) and (2), are symmetry adapted to the group hierarchy $R_{3i} \supset D_{\infty h} \supset D_{2h}$ as

also described in the expressions. All the functions are defined on the surface of the unit sphere, $x^2 + y^2 + z^2 = 1$:

$$
\begin{aligned}
&a_{2u}(D_{\infty h})b_{1u}(D_{2h}) \quad && p_z = p\sigma = p0 = \left(\sqrt{3/4\pi}\right)z = \left(\sqrt{3/4\pi}\right)[\cos\theta] \\
&e_{1u}(D_{\infty h})b_{2u}(D_{2h}) \quad && p_y = p\pi s = p1 = \left(\sqrt{3/4\pi}\right)y = \left(\sqrt{3/4\pi}\right)[\sin\theta\,\sin\phi] \\
&e_{1u}(D_{\infty h})b_{3u}(D_{2h}) \quad && p_x = p\pi c = p2 = \left(\sqrt{3/4\pi}\right)x = \left(\sqrt{3/4\pi}\right)[\sin\theta\,\cos\phi]
\end{aligned} \tag{1}
$$

$$
\begin{aligned}
&a_{1g}(D_{\infty h})a_g(D_{2h}) \quad && d_\theta = d\sigma = d0 = \left(\sqrt{5/4\pi}\right)\left[z^2 - (1/2)x^2 - (1/2)y^2\right] \\
& && \quad = \left(\sqrt{5/4\pi}\right)\left[\cos^2\theta - (1/2)\sin^2\theta\right] \\
&e_{1g}(D_{\infty h})b_{3g}(D_{2h}) \quad && d_\xi = d\pi s = d1 = \left(\sqrt{5/4\pi}\right)\sqrt{3}\,[yz] \\
& && \quad = \left(\sqrt{15/8\pi}\right)[\sin 2\theta\,\sin\phi] \\
&e_{1g}(D_{\infty h})b_{2g}(D_{2h}) \quad && d_\eta = d\pi c = d2 = \left(\sqrt{5/4\pi}\right)\sqrt{3}\,[zx] \\
& && \quad = \left(\sqrt{15/8\pi}\right)[\sin 2\theta\,\cos\phi]
\end{aligned} \tag{2}
$$

$$
\begin{aligned}
&e_{2g}(D_{\infty h})b_{1g}(D_{2h}) \quad && d_\xi = d\delta s = d3 = \left(\sqrt{5/4\pi}\right)\sqrt{3}\,[xy] \\
& && \quad = \left(\sqrt{15/16\pi}\right)[(1 - \cos 2\theta)\sin 2\phi] \\
&e_{2g}(D_{\infty h})a_g(D_{2h}) \quad && d_\epsilon = d\delta c = d4 = \left(\sqrt{5/4\pi}\right)\left(\sqrt{3/4}\right)\left[x^2 - y^2\right] \\
& && \quad = \left(\sqrt{15/16\pi}\right)[(1 - \cos 2\theta)\cos 2\phi]
\end{aligned}
$$

It may be noted that each function, independent of its l value, is numbered with a non-negative integer. The σ functions, numbered zero, and the cosine functions, numbered with even positive numbers, are even with respect to reflection in the ZX plane. The sine functions, numbered with odd integers, are odd with respect to this reflection. The function sets of eqns. (1) and (2) have sometimes [1] been denoted the $1\lambda\varsigma$ sets where $\lambda = 0$, 1 and 2 correspond to σ, π and δ functions just as $l = 0$, 1 and 2 correspond to s, p and d functions. For $\lambda = 0$ the extra denotation ç is superfluous, but for $\lambda > 0$, ç may represent either c or s.

As they stand, the functions in eqns. (1) and (2) are normalized to unity over the unit sphere but we shall nevertheless in the rest of the paper use their Cartesian expressions without the factor $\sqrt{(2l+1)/4\pi}$ and yet imply that they are normalized to unity.

(ii) An axial ligand field. Pseudoabsolute energies

Strictly speaking an l electron is a concept that only has full meaning for systems of spherical symmetry. However, the concept may be used for

qualitative classification purposes [21], and the assumption that, further, quantification is possible leads to what is known as ligand field theory. One can in the case of p electrons speak about the parametrical p^q model which means that the chemical situation is parametrized under the restriction that its eigenfunctions can be described by the full set of functions of the p^q configuration.

A p electron has 3 orbitals among which to choose. If one has a Cartesian coordinate system XYZ, then the orbital functions are most naturally chosen as p_x, p_y and p_z, simply denoted x, y and z and assumed to be normalized to unity as in (1). The orbitals have a mutual relationship like the three unit vectors of the Cartesian coordinate system. The energies associated with them are identical in spherical symmetry and in actual fact the concept of p means that the three functions span the three-dimensional irreducible representation of the three-dimensional rotation group R_3. In the octahedral group O, p transforms as the three-dimensional irreducible representation $t_1(O)$, meaning that the p orbitals remain degenerate in an octahedral ligand field. This in turn means that there is no ligand field parameter (no ligand field observable) to monitor the octahedral part of the Hamiltonian within the parametrical p^q model. However, if, for example, the symmetry is lowered to D_4, then the three p orbitals fall into two classes, p_z or $pa_2(D_4)$, consisting of the p orbital whose symmetry axis is directed along the tetragonal axis, chosen as the Z axis, and $\{p_x, p_y\}$ or $pe(D_4)$, consisting of the two remaining p orbitals. The situation is analogous if the symmetry is lowered from R_3 to D_3: the orbital p_z is now $pa_2(D_3)$, directed along the trigonal axis. This orbital forms one class while the two orthogonal orbitals $pe(D_3)$ form the other class.

We are concerned with situations where the term axial symmetry is appropriate. Axial means effectively full rotational symmetry about one axis (like a σ orbital, or in this context, like a σ operator) and from the point of view of p orbitals, the symmetries D_3 and D_4 are indistinguishable from D_∞. In more general terms the way in which the p orbitals are divided into classes does not allow a distinction between D_n symmetries for varying n provided $n > 2$; even D_∞ gives rise to this same situation with two classes of orbitals, one consisting of the orbital directed along the principal axis and one consisting of the two remaining orbitals. The p orbital whose rotational symmetry axis is along the ∞ axis, i.e. $p_z = pa_2(D_\infty)$ is according to eqn. (1) the $p\sigma$ orbital. In D_∞, orbitals of symmetry $a_2(D_\infty)$ and $a_1(D_\infty)$ (as d_{z^2}) are both referred to as σ. The two remaining p orbitals whose symmetry axes are perpendicular to the ∞ axis are then the $pe_1(D_\infty)$ or $p\pi$ set. The terms σ and π have their usual chemical meaning provided it is remembered that this meaning is bound together with the circularly cylindrical or conical symmetry of the ∞ axis.

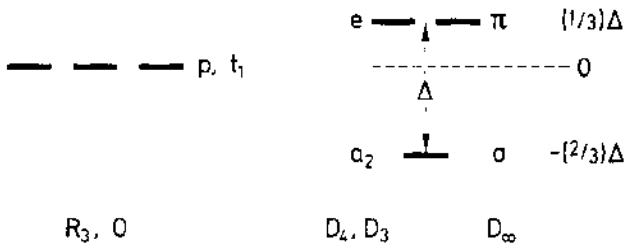

Fig. 1. The splitting Δ of the p-orbital level caused by a ligand field of axial symmetry. Passing from spherical (R_3) to octahedral (O) symmetry, the three p orbitals remain degenerate. Under D_3 or D_4 symmetry perturbations, however, the set is split into a non-degenerate orbital of symmetry $a_2(D_3)$ or $a_2(D_4)$ and a doubly degenerate set of symmetry $e(D_3)$ or $e(D_4)$ under preservation of the barycentre. As pointed out in Section B(ii) the p orbitals cannot distinguish D_n symmetry ($n > 2$) from D_∞ symmetry. This means that we can alternatively choose to label the orbitals according to linear symmetry. The $a_2(D_\infty)$ orbital is then of σ symmetry and the $e(D_\infty)$ set becomes a set of π orbitals. The sign of Δ in the figure corresponds to a negative sign of the parameter N_θ^σ associated with the sign-fixed operator $\hat{N}_\theta^\sigma$ (eqn. (32)). The sign of this operator is based upon phase-fixed coupling coefficients [22]. The sign of Δ shown on the figure is that expected for a square-planar molecule such as XeF_4 (see Section B(viii)).

The fact that it is possible to label the orbital levels in $D_n (n > 2)$ according to irreducible representations of D_∞ is carried over to the poly-electron levels of all p^q configurations. This has the important consequence that multiplet terms of $D(R_3)$ symmetry do not split up as expected in tetragonal symmetry. This will be illustrated in Section E.

The one-electron energy situation described is depicted in Fig. 1 where the ligand field parameter Δ is defined with an arbitrary choice of sign, placing the π orbitals above the σ orbital. This parameter is an observable of the parametrical p^q model and in fact the only ligand field observable when the symmetry is axial.

The observable Δ is an energy difference, and it is important to realize that absolute energies are never ligand field observables. However, it is useful to introduce pseudoabsolute energies. This is done by choosing a zero point for the orbital energies. We choose this zero point as the average energy of the orbitals present, here the three p orbitals. This average is $2\Delta/3$ in Fig. 1. The pseudoabsolute energies $\bar{h}$ are then

$$\begin{aligned} \bar{h}(p\pi) &= \Delta - 2\Delta/3 = (1/3)\Delta \\ \bar{h}(p\sigma) &= 0 - 2\Delta/3 = -(2/3)\Delta \end{aligned} \tag{3}$$

with the consequence that these energies, summed over the three p orbitals, are zero. The process of enforcing this sum rule is called barycentration.

We shall now proceed to combine our knowledge about the axial field with the particular choice of p-function basis made in Section B(i). This will lead us to the important concepts of a ligand field operator and its associated matrix representation.

(iii) A matrix representation of the tetragonal ligand field operator

In this section we shall discuss different ways of expressing the symmetry results of eqn. (3), i.e. the action of, for example, a tetragonal ligand-field operator on a p-orbital space. These ways contain by their example several general features of both ligand field theory itself and of the formalism we advocate here. In this formalism the concept of the tetragonal ligand field operator, here called $\hat{V}(D_4)$, is very important. Operators will in the following be characterized by a caret (a hat). We stress that we never need to let the operators operate in any tangible way, i.e. by using rules of operation. We need them only as part of the formalism, i.e. as part of the conceptual framework, and as a highly useful component of the system of notation. All the information required about the action of an operator will be contained in one of its matrix representations.

We are able to write eqn. (3) in the alternative form given in eqn. (4):

$$\begin{aligned}
&\langle z|\hat{V}(D_4)|z\rangle = \langle \sigma|\hat{V}(D_4)|\sigma\rangle = -(2/3)\Delta \\
&\langle y|\hat{V}(D_4)|y\rangle = \langle \pi s|\hat{V}(D_4)|\pi s\rangle = (1/3)\Delta \\
&\langle x|\hat{V}(D_4)|x\rangle = \langle \pi c|\hat{V}(D_4)|\pi c\rangle = (1/3)\Delta
\end{aligned} \tag{4}$$

where s and c represent sine and cosine and refer to the functional form (ϕ dependence) of the pπ orbitals when these are written in spherical polar coordinates as in eqn. (1).

Another way of expressing the same results is by using matrix notation as shown in matrix (5):

$$\hat{V}(D_4) \begin{matrix} \\ x \\ y \\ z \end{matrix} \begin{matrix} \begin{matrix} x & \quad y & \quad z \end{matrix} \\ \begin{bmatrix} 1/3 & 0 & 0 \\ 0 & 1/3 & 0 \\ 0 & 0 & -2/3 \end{bmatrix} \end{matrix} \Delta \tag{5}$$

The 3×3 array of numbers is called the coefficient matrix to the parameter Δ. The matrix contains the coefficients to Δ in the energy expressions (4) for the different orbitals. We define also the coefficient operator $\hat{Q}_\Delta$ by eqn. (6):

$$\hat{V}(D_4) = \hat{Q}_\Delta \Delta \tag{6}$$

Since the parameter is only a multiplication factor, $\hat{V}(D_4)$ may equally well be written $\Delta\hat{Q}_\Delta$. As a convention we shall, however, always write the parameter after the operator as in eqn. (6). We can now alternatively express the information of matrix (5) by writing the coefficient matrix (7) alone:

$$\begin{array}{c} \hat{Q}_\Delta \\ \mathrm{x} \\ \mathrm{y} \\ \mathrm{z} \end{array} \begin{array}{c} \begin{array}{ccc} \mathrm{x} & \mathrm{y} & \mathrm{z} \end{array} \\ \begin{bmatrix} 1/3 & 0 & 0 \\ 0 & 1/3 & 0 \\ 0 & 0 & -2/3 \end{bmatrix} \end{array} \tag{7}$$

The matrix (7) is the matrix representation of the operator $\hat{Q}_\Delta$ with respect to our particular basis of p orbitals (eqn. (1)). The numbers of the matrix are the matrix elements of $\hat{Q}_\Delta$. When each element is multiplied by the energy parameter Δ, we obtain the matrix of $\hat{V}(D_4)$. The whole example shows how simple it is to obtain a matrix representation of $\hat{V}(D_4)$ from the symmetry results of eqn. (3).

The matrices (5) and (7) consist of numbers that are different from zero only along the diagonal; we say that the matrices are diagonal. Further, the sum of the diagonal elements is equal to zero, i.e. the trace of the matrices is equal to zero. The matrices are traceless. This is a consequence of the barycentration introduced in connection with the pseudoabsolute energies in eqn. (3). The diagonality implies that our particular p basis functions are eigenfunctions of $\hat{V}(D_4)$ as well as of $\hat{Q}_\Delta$. For example, the equality (eqn. (8))

$$\hat{Q}_\Delta |\mathrm{z}\rangle = -(2/3)\,|\mathrm{z}\rangle \tag{8}$$

can be verified by noting eqn. (9):

$$\langle \mathrm{z}\,|\,\hat{Q}_\Delta\,|\mathrm{z}\rangle = -(2/3)\langle \mathrm{z}|\mathrm{z}\rangle = -2/3 \tag{9}$$

The fact that the real p functions are eigenfunctions of the tetragonal ligand field operator $\hat{V}(D_4)$ and thereby of $\hat{Q}_\Delta$ was actually already revealed in eqn. (1) where the transformation properties of the three orbitals in the hierarchy $R_3 \supset D_{\infty h} \supset D_{2h}$ were given. These properties were also our reason for choosing this real set of p orbitals in the first place. The manifestation of the operators $\hat{V}(D_4)$ and $\hat{Q}_\Delta$ is fully covered in their matrices (5) and (7). This is the reason why we do not have to operate with them except in a rather formal sense. This will be further illustrated in Section B(v). First we look at operators from a point of view that may still be considered rather new in chemistry: orthogonality and normalization of operators.

(iv) Magnitude of an operator and the mutual operator properties of overlap and orthogonality

The concept of overlap between two orbitals is well known in chemistry. The concept of normalization of an orbital is also commonplace, although the fact that this is the same as requiring the orbital self-overlap to take on a particular value is less commonly appreciated. These overlap concepts for functions can be defined also for operators and this leads, for example, to such a concept as a complete set of orthonormal operators. This will be further elaborated in Section B(v). Here we restrict ourselves to discussing pairs of operators, including the special case of two identical operators.

The overlap, or, what is the same, the scalar product, of two operators $\hat{A}$ and $\hat{B}$ is defined by eqn. (10):

$$\langle \hat{A}|\hat{B}\rangle = \mathrm{Tr}(\hat{A}^{\dagger}\hat{B}) = \mathrm{Tr}(\mathbf{A}^{\dagger}\mathbf{B}) = \sum_{i,j} \mathbf{A}^{\dagger}_{ji}\mathbf{B}_{ij}$$

$$= \sum_{i,j} \mathbf{A}^{*}_{ij}\mathbf{B}_{ij} = \sum_{i,j} \mathbf{A}_{ij}\mathbf{B}_{ij} \qquad (10)$$

For the present purpose we need only consider the final result. It is seen that matrix representations **A** and **B** of the two operators are involved. It is understood that these matrices are set up in the same basis, and in the present paper the last expression applies because it has been seen to that only real matrix elements occur. The algorithm is then extremely simple. One has to take products of corresponding elements of the two matrices and then add all the products to obtain the operator overlap or scalar product. The reason that the formalism works is that the operator overlap is a scalar and thus independent of the function basis in which the matrices of the operators are set up.

For completeness we briefly discuss the intermediate expressions in eqn. (10). $\hat{A}^{\dagger}$ means the Hermitian conjugate of $\hat{A}$. Tr is an abbreviation of the word trace which means the sum of the diagonal elements.

Operator orthogonality is an extremely important concept that comes into being as a special case of eqn. (10). When the overlap between two operators is equal to zero, we say that the two operators are orthogonal. The concept of operator orthogonality will be used time and time again in this paper and in Section E it will turn out to be a major prerequisite and even a condition for the new quantifications illustrated there.

We next consider the special situation where $\hat{A} = \hat{B}$. The expression (10) then means the self-overlap which is seen to be equal to the sum of the squares of all the matrix elements. This quantity is also called the norm square of the operator and its positive square root is called the magnitude (length) of the operator. If an operator is divided by its magnitude, the

operator thus obtained is said to be normalized to unity. In general, an operator is said to be normalized to its own norm square.

We now apply eqn. (10) to the cases of $\hat{V}(D_4)$ in matrix (5) and $\hat{Q}_\Delta$ in matrix (7) to obtain eqns. (11) and (12):

$$\langle \hat{V}(D_4)|\hat{V}(D_4)\rangle = \langle \hat{Q}_\Delta\Delta|\hat{Q}_\Delta\Delta\rangle = \langle \hat{Q}_\Delta|\hat{Q}_\Delta\rangle\Delta^2$$
$$= \left[(1/3)^2 + (1/3)^2 + (-2/3)^2\right]\Delta^2 = (2/3)\Delta^2 \tag{11}$$

$$\langle \hat{Q}_\Delta|\hat{V}(D_4)\rangle = \langle \hat{Q}_\Delta|\hat{Q}_\Delta\rangle\Delta = (2/3)\Delta \tag{12}$$

Equation (11) shows that $\hat{V}(D_4)$ and $\hat{Q}_\Delta$ are normalized to $(2/3)\Delta^2$ and $(2/3)$ respectively, while eqn. (12) gives their overlap as $(2/3)\Delta$.

The next section can be anticipated in eqn. (13) by rewriting $\hat{V}(D_4)$ in terms of an irreducible tensor operator $\hat{N}_\theta^{\mathrm{d}}$, normalized to unity when acting on the p-orbital space, and its associated parameter N_θ^{d} whose symbol does not contain a hat:

$$\hat{V}(D_4) = \hat{N}_\theta^{\mathrm{d}} N_\theta^{\mathrm{d}} \tag{13}$$

When $\hat{V}(D_4)$ is written as in eqn. (13), the expressions (11) and (12) read as the expressions (14) and (15) respectively:

$$\langle \hat{V}(D_4)|\hat{V}(D_4)\rangle = (N_\theta^{\mathrm{d}})^2 \tag{14}$$

$$\langle \hat{N}_\theta^{\mathrm{d}}|\hat{V}(D_4)\rangle = N_\theta^{\mathrm{d}} \tag{15}$$

A comparison of eqns. (11) and (12) with eqns. (14) and (15) respectively shows how the use of normalized operators emphasizes the importance of the empirical parameters, in this case N_θ^{d}, of the model.

We finish this section by asking the reader to realize that a unit matrix and a traceless matrix are mutually orthogonal. This means that an operator whose matrix representations are proportional to the unit matrix is orthogonal to a traceless operator. When in l-orbital ligand field models, operators of the former kind are used as energy operators (see Section B(v)), then they are totally symmetrical under R_{3j}, i.e. they have s_g symmetry and do not represent observables within the model. The latter operators, the traceless ones, carry the observable energy parameters that make up the empirical part of the model. This will be further discussed in the following section.

(v) Complete sets of operators acting on the p-orbital space

In this section we shall begin by discussing general operators acting on the p-orbital space and eventually show how it is possible on the basis of

point group character tables alone to obtain completely defined explicit expressions for the ligand field operators for a chemical system of a particular symmetry.

Just as one may choose a function basis for the p-orbital space, one may also choose a basis for the operators acting on this space. An infinite number of such operator bases exist but we shall here focus on two special kinds, one characterized by its simple relationship to the functional basis, and the other distinguished by referring directly to the observable orbital-energy differences of a chemical system. When we have introduced these two operator bases and derived their mutual relationship, we shall be able to compare this relationship with the well-known coupling of angular momenta. The two kinds of orthonormal operator bases will be denoted by $\hat{S}$ and $\hat{N}$; the $\hat{S}$ operators are called basic operators because they are closely related to a particular basis of the function space on which they act, while the $\hat{N}$ operators are irreducible tensor operators of some group.

It will turn out that the expression for a ligand field operator obtains the form either $\sum_{\alpha,\beta}\hat{S}_{\alpha\beta}S_{\alpha\beta}$ or $\sum_{\Gamma,\gamma}\hat{N}_{\gamma}^{\Gamma}N_{\gamma}^{\Gamma}$ where the dummy indices α and β refer to basis functions while the dummy index Γ refers to an irreducible representation of some group and γ to its component (see eqn. (13)). In these expressions, $S_{\alpha\beta}$ and N_{γ}^{Γ} are energy quantities, i.e. parameters. For a given symmetry of the ligand field and a given function space (here p), the number of independent ligand field parameters is fixed and this number is equal to the number of linearly independent, totally symmetrical operators, i.e. operators belonging to the unit representation of the point group of the central atom, taken together with its environment.

A matrix representation of the most general operator on the p space can be written as

$$\begin{array}{c} \\ \mathrm{x} \\ \mathrm{y} \\ \mathrm{z} \end{array}\begin{array}{c} \begin{array}{ccc} \mathrm{x} & \mathrm{y} & \mathrm{z} \end{array} \\ \begin{bmatrix} S_{xx} & S_{xy} & S_{xz} \\ S_{yx} & S_{yy} & S_{yz} \\ S_{zx} & S_{zy} & S_{zz} \end{bmatrix} \end{array} \tag{16}$$

where no special conditions have been placed on the nine S-parameters that define the values of the matrix elements. This means that nine independent operators are required, one corresponding to each of the nine parameters, in order to span the full space of operators acting on a p space of functions. There are, of course, an infinite number of ways of choosing a nine-dimensional basis of operators spanning this operator space, but as mentioned above, some choices are more appealing than others.

One natural choice is that of the basic operators (eqn. (17)):

$$\hat{S}_{xx},\ \hat{S}_{yy},\ \hat{S}_{zz},\ \hat{S}_{xy},\ \hat{S}_{yx},\ \hat{S}_{xz},\ \hat{S}_{zx},\ \hat{S}_{yz},\ \hat{S}_{zy} \tag{17}$$

where $\hat{S}_{xz}$, for example, is defined as in eqn. (18):

$$\hat{S}_{xz} = |x\rangle\langle z| \tag{18}$$

The combination of two sets in the way shown here for two p sets is called the formation of the simple tensor product or of the non-commutative product (see also eqn. (34) in Section C). In the present example the first factor is invariably a ket and the second factor a bra, thereby making the combination an operator. The operator of eqn. (18) is fully characterized by having the matrix representation (19):

$$\begin{array}{c} \hat{S}_{xz} \\ \\ x \\ y \\ z \end{array} \begin{array}{c} \begin{array}{ccc} x & y & z \end{array} \\ \begin{bmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \end{array} \tag{19}$$

As can be seen from eqns. (18) or (19), the operator $\hat{S}_{xz}$ has the property $\langle x|\hat{S}_{xz}|z\rangle = 1$, which may alternatively be written either as $\hat{S}_{xz}|z\rangle = |x\rangle$ or $\langle x|\hat{S}_{xz} = \langle z|$. In either case, $\hat{S}_{xz}$ is a shift operator that takes one real p function into another. Similarly, $\hat{S}_{zz}$ acts on $|z\rangle$ to produce $|z\rangle$ again so that $\hat{S}_{zz} = (\hat{S}_{zz})^2$. $\hat{S}_{zz}$ is called an idempotent which means that it can be used any number of times with the same result. It is also called the projection operator of z because if it acts on a linear combination of p functions, for example, $\alpha z + \beta y$, where α and β are numbers, then its result is αz, i.e. it has "projected" out the z part of the linear combination.

The most general operator on a p-orbital space can be written as the linear combination (20) of basic operators:

$$\hat{S}_{xx}S_{xx} + \hat{S}_{yy}S_{yy} + \hat{S}_{zz}S_{zz} + \hat{S}_{xy}S_{xy} + \hat{S}_{yx}S_{yx} + \hat{S}_{xz}S_{xz} + \hat{S}_{zx}S_{zx} + \hat{S}_{yz}S_{yz} + \hat{S}_{zy}S_{zy} \tag{20}$$

The representation of this operator in our standard p function basis is the matrix (16). The basic operators of set (17) are dimensionless, and consequently the associated parameters have the dimension of the total operator of the form (20).

Referring to the discussion in Section B(iv), it is easily seen that the basic operators of set (17) make up an orthonormal operator basis on the p space. The completeness of this basis within the p space is the same as the generality of the operator (20).

It is useful for us to note the resemblance between orthonormal sets of functions and those of operators. Let us as an example consider the two operators, $\hat{S}_{xx}$ and $\hat{S}_{yy}$, that form an orthonormal operator subspace of the

operator space (17). If α and β are real numbers and $\alpha^2 + \beta^2 = 1$, then the two linear combinations of $\hat{S}_{xx}$ and $\hat{S}_{yy}$

$$\begin{aligned} &\alpha\hat{S}_{xx} + \beta\hat{S}_{yy} \\ &\beta\hat{S}_{xx} - \alpha\hat{S}_{yy} \end{aligned} \tag{21}$$

form a new orthonormal set of operators spanning the same subspace. The property of operator spaces (and subspaces) exemplified in connection with expression (21) will be of immediate use to us when permutational symmetry breaks up the set (17) into the mutually orthogonal subsets (22) and (23).

When our interest is in energy operators (or more generally in operators corresponding to observables), the demand of real eigenvalues imposes the constraint on the operators, that they be Hermitian, or, in our case where the function bases are invariably real, that they have symmetrical matrix representations. This is not a property of all the operators of set (17). The maximum number of independent Hermitian operators that can be constructed from the set of basic operators is six. These have been written out as the set (22) and they include the permutationally symmetrical and normalized linear combinations of basic operators of set (17):

$$\hat{S}_{xx},\ \hat{S}_{yy},\ \hat{S}_{zz},\ \sqrt{1/2}\left(\hat{S}_{xy} + \hat{S}_{yx}\right),\ \sqrt{1/2}\left(\hat{S}_{xz} + \hat{S}_{zx}\right),\ \sqrt{1/2}\left(\hat{S}_{yz} + \hat{S}_{zy}\right) \tag{22}$$

The three operators, which hereby are excluded as energy operators and which together with the six operators of set (22) form an orthonormal set that spans the same space as the set (17), are then naturally chosen as the permutationally antisymmetric ones of set (23):

$$\sqrt{1/2}\left(\hat{S}_{xy} - \hat{S}_{yx}\right),\ \sqrt{1/2}\left(\hat{S}_{zx} - \hat{S}_{xz}\right),\ \sqrt{1/2}\left(\hat{S}_{yz} - \hat{S}_{zy}\right) \tag{23}$$

We have now redistributed the members of the operator space (17) according to their permutational symmetry. We then look at their spatial symmetry. First we consider the component operators of set (17) and note that we have used the standard basis (eqn. (1)) for the p space of functions to construct them. This standard orbital set has the property that its individual functions transform irreducibly under the point group D_{2h}. Since the irreducible representations of D_{2h} are all one-dimensional, the operators $\hat{S}_{\alpha\beta}$ of set (17) also transform irreducibly under D_{2h} when α and β refer to the standard set (1), and the immediate conclusion is that the first three operators of set (17), the idempotents, transform as $A_g(D_{2h})$ and the six others pair-wise as $B_{1g}(D_{2h})$, $B_{2g}(D_{2h})$ and $B_{3g}(D_{2h})$ respectively. By re-examining sets (22) and (23) in the light of this conclusion, it is further seen that the permutational symmetry adaptation does not influence the spatial one. This means that the permutational symmetry adaptation takes place inside the pairs that contain components of equal spatial symmetry.

Until now we have been concerned with the spatial symmetry under D_{2h} only. However, the p-function basis and thereby the operator basis has a much higher symmetry: the p functions transform as the three-dimensional irreducible representation p_u of R_{3i}. Using this we shall be able to symmetry-characterize in R_{3i} also the set of all operators acting on p space, just as we did above in D_{2h}.

The formation of the set of all ordered ket bra juxtapositions (products) of components of two p sets is called the formation of the tensor product of these sets. This tensor product spans a gerade reducible representation of R_{3i} that may be reduced to three irreducible subsets. This statement is expressed in eqn. (24) apart from the parities (see below):

$$|p\} \otimes \{p| = [\,|p\}\{p|\,]^s \oplus \underline{[\,|p\}\{p|\,]^p} \oplus [\,|p\}\{p|\,]^d \tag{24}$$

In eqn. (24), set notation has been used. $|\}$ means the orthonormal set of all the kets and $\{|$ the orthonormal set of all the bras. $\otimes$ denotes the formation of the tensor product, and $\oplus$ denotes the tensor sum (a sum of sets). The left-hand expression of eqn. (24) is thus a short-hand way of writing the set of the nine $|\ \rangle\langle\ |$-type (S-type) orthonormal operators * of set (17). The right-hand expression is a symmetry reformulation of the well-known vector coupling rule result from atoms that the tensor product of two p-sets is equal to the tensor sum of three sets of s, p and d types respectively, where these symbols refer to the one-dimensional, the three-dimensional and the five-dimensional irreducible representation of the group R_3.

The first term $[\,|p\}\{p|\,]^s$ is thus the spherically symmetrical, normalized linear combination of the $\hat{S}$ operators of set (17) and it is actually equal to the algebraic sum of the first three operators of set (17), normalized by being multiplied by the factor $\sqrt{1/3}$. This factor is the so-called Clebsch Gordan coefficient, a number. It is normally written as $\langle px\ px\,|s\rangle = \langle py\ py\,|s\rangle = \langle pz\ pz\,|s\rangle$ and is, for example, equal [1] to the operator overlap $\langle \hat{S}_{zz}\,|[\,|p\}\{p|\,]^s\rangle$. The second term $[\,|p\}\{p|\,]^p$ has been underlined to signify that this term is permutationally antisymmetrical. Since in this particular case, $[\,|p\}\{p|\,]^p$ is the only antisymmetrical set in tensor product space, its orthonormal components were already isolated in set (23) as a consequence of the permutational symmetry adaptation. In set (23) the components occur in the order $[\,|p\}\{p|\,]^p_z$, $[\,|p\}\{p|\,]^p_y$ and $[\,|p\}\{p|\,]^p_x$ respectively, referring to eqn. (1). Incidentally, the three last operators of set (22) are the orthonormal components $[\,|p\}\{p|\,]^d_\xi$, $[\,|p\}\{p|\,]^d_\eta$ and $[\,|p\}\{p|\,]^d_\zeta$ respectively, referring to

* It is customary to use lower-case letters for one-electron functions and capital letters for all other purposes. We have chosen to use lower-case letters also for irreducible representations associated with one-electron operators.

eqn. (2). The two remaining operators must transform as $[|p\}\{p|]^q_\theta$ and $[|p\}\{p|]^d_\epsilon$ with reference to eqn. (2), and these operators must be orthonormal linear combinations of the first three operators of set (22). Their explicit expressions will be derived shortly. All the operators of set (23) have gerade inversion symmetry because they are tensor products of two ungerade sets (see also Section B(vi)). In spite of the gerade symmetry, the set $[|p\}\{p|]^p$ cannot, as already discussed above, be used as energy operators because of their permutational antisymmetry.

Referring to the last remarks in Section B(iv), the operator $[|p\}\{p|]^s$ carries the whole trace [22, p. 251] of the set (22) and has therefore no observable consequences in a ligand field context. It is the five operators of $[|p\}\{p|]^d$ type that are traceless and therefore are potentially able to carry ligand field observables.

We are therefore now able to conclude that in the most general ligand field on a p space, i.e. a field without any symmetry at all, there are five linearly independent operators that may correspond to observables, and these five operators span a d space. We have thus limited our problem to some extent. In set (22) we have a set of six operators that can be used as a basis for the most general ligand field operator, but though the operators of set (22) are fully symmetry adapted with respect to their permutational symmetry, this is only partially true with respect to their spatial symmetry. We now proceed by returning to the general operator (20) in order to illustrate a property of it which will be used in performing the spatial symmetry adaptation.

So far we have mainly been concerned with the operator basis for energy operators rather than with the energy operators themselves. We aim at finding the latter for a particular chemical situation. In order to progress, we focus attention upon an operator that may exemplify an energy operator and note the identity (25) for $\alpha^2 + \beta^2 = 1$:

$$\hat{S}_{xx}S_{xx} + \hat{S}_{yy}S_{yy} = \left(\alpha\hat{S}_{xx} + \beta\hat{S}_{yy}\right)\left(\alpha S_{xx} + \beta S_{yy}\right) + \left(\beta\hat{S}_{xx} - \alpha\hat{S}_{yy}\right)\left(\beta S_{xx} - \alpha S_{yy}\right) \tag{25}$$

This identity illustrates the statement that any orthogonal transformation of the ordered set of component operators of a general operator (20) implies the same orthogonal transformation of the ordered parameters associated with the operators. The reverse implication is also true [2,3], and we shall use this in the following as one of the means of performing our spatial symmetry adaptation.

As an example we consider a chemical system of orthorhombic rotational symmetry D_2. We choose the C_2 axes of D_2 as the Cartesian axes X, Y and Z which define the p-orbital set (1). With this choice the ligand field

operator $\hat{W}(D_2)$ of the form (20) has only three terms since each term has to have the full symmetry of the chemical system, i.e. $A(D_2)$, and this is only true of the idempotent operators $\hat{S}_{xx}$, $\hat{S}_{yy}$ and $\hat{S}_{zz}$, as discussed in connection with the spatial symmetry properties of the operators of sets (17) and (22). $\hat{W}(D_2)$ then has the form

$$\hat{W}(D_2) = \hat{S}_{xx}S_{xx} + \hat{S}_{yy}S_{yy} + \hat{S}_{zz}S_{zz} \tag{26}$$

where $\langle x | \hat{W}(D_2) | x \rangle = S_{xx}$ is the energy of the p_x orbital perturbed by $\hat{W}(D_2)$. Equation (26) is the expression for the ligand field operator in terms of basic operators. We now proceed with the aim of obtaining the expression for the same operator $\hat{W}(D_2)$ in terms of hierarchic irreducible tensor operators.

Firstly we have to establish a symmetry hierarchy. The situation is the following. We begin with a set of unperturbed p orbitals, i.e. p orbitals in spherical symmetry R_3, where they make a basis for the three-dimensional irreducible representation. We now gradually reduce the symmetry passing through the octahedral rotation group O and the dihedral tetragonal rotation group D_4 to the holohedral orthorhombic rotation group D_2. Character tables for these groups immediately tell us that the p set transforms as $t_1(O)$, as $e(D_4) \oplus a_2(D_4)$ and as $b_3(D_2) \oplus b_2(D_2) \oplus b_1(D_2)$. In Fig. 2 these symmetry results are illustrated by depicting the hierarchic splittings associated with our ligand field operator $\hat{W}(D_2)$. This total orthorhombic operator may accordingly be written as in eqn. (27) where $\hat{V}(D_2)$ is now the orthorhombic part of the total perturbation:

$$\hat{W}(D_2) = \hat{W}(O) + \hat{V}(D_4) + \hat{V}(D_2) \tag{27}$$

This lowest symmetry part $\hat{V}(D_2)$ of the ligand field dictates the symmetry

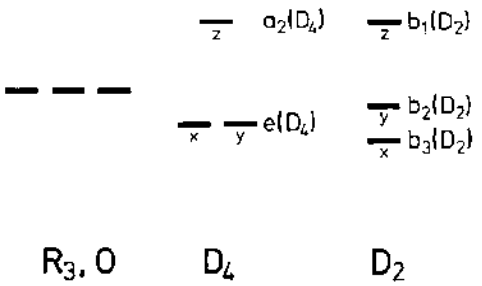

Fig. 2. Symmetry-based orbital energy level diagram for p electrons. The p-orbital basis {x,y,z} (see eqn. (1)) is symmetry adapted to the group hierarchy $R_3 \supset O \supset D_4 \supset D_2$. This figure, apart from showing the transformation properties of the p set on descent in symmetry, also shows, with signs, the ligand field splittings, associated with the tetragonal and the orthorhombic field components. The diagram thereby completely defines the hierarchic irreducible tensorial operators, including their signs, as discussed in Section B(v).

of the total field $\hat{W}(D_2)$. The three terms on the right-hand side of eqn. (27) must now be found among the six operators of $[|p\}\{p|]^s \oplus [|p\}\{p|]^d$ as discussed in connection with eqn. (24).

Looking at Fig. 2, we observe that the orthorhombic splitting of the orbital level e(D_4) is $S_{yy} \quad S_{xx}$. The associated operator is therefore (see eqn. (25)) $\hat{S}_{yy} - \hat{S}_{xx}$, the normalized operator is $\sqrt{1/2}(\hat{S}_{yy} - \hat{S}_{xx})$ and the orthorhombic part to the total energy operator is then as given in eqn. (28):

$$\hat{V}(D_2) = \sqrt{1/2}\left(\hat{S}_{yy} - \hat{S}_{xx}\right)\sqrt{1/2}\left(S_{yy} - S_{xx}\right)$$
$$= \sqrt{1/2}\left(\hat{S}_{xx} - \hat{S}_{yy}\right)\sqrt{1/2}\left(S_{xx} - S_{yy}\right) \tag{28}$$

The purpose of the last part of this equation is to illustrate the fact that there is no chemistry in the sign defining the splitting operator. There is only convention. However, once such a convention has been made, then there is chemistry in the sign of the associated empirical parameter. In eqn. (28) the first expression, combined with a positive empirical energy parameter, leads to the splitting situation shown in Fig. 2. Further, we note that the operator of eqn. (28) transforms under all rotations and reflections under R_{3i} as the d orbital d_ϵ of eqn. (2). What is especially important here is that this operator is non-totally symmetrical in the groups O and D_4 but totally symmetrical in D_2, i.e. has a(D_2) symmetry. The operator is the component $\hat{N}^d_\epsilon = [|p\}\{p|]^d_\epsilon$ of the set $[|p\}\{p|]^d$ in eqn. (24).

By analogy [2,3] to the method used for obtaining eqn. (28), we obtain eqns. (29) and (30):

$$\hat{V}(D_4) = \sqrt{1/6}\left(2\hat{S}_{zz} - \hat{S}_{xx} - \hat{S}_{yy}\right)\sqrt{1/6}\left(2S_{zz} - S_{xx} - S_{yy}\right) = \hat{N}^d_\theta N^d_\theta \tag{29}$$

$$\hat{W}(O) = \sqrt{1/3}\left(\hat{S}_{zz} + \hat{S}_{xx} + \hat{S}_{yy}\right)\sqrt{1/3}\left(S_{zz} + S_{xx} + S_{yy}\right) = \hat{N}^s N^s$$
$$= \hat{V}(R_3) + \hat{V}(O) \tag{30}$$

We have now finished developing the ligand field operators of eqn. (27) in terms of the basic operators. The linear combinations that we have obtained are so-called irreducible tensor operators of R_3 and the coefficients to the basic operators in the linear combinations are the so-called coupling coefficients or Clebsch–Gordan coefficients of this group. The irreducible tensor operators are the $\hat{N}$ operators mentioned at the beginning of this section and the three terms of eqn. (27) can then be rewritten as in eqn. (31) using eqn. (30), eqn. (29) and eqn. (28) respectively:

$$\hat{W}(D_2) = \hat{N}^s N^s + \hat{N}^d_\theta N^d_\theta + \hat{N}^d_\epsilon N^d_\epsilon \tag{31}$$

The first term on the right-hand side is $\hat{W}(O)$ of octahedral symmetry, but because of the restriction that lies in the fact that $\hat{W}(D_2)$ acts on p orbitals, $\hat{W}(O)$ has spherical symmetry or s symmetry. The symmetry of the tetrago-

nal operator $\hat{N}_\theta^{\mathrm{d}}$ is also too high because of the restricted space on which it acts, and $\hat{N}_\theta^{\mathrm{d}}$ has cylindrical symmetry, or symmetry $\mathrm{a}_1(D_\infty)$ as does the $\mathrm{d}\sigma$ orbital of eqn. (2).

The symmetry operator part of $\hat{W}(D_2)$ embodies only the three permutationally symmetrical operators of set (17), the idempotents, since they are the only ones that are totally symmetrical in D_2. One of these will now be written out explicitly to show how we have actually derived Clebsch–Gordan coefficients by our procedure.

The Clebsch–Gordan coefficients are, as also mentioned above, expansion coefficients of an orthogonal transformation. The use of the notation $\langle \quad | \quad \rangle$ should, by analogy with the usual bra(c)ket notation, be thought of as an overlap or a scalar product. In this specific case, the bra side contains one of the tensor product operators of the orthonormal operator set (17) and the ket side a component of the complete orthonormal set of R_3 symmetry-adapted operators.

We have, for example, for the second symmetry operator of eqns. (27) and (31) by using the numerical results of eqn. (29):

$$\begin{aligned}
\hat{N}_\theta^{\mathrm{d}} &= [\,|\mathrm{p}\rangle\{\langle\mathrm{p}|\,]_\theta^{\mathrm{d}} \\
&= \langle \mathrm{pz}\ \mathrm{pz}\,|\mathrm{d}\theta\rangle\,|\mathrm{z}\rangle\langle\mathrm{z}| + \langle \mathrm{px}\ \mathrm{px}\,|\mathrm{d}\theta\rangle\,|\mathrm{x}\rangle\langle\mathrm{x}| + \langle \mathrm{py}\ \mathrm{py}\,|\mathrm{d}\theta\rangle\,|\mathrm{y}\rangle\langle\mathrm{y}| \\
&= \sqrt{2/3}\,|\mathrm{z}\rangle\langle\mathrm{z}| - \sqrt{1/6}\,|\mathrm{x}\rangle\langle\mathrm{x}| - \sqrt{1/6}\,|\mathrm{y}\rangle\langle\mathrm{y}| \\
&= \sqrt{2/3}\,\hat{S}_{\mathrm{zz}} - \sqrt{1/6}\,\hat{S}_{\mathrm{xx}} \quad \sqrt{1/6}\,\hat{S}_{\mathrm{yy}} \qquad (32)
\end{aligned}$$

where the coefficients to the $\hat{S}$ operators are the Clebsch–Gordan coefficients of R_3 which are required to obtain the $\mathrm{d}\theta$ component of the tensor product of the two real standard p sets. * Incidentally, these coefficients also apply to the group O, and similarly the coefficients occurring in eqn. (28), which are of $[\,|\mathrm{p}(R_3)\}\{\mathrm{p}(R_3)|\,]_\epsilon^{(\mathrm{d}(R_3)}$ (or simply $[\,|\mathrm{p}\}\{\mathrm{p}|\,]_\epsilon^{\mathrm{d}}$) type in R_3, of $[\,|\mathrm{t}_1(O)\}\{\mathrm{t}_1(O)|\,]_\epsilon^{\mathrm{e}(O)}$ (or simply $[\,|\mathrm{t}_1\}\{\mathrm{t}_1|\,]_\epsilon^{\mathrm{e}}$) type in O and of $[\,|\mathrm{e}(D_4)\}\{\mathrm{e}(D_4)|\,]^{\mathrm{b}_1(D_4)}$ (or simply $[\,|\mathrm{e}\}\{\mathrm{e}|\,]^{\mathrm{b}_1}$) type in D_4, are simultaneously Clebsch–Gordan coefficients of R_3, O and D_4 respectively. It may be observed that the operator of $\mathrm{b}_1(D_4)\mathrm{a}(D_2)$ symmetry has no component designation. This is because $\mathrm{b}_1(D_4)$ is one-dimensional so that the concept of component is trivial. As we saw in connection with eqn. (28), the signs of the coefficients have a certain arbitrariness attached to them and it turns out

* It is a feature of the orthogonal transformation that the sum of the squares of the coefficients to a given operator is invariably equal to unity. For example, $\hat{S}_{\mathrm{zz}}$ occurs only in $\hat{N}^{\mathrm{s}} = [\,|\mathrm{p}\}\{\langle\mathrm{p}|\,]^{\mathrm{s}}$ and in $\hat{N}_\theta^{\mathrm{d}} = [\,|\mathrm{p}\}\{\langle\mathrm{p}|\,]_\theta^{\mathrm{d}}$. In $\hat{N}^{\mathrm{s}}$ its coefficient is $\sqrt{1/3}$, as discussed in connection with eqn. (24), and in $\hat{N}_\theta^{\mathrm{d}}$ its coefficient is $\sqrt{2/3}$ according to eqn. (32) so that the square sum of the coefficients is equal to unity.

that if phase fixation is established using the proposals of ref. 22, then the signs of the coefficients of eqn. (28) depend on whether they are considered to be D_4 coefficients (top row) or R_3, O coefficients (bottom row). By the hierarchic irreducible tensor operators [3], we mean, using this particular example, the octahedral tensor operator $[|t_1(O)\}\{t_1(O)|]_\theta^{a(O)} = [|t_1\}\{t_1|]_\theta^{s}$ of tetragonal symmetry, giving the tetragonal splitting, and the tetragonal tensor operator $[|e(D_4)\}\{e(D_4)|]^{b_1(D_4)} = [|e\}\{e|]^{b_1}$ of orthorhombic symmetry, giving the orthorhombic splitting. Our phase-fixation procedure of ref. 22 then leads to the signs of the top row in eqn. (28) (see also Fig. 2).

In closing this section we point out that the detailed form of the symmetry operators (28), (29) and (30) was obtained here by using only the results given in Fig. 2, which are obtainable from character tables of the groups. The group hierarchy is enough to define the particular function bases necessary to specify the coefficients of the basic operators and thereby the particular coupling coefficients for R_3, O and D_4. It is generally true that the necessary coupling coefficients for the purpose, apart from their phase, can be obtained in this way.

(vi) Function space and holohedral rotational point group symmetry

Functions of l^q configurations always have gerade inversion symmetry except when l and q simultaneously are odd, in which case the l^q functions have ungerade inversion symmetry. In other words, l^q functions are always eigenfunctions of the inversion operator $\hat{S}_2$ and since in any concrete chemical application l and q are fixed, the parametrical l^q model is invariably concerned with functions of one particular parity. This means that only the gerade part of any model Hamiltonian will give a non-vanishing contribution to the energy matrix elements or, what amounts to the same thing, the effective Hamiltonian of the l^q model always has gerade inversion symmetry.

The Hamiltonian for a complex has the same symmetry as the complex itself, and if the point group of the complex does not contain inversion, then its Hamiltonian may be expressed as a sum of g and u parts. The former is the effective part of the Hamiltonian within the l^q space (l and q fixed) and the latter has only vanishing matrix elements within this space. In order to find the symmetry of the effective part of the Hamiltonian, it is useful to introduce an artificial centre of inversion into the complex. An example will illustrate the procedure.

Bromine trifluoride is T-shaped and its point group is C_{2v}. The Hamiltonian therefore has the symmetry C_{2v}, or, put in another way, the Hamiltonian transforms as the totally symmetrical representation A_1 of the group C_{2v}. If an artificial system is formed by the introduction of a centre of

inversion, then the symmetry group of this system is found as the direct product of the two commuting point groups C_{2v} and S_2, the hemihedral orthorhombic group and the inversion group. This direct product is D_{2h}. Provided that the original Hamiltonian has been symmetry adapted to D_{2h}, i.e. written as a linear combination of terms belonging to irreducible representations of this group, then it contains only two kinds of terms. These kinds belong to either $A_g(D_{2h})$ or $B_{1u}(D_{2h})$ since these are the only irreducible representations of D_{2h} that transform as $A_1(C_{2v})$ in the subgroup C_{2v}. Of these two kinds of Hamiltonian terms, the gerade term, that of $A_g(D_{2h})$ symmetry, contains the effective Hamiltonian on the l^q space.

We have here seen how the inversion symmetry restriction on the function space carries over to the Hamiltonian operator whose effective symmetry is increased from $A_1(C_{2v})$ to $A_g(D_{2h})$. This higher effective symmetry has been called the holohedral symmetry (in this case the holohedral orthorhombic point group which is the orthorhombic point group that allows the highest number of kinds of faces possible in the orthorhombic crystal class) in an abstract sense and the holohedrized symmetry in a concrete sense where the effective operator is extracted or projected out explicitly.

Since, as we have seen, the parities of the function space and of the effective Hamiltonian are trivially fixed within the parametrical l^q model, the inversion symmetry can hereafter be ignored and the rotation group of the holohedral group of a complex can be used for classifying functions and operators. This group may be called the holohedral rotation group and in the case of our example of BrF_3 this group is D_2.

It is advantageous that the effective symmetry of our problem is a pure rotation point group because for these groups particularly simple phase-fixing rules for coupling coefficients have been devised [22]. These rules fix the signs of the hierarchic irreducible tensor operators of the observable ligand field as discussed in connection with eqn. (28).

(vii) The holistic and the partitioned view of the ligand field. An example of a difference in effective symmetry

It has been understood until now that the ligand field was conceived from the holistic point of view where the individuality of the ligands is not a part of the model, but where the symmetries of the function space and of the central ion plus its ligands form the complete symmetry basis of the Hamiltonian. This view is also referred to as the non-additive field model.

The ligand field can alternatively be conceived from the partitioned point of view: it then consists of parts and the total ligand field operator is written as a sum of terms either referring to the individual coordinating atoms

(ligators) or to the individual ligands or groups of ligands. This view is usually referred to as the additive field model.

The holohedral rotation point group of a ligand field, and thereby the effective symmetry, sometimes depends on whether the holistic or the partitioned, the non-additive or the additive, view is taken. The reason for this is that the holistic view only knows symmetry while the partitioned view also knows geometry and embodies ligand–ligand positional relationships. These relationships [10] in general involve the angular positions of ligators (θ and ϕ) as well as orientational angles of the ligands (ψ). Since this paper is mainly concerned with holistic ligand fields, we restrict ourselves to a single example of how the effective symmetry may depend on the description adopted.

We choose the angular molecule BrF_2^+ whose symmetry is C_{2v} irrespective of the valence angle at Br, and whose holohedral rotation group from a holistic point of view therefore is always D_2 (see Section B(vi)). However, if the partitioned view is taken for BrF_2^+ and if the valence angle at Br happens to be exactly 90°, then the holohedral rotation symmetry of BrF_2^+ increases to D_4. The reason for this is that the introduction of a centre of inversion transforms BrF_2^+ of symmetry C_{2v} to $Br(F_{1/2})_4^+$ of symmetry D_{4h}. Here the symbol $F_{1/2}$ refers to the perturbation effect of one half F. Since these results concerning the holohedral rotation group are not black and white when applied to the effective Hamiltonian, it can be concluded that for BrF_2^+ with a valence angle slightly different from 90°, $\hat{V}(D_4)$ is much greater than $\hat{V}(D_2)$ (see eqn. (27)). Further, this latter statement can be quantified by comparing the norm squares of the two operators [2], as illustrated for $\hat{V}(D_4)$ and the repulsion operator $\hat{Q}_D D$ in Sections E(iii) and E(iv).

(viii) The p-only, σ-only Angular Overlap Model. Global and local p-orbital bases

As already mentioned, quantitative ligand field theory consists of empirical parameters whose coefficients are theoretical and, for systems of high symmetry, symmetry determined in a non-trivial way. In this semiempirical model, the empirical parameters are determined from the ligand field spectra and may in principle take any values and any signs. It is therefore remarkable that a partitioned view of the ligand field is useful in inorganic practice. This view is in the general case, a more restricted version of the ligand field in which this is written as a sum of contributions from the individual ligands, the so-called additive ligand field. It is remarkable that the partitioned view, combined with an extremely simple model of chemical bonding, can be used to predict, at least qualitatively, the spectral properties of

complexes. To our knowledge there is no exception as yet to a correct prediction of the sign of the main splitting of an l orbital set using the l-only, σ-only Angular Overlap Model. This section therefore gives these predictions of the p-only, σ-only model for our p^2 and p^4 examples XeF_4 and XeF_2 respectively. The discussion that follows will be used further to illustrate the concept of local function bases and their relationships to the conventional global basis already discussed in the previous sections.

In the p^4 system XeF_2 of symmetry $D_{\infty h}$ the global and local bases coincide. The Z axis is chosen as the ∞ axis, and the p_z orbital of xenon has the symmetry $a_{2u}(D_{\infty h})$, or, in other words, σ symmetry. The p_x and p_y orbitals together make up the $e_{1u}(D_{\infty h})$ set or π set. This was the characterization of the p basis from the point of view of the symmetry of the whole molecule; the global basis.

Alternatively, if we look at the same xenon p basis from the point of view of its bonding capability relative to the two fluorine ligands, then the p_z orbital, being 100% $\sigma^+(C_{\infty v})$ in character, has a perfect angular overlap with the σ orbitals, σ_1 and σ_2, of the two fluorine atoms while the $\{p_x,p_y\}$ set, being 100% $\pi(C_{\infty v})$ in character, has a perfect angular overlap with appropriately chosen fluorine π orbitals.

Perturbed now by the σ-bonding interaction, the energies of the antibonding, essentially xenon p_z and the non-bonding xenon $\{p_x,p_y\}$ are according to the p-only, σ-only Angular Overlap Model equal to $2e_\sigma$ and 0 respectively. The factor 2 arises from the two fluorine ligands each of which contributes e_σ to the antibonding energy of p_z. Therefore the splitting pattern is that shown in Fig. 3, i.e. the opposite to that shown in Fig. 1.

In this σ-only model, each fluorine atom provides one valence electron to the system, and in addition one has to account for all the eight electrons of the xenon valence shell. The xenon s orbital and the $(\sigma_1 - \sigma_2)$ orbital of the

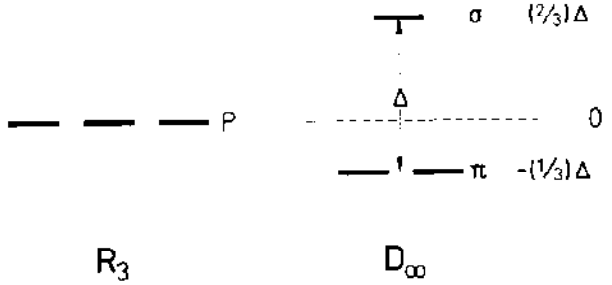

Fig. 3. The p-orbital level splitting inverted relative to that in Fig. 1. The sign shown is that expected for a linear molecule such as XeF_2. The sign here refers to positive values of the parameter N_θ^d, associated with the phase-fixed irreducible tensor operator $\hat{N}_\theta^d$ (see eqn. (32)).

fluorine atoms, both of symmetry $a_{1g}(D_{\infty h})$, have an energetically unfavourable encounter resulting from overlap and interaction between two filled orbitals, and they account for four out of the ten valence electrons. The bonding combination of xenon p_z and fluorine $(\sigma_1 - \sigma_2)$ contains another two electrons and provide a bond order of one half to each Xe–F bond. The non-bonding xenon $\{p_x,p_y\}$ set contains the remaining four electrons and thus substantiates the book-keeper characterization of XeF_2 as a p^4 system [19].

In the p^2 system XeF_4 of symmetry D_{4h} the global coordinate system is chosen according to convention so that the Z axis coincides with the principal axis of the molecule, in this case the fourfold axis. Further, we choose the X and Y axes so that each passes through two fluorine atoms. The XYZ coordinate system is now the global coordinate system relative to which the standard sets of p orbitals of eqn. (1) and of d operators transforming as the d functions of eqn. (2) are defined and used in the holistic description of the ligand field. The p_z orbital is the $p\sigma$ orbital, when described in this coordinate system, the set $\{p_x,p_y\}$ is the $p\pi$ set, and the symbols σ and π do not in this context refer to the individual xenon-to-fluorine bonds. However, as found in Section B(v), a ligand field of symmetry D_4 acting on p orbitals, has the symmetry D_{∞}, or in other words, cylindrical symmetry so that the concepts σ and π refer to irreducible representations of the point group of the effective Hamiltonian and thereby to the symmetries of eigenstates.

Let us then look at the p^2 system of symmetry D_{4h} from the point of view of the individual Xe–F bonds—the four local views. Let us first focus attention at the fluorine atoms on the X axis. From their point of view the xenon p_x orbital is a 100% σ orbital while the set $\{p_y,p_z\}$ makes up a perfect π set. The p_x orbital becomes antibonding with an energy $2e_\sigma$, e_σ from each fluorine atom on the X axis. Similarly, the xenon p_y orbital is a 100% σ orbital for the two fluorine ions on the Y axis and its energy will also be $2e_\sigma$. Since all the four fluorine atoms are situated in the nodal plane of xenon p_z, this orbital will be non-bonding in the σ-only model. In conclusion the splitting pattern will be that shown in Fig. 1, with the orbital set $\{p_x,p_y\}$ degenerate at energy $2e_\sigma$ and the orbital p_z at energy zero.

The conceptual point that we want to make by this example of XeF_4 is the relativity of the symmetry concepts of σ and π. A central ion orbital may be a σ orbital when referred to the global coordinate system and a π orbital when referred to one or more of the local coordinate systems that define also the local central ion bases.

In this connection, it is important to realize that if the ligand field is viewed as partitioned into contributions from different parts of the ligand system, then addition of these contributions cannot be made unless they are

first referred to some common basis, the global basis. Reference to this common basis may be obtained by means of the mathematical framework used with the Angular Overlap Model [10].

Finally, we shall add some chemical remarks. There is an analogy between XeF_2 and XeF_4 on the one hand and $CrCl_6^{3-}$ and $CoCl_4^{2-}$ on the other hand. The two xenon compounds have effectively an axial ligand field which for p orbitals is represented by one parameter. According to the p-only, σ-only Angular Overlap Model, this parameter has the *opposite sign* for the two molecules which have p^q configurations which *add up* to a *full* p shell, a p^6 shell. These three correlative properties, marked in italics, are analogous to those of the d systems of holohedral symmetry O, mentioned above, and result in identical ligand field energy diagrams as will be discussed further in Section E(iv).

The classification of these xenon and bromine fluorides as p^q systems [19,23] and the use of the Angular Overlap Model in connection with a discussion of their bonding situation [24,25] is not new with us. However, the use of the holistic ligand field on these systems is new but only a minor consideration of the present paper. For high symmetry systems, it is always illuminating to have both the holistic and the partitioned view. When we have used the term "l-only model", particularly for the present purpose where the meaning is "p-only model", it is because s orbitals are sometimes likely to play an important role at least with respect to the stereochemistry of these p^q systems [24,25].

C. THE p^q CONFIGURATIONS IN A TETRAGONAL LIGAND FIELD

In Section B we discussed the action of ligand fields of different symmetries on the p-orbital space. It was shown that the transformation properties of the three p orbitals allowed one to deduce if and how the p-orbital level is split by the action of a field. In this section we shall focus on a field of tetragonal symmetry which splits the p set of orbitals {x,y,z} into z spanning the irreducible representation $a_2(D_4)$ and the set {x,y} spanning $e(D_4)$. The tetragonal ligand field $\hat{V}(D_4)$ is, at least in principle, observable and the energy difference between the x and y orbitals and the z orbital is expressed by the parameter Δ (see Fig. 1 and eqn. (3)).

The purpose of this section is to extend these results to systems with more than one p electron. Firstly, we shall include the electron spin in the one-electron wavefunctions and thereby go from the three-dimensional p-orbital space to the six-dimensional p-spin-orbital space which is the space of the p^1 configuration. Secondly, we shall consider the many-electron wavefunctions corresponding to the p^2 and p^3 configurations. In spite of the fact that the ligand field operator does not contain electron spin, spin

influences the form of the many-electron wavefunctions and the number of p^q states through the Pauli principle.

Most of what is said in this section is well known from textbooks. However, the function space on which ligand field operators act is almost always implied in textbooks as well as in scientific papers. In orthonormal operators' modelling, special focus on the function space is necessary, and it is the main purpose of this section to emphasize this necessity.

(i) The p^1 configuration

Since the ligand field operator does not contain spin, knowledge about its action on the p-orbital space can easily be generalized to knowledge about its action on the p-spin-orbital space.

Each of the three p orbitals may be combined with either a spin-up spin function (α) or a spin-down spin function (β). For the z orbital, for example, we thus obtain zα with $m_s = 1/2$ and zβ with $m_s = -1/2$ both of which have the same ligand field energy. The matrix (33) for the tetragonal ligand field coefficient operator $\hat{Q}_\Delta$ in the spin-orbital basis is therefore simply made by doubling up the matrix (7):

$$\hat{Q}_\Delta \begin{array}{c} \\ x\alpha \\ y\alpha \\ z\alpha \\ x\beta \\ y\beta \\ z\beta \end{array} \begin{array}{c} \begin{array}{cccccc} x\alpha & y\alpha & z\alpha & x\beta & y\beta & z\beta \end{array} \\ \left[\begin{array}{cccccc} 1/3 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1/3 & 0 & 0 & 0 & 0 \\ 0 & 0 & -2/3 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1/3 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1/3 & 0 \\ 0 & 0 & 0 & 0 & 0 & -2/3 \end{array}\right] \end{array} \tag{33}$$

All matrix elements between spin orbitals of different m_s values vanish due to the orthogonality of the two spin functions. The norm square of the matrix (33) is equal to 4/3 which of course is twice the value found for the matrix (7). The six spin orbitals that are basis functions of the matrix (33) span the space of the p^1 configuration.

The step of going from the p-orbital space to the p-spin-orbital space or the p^1 configuration space is an important step since this space is the natural foundation for the normalization of one-electron operators on p^q spaces. There is yet another reason for this, namely, that a general normalization of all one-electron operators, not only ligand field operators, can thereby be obtained (see eqn. (89)). The existence of operators, which, like the spin-orbit

coupling operator [4], act on both the spin part and the orbital part of the space, also makes the spin-orbital space the natural foundation.

(ii) The strong-field limit of the p^2 configuration. Permutational antisymmetry

A main group molecule such as, for example, the square-planar XeF_4 is best conceived in the parametrical p^q model as a p^2 electronic system with tetragonal symmetry (see Section B(viii)). In order to describe such a system, we have to investigate how a tetragonal ligand field acts on two-electron functions. We first examine the simple orbital product functions and then include spin to obtain all those functions that are allowed by the Pauli principle, i.e. those which are antisymmetric with respect to permutation of two electrons.

We first look at the non-commutative or tensor product (sometimes called direct product) of a p set {x,y,z} which is itself given in eqn. (34):

$$p \otimes p = xx \oplus yy \oplus zz \oplus xz \oplus zx \oplus yx \oplus xy \oplus zy \oplus yz \tag{34}$$

Here zx could, for example, with a more detailed notation be written as z(1)x(2) since it means the product of the p_z orbital, occupied by electron number 1, and the p_x orbital, occupied by electron number 2. Because of these electron coordinates, which are understood, zx is not the same as xz so that $zx - xz$ is different from zero. Here the non-commutativity is caused by the fact that the first factor refers to a particle different from that referred to by the second factor.

Let us classify the nine product functions of eqn. (34) according to their ligand field energies obtained as a sum of the individual orbital energies (see Fig. 1):

e^2	π^2	xx, yy, xy, yx	$(2/3)\Delta$
ea_2	$\pi\sigma$	xz, zx, zy, yz	$-(1/3)\Delta$
a_2^2	σ^2	zz	$-(4/3)\Delta$

(35)

In array (35) the D_4 and D_{∞} subconfigurations of p^2 are stated in the first two columns, the non-commutative product functions in the third and their energies in the fourth column. The barycentre rule that applies to the one-electron functions automatically carries over to the two-electron functions and the sum of the nine energies is therefore zero.

Because of the indistinguishability of electrons, zx and xz, for example, could never have been proper two-electron functions. However, the functions $zx + xz$ and $zx - xz$, which are symmetrical and antisymmetrical respectively to permutation of the two electrons, have squared values that are invariant to this permutation and these are therefore proper two-electron

space functions. In array (36), all the functions have been rewritten in permutationally symmetry-adapted and still normalized form:

$$\begin{array}{lll} e^2 \quad \pi^2 & xx,\ yy,\ \sqrt{1/2}\,(xy+yx),\ \sqrt{1/2}\,(xy-yx) & (2/3)\Delta \\ ea_2 \quad \pi\sigma & \sqrt{1/2}\,(zx+xz),\ \sqrt{1/2}\,(zx-xz), & -(1/3)\Delta \\ & \sqrt{1/2}\,(yz+zy),\ \sqrt{1/2}\,(yz-zy) & \\ a_2^2 \quad \sigma^2 & zz & -(4/3)\Delta \end{array} \tag{36}$$

The Pauli principle requires the total two-electron functions to be antisymmetrical to permutation of the two electrons. This can be achieved either by having a symmetrical space function combined with (i.e. multiplied by) an antisymmetrical spin function or vice versa. The three space functions of array (36) containing minus signs are antisymmetrical while the remaining ones are symmetrical. The six symmetrical space functions have to be combined with the antisymmetrical spin function, the spin singlet function, of eqn. (37)

$$\sqrt{1/2}\,(\alpha\beta - \beta\alpha) \quad M_S = 0 \tag{37}$$

while the three antisymmetrical space functions have to be combined with symmetrical spin functions of which there are three:

$$\begin{array}{ll} \alpha\alpha & M_S = 1 \\ \sqrt{1/2}\,(\alpha\beta + \beta\alpha) & M_S = 0 \\ \beta\beta & M_S = -1 \end{array} \tag{38}$$

Together, these three functions form a set of eigenfunctions of $\hat{S}^2$ with the eigenvalue $S = 1$ and therefore $2S + 1 = 3$, i.e. a set of spin-triplet functions.

The following classification of the Pauli-allowed two-electron functions of the p^2 configuration may be made. The subconfiguration e^2 consists of the three spatially symmetrical functions, counting as three, and the antisymmetrical one, also counting as three, because of spin, giving altogether six functions. This number is equal to $\binom{4}{2} = 6$ which is the number of times two electrons can be accomodated in the four spin orbitals (of e type). The subconfiguration ea_2 is not Pauli restricted and therefore contains $4 \times 2 = 8$ functions altogether. Finally, there is the subconfiguration a_2^2 consisting of one symmetrical space function, which, when combined with the proper antisymmetrical spin function gives rise to only one function. Adding up the number of allowed functions over the three subconfigurations, one obtains $6 + 8 + 1 = 15$ which is $\binom{6}{2}$, i.e. the number of times two electrons can be accomodated in the six spin orbitals (of p type). All the two-electron functions we have been concerned with here are the so-called tetragonal strong-field functions.

The 15×15 matrix of $\hat{Q}_\Delta\Delta$ over p^2 in the subconfiguration basis can now in an abbreviated form be written as matrix (39):

$$\begin{array}{cc} & \hat{Q}_\Delta\Delta \\ 6 & e^2 \\ 8 & ea_2 \\ 1 & a_2^2 \end{array} \begin{array}{c} \begin{array}{ccc} e^2 & ea_2 & a_2^2 \end{array} \\ \begin{bmatrix} 2/3 & 0 & 0 \\ 0 & -1/3 & 0 \\ 0 & 0 & -4/3 \end{bmatrix} \end{array} \Delta \tag{39}$$

where the barycentre rule again can be seen to apply, provided the weight factors given to the left of the matrix are observed. Including these, the norm square of $\hat{Q}_\Delta$ may be calculated as in eqn. (40):

$$\langle \hat{Q}_\Delta \mid \hat{Q}_\Delta \rangle_{p^2} = 6(2/3)^2 + 8(-1/3)^2 + 1(-4/3)^2 = 16/3 = 4(4/3) \tag{40}$$

This result shows that the norm square of $\hat{Q}_\Delta$ over the p^2 configuration is four times that found for $\hat{Q}_\Delta$ over the p^1 configuration (see the matrix (33)). This factor of 4 on going from the p^1 to the p^2 function space is general for one-electron operators (see Section E(iii)).

The subconfiguration basis of matrix (39) makes up the tetragonal strong-field basis of the p^2 configuration. The strong-field basis is in this case completely defined by being the eigenbasis of the tetragonal ligand field operator $\hat{V}(D_4)$ and its identity to the basis of matrix (39) is therefore established by the diagonality of this matrix. As opposed to strong-field bases, we have weak-field bases which in most cases are eigenbases of the interelectronic repulsion. We shall return to the properties of both strong-field and weak-field bases in Sections D and E.

(iii) The p^3 configuration

We shall not here discuss the p^3 configuration in much detail since it is of little chemical interest. Being an odd-electron configuration, very few, if any, molecules are known which may be described as p^3 systems although, of course, several atoms and ions are p^3 systems, e.g. the nitrogen atom.

We shall therefore in the usual brief form simply state the 20×20 matrix (41) of the tetragonal ligand field operator $\hat{V}(D_4)$ in the strong-field basis and add a few comments:

$$\begin{array}{cc} & \hat{Q}_\Delta\Delta \\ 4 & e^3 \\ 12 & e^2a_2 \\ 4 & ea_2^2 \end{array} \begin{array}{c} \begin{array}{ccc} e^3 & e^2a_2 & ea_2^2 \end{array} \\ \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix} \end{array} \Delta \tag{41}$$

The non-existence of the subconfiguration a_2^3 is an obvious consequence of the Pauli principle for the p^3 configuration. The subconfiguration e^2a_2 has the ligand field energy zero since the barycentration requires the a_2 orbital to be stabilized twice as much as the e orbitals are destabilized (see Fig. 1 and eqn. (3)).

The matrix of $\hat{Q}_\Delta$ is as usual barycentred and its norm square is equal to eight which may be compared with the value 4/3 found for the p^1 configuration. Generally, the norm square will increase when the dimension of the space increases. In Section E(iii) the relation between the norm square of an operator and the space upon which it acts will be given.

D. INTERELECTRONIC REPULSION INSIDE p^q CONFIGURATIONS

The three p orbitals have the same energies when the symmetry is spherical. Nevertheless a p system containing q electrons, i.e. a p^q configuration, gives rise to more energy levels when $q > 1$. When the spin–orbit interaction is small enough to be neglected, these energy levels are multiplet terms ^{2S+1}L with degeneracy $(2S + 1)(2L + 1)$, selected out by occupying the six p spin orbitals by q electrons under the restriction of the Pauli principle. The energy levels of p^q have different energies because the electrons repel each other to different extents depending on how the electrons' mutual relationship is restricted by S and L. The Hamiltonian operator, $\hat{H}_{\text{rep}}$, for electrostatic repulsion between the electrons is formally written as $\sum_{i<j}(e^2/r_{ij})$ where e is the charge of the electron and r_{ij} is the distance between electron i and electron j. The inequality sign ensures that every pair i, j of electrons is counted only once. By containing only one pair of electrons, the p^2 configuration represents a particularly simple case but general enough for the two-electron operator. We shall therefore in this section use this configuration to illustrate how the interelectronic repulsion may be parameterized.

As in Section C, in this section also the function space is gradually built up. Section D(i) considers simple product functions for two electrons and the matrix of the interelectronic repulsion operator in this basis. This matrix contains the coulomb and exchange integrals. In Section D(ii) the matrix is diagonalized to obtain the spatial eigenfunctions of the electron repulsion. In Section D(iii) spin functions are multiplied onto the space functions to obtain the so-called weak-field functions. The spin-pairing energy parameter D and its associated coefficient operator is also introduced here, and in Section D(iv) this operator is split up into a sum of two mutually orthogonal component operators. Finally, in Section D(v) a brief account of interelectronic repulsion in the p^3 configuration is given.

(i) Interelectronic repulsion integrals: the spatial matrix elements

The Hamiltonian operator for interelectronic repulsion $\hat{H}_{\text{rep.}}$ is a two-electron operator and its matrix elements therefore involve two-electron product functions of the kind presented in eqn. (34). The problem of setting up an energy matrix representing the interelectronic repulsion between two p electrons is simply that of finding the values of all matrix elements of $\hat{H}_{\text{rep.}} = e^2/r_{12}$ which have the nine two-electron functions of eqn. (34) as basis functions. We recapitulate that the first factor in these products of p functions represents electron number 1 and the second factor electron number 2. It follows immediately from the congruence and symmetry properties of the three p orbitals that there are only four formally different types of matrix elements, all the rest of the 9×9 matrix elements being either obtainable from these by suitable permutations of the p orbitals or else being equal to zero for symmetry reasons. These symmetry reasons will be discussed after matrix (47). The four types of matrix elements are exemplified in eqns. (42)–(45):

$$J = \langle \mathrm{x}(1)\mathrm{y}(2)|e^2/r_{12}|\mathrm{x}(1)\mathrm{y}(2)\rangle = \langle \mathrm{xy}|e^2/r_{12}|\mathrm{xy}\rangle \tag{42}$$

$$K = \langle \mathrm{x}(1)\mathrm{y}(2)|e^2/r_{12}|\mathrm{y}(1)\mathrm{x}(2)\rangle = \langle \mathrm{xy}|e^2/r_{12}|\mathrm{yx}\rangle \tag{43}$$

$$J' = \langle \mathrm{x}(1)\mathrm{x}(2)|e^2/r_{12}|\mathrm{x}(1)\mathrm{x}(2)\rangle = \langle \mathrm{xx}|e^2/r_{12}|\mathrm{xx}\rangle \tag{44}$$

$$\langle \mathrm{xx}|e^2/r_{12}|\mathrm{yy}\rangle = \langle \mathrm{xy}|e^2/r_{12}|\mathrm{yx}\rangle = K \tag{45}$$

We shall discuss them one at a time. J is the so-called coulomb integral which represents the electrostatic repulsion between the two charge clouds x^2 and y^2 and which may be obtained by an integration over the two three-dimensional spaces of the two electrons. In principle, J is classical and the same is true of J' which represents the repulsion of the two electrons in the same orbital. K is the exchange integral which is non-classical in the sense that it formally represents the repulsion between the "charge cloud" xy (the first factors on the two sides of the operator) and the "charge cloud" yx (the second factors). J, J' and K are always positive quantities. The fourth type of matrix element shown in eqn. (45) happens to be equal to the K integral because the functions are real and the operator just a multiplication factor so that the two second factors can be permuted. We are therefore left with the three quantities J, K and J' which are needed for setting up the 9×9 energy matrix. This matrix consists of one 3×3 matrix and three 2×2 matrices placed about the diagonal of the 9×9 matrix, the rest of the matrix elements being zero. The 3×3 matrix is given as the

matrix (46):

$$\begin{array}{c} \\ \\ a(D_2) \end{array} \begin{array}{c} e^2/r_{12} \\ \text{xx} \\ \text{yy} \\ \text{zz} \end{array} \begin{array}{c} \text{xx} \quad \text{yy} \quad \text{zz} \\ \begin{bmatrix} J' & K & K \\ K & J' & K \\ K & K & J' \end{bmatrix} \end{array} \tag{46}$$

and one of the 2×2 matrices as the matrix (47):

$$\begin{array}{c} \\ b_1(D_2) \end{array} \begin{array}{c} e^2/r_{12} \\ \text{xy} \\ \text{yx} \end{array} \begin{array}{c} \text{xy} \quad \text{yx} \\ \begin{bmatrix} J & K \\ K & J \end{bmatrix} \end{array} \tag{47}$$

where the symmetries of the product functions have been given as irreducible representations of the point group D_2. The remaining two 2×2 matrices are both identical with the matrix (47) but they involve product functions of symmetries $b_2(D_2)$, zx and xz, and $b_3(D_2)$, yz and zy (see also Section E(i)). The purpose of classifying the functions according to D_2 is the following. The repulsion operator has spherical symmetry and thereby also $a(D_2)$ symmetry. This latter property is sufficient to secure that all matrix elements connecting functions belonging to different irreducible representations of D_2 are equal to zero. The energy matrices (46) and (47) are thus independent, and may accordingly also be diagonalized independently.

(ii) The spatial eigenfunctions of the interelectronic repulsion operator

The non-diagonality of the energy matrices (46) and (47) shows that the product functions of eqn. (34) are not eigenfunctions of the interelectronic repulsion operator $\hat{H}_{\text{rep.}} = e^2/r_{12}$. The eigenfunctions of $\hat{H}_{\text{rep.}}$ are those linear combinations of the orbital product functions which, when used as basis functions for $\hat{H}_{\text{rep.}}$, yield a diagonal matrix. These eigenfunctions may be obtained together with the eigenvalues by a diagonalization of the matrix of $\hat{H}_{\text{rep.}}$ in the product function basis. Here we shall not actually perform this diagonalization but instead obtain the eigenfunctions by symmetry arguments.

The spatial symmetries of these eigenfunctions of $\hat{H}_{\text{rep.}}$ emerge directly when eqn. (34) is rewritten as eqn. (48) by using the vector coupling rules (see here also eqn. (24)):

$$|\text{p}\} \otimes |\text{p}\} = \text{S} \oplus \underline{\text{P}} \oplus \text{D} \tag{48}$$

The letters on the right-hand side have been written as capital letters because here they represent two-electron functions. P has been underlined to mean that P lies in the antisymmetric part of the tensor product while S and D lie in the symmetric part. This means that an interchange of the order of

the two p sets, whose tensor product is formed, will lead to change of sign of the resulting P set (see eqn. (23)) while the signs of the S and D sets remain unaffected (see eqn. (22)). A comparison of eqns. (34) and (48) shows that the product functions of eqn. (34) can be linearly combined to give functions which transform irreducibly under R_3 as sets of S, P and D symmetry. The coefficients in these linear combinations are coupling coefficients that could have been looked up in a table [22]. Alternatively, they could be obtained, as explained above, as the components of the eigenvectors associated with the matrices (46) and (47). Here we proceed by a third, but related route.

We use the analogy between ket–bra operators (eqn. (17)) and two-electron product functions (eqn. (34)), an analogy that is particularly strong when real functions are used. If the results of eqns. (27)–(32) are studied, it becomes an easy matter to guess the eigenvectors of the matrix (46) and thereby the eigenfunctions of $\hat{H}_{\text{rep.}}$ which consist of xx, yy and zz terms only. These are given in eqn. (49) together with various expressions for their symmetry properties:

$$\begin{array}{llll} S\Sigma & A_1(D_4)A(D_2) & S = \sqrt{1/3}\,(xx + yy + zz) & A_1(O) \\ D\Sigma & A_1(D_4)A(D_2) & D(z^2) = \sqrt{1/6}\,(2\,zz - xx - yy) & \left.\begin{array}{l}\\ E(O)\end{array}\right\} \\ D\Delta c & B_1(D_4)A(D_2) & D(x^2 - y^2) = \sqrt{1/2}\,(xx - yy) & \end{array} \tag{49}$$

The symmetry designations to the far left specify the rotational symmetry properties under R_3 using the lλç notation of eqns. (1) and (2). We further notice the resemblance of the two D functions to the corresponding d orbitals. We may now check our guess by calculating in eqn. (50) the few matrix elements which are non-zero:

$$\begin{aligned} \langle S|e^2/r_{12}\,S\rangle &= (1/3)[3J' + 6K] &&= J' + 2K \\ \langle D(z^2)|e^2/r_{12}|D(z^2)\rangle &= (1/6)[6J' - 8K + 2K] &&= J' - K \\ \langle D(x^2 - y^2)|e^2/r_{12}|D(x^2 - y^2)\rangle &= (1/2)[2J' - 2K] &&= J' - K \end{aligned} \tag{50}$$

The matrix of e^2/r_{12} in the basis of eqn. (49) is then given as the matrix (51) and the fact that there are no further non-zero matrix elements can be checked by noting the norm square invariance on going from the matrix (46) to the matrix (51):

$$\begin{array}{c} e^2/r_{12} \\ S \\ D(z^2) \\ D(x^2 - y^2) \end{array} \begin{array}{c} \begin{array}{ccc} S & D(z^2) & D(x^2 - y^2) \end{array} \\ \begin{bmatrix} J' + 2K & 0 & 0 \\ 0 & J' - K & 0 \\ 0 & 0 & J' - K \end{bmatrix} \end{array} \tag{51}$$

Similarly, we guess in eqn. (52) the eigenfunctions of the matrix (47):

$$\begin{array}{lll} D\Delta s & B_2(D_4)B_1(D_2) & D(xy) = \sqrt{1/2}\,(xy + yx) \\ P\Sigma & A_2(D_4)B_1(D_2) & P(z) = \sqrt{1/2}\,(xy - yx) \end{array} \tag{52}$$

where the expression for P(z) reminds one of the fact that the vector product of the X unit vector and the Y unit vector is the Z unit vector. The diagonalized matrix is given as matrix (53):

$$\begin{array}{c} e^2/r_{12} \\ D(xy) \\ P(z) \end{array} \begin{array}{c} \begin{array}{cc} D(xy) & P(z) \end{array} \\ \begin{bmatrix} J + K & 0 \\ 0 & J - K \end{bmatrix} \end{array} \tag{53}$$

Expressing from eqns. (50) and (53) that the D functions are degenerate, one obtains the relation $J' - K = J + K$, i.e. *

$$J' = J + 2K \tag{54}$$

Summing up the results from matrices (51) and (53) and the associated eqn. (54), the 9×9 matrix of our new basis—the spatial eigenbasis of $\hat{H}_{rep.}$ - can in an abbreviated form be written as matrix (55):

$$\begin{array}{ccc} & e^2/r_{12} & \begin{array}{ccc} S & D & P \end{array} \\ 1 & S & \begin{bmatrix} J + 4K & 0 & 0 \\ 5 & D & 0 & J + K & 0 \\ 3 & P & 0 & 0 & J - K \end{bmatrix} \end{array} \tag{55}$$

This matrix contains the results for spherical symmetry in the nine-dimensional basis of the spatial p^2 functions.

(iii) The weak-field limit of the p^2 configuration. The spin-pairing energy parameter

Until now we have looked at the electronic repulsion in a purely spatial basis, which is fair enough since the repulsion operator contains no spin. We have found eigenfunctions which obey the indistinguishability rule for electrons. We now introduce the spin into the two-electron functions as we did in connection with expression (36) in Section C(ii). We recapitulate that the P functions lie in the antisymmetrical tensor product space of eqn. (48), which means that the P functions are antisymmetrical to permutation of the

* Equation (54) is a result also valid for pairs of the usual real d and f orbitals even though we have here different kinds of J (and their associated K) integrals.

two electrons, as can also be seen directly from eqn. (52). This means that each of the three P functions have to be multiplied with each of the three symmetrical spin functions of eqn. (38) to form the nine-dimensional ^{3}P term. By similar arguments the S and D functions become ^{1}S and ^{1}D by being multiplied with the antisymmetrical spin function of eqn. (37). Summing up, the introduction of spin is accompanied by an increase in the number of functions from $1 + 3 + 5 = 9$ to $(1 \times 1) + (3 \times 3) + (1 \times 5) = 15$. The latter number is equal to the number of ways $\binom{6}{2}$ in which two electrons may be distributed among six spin orbitals. Our 15 functions make up the weak-field basis of the p^2 configuration.

All functions belonging to a particular multiplet term are degenerate. The coulomb integral J of the matrix (55) is not observable since it is common to all three term energies. It is in this sense in line with absolute energies and can therefore by barycentration be subtracted here. It is only the energy differences that are observable, and these are all expressed in terms of the exchange parameter K. We notice that when the term degeneracies are used as weights, the interelectronic repulsion energy matrix already possesses the barycentration with respect to K, which it otherwise would have been desirable to introduce. We shall now rewrite the energies in terms of the spin-pairing energy parameter D [20].

The parameter D is defined so that the average energy of all the spin states with a total spin quantum number of $(S_0 \quad 1)$ minus the average energy of those with a total spin quantum number of S_0 is equal to $2S_0D$. In our particular case the ^{3}P term with energy $-K$ relative to the barycentre contains all the $S = 1$ functions. The average energy of the $S = 0$ functions, i.e. those making up ^{1}S and ^{1}D, is $[4K + 5(K)]/6 = (3/2)K$ so that $D = (5/4)K$ and $K - (4/5)D$. By omitting the constant energy contribution from J, this expression for K may now be used to rewrite the matrix (55) as matrix (56):

$$\begin{array}{cc} \hat{Q}_D D & \begin{array}{ccc} {}^1\mathrm{S} & {}^1\mathrm{D} & {}^3\mathrm{P} \end{array} \\ \begin{array}{c} 1 \\ 5 \\ 9 \end{array} & \begin{array}{c} {}^1\mathrm{S} \\ {}^1\mathrm{D} \\ {}^3\mathrm{P} \end{array} \begin{bmatrix} 16/5 & 0 & 0 \\ 0 & 4/5 & 0 \\ 0 & 0 & -4/5 \end{bmatrix} D \end{array} \qquad (56)$$

The basis has at the same time been extended to cover all the 15 Pauli allowed states of the full p^2 configuration. The symmetry part of the repulsion operator $\hat{Q}_D D$ is its coefficient operator $\hat{Q}_D$ and D is the empirical repulsion parameter. The value of D for free atoms and ions may be determined by confronting the model expression (56) with experimentally found atomic energy levels for p^2 or p^4 configurations. For p^q complexes a determination of D from the experimental energy levels of a complex will

necessarily involve a co-determination of the ligand field parameters which are necessary to describe the symmetry of the complex in question. It is noted that $\hat{Q}_D$ is a traceless operator over p^2 and that it has a norm square of 96/5 over these 15 states. Alternatively, we may write eqn. (57):

$$\left\langle \hat{Q}_D D \middle| \hat{Q}_D D \right\rangle_{p^2} = (96/5) D^2 \tag{57}$$

It is noteworthy that even though $\hat{Q}_D D$ is spin free, its barycentration and norm square depend on spin through the Pauli principle. The p^2 configuration space is the natural foundation for normalization of two-electron operators on p^q spaces (section E(iii)).

(iv) A decomposition of the spin-pairing energy coefficient operator $\hat{Q}_D$ into mutually orthogonal components

The following considerations are typical of the ideas of the orthonormal operators' formalism, and at the same time provide a new illustration of the concept of orthogonal operators.

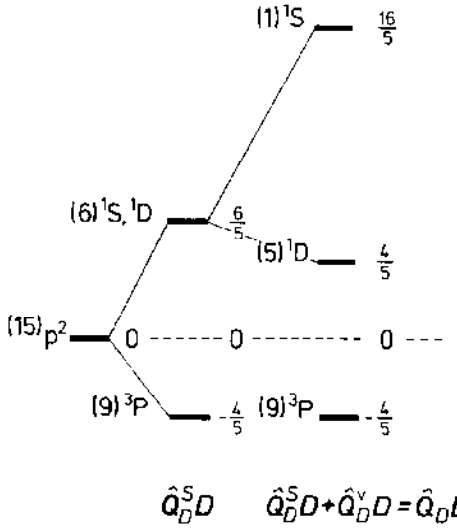

Fig. 4. The interelectronic repulsion splitting of the p^2 configuration, described by the operator $\hat{Q}_D D$, can conceptually be divided into two ordered steps. First, the 15 states of p^2 are split by the spin-separating operator $\hat{Q}_D^S D$ into six spin-singlet states ^{1}S, ^{1}D and nine spin-triplet states ^{3}P. The former are increased in energy by $(6/5)D$ while the latter are decreased by $(4/5)D$ so that the barycentre rule applies. Second, when the seniority-separating operator $\hat{Q}_D^V D$ is allowed to act, the six spin-singlet states are split into ^{1}S and ^{1}D of energies $(10/5)D$ and $-(2/5)D$, relative to their common origin. Again the barycentre rule applies.

Let us think of the coefficient operator for interelectronic repulsion $\hat{Q}_D$ as acting on the space of the p^2 configuration in two steps. In the first step it separates the triplet term ^3P from the singlet terms ^1S and ^1D which remain degenerate. The part of the $\hat{Q}_D$ operator doing this, we call the spin-separating operator and denote it $\hat{Q}_D^S$. In the second step $\hat{Q}_D$ separates ^1S and ^1D by what we call the seniority-separating operator $\hat{Q}_D^v$. Seniority is a concept based upon looking at all p^q configurations, with varying q, as a whole. It is in itself quite unimportant here and we shall only mention that one says that the seniority of the p^2 ^1S is zero because ^1S occurred already among p^q configurations for $q = 0$ while the other two p^2 terms have $v = 2$ because they occur for the first time for $q = 2$. The two singlet terms of the p^2 configuration may therefore be distinguished by their seniority *.

The two-step splitting is depicted in Fig. 4. It is illustrative of the ideas in this paper to express the two-step splitting in more ways: by the operator eqn. (58) and by the matrix eqn. (59):

$$\hat{Q}_D = \hat{Q}_D^S + \hat{Q}_D^v \tag{58}$$

$$\begin{bmatrix} 16/5 & 0 & 0 \\ 0 & 4/5 & 0 \\ 0 & 0 & -4/5 \end{bmatrix} = \begin{bmatrix} 6/5 & 0 & 0 \\ 0 & 6/5 & 0 \\ 0 & 0 & -4/5 \end{bmatrix} + \begin{bmatrix} 10/5 & 0 & 0 \\ 0 & -2/5 & 0 \\ 0 & 0 & 0 \end{bmatrix} \tag{59}$$

The matrices of the individual component operators $\hat{Q}_D^S$ and $\hat{Q}_D^v$, given in eqn. (59), are found by combining the requirement that their sum matrix be that of $\hat{Q}_D$ (eqn. (56)) and that both component matrices be traceless or barycentred. The procedure is simple. We first use the sum requirement together with the fact that $\hat{Q}_D^v$ does not act on the triplet, i.e. that $\langle {}^3P | \hat{Q}_D^v | {}^3P \rangle = 0$, to obtain $\langle {}^3P | \hat{Q}_D^S | {}^3P \rangle = \langle {}^3P | \hat{Q}_D | {}^3P \rangle = -4/5$. Secondly, we use the tracelessness of $\hat{Q}_D^S$ to find the value of $\langle {}^1S | \hat{Q}_D^S | {}^1S \rangle = \langle {}^1D | \hat{Q}_D^S | {}^1D \rangle$ as $6/5$. In doing this the weight factors in eqn. (56) should be remembered. Having now obtained the complete matrix of $\hat{Q}_D^S$, we finally subtract it from the matrix of $\hat{Q}_D$ to obtain the matrix of $\hat{Q}_D^v$. The three matrices of eqn. (59), all in the same basis as matrix (56), correspond to the three operators in eqn. (58) and are the coefficient matrices to D. $\hat{Q}_D^S$ acts in one way on all the singlet states and in another way on all the triplet states.

* The two singlet terms are of course distinguished also by their orbital angular momentum quantum number L. However, repulsion coefficient operators which are analogous to $\hat{Q}_D$ exist for all other l^q configurations [4] and these operators have properties which clearly associate a part of their splitting effect with the seniority.

$\hat{Q}_D^v$ acts only on the singlets and in a different way on the two terms with different seniority numbers.

We now use eqns. (58) and (59) to illustrate the concepts of operator overlap and operator orthogonality. We can here refer to the discussion of $\langle \hat{V}(D_4) | \hat{V}(D_4) \rangle$ in Section B(iv). In eqn. (60) the norm square or self-overlap of $\hat{Q}_D$ is written out in terms of its expression on the right-hand side of eqn. (58) by using the well-known formalism for functions when these are real:

$$\langle \hat{Q}_D | \hat{Q}_D \rangle = \langle \hat{Q}_D^S | \hat{Q}_D^S \rangle + \langle \hat{Q}_D^v | \hat{Q}_D^v \rangle + 2 \langle \hat{Q}_D^S | \hat{Q}_D^v \rangle \tag{60}$$

The last term in eqn. (60) is, according to the definition in eqn. (10), given by eqn. (61):

$$\langle \hat{Q}_D^S | \hat{Q}_D^v \rangle = \sum_{i,j} [\mathbf{Q}_D^S]_{ij} [\mathbf{Q}_D^v]_{ij} \tag{61}$$

By using the matrices of eqn. (59) and the weight factors of matrix (56), eqn. (60) may be rewritten in numerical form in eqn. (62):

$$\begin{aligned} &(1/5)^2 \{16^2 + 5(4)^2 + 9(-4)^2\} \\ &\quad = (1/5)^2 \{[(6)^2 + 5(6)^2 + 9(-4)^2] + [(10)^2 + 5(-2)^2 + 9(0)^2] \\ &\qquad + 2[(6)(10) + 5(6)(-2) + 9(-4)(0)]\} \\ &\quad \Leftrightarrow 480/25 = 360/25 + 120/25 + 0 \end{aligned} \tag{62}$$

Since the operator overlap $\langle \hat{Q}_D^S | \hat{Q}_D^v \rangle$ is equal to zero, $\hat{Q}_D^S$ and $\hat{Q}_D^v$ are orthogonal. The orthogonality has the important implication that the norm square of $\hat{Q}_D$ is equal to the sum of the norm square of $\hat{Q}_D^S$ and the norm square of $\hat{Q}_D^v$. Equation (62) then tells that the spin-separating operator $\hat{Q}_D^S$ accounts for $360/480 = 75\%$ and the seniority-separating operator $\hat{Q}_D^v$ accounts for $120/480 = 25\%$ of the total norm square of $\hat{Q}_D$. These relative contributions of $\hat{Q}_D^S$ and $\hat{Q}_D^v$ are independent of the value of the empirical parameter D, since both coefficient operators are associated with this parameter.

(v) The p^3 configuration

The p^3 configuration contains $\binom{6}{3} = 20$ states, grouped into one spin-quartet term and two spin-doublet terms. The orbital degeneracy of the spin quartet is $\binom{3}{3} = 1$ since this is the number of ways in which it is possible for all three electrons to have α spin. The spin quartet is accordingly ^4S. Further analysis shows that the doublets are ^2P and ^2D.

The matrix of the interelectronic repulsion operator $\hat{Q}_D D$, analogous to matrix (56) for p^2, is matrix (63):

$$\begin{array}{cc|ccc} & \hat{Q}_D D & {}^2P & {}^2D & {}^4S \\ 6 & {}^2P & 8/5 & 0 & 0 \\ 10 & {}^2D & 0 & 0 & 0 \\ 4 & {}^4S & 0 & 0 & -12/5 \end{array} \Bigg] D \qquad (63)$$

Since the configuration p^3 as mentioned in Section C is of little chemical interest, we content ourselves with pointing out a few properties of the coefficient matrix $\mathbf{Q}_D$: this 20×20 matrix is traceless and has a norm square of 192/5 which is two times that of $\mathbf{Q}_D$ for p^2 (matrix (56)) in agreement with eqn. (90) in section F(iii). Finally, the energy difference between the barycentre of the doublet states and the quartet state is $(3/5)D - (-(12/5)D) = 3D = 2S_0 D$ since $S_0 = 3/2$.

E. THE COMBINED EFFECT OF A TETRAGONAL LIGAND FIELD AND THE INTERELECTRONIC REPULSION ON THE p^2 CONFIGURATION

The preceding two sections (Sections C and D) were concerned with two different kinds of perturbations on the p^2 configuration: the ligand field $\hat{H}_{l.f.}$ and the interelectronic repulsion $\hat{H}_{rep.}$. In real chemical systems such as, for example, XeF_4, both these perturbations are simultaneously present and we shall therefore in this section consider their sum:

$$\hat{H} = \hat{H}_{l.f.} + \hat{H}_{rep.} \qquad (64)$$

We shall discuss the different bases that may be chosen for the total Hamiltonian $\hat{H}$ and the relationships between them. Moreover, we shall show how the orthonormal operators' formalism allows a quantitative comparison to be made between the relative contributions of the ligand field $\hat{H}_{l.f.}$ and the interelectronic repulsion $\hat{H}_{rep.}$ to the total Hamiltonian $\hat{H}$. Finally, we shall discuss how the eigenenergies of a configuration may be visualized in different kinds of energy level diagrams.

(i) Weak-field and strong-field bases for p^2

A weak-field basis is a basis that is an eigenbasis of $\hat{Q}_D$ and a strong-field basis is analogously an eigenbasis of $\hat{Q}_\Delta$. When the combined effect of a tetragonal ligand field and the interelectronic repulsion is sought, the same basis has to be used for both operators in order to make it meaningful to add their matrices. In Sections C and D, we have already discussed $\hat{Q}_\Delta$ in the strong-field basis and $\hat{Q}_D$ in the weak-field basis respectively. These two

bases are the eigenbases for the two operators and are therefore the natural bases to choose for setting up their matrix representations. When adding the two operators, it is, however, necessary to consider at least one of the operators in a less natural basis. In the cases to be discussed here, we shall include both $\hat{Q}_\Delta$ in the weak-field basis and $\hat{Q}_D$ in the strong-field basis.

As far as the weak-field situation is concerned, it should be noted that several weak-field bases exist. The weak field basis of the matrix (56) is written in the most general way since the particular functions which span the individual $^{2S+1}$L terms are not stated. For the basis to be completely specified, these functions must be given. A fully specified basis, which has the special property of being hierarchically symmetry adapted, is made up from the functions given in eqns. (49) and (52) and include the functions in eqns. (65) and (66) *:

$$\begin{array}{lll} \mathrm{D\Pi c} & \mathrm{E}(D_4)\mathrm{B}_2(D_2) & \mathrm{D(zx)} = \sqrt{1/2}\,(\mathrm{zx} + \mathrm{xz}) \\ \mathrm{P\Pi s} & \mathrm{E}(D_4)\mathrm{B}_2(D_2) & \mathrm{P(y)} = \sqrt{1/2}\,(\mathrm{zx} - \mathrm{xz}) \end{array} \tag{65}$$

$$\begin{array}{lll} \mathrm{D\Pi s} & \mathrm{E}(D_4)\mathrm{B}_1(D_2) & \mathrm{D(yz)} = \sqrt{1/2}\,(\mathrm{yz} + \mathrm{zy}) \\ \mathrm{P\Pi c} & \mathrm{E}(D_4)\mathrm{B}_1(D_2) & \mathrm{P(x)} = \sqrt{1/2}\,(\mathrm{yz} - \mathrm{zy}) \end{array} \tag{66}$$

This basis is symmetry adapted to the group D_4 which is the holohedral rotation group of the tetragonal ligand field, and this weak-field basis will be used in the following development. As discussed in Section D, the weak-field basis of p^2 including spin, adapted to the tetragonal hierarchy, then consists of the following terms: two $^1\mathrm{A}_1(D_4)$ (eqn. (49)), one $^1\mathrm{B}_1(D_4)$ (eqn. (49)), one $^1\mathrm{B}_2(D_4)$ (eqn. (52)), one $^3\mathrm{A}_2(D_4)$ (three functions) (eqn. (52)), one $^1\mathrm{E}(D_4)$ (two functions) (eqns. (65) and (66)), and one $^3\mathrm{E}(D_4)$ (six functions) (eqns. (65) and (66)). The tetragonal strong-field basis of p^2 consists of the same seven terms, but the expressions for the strong-field functions are in general not the same as those for the weak-field functions.

We observe that the different symmetry types $^{2S+1}\Gamma(D_4)$ occur only once, with the exception of $^1\mathrm{A}_1(D_4)$ which occurs twice. This means that the matrices of both the ligand field operator $\hat{Q}_\Delta\Delta$ and the repulsion operator $\hat{Q}_D D$ will be diagonal in bases, symmetry adapted to D_4, except for a (possible) non-diagonal element connecting the two $^1\mathrm{A}_1(D_4)$ functions. This is the same as saying that for all symmetry types except $^1\mathrm{A}_1(D_4)$, no distinction can be made between the weak-field and the strong-field func-

* Other examples of weak-field bases are the two SL bases whose functions are complex: the $\mathrm{SLM_SM_L}$ basis and the SLJM basis. The energy matrices in these bases are of course diagonal in the interelectronic repulsion parameter D, but matrices in the SLJM basis are furthermore diagonal in the spin–orbit coupling within each $^{2S+1}$L term.

tions or, in other words, between the multiplet terms of the spherically symmetrical situation and the terms belonging to tetragonal subconfigurations *.

Let us now set up a matrix for the ligand field and the interelectronic repulsion in the tetragonally adapted bases. We shall consider the triplets first. These are invariably ^3P functions independent of the magnitude of the ligand field. They therefore have the repulsion energy $-(4/5)D$ according to matrix (56). As far as the ligand field is concerned, a comparison of eqns. (36) and (52) shows that $^3P^3A_2(D_4)$ belongs to the subconfiguration $e^2(D_4)$ or π^2 with the energy $(2/3)\Delta$ independent of the repulsion, while a comparison of eqns. (36), (65) and (66) shows that $^3P^3E(D_4)$ belongs to the subconfiguration $ea_2(D_4) = \pi\sigma$ with energy $-(1/3)\Delta$. We summarize the triplet results in eqn. (67) where the barycentre rule is observed to apply for Δ inside the ^3P term.

$$\begin{aligned} &^3P^3A_2(D_4) = {}^3P^3\Sigma \quad -(4/5)D + (2/3)\Delta \quad e^2 \quad \pi^2 \\ &^3P^3E(D_4) = {}^3P^3\Pi \quad -(4/5)D - (1/3)\Delta \quad ea_2 \quad \pi\sigma \end{aligned} \tag{67}$$

We next consider the singlets in a similar way (except for those of $^1A_1(D_4)$ symmetry) referring to eqns. (36), (56), (49), (52), (65) and (66) to obtain eqn. (68):

$$\begin{aligned} &^1D^1E(D_4) = {}^1D^1\Pi \qquad (4/5)D - (1/3)\Delta \quad ea_2 \quad \pi\sigma \\ &^1D^1B_1(D_4) \text{ and } {}^1D^1B_2(D_4) = {}^1D^1\Delta \quad (4/5)D + (2/3)\Delta \quad e^2 \quad \pi^2 \end{aligned} \tag{68}$$

The two tetragonal terms $^1B_1(D_4)$ and $^1B_2(D_4)$ are both associated with the term ^1D and the tetragonal subconfiguration e^2 and are degenerate. This degeneracy may be considered accidental since the two terms transform differently in the group D_4 (as $^1B_1(D_4)$ and $^1B_2(D_4)$ respectively) but it is easily explained. As discussed in Section B(ii), the p orbital set is not able to distinguish between ligand fields of symmetry $D_n (n > 2)$ and D_∞. Collectively, these fields may therefore (when acting on p^q configurations) be called axial fields, and they split a ^1D term into $^1D^1\Sigma$, $^1D^1\Pi$ and $^1D^1\Delta$. In our case the two degenerate tetragonal terms make up the $^1D^1\Delta$.

Finally, we consider the weak-field matrix elements whose basis functions are the $^1A_1(D_4)$ functions. The interelectronic repulsion part of these elements we know already from matrix (56): $^1S^1A_1$ has a repulsion energy of $(16/5)D$ and $^1D^1A_1$ an energy of $(4/5)D$. To obtain the ligand field part, we use eqn. (49) and Fig. 1, remembering that z spans $a_2(D_4)$ and the set {x,y}

* Since none of the operators in eqn. (64) contains spin, matrix elements between spin-singlet and spin-triplet functions would have been zero anyway because of the spin orthogonality. It is therefore always possible to treat the triplets and the singlets independently.

spans e(D_4):

$$\left\langle {}^1\mathrm{S}\middle|\hat{V}(D_4)\middle|{}^1\mathrm{S}\right\rangle = \left\langle \sqrt{1/3}\,(\mathrm{xx}+\mathrm{yy}+\mathrm{zz})\middle|\hat{V}(D_4)\middle|\sqrt{1/3}\,(\mathrm{xx}+\mathrm{yy}+\mathrm{zz})\right\rangle$$
$$= (1/3)[(2/3)+(2/3)-(4/3)]\,\Delta = 0 \tag{69}$$

$$\left\langle {}^1\mathrm{D}(z^2)\middle|\hat{V}(D_4)\middle|{}^1\mathrm{D}(z^2)\right\rangle$$
$$= \left\langle \sqrt{1/6}\,(2\,\mathrm{zz}-\mathrm{xx}-\mathrm{yy})\middle|\hat{V}(D_4)\middle|\sqrt{1/6}\,(2\,\mathrm{zz}-\mathrm{xx}\quad\mathrm{yy})\right\rangle$$
$$-(1/6)[4(-4/3)+(2/3)+(2/3)]\,\Delta = -(2/3)\,\Delta \tag{70}$$

$$\left\langle {}^1\mathrm{S}\middle|\hat{V}(D_4)\middle|{}^1\mathrm{D}(z^2)\right\rangle$$
$$= \left\langle \sqrt{1/3}\,(\mathrm{zz}+\mathrm{xx}+\mathrm{yy})\middle|\hat{V}(D_4)\middle|\sqrt{1/6}\,(2\,\mathrm{zz}-\mathrm{xx}-\mathrm{yy})\right\rangle$$
$$= \sqrt{1/18}\,[2(-4/3)-(2/3)-(2/3)]\,\Delta = -\sqrt{8/9}\,\Delta \tag{71}$$

The results for the diagonal elements in eqns. (69) and (70) could also have been obtained without direct calculation by using the barycentre rule on ^{1}S and ^{1}D respectively, in the latter case by including the results from eqn. (68). The magnitude of the non-diagonal element in eqn. (71) could have been obtained from the norm square invariance inside the two-dimensional subspace of p^2 whose components are characterized as $^1A_1(D_4)$. This method requires knowledge of the strong-field matrix (73) but this is easy to obtain directly from a knowledge of the subconfigurations and from Fig. 1.

The results of eqns. (69)–(71) may be combined, yielding the $^1A_1(D_4)$ weak-field matrix (72):

$$^1\mathrm{A}_1(D_4)\,{}^1\Sigma \qquad \begin{matrix} & \hat{V}(D_4) & {}^1\mathrm{S} & {}^1\mathrm{D}(z^2) \\ {}^1\mathrm{S} & & 0 & -\sqrt{8/9} \\ {}^1\mathrm{D}(z^2) & & -\sqrt{8/9} & -2/3 \end{matrix} \Delta \tag{72}$$

We now turn to the strong-field matrix and its relationship to the weak-field matrix derived above. Since for most of the tetragonal p^2 terms there is no difference between the weak- and strong-field forms, we shall in the following discussion focus attention on the two $^1A_1(D_4)$ terms, the only terms for which such a difference exists. The strong-field basis is the eigenbasis of $\hat{Q}_\Delta$. A diagonalization of the weak-field $^1A_1(D_4)$ matrix (72) will therefore yield the corresponding strong-field matrix (73):

$$\begin{matrix} & & & \hat{V}(D_4) & \mathrm{e}^2(D_4) & \mathrm{a}_2^2(D_4) \\ \sqrt{1/2}\,(\mathrm{xx}+\mathrm{yy}) = \sqrt{2/3}\,{}^1\mathrm{S} - \sqrt{1/3}\,{}^1\mathrm{D}(z^2) = \mathrm{e}^2(D_4) & & & 2/3 & 0 \\ \mathrm{zz} = \sqrt{1/3}\,{}^1\mathrm{S} + \sqrt{2/3}\,{}^1\mathrm{D}(z^2) = \mathrm{a}_2^2(D_4) & & & 0 & -4/3 \end{matrix} \Delta \tag{73}$$

The strong-field functions have here been characterized by their tetragonal subconfigurations, by the linear combinations of weak-field functions found by the diagonalization, and by the explicit function expressions. The relationship between the weak- and strong-field ${}^1A_1(D_4)$ bases may be expressed as the overlap matrix (74):

$$\begin{array}{c} {}^1A_1(D_4) \\ (pe)^2 \\ (pa_2)^2 \end{array} \begin{array}{c} {}^1S \qquad\quad {}^1D \\ \begin{bmatrix} \sqrt{2/3} & -\sqrt{1/3} \\ \sqrt{1/3} & \sqrt{2/3} \end{bmatrix} \end{array} \tag{74}$$

This matrix is a so-called Racah lemma [1,22] matrix which expresses some basis-independent symmetry relations between the groups R_3 and D_4, basis independent meaning here independent of the matrix forms chosen for the irreducible representations of these two groups. The content of the matrix can be expressed verbally in various ways. As examples, the a_2^2 tetragonal subconfiguration of p^2 has in the squares one third ${}^1S$ and two thirds ${}^1D$ character as can be read from the second row of matrix (74), or, the ${}^1D{}^1A_1(D_4)$ function of p^2 belongs (in the squares) $1/3$ to $e^2(D_4)$ and $2/3$ to $a_2^2(D_4)$.

Transforming the 2×2 upper left part of the matrix of $\hat{Q}_D$ (matrix (56)) to the strong-field basis using matrix (74), the strong-field interelectronic repulsion matrix (75) is obtained:

$$\begin{array}{c} \hat{Q}_D D \\ e^2\,{}^1A_1(D_4) \\ a_2^2\,{}^1A_1(D_4) \end{array} \begin{array}{c} e^2\,{}^1A_1(D_4) \qquad a_2^2\,{}^1A_1(D_4) \\ \begin{bmatrix} 12/5 & \sqrt{32/25} \\ \sqrt{32/25} & 8/5 \end{bmatrix} \end{array} D \tag{75}$$

To summarize the discussion of the two ${}^1A_1(D_4)$ levels of p^2, we give the strong- and weak-field energy matrices of the combined perturbations in eqns. (76) and (77) respectively:

$$\begin{array}{c} \hat{Q}_\Delta \Delta + \hat{Q}_D D \\ e^2\,{}^1A_1(D_4) \\ a_2^2\,{}^1A_1(D_4) \end{array} \begin{array}{c} e^2\,{}^1A_1(D_4) \qquad\qquad a_2^2\,{}^1A_1(D_4) \\ \begin{bmatrix} (2/3)\Delta + (12/5)D & \left(\sqrt{32/25}\right)D \\ \left(\sqrt{32/25}\right)D & -(4/3)\Delta + (8/5)D \end{bmatrix} \end{array} \tag{76}$$

$$\begin{array}{c} \hat{Q}_D D + \hat{Q}_\Delta \Delta \\ {}^1S{}^1A_1(D_4) \\ {}^1D{}^1A_1(D_4) \end{array} \begin{array}{c} {}^1S{}^1A_1(D_4) \qquad\quad {}^1D{}^1A_1(D_4) \\ \begin{bmatrix} (16/5)D & \left(-\sqrt{8/9}\right)\Delta \\ \left(-\sqrt{8/9}\right)\Delta & -(2/3)\Delta + (4/5)D \end{bmatrix} \end{array} \tag{77}$$

By merging eqn. (76) with eqns. (67) and (68) the total strong-field matrix (78) is obtained:

			$^1A_1$ $^1\Sigma$	$^1B_1, {}^1B_2$ $^1\Delta$	$^3A_2$ $^3\Sigma$	^1E $^1\Pi$	^3E $^3\Pi$	$^3A_1$ $^1\Sigma$
1	e^2	$^1\Sigma$	$(2/3)\Delta + (12/5)D$	0	0	0	0	$(\sqrt{32/25})D$
2	e^2	$^1\Delta$	0	$(2/3)\Delta + (4/5)D$	0	0	0	0
3	e^2	$^1\Sigma$	0	0	$(2/3)\Delta - (4/5)D$	0	0	0
2	a_2e	$^1\Pi$	0	0	0	$-(1/3)\Delta + (4/5)D$	0	0
6	a_2e	$^3\Pi$	0	0	0	0	$-(1/3)\Delta - (4/5)D$	0
1	a_2^2	$^1\Sigma$	$(\sqrt{32/25})D$	0	0	0	0	$-(4/3)\Delta + (8/5)D$

(78)

The total weak-field matrix (79) is similarly obtained by substituting matrix (77) for matrix (76) in the strong-field matrix:

			$^3A_1$ $^1S^1\Sigma$	^1E $^1D^1\Pi$	$^1B_1, {}^1B_2$ $^1D^1\Delta$	$^3A_2$ $^3P^3\Sigma$	^3E $^3P^3\Pi$	$^1A_1$ $^1D^1\Sigma$
1	^1S	$^1\Sigma$	$(16/5)D$	0	0	0	0	$(-\sqrt{8/9})\Delta$
2	D	$^1\Pi$	0	$(4/5)D - (1/3)\Delta$	0	0	0	0
2	^1D	$^1\Delta$	0	0	$(4/5)D - (2/3)\Delta$	0	0	0
3	^1P	$^1\Sigma$	0	0	0	$-(4/5)D + (2/3)\Delta$	0	0
6	^1P	$^1\Pi$	0	0	0	0	$-(4/5)D - (1/3)\Delta$	0
1	^1D	$^1\Sigma$	$(\sqrt{8/9})\Delta$	0	0	0	0	$(4/5)D - (2/3)\Delta$

(79)

Both the matrices (78) and (79) are brief forms. (weight factors to the left) of 15×15 matrices.

If one notices in the weak-field matrix (79) at the same time the barycentration of $\hat{Q}_\Delta$ within each of the spherical terms and the fact that the coefficient to D is a constant within each such term, then one may conclude that the ligand field matrix and the repulsion matrix have zero overlap, i.e. they are orthogonal. As discussed in Section B(iv), such a matrix orthogonal-

ity reflects the more general operator orthogonality and we may therefore conclude that the two coefficient operators $\hat{Q}_\Delta$ and $\hat{Q}_D$ are orthogonal. This orthogonality is important because it allows quantitative comparisons to be made between the relative magnitudes of the ligand field and the interelectronic repulsion. How this is done will be discussed in Section E(iii).

(ii) Intermediate ligand field bases and rediagonalizations

The total Hamiltonian operator $\hat{H}$ may be written in terms of parameters and coefficient operators as in eqn. (80):

$$\hat{H} = \hat{Q}_\Delta \Delta + \hat{Q}_D D \tag{80}$$

The Hamiltonian operator (eqn. (80)) depends on empirical parameters. We therefore call it a parametrical Hamiltonian. When the ligand field term $\hat{Q}_\Delta \Delta$ completely dominates the Hamiltonian, i.e. when $\Delta/D = \infty$, the eigenbasis of $\hat{H}$ is the strong-field basis. Conversely, when the repulsion term completely dominates the Hamiltonian, i.e. when $\Delta/D = 0$, the eigenbasis of $\hat{H}$ is the weak-field basis. Real chemical systems, such as for example XeF_4, are found between these two extreme situations and their eigenbases are what we call intermediate ligand field bases. An infinite number of such intermediate-field bases exist, none of which is defined by symmetry, as is the case for the strong-field and weak-field bases. Intermediate-field matrices are therefore neither diagonal in Δ nor in D. An intermediate-field basis is the eigenbasis of the parametrical Hamiltonian for particular magnitudes of the ligand field term and the repulsion term. A slightly different way to specify an intermediate-field basis is by the parameter ratio Δ/D where the use of the ratio for this purpose is possible because the eigenbasis of a parametrical energy matrix is independent of the absolute magnitudes of the parameters but depends only upon their relative magnitudes. Doubling the values of both Δ and D thus leaves the eigenbasis of $\hat{H}$ unchanged.

Strong-field and weak-field matrices have bases that are symmetry defined, and it is therefore possible to set up these matrices as illustrated in Section E(i). Intermediate-field matrices cannot be set up in this way but must instead be obtained indirectly by transformations of matrices already set up in one of the symmetry-defined bases. In the following discussion we shall detail how intermediate-field matrices may be formed by such transformations. First, the particular intermediate-field basis in which we are interested must be fully specified. It is specified as the eigenbasis of the parametrical Hamiltonian, defined by the particular numerical values of the parameters. Often the intermediate-field basis is the eigenbasis of a particular complex and in that case the parameter values may be said also to describe the complex. Assuming that the intermediate-field basis is specified,

we next require a parametrical energy matrix such as the strong-field matrix (78) or the weak-field matrix (79), which may be subjected to the transformation. We are then ready to begin. The parameter values which characterize our intermediate-field basis are inserted into the parametrical energy matrix, and the matrix, now containing only numbers, is then diagonalized to give a set of eigenvalues and eigenvectors. The basis of the diagonalized matrix is our desired intermediate-field basis. However, in order to arrive at this basis, the energy contributions from the ligand field and the interelectronic repulsion have been added together and the information about their individual contributions lost.

This information may be retrieved by the following procedure which we call a rediagonalization [26]. The eigenvectors obtained in the diagonalization relate the intermediate-field basis to the basis of the original parametrical energy matrix, for example the weak-field matrix. The eigenvectors may be used to transform this matrix (eqn. (81)) to the intermediate-field basis according to eqn. (82):

$$\mathbf{H} = \mathbf{Q}_{\Delta}\Delta + \mathbf{Q}_{D}D \tag{81}$$

$$\begin{aligned}\mathbf{H}' = \mathbf{U}\mathbf{H}\mathbf{U}^{-1} &= \left[\mathbf{U}\mathbf{Q}_{\Delta}\mathbf{U}^{-1}\right]\Delta + \left[\mathbf{U}\mathbf{Q}_{D}\mathbf{U}^{-1}\right]D \\ &= \mathbf{Q}'_{\Delta}\Delta + \mathbf{Q}'_{D}D\end{aligned} \tag{82}$$

Here matrices that are in the intermediate-field basis are characterized by a prime. $\mathbf{U}$ is the unitary matrix containing the eigenvectors, i.e. containing the information regarding the relationship between the two bases, in the example between the weak-field basis and the intermediate-field basis. By this rediagonalization process (eqn. (82)) we have obtained a matrix representation $\mathbf{H}'$ of the general parametrical Hamiltonian operator $\hat{H}$ (eqn. (80)) in the particular intermediate-field basis desired here. The matrix representations of the two coefficient operators are both non-diagonal, but possess the special feature that corresponding non-diagonal elements in the two matrices are of equal magnitude but of opposite sign when weighted by their respective empirical parameters. Inserting the empirical parameter values into $\mathbf{H}'$ therefore yields a diagonal matrix. The diagonal elements are the eigenvalues of our complex. However, while the diagonalization gives only the eigenvalues themselves, the rediagonalization provides additional information: the eigenvalues are in the diagonal of $\mathbf{H}'$ expressed as a linear combination of Δ and D, and we can therefore read the individual contributions of the ligand field and the interelectronic repulsion to each of the eigenvalues. Furthermore, the form of this information is useful because the diagonal elements of the coefficient matrices are the partial derivatives of the eigenvalues with respect to the associated parameters.

(iii) Quantitative comparison of Hamiltonian operator terms. Their individual contributions to the total Hamiltonian

Throughout this review, we have discussed and illustrated the two concepts of operator magnitude and operator orthogonality. The point has now been reached where the full significance of these concepts in connection with the parametrical 1^q model may be appreciated. Below we shall therefore show how the properties of orthogonal operators make quantitative comparisons possible between the constituent perturbations of the sum Hamiltonian operator.

The orthogonality of $\hat{H}_{\text{l.f.}}$ and $\hat{H}_{\text{rep}}$ found in Section E(i) allows us to write the norm square of the total Hamiltonian as in eqn. (83):

$$\langle \hat{H} \mid \hat{H} \rangle = \left\langle \hat{H}_{\text{l.f.}} \middle| \hat{H}_{\text{l.f.}} \right\rangle + \left\langle \hat{H}_{\text{rep.}} \middle| \hat{H}_{\text{rep}} \right\rangle \tag{83}$$

where the cross term $\langle \hat{H}_{\text{l.f.}} \mid \hat{H}_{\text{rep.}} \rangle$ is not present because of the orthogonality. Rewriting eqn. (83) in terms of parameters and coefficient operators we obtain eqn. (84):

$$\langle \hat{H} \mid \hat{H} \rangle = \Delta^2 \left\langle \hat{Q}_\Delta \middle| \hat{Q}_\Delta \right\rangle + D^2 \left\langle \hat{Q}_D \middle| \hat{Q}_D \right\rangle \tag{84}$$

This equation shows that the norm square of the total Hamiltonian may be calculated as the sum of a ligand field contribution and an interelectronic-repulsion contribution. In Fig. 5 a number of geometrical illustrations of eqn. (83) and (84) have been given by conceiving the operators as generalized vectors. In the figure the operator property magnitude or length, as mentioned in Section B(iv), corresponds to the vector property length. The figure further illustrates that eqn. (83) is a generalization of the Pythagorean theorem and that it applies to our two component operators because they are orthogonal. Finally, it is seen from Fig. 5 and eqns. (83) and (84) that the norm square of a sum of two (or more) orthogonal operators is the sum of the norm squares of the constituent operators. For this reason the norm square rather than the magnitude (to which this does not apply) plays such an important role in the orthonormal operators' formalism.

As mentioned previously, the norm square of an operator is independent of the particular matrix representation used for calculating it. If the matrix of $\hat{H}$ used for calculating the norm square of $\hat{H}$ is chosen to be diagonal, then the norm square is the sum of the squares of the diagonal elements (see eqn. (10)). Generally, the norm square of $\hat{H}$ is therefore equal to the sum of the squared eigenvalues. Since $\hat{H}$ is barycentred, its eigenvalues $\bar{h}_i$ express energy deviations from the configuration barycentre, i.e. they are the splitting energies of the configuration. The Hamiltonian operator norm square in

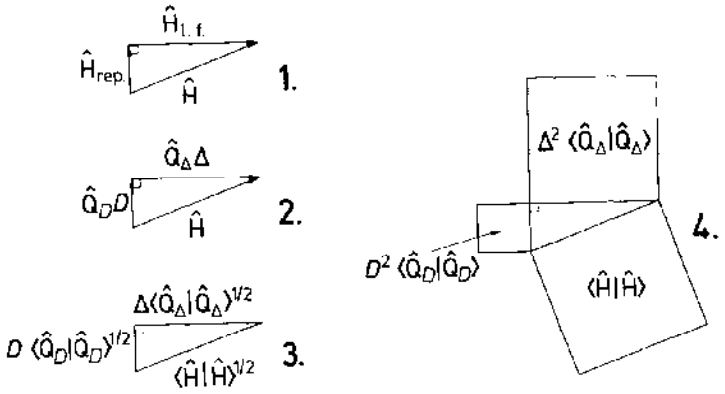

Fig. 5. There are both conceptual and pedagogical advantages in thinking about operators as vectors in a vector space. This is exemplified here by considering the total Hamiltonian (eqn. (64)). The orthogonality of the ligand field and interelectronic repulsion operators is illustrated in general in **1**, and for our specific parametrization of p^q systems (eqn. (80)) in **2**. The important consequences of the orthogonality is illustrated in **3** for the magnitudes (lengths) of the operators and in **4** for their norm squares.

eqn. (85) has therefore been called the sum square splitting [2]:

$$\langle \hat{H} \mid \hat{H} \rangle = \langle \mathbf{H}_{\text{diag}} \mid \mathbf{H}_{\text{diag}} \rangle = \sum_i (\bar{h}_i)^2 \tag{85}$$

Having now obtained an understanding of the purely mathematical concept of a Hamiltonian operator norm square in terms of splitting energies, we may return to the decomposition of $\langle \hat{H} \mid \hat{H} \rangle$ in eqn. (84).

According to eqn. (84) the sum square splitting is the sum of the norm squares of the component operators $\hat{H}_{\text{l.f.}}$ and $\hat{H}_{\text{rep.}}$. This gives directly a means of dividing the sum square splitting into parts associated with these components of the total perturbation. Dividing eqn. (83) by $\langle \hat{H} \mid \hat{H} \rangle$, we obtain in eqn. (86) a formulation giving the fractions of the sum square splitting to be attributed to the ligand field and to the interelectronic repulsion:

$$\frac{\langle \hat{H}_{\text{l.f.}} | \hat{H}_{\text{l.f.}} \rangle}{\langle \hat{H} \mid \hat{H} \rangle} + \frac{\langle \hat{H}_{\text{rep}} | \hat{H}_{\text{rep.}} \rangle}{\langle \hat{H} \mid \hat{H} \rangle} = 1 \tag{86}$$

If we call the fraction of the sum square splitting that is caused by the tetragonal ligand field $x(\Delta)$ and the fraction caused by the interelectronic

repulsion $x(D)$, we have according to eqn. (84) the following expressions:

$$x(\Delta) = \frac{\Delta^2 \langle \hat{Q}_\Delta | \hat{Q}_\Delta \rangle}{\Delta^2 \langle \hat{Q}_\Delta | \hat{Q}_\Delta \rangle + D^2 \langle \hat{Q}_D | \hat{Q}_D \rangle} \tag{87}$$

$$x(D) = \frac{D^2 \langle \hat{Q}_D | \hat{Q}_D \rangle}{\Delta^2 \langle \hat{Q}_\Delta | \hat{Q}_\Delta \rangle + D^2 \langle \hat{Q}_D | \hat{Q}_D \rangle} \tag{88}$$

where the norm squares of the two coefficient operators $\hat{Q}_\Delta$ and $\hat{Q}_D$ may be calculated once and for all for a given p^q configuration.

These norm squares depend on the p^q configuration considered. For p^1 we have $\langle \hat{Q}_\Delta | \hat{Q}_\Delta \rangle = 4/3$ (eqn. (33)) and for p^2 we have $\langle \hat{Q}_D | \hat{Q}_D \rangle = 96/5$ (eqn. (57)). General formulae exist [4] which allow calculation of the coefficient operator norm squares as a function of l and q in l^q. For p^q configurations these formulae are

$$\langle \hat{Q}_\Delta | \hat{Q}_\Delta \rangle_{p^q} = \langle \hat{Q}_\Delta | \hat{Q}_\Delta \rangle_{p^1} \binom{4}{q-1} \tag{89}$$

$$\langle \hat{Q}_D | \hat{Q}_D \rangle_{p^q} = \langle \hat{Q}_D | \hat{Q}_D \rangle_{p^1} \binom{2}{q-2} \tag{90}$$

The way in which the norm squares depend on q is not the same for $\hat{Q}_\Delta$ and $\hat{Q}_D$. This arises from the fact that $\hat{Q}_\Delta$ is a one-electron operator whose foundation is the p^1 system and $\hat{Q}_D$ a two-electron operator whose foundation is a p^2 system (see also Section C(i)).

In conclusion, the orthonormal operators' formalism allows us to quantify the ligand field as well as the interelectronic repulsion. Furthermore, this quantification allows a comparison between the magnitudes of the two perturbations. In the strong-field limit the ligand field completely dominates the issue, a situation which in the formalism is described as $x(\Delta) = 1$ and $x(D) = 0$. In the weak-field limit the situation is reversed with $x(\Delta) = 0$ and $x(D) = 1$. Intermediate-field situations are characterized by $x(\Delta)$ and $x(D)$, both having values between zero and unity. According to eqns. (87) and (88) their sum is, however, always equal to unity. In the next section we look at the values of these ligand field fractions and repulsion fractions for some special p^2 intermediate-field situations.

(iv) Visualizing the combined effect of ligand field and interelectronic repulsion by means of energy level diagrams

Each of the parametrical energy matrices (78) and (79) contains all the information of the parametrical p^2 model concerning the energy levels of

tetragonal p^2 systems. For the p^2 configuration, the full energy matrix has a rather small size, and with only two basis functions of equal symmetry type (the two $^1A_1(D_4)$ functions), the number of non-diagonal elements is limited to the two connecting these functions. It is, in this particular case, not difficult to obtain an impression of the dependence of the eigenenergies of the different tetragonal terms on Δ and D just by examining one or both of the matrices. In general, however, for example in the case of d^q configurations, the simultaneous presence of ligand field and interelectronic repulsion creates a complex situation as far as the energy matrices, and thereby the eigenenergies, are concerned. In order to clarify the picture and make understanding of the intermediate-field situations easier, ligand field energy level diagrams have been invented.

There exist several types of these diagrams and variants of these types, the classical and most commonly encountered types being the Orgel diagrams and the Tanabe–Sugano diagrams. These are geometrically similar in a mathematical sense if the variants are chosen so as to attribute the same slope to the ground level in the two types of diagrams. Both of these were introduced originally with the purpose of describing the energy levels of d^q configurations under the influence of cubic ligand fields. These types of diagrams may, however, equally well be used for p^q configurations when these are under the influence of ligand fields that give rise to only one splitting parameter, e.g. fields of tetragonal symmetry. In this review we have denoted this splitting parameter Δ to emphasize its analogy to the spectrochemical parameter which for d^q systems measures the magnitude of the cubic ligand field splitting of the d orbital level into an e and a t_2 level. Similarly, our repulsion parameter D, introduced in Section D(iii), plays almost the same role in p^q systems as does the Racah parameter B in d^q systems. In an Orgel diagram the energies of the different cubic terms are depicted vs. the ligand field parameter Δ, and the diagram implies a constant and finite value of the interelectronic repulsion parameter (D or B). In the Tanabe–Sugano diagrams the d^q term energies (relative to the ground state), measured in units of B, are plotted vs. Δ/B. The latter ratio has been named "the internal field-strength parameter" [27]. The use of this parameter as abscissa in such diagrams has the advantage that this parameter alone determines the eigenfunctions in cubic d^q systems. In other words, when Δ/B is fixed, then relative eigenenergy differences are determined and the only degree of freedom left for obtaining the energy differences explicitly is a scale factor with the dimension of energy.

In Fig. 6 a Tanabe–Sugano-type energy level diagram for the p^2 and p^4 configurations in tetragonal symmetry has been constructed by use of the matrices (78) and/or (79). In the particular variant of the diagram the barycentre of the configuration rather than the ground state has been chosen

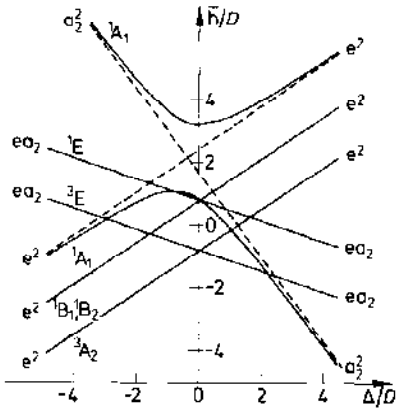

Fig. 6. Tanabe–Sugano-like diagram for the p^2 configuration in tetragonal symmetry (see Fig. 1 for definition of sign of Δ). The internal field-strength parameter Δ/D is the abscissa and the zero-point of the ordinate axis is defined by the barycentre energy of all the p^2 states. The weak-field situation is on the ordinate axis in the middle of the diagram, where the crossing of the energy curves are found at $16/5(^1S)$, $4/5(^1D)$ and $-4/5(^3P)$ (cf. the weak-field matrix (79)). The strong-field limits, corresponding to opposite signs of the tetragonal splitting, are approached to the left and to the right in the diagram. The ground level is seen to be $^3A_2(D_4)$ for $(\Delta/D) < 0$, $^1E(D_4)$ for $0 < (\Delta/D) < 2.16$, and $^1A_1(D_4)$ for $(\Delta/D) > 2.16$. As mentioned in Section F(i) the $^1B_1(D_4)$ and $^1B_2(D_4)$ terms are accidentally degenerate because of the inability of p electrons to distinguish between D_4 and D_{∞} symmetry. The energies of the $^1A_1(D_4)$ functions, which are the only functions of a repeated symmetry type, do not vary linearly through the diagram. The strong-field asymptotes (— — —) of their energy curves are included. The strong-field approximation to the spin cross-over point is the crossing point between the $^3E(ea_2)$ energy graph (a straight line) and the $^1A_1(a_2^2)$ asymptote, i.e. at $\Delta/D = 2.40$.

as the zero point of the energy. The diagram has been drawn for negative as well as for positive values of the internal field-strength parameter. The right-hand side of the diagram represents the p^2 situation $N_\theta^{\mathrm{d}} < 0$ (Fig. 1), and by the hole equivalence principle, the p^4 situation $N_\theta^{\mathrm{d}} > 0$ (Fig. 3) while the left-hand side represents the same situations except for opposite signs of N_θ^{d}. As discussed in Section B(viii), the sign of the splitting of the p-orbital level is expected to be reversed on going from a linear to a square-planar molecule. The right-hand side of the diagram therefore represents linear p^4 configurations (e.g. XeF_2) and square-planar p^2 configurations (e.g. XeF_4) while the left-hand part of the diagram has no chemical examples associated with it.

The extension of the diagram to negative Δ/D values has been included here only to show some general features of parametrical l^q models. First, all energy levels that only occur once are represented by straight lines throughout

the diagram. The slopes of these lines are the diagonal elements of $\hat{Q}_\Delta$ and the intercepts those of $\hat{Q}_D$ [26]. Second, for the l^2 configuration (and the hole equivalent l^{4l} configuration), the mixing of energy levels as Δ/D varies from zero to infinity or vice versa is quantitatively given by Racah lemma matrices [1] that contain an absolute measure of the amounts of subconfigurations in the gaseous terms (and vice versa, see discussion after matrix (74)). In the following discussion, some consequences of bringing this absoluteness, concerning the eigenfunctions, together with the relativity (upper and lower), concerning the eigenenergies, will be revealed. The Racah lemma matrix (74) can be read as follows in connection with the diagram in Fig. 6. The eigenenergies of $^1A_1(D_4)$ are roots of a quadratic equation in Δ and D. For $\Delta = 0$ the upper root is ^1S and the lower ^1D. Both this statement and that following apply to p^2 as well as to p^4. When the internal field strength increases from zero to infinity along the right-hand side of the diagram, the upper $^1A_1(D_4)$ level loses $1/3$ of its ^1S character and obtains $1/3$ ^1D character in return. Conversely, the lower $^1A_1(D_4)$ level loses $1/3$ of its ^1D character to obtain $1/3$ ^1S character instead. In conclusion, the upper level of the strong-field limit contains $2/3$ of the upper level of the weak-field limit. Therefore if we wrote, for example for p^2, $e^2(S)$, then this could be taken to mean that e^2 is mainly S in character. Now comes the new point. Analogously, for the left-hand side of the diagram, also taking p^2 as an example and still using the Racah lemma matrix (74), then the conclusion is that the upper level in the strong-field limit $a_2^2\ ^1A_1(D_4)$ contains only $1/3$ of the upper level ^1S of the weak-field limit, but $2/3$ of the lower level ^1D of this limit. Therefore with the logic introduced above, this upper level ought to be designated $a_2^2(D)$. The problem under discussion can also be qualitatively revealed by noting that in absorption the transition which in the strong-field limit is $^1A_1(a_2^2) \rightarrow {}^1A_1(e^2)$, a two-electron jump, only slowly obtains one-electron-jump character when the field strength becomes finite (right-hand side of Fig. 6), while this happens much faster for the transition $^1A_1(e^2) \rightarrow {}^1A_1(a_2^2)$ (left-hand side of Fig. 6).

Focusing now on the right-hand part of the diagram, it is observed that for low values of Δ relative to D, a $^3E(D_4)$ high-spin ground term is expected. For higher values of Δ/D, i.e. closer to the strong-field limit, a $^1A_1(D_4)$ low-spin ground term is expected. Since the $^1A_1(D_4)$ block of the matrix (78) is only of dimension two, an explicit expression for its lower eigenvalue can be found. Equating this expression with the expression for the $^3E(D_4)$ energy (from matrix (78)), an equation is obtained from which the exact ratio Δ/D for the high-spin/low-spin crossing point may be determined (eqn. (91)):

$$\Delta/D = (2/5)(\sqrt{41} - 1) \approx 2.16 \tag{91}$$

This parametric condition for spin crossing in tetragonal p^2 systems is based on symmetry only and may in view of this seem to be a somewhat odd result. *

The percentage of the total perturbation accounted for by the ligand field at the high-spin/low-spin crossing point may be calculated according to eqn. (92):

$$x(\Delta) = \frac{(2.16)^2(16/3)}{(2.16)^2(16/3) + (96/5)} \approx 56\% \tag{92}$$

The values of the coefficient operators' norm squares used in this equation have been obtained from eqns. (40) and (57). The result from eqn. (92) illustrates that high-spin/low-spin crossing and equal contributions to the total perturbation from ligand field and interelectronic repulsion are two different things.

For the situation where the two perturbations contribute equally to $\langle \hat{H} \mid \hat{H} \rangle$, we have the condition of eqn. (93):

$$\Delta^2 \langle \hat{Q}_\Delta | \hat{Q}_\Delta \rangle = D^2 \langle \hat{Q}_D | \hat{Q}_D \rangle \tag{93}$$

from which we obtain eqns. (94) and (95), valid for p^2: **

$$(16/3)\Delta^2 = (96/5)D^2 \tag{94}$$

$$\Delta/D = \sqrt{18/5} \approx 1.90 \tag{95}$$

Incidentally, this value is not very different from that in eqn. (91). Since D is always finite, this value of Δ/D may be considered to represent the midpoint between $\Delta = 0$ and $\Delta = \infty$, or in other words, to represent the midway through the unsymmetrical right-hand side of the diagram in Fig. 6 when the ligand field provides 50% of $\langle \hat{H} \mid \hat{H} \rangle$.

As a final remark in connection with Fig. 6, we return to the fact that the p^4 system XeF_2 has an energy level diagram identical to that of the p^2

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* The strong-field approximation is the use of the diagonal elements of the strong-field matrix. If this is used here rather than the lowest root of the $^1A_1(D_4)$ matrix, the following equation is obtained as the strong-field approximation to the high-spin/low-spin crossing point:

$$-(4/3)\Delta + (8/5)D = -(1/3)\Delta - (4/5)D$$

$$\Delta/D = 12/5 = 2.40$$

This value is also the value at the crossing point of $^3P^3E$ with the asymptote $a_2^2\,{}^1A_1$.

** In eqn. (93) the norm squares of the two coefficient operators depend differently on the number q of p electrons according to eqns. (89) and (90). The result from eqn. (95) is therefore valid only for p^2. For p^3 the condition of eqn. (93) leads to $\Delta/D = \sqrt{24/5} = 2.19$.

system XeF_4 (the right-hand side of Fig. 6). This is so because the effect of changing the sign of Δ upon going from tetragonal to linear symmetry is cancelled out by the effect of going at the same time from the p^2 configuration to its hole equivalent configuration p^4. In the weak-field situation the terms ^3P, ^1D, ^1S and their energetic ordering are the same for XeF_2 as for XeF_4, understanding though that they refer to p^4 and p^2 respectively. The strong-field situation $e^4\ {}^a a_2^{2-b\ 2S+1}\Gamma(D_4)$ of XeF_2 similarly corresponds to $e^a a_2^{b\ 2S+1}\Gamma(D_4)$ of XeF_4 ($a+b=2$). The degeneracy of the $^1\Delta$ functions in XeF_2 is, of course, not accidental. These ligand field theory relationships between XeF_4 and XeF_2 are analogous to the well-known relationships between, for example, $CrCl_6^{3-}$ (d^3) in octahedral symmetry and $CoCl_4^{2-}$ (d^7) in tetrahedral symmetry. In both cases the ligand field splitting parameter changes sign as one passes to the hole equivalent electron configuration. In the p systems the effective symmetry group is axial (D_∞), while in the d systems it is the holohedral rotation group O.

One of the characteristics of the classical ligand field energy diagrams, including Fig. 6, is their unequal treatment of the two perturbations, the ligand field and the interelectronic repulsion. In both Orgel diagrams and Tanabe–Sugano diagrams the constant presence of the interelectronic repulsion implies that even if the ligand field is allowed to gain significance, it never achieves absolute dominance. In other words, the strong-field basis is never an eigenbasis in any of these types of diagrams, whereas the weak-field basis is an eigenbasis when $\Delta = 0$ or $\Delta/D = 0$. When reasoning within ligand field (or molecular orbital) models, this asymmetry has a particular disadvantage since these models, from a chemical point of view, are fundamentally one-electron models for which the strong-field basis for many-electron systems is the natural choice. It would therefore add an extra dimension to the pedagogics of energy level diagrams, if a diagram that treated ligand field and repulsion on an equal footing could be invented.

Our discussion in Section E(iii), may together with Fig. 5 inspire one to solve the problem by using the abscissa of eqn. (96)

$$\frac{\Delta\left\langle \hat{Q}_\Delta | \hat{Q}_\Delta \right\rangle^{1/2}}{\Delta\left\langle \hat{Q}_\Delta | \hat{Q}_\Delta \right\rangle^{1/2} + D\left\langle \hat{Q}_D | \hat{Q}_D \right\rangle^{1/2}} = \frac{\Delta^{\text{norm.}}}{\Delta^{\text{norm.}} + D^{\text{norm.}}} \tag{96}$$

together with the ordinate of eqn. (97)

$$\frac{\bar{h}}{\Delta\left\langle \hat{Q}_\Delta | \hat{Q}_\Delta \right\rangle^{1/2} + D\left\langle \hat{Q}_D | \hat{Q}_D \right\rangle^{1/2}} \tag{97}$$

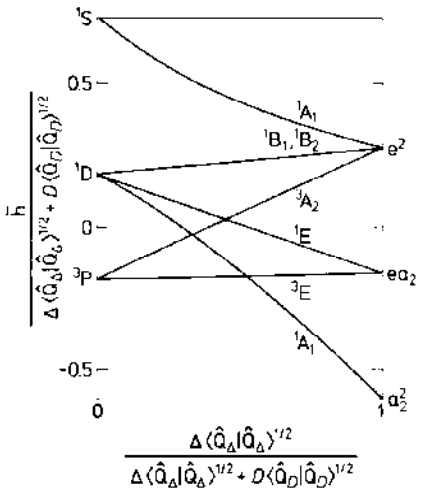

Fig. 7. Symmetrized energy level diagram for the p^2 configuration under the influence of a tetragonal ligand field. The abscissa expresses the magnitude of the ligand field operator relative to the sum of the magnitudes of the ligand field and the repulsion operators, i.e. it expresses a magnitude fraction. This magnitude fraction takes the value 0 for the weak-field situation and the value unity for the strong-field situation. Compared with the Tanabe–Sugano diagram (Fig. 6), this magnitude-fraction diagram has the advantage that only a finite range of abscissa values is necessary for describing the weak-field, the strong-field and all intermediate-field situations. The weak-field degeneracies (the same as those of gaseous terms) and the strong-field degeneracies (those of the subconfigurations without repulsion) show up at the left-hand side and at the right-hand side of the diagram respectively. The energy graphs associated with terms of a symmetry type which occurs only once are straight lines as in Tanabe–Sugano diagrams. This would not have been the case if the norm square fraction of eqn. (87) had been chosen as abscissa.

assuming at all times that $\Delta > 0$ and $D > 0$. The diagram in Fig. 7 has been constructed in this way by using the definition of Δ given in Fig. 1. This diagram represents an alternative to that in Fig. 6 in depicting the symmetry part of the p^2 model. It does this in the sense of being independent of the values of the empirical parameters but dependent only on their ratio, in this case Δ/D. This is true of the abscissa as well as of the ordinate which are both pure numbers.

The abscissa of Fig. 7 is the magnitude fraction of the operator terms containing the parameters Δ and D. It is understood that the abscissa can be read equally well from left to right as from right to left with the appropriate change in its meaning (as in a mole fraction diagram). The abscissa is also a parameter fraction, provided its parameters are those associated with coefficient operators that are renormalized to unity, as

illustrated for Δ in eqn. (98):

$$\hat{Q}_\Delta \Delta = \hat{Q}_\Delta^{\text{norm.}} \Delta^{\text{norm.}} = \left(\hat{Q}_\Delta / \langle \hat{Q}_\Delta | \hat{Q}_\Delta \rangle^{1/2}\right)\left[\Delta \langle \hat{Q}_\Delta | \hat{Q}_\Delta \rangle^{1/2}\right] \tag{98}$$

with a similar expression being valid for D.

The expression in the square brackets (eqn. (98)) contains the definition of the parameter $\Delta^{\text{norm.}}$ as the parameter associated with the operator $\hat{Q}_\Delta^{\text{norm.}}$ which is normalized to unity. This parameter and the corresponding $D^{\text{norm.}}$ have already been introduced into eqn. (96). One should be aware of the eqns. (89) and (90) which limit the usefulness in applying this kind of parameter to particular configurations. Here we are considering only p^2 and p^4 configurations for which configurations the norm square of any given operator is the same.

The ordinate of Fig. 7 contains the eigenenergies reduced to pure numbers in such a way that only their relative values are in essence depicted. For every value of the abscissa the sum square energy splitting is, according to eqns. (85), (84) and (98), equal to $(\Delta^{\text{norm.}})^2 + (D^{\text{norm.}})^2$. This means that the sum square reduced energy splitting is not independent of the abscissa since its expression is that of eqn. (99):

$$\frac{(\Delta^{\text{norm.}})^2 + (D^{\text{norm.}})^2}{(\Delta^{\text{norm.}} + D^{\text{norm.}})^2} \tag{99}$$

This expression is symmetrical about the abscissa value of one-half, i.e. $\Delta^{\text{norm.}} = D^{\text{norm.}}$, when it incidentally takes on the value of one-half. Furthermore, it is equal to unity when the abscissa is zero or unity, and, for example, equal to 5/9 when the abscissa is equal to 1/3 or 2/3, i.e. $\Delta^{\text{norm.}}/D^{\text{norm.}} = 1/2$ or 2. The example of the abscissa equal to 2/3 will be taken up again below.

The type of diagram in Fig. 7 has the advantage of illustrating the degeneracies in both the weak-field limit and the strong-field limit. Furthermore, it is seen and can easily be proven that this diagram preserves the straight lines of symmetry-unique energy levels from the Tanabe–Sugano and Orgel diagrams. A p^2 energy level having a linear energy dependence on both Δ and D, i.e.

$$E = \delta\Delta + dD = \delta \langle \hat{Q}_\Delta | \hat{Q}_\Delta \rangle^{-1/2} \Delta^{\text{norm.}} + d \langle \hat{Q}_D | \hat{Q}_D \rangle^{-1/2} D^{\text{norm.}} \tag{100}$$

is in a Tanabe–Sugano-like diagram depicted as a straight line with a slope of δ. In the new type of diagram, the mapping is also a straight line, but this time with the slope

$$\delta \langle \hat{Q}_\Delta | \hat{Q}_\Delta \rangle^{-1/2} - d \langle \hat{Q}_D | \hat{Q}_D \rangle^{-1/2} \tag{101}$$

where the two terms are the coefficients to $\Delta^{\text{norm.}}$ and $D^{\text{norm.}}$ respectively in eqn. (100). Especially in the light of our discussion in section E(iii), it might seem that $x(\Delta)$ of eqn. (87) would be a more natural choice for the abscissa than eqn. (96) in such a symmetrized energy diagram. However, such a choice would have several disadvantages. The most important disadvantage is that the levels whose energies are of the form of eqn. (100) are no longer depicted as straight lines. In any case, the abscissa in Fig. 7 can easily be translated into the quantity $x(\Delta)$. A simple example will illustrate this. Let us assume that we have observed two p–p transitions in a spectroscopic experiment on a tetragonal p^2 system and that we can assign these as transitions from the $^1A_1$ ground term to the ^1E and ^3E excited terms. We then search the diagram in Fig. 7 to find where the experimental ratio between the two transition energies is reproduced. Say that this happens, as in one of the examples above, for the value 2/3 on the abscissa. We then have the condition (eqn. (102))

$$\frac{\Delta^{\text{norm.}}}{\Delta^{\text{norm.}} + D^{\text{norm.}}} = \frac{\Delta\langle \hat{Q}_\Delta | \hat{Q}_\Delta \rangle^{1/2}}{\Delta\langle \hat{Q}_\Delta | \hat{Q}_\Delta \rangle^{1/2} + D\langle \hat{Q}_D | \hat{Q}_D \rangle^{1/2}} = 2/3 \tag{102}$$

meaning that

$$\frac{\Delta^{\text{norm.}}}{D^{\text{norm.}}} = \frac{\Delta\langle \hat{Q}_\Delta | \hat{Q}_\Delta \rangle^{1/2}}{D\langle \hat{Q}_D | \hat{Q}_D \rangle^{1/2}} = 2 \tag{103}$$

or

$$\frac{(\Delta^{\text{norm.}})^2}{(D^{\text{norm.}})^2} = \frac{\Delta^2\langle \hat{Q}_\Delta | \hat{Q}_\Delta \rangle}{D^2\langle \hat{Q}_D | \hat{Q}_D \rangle} = 4 \tag{104}$$

giving the quantity sought ($x(\Delta)$ defined in eqn. (87)) in eqn. (105):

$$x(\Delta) = \frac{(\Delta^{\text{norm.}})^2}{(\Delta^{\text{norm.}})^2 + (D^{\text{norm.}})^2} = \frac{4}{4+1} = 0.8 \tag{105}$$

Thus the ligand field in the example is responsible for 80% (and thereby the repulsion is responsible for 20%) of the total squared splitting.

To conclude this section, we stress that intermediate ligand field situations are those corresponding to chemical systems. The eigenfunctions of these systems, described within the l^q model, depend on ratios between empirical parameters, while their eigenenergies depend on the empirical parameters themselves. In any comparison made within the model, empirical

parameters have to be weighted by the magnitude of their associated operators, which serve as their units of magnitude.

F. CONCLUSION

The introduction contained a few historical remarks to place the contents of the paper into perspective. To appreciate the results of the paper, more history is required.

The invention of electron spin resonance spectroscopy gave rise in the fifties to a second wave of interest among the physicists in the magnetic behaviour of transition metal complexes. Shortly afterwards recording spectrophotometers helped make the chemistry inspired by ligand field theory the forefront of inorganic chemistry. Ligand field theory was therefore used by many researchers with many different backgrounds, and various kinds of parametrizations flourished, together with analyses of various kinds of experiments using various kinds of numerical approximations to what could have been quantitative ligand field theory.

The situation became inexpedient. The literature became almost impossible to use, especially for newcomers. It was time for conceptual clarification. Here we are not talking about the chemistry or physics behind ligand field theory, but rather about the concepts within the model-theory itself, i.e. within the mathematical framework which we have called here quantitative ligand field theory or the parametrical l^q model.

The existence of atomic (or spherical harmonic, or multipole, or spherical irreducible tensor) and molecular (or orbital energy, or point group irreducible tensor) parametrizations combined with holistic and partitioned models of the ligand field gives four versions of the ligand field part of the parametrical l^q model, each one illuminative in its own way, as briefly reviewed previously [28]. Even within each of these versions, several systems of parameters appeared in the literature, and therefore standardization seemed unavoidable. An atomic parametrization scheme of the holistic field using group hierarchies [16] was incidentally agreed upon [14,17] and developed quite extensively [18] under the name of normalized spherical harmonic Hamiltonians. These Hamiltonians are k-sets of surface spherical harmonics C^k (containing $(2k+1)$ components, each specified by a q) that act as multiplicative operators. They are orthonormal as functions over the unit sphere in such a way that $\langle C_q^k \mid C_{q'}^{k'} \rangle = [4\pi/(2k+1)]\delta_{kk'}\delta_{qq'}$. This implies that they are orthogonal also in the operator sense of this concept (eqn. (10)) and their overlap over d space is then [3] equal to $\langle \hat{C}_q^k \mid \hat{C}_{q'}^{k'} \rangle = [(10/7)/(2k+1)]\delta_{kk'}\delta_{qq'}$, which means that their self-overlap, in both a function sense and an operator sense, depends on k. It further means that linear combinations of such spherical harmonic operators belonging to different k sets, as

they occur in a molecular parametrization, in general will have strange values of their self-overlaps. For this reason it would probably have been better to define the normalized spherical harmonics as, for example, in eqns. (1) and (2), perhaps dropping the factor $\sqrt{4\pi}$.

A standardization of the partitioned ligand field is that of the Angular Overlap Model [8–11].

The standardization ideas concerning the ligand field itself were further developed [1–3] using orthonormal operators and group hierarchies as a tool together with phase fixation of coupling coefficients [22]. Thereby the hierarchic molecular parametrization scheme, which is closely related to the l-orbital splitting by the ligand field (Section B(v)), was worked out [3,22].

Later [4] the interelectronic repulsion operator on d^q configurations was written as a sum of two mutually orthogonal and normalized components, both of which are orthogonal also to the operator of spin–orbit coupling as well as to ligand field operators. This allowed, for example, a monoatomic ion to be placed quantitatively at its own specific point between LS-coupling and jj-coupling, known as (its own) intermediate coupling.

The investigations on one-electron operators [1–3] and also two-electron operators [4] revealed that all the operators which are associated with observables of ligand field theory can be made mutually orthogonal. Moreover, this orthogonality applies to the operators when they act on all the different l^q configurations ($q \geqslant 2$). However, a dilemma for standardization is that a common normalization of one-electron operators and two-electron operators is only possible for a fixed value of q, another value of q requiring a renormalization of at least one of these kinds of operators (eqns. (89) and (90)). Weighting of empirical parameters by the magnitudes of their associated operators may be the way out of this dilemma (see eqn. (94)).

The present review has illustrated the orthonormal operators' model of the ligand field by discussing an orthorhombic field on p orbitals and obtaining a set of hierarchic molecular operators and their associated parameters. Moreover, the review has discussed the interelectronic repulsion on p^q configurations in terms of the spin-pairing energy operator and parameter. This operator was further written as a sum of two mutually orthogonal components, a spin separator and a seniority separator. Then the interplay of the ligand field and the repulsion was studied to obtain the strong- and weak-field energy matrices of the parametrical $p^2(p^4)$ models of, for example, $XeF_4(XeF_2)$. These matrices were illustrated by a variant of a Tanabe–Sugano-type diagram using barycentred energies and also by introducing a new type of energy level diagram which symmetrizes the description of the interelectronic repulsion and the ligand field.

Quantitative ligand field theory or the parametrical l^q model [26] is quantitative in the following sense: if adequate and sufficient quantitative

spectroscopic data are available, then the theory allows these data to be transformed into empirical parameters of the theory in a well-defined way. These parameters make it possible to compare phenomenological properties which are associated with different chemical compounds or which, for the same compound, are not directly related such as, for example, spectra and magnetism. To this fact the following statements may be added: on the one hand, the quantitative part of the parametrical l^q model is a mathematical machine rather than physical theory; on the other hand, the basis of the quantitative data, i.e. the results regarding the classificatory electron configuration [19] and particularly the symmetry assignments of the energy levels, is chemically significant (see introduction). This means that these results are qualitatively correct in a very strong sense of the word qualitative, much stronger than when this word has the meaning of non-quantitative. In recent years, evidence has been provided that the interelectronic repulsion part of ligand field theory, i.e. the Slater–Condon–Shortley formalism, is perhaps even more a parametrical model than is the ligand field part of quantitative ligand field theory [29–31]. Ultimately, a bridge between these model theories and a more fundamental quantum chemical understanding is, of course, the obvious aim. However, until then, ligand field theory is the best we have, and quantitative ligand field theory is the only means of handling a large body of apparently unrelated data by making it related through a scheme of empirical parameters. As such, the parametrical l^q model will remain an important tool of inorganic chemistry until the advent of a competitive successor.

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