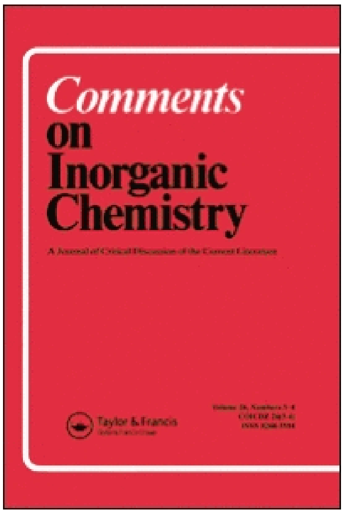

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Quantitative Comparison of the Symmetry Components of a Ligand Field: Illustrations of the Orthonormal Operators Formalism

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Quantitative Comparison of the Symmetry Components of a Ligand Field: Illustrations of the Orthonormal Operators Formalism

A recently proposed formulation of ligand field models in terms of *orthonormal operator sets* allows a *quantitative* comparison of the various symmetry components of a ligand field operator in terms of percentages. This is illustrated here by the detailed analysis of an orthorhombic system using the hierarchy $O \supset D_4 \supset D_2$ of cubic, tetragonal and orthorhombic symmetries. The first part of the analysis pertains to a set of general octahedral e functions. The formalism introduced is later applied to an entire set of d orbitals, and in this connection we further discuss the concepts of *atomic* and *molecular ligand field theory*. In the present treatment all ligand field parameters and splittings are defined with respect to *sign* as well as *magnitude*. In the example cited the tetragonal splitting in the e space may be positive as well as negative, whereas the total splitting and the quantity called the orthorhombic splitting are non-negative. It is demonstrated that for any ligand field component of octahedral E symmetry it is possible to choose a coordinate frame in such a way that the resulting decomposition of the field component into tetragonal and orthorhombic parts will describe the system as being *at least* 75% tetragonal.

I. INTRODUCTION

A general formulation of ligand field models has recently been introduced.[1] The formalism used is based on *orthonormal sets of operators* and permits a given ligand field experiment to be analyzed in such a way that the empirical ligand field parameters not only have well-defined individual magnitudes and signs, but also chemically significant *relative magnitudes*. This means, for example, that the magnitude of a low symmetry field component can be expressed as a percentage of the total

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field. Comparisons with previous formulations are easy because these can be based upon the simple concept of overlap between operators.

In the semiclassical physical model of the crystalline field potential and in the point-charge and point-dipole models of the ligand field in complex ions, the Hamiltonian is a sum of terms referring to the individual atoms (or groups of atoms) creating the "field", i.e., the field is *additive*. The angular overlap model (AOM) took over this additivity[2] as an assumption. A later analysis[3] showed that if one wishes to apply the angular overlap model just as a semiempirical model, it is only necessary to assume additivity for the nonspherical part of its Hamiltonian.

Griffith[4] introduced a purely symmetry-based ligand field model which did not have any additivity assumption built in. This was later described as a model of a *nonadditive* field,[5,6] i.e., a field which is not necessarily additive.

The orthonormal operator formalism is directly applicable to symmetry-based nonadditive field models. When additivity is assumed in such a formulation the terms referring to the individual ligands are described in the same way as in the symmetry-based angular overlap model.[7] In particular, the operators representing the effect of an individual ligand in the angular overlap model are orthonormal.

Ligand field theory has, as we see it, two characteristics: it is semiempirical and symmetry-based. "Semiempirical" means in this context that ligand field models contain so-called empirical parameters whose values may be found by confronting the model with experiments. The model Hamiltonian acts in a space which for computational purposes is often represented by functions, e.g., *d* functions. However, the essential thing about the space is its transformation properties, i.e., the fact that it embodies bases for irreducible representations of a certain group. This is how the concept "symmetry-based" comes in. Thus the space may in principle be a molecular orbital space. Ligand field theory does not, however, operate *explicitly* with the mixing of central ion and ligand orbitals.

A ligand field model can further be viewed as a perturbation model which is first order in the sense that it only uses functions taken from the space mentioned, but which on the other hand is of infinite order in the sense that all interactions within this limited space are taken into account.

As we have seen here, a ligand field model is based mathematically on a carrier space, usually a d space or an f space where d and f refer to irreducible[8] representations of the three-dimensional rotation group R_3. In these latter cases we shall speak about *atomic ligand field theory*. However, the space may also be chosen as a carrier space for irreducible representations of a *subgroup* of R_3. In this case we shall speak about *molecular ligand field theory*.

In atomic ligand field theory it is possible to suppress the spherical symmetry of the basis and describe the whole situation in terms of symmetry by reference only to the molecular subgroup of R_3. In this case we speak about a *molecular scheme*[9] of atomic ligand field theory. If R_3 symmetry is used in the parametrization we speak about the *atomic scheme*. The two schemes can be shown to be related by a unitary transformation.[1]

Section II of this Comment exemplifies molecular ligand field theory by a space $V^{e(O)}$, which carries the irreducible representation e of the octahedral rotation group, while Section III illustrates atomic ligand field theory, mainly in a molecular scheme. Sections II.1 and II.2 describe the two-dimensional space $V^{e(O)}$ spanned by an orthonormal function basis and its associated four-dimensional operator space. Sections II.3 and II.4 describe the ligand field parametrized by the one-electron energies in the basic operator scheme and, equivalently, in the so-called irreducible tensor operator scheme. Section II.5 explains how Clebsch–Gordan coefficients relate the two schemes. Section II.6 contains a detailed analysis of a chemical example. Section III.1 introduces a full d orbital space, $V^{d(R_3)}$, and Sections III.2 and III.3 discuss the molecular scheme of atomic ligand field theory within the de and dt_2 subspaces, respectively. Section III.4 introduces the important cubic field, which in Section III.5 is compared with the field components of tetragonal and orthorhombic symmetry.

In the following we shall need the usual real d orbitals. It is well known that these five orbitals, which are degenerate in spherical symmetry, split up in an octahedral ligand field into a two-dimensional $e(O)$ space spanned by the component functions $|de\theta\rangle$ and $|de\varepsilon\rangle$ given in Eq.(1) and a three-dimensional $t_2(O)$ space consisting of the components $|dt_2\xi\rangle$, $|dt_2\eta\rangle$, and $|dt_2\zeta\rangle$ given in Eq.(2). All the d orbitals are normalized to $4\pi/(2l + 1) = 4\pi/5$ by integration over the unit sphere:

$$|de\theta\rangle = z^2 - \tfrac{1}{2}x^2 - \tfrac{1}{2}y^2; \; |de\varepsilon\rangle = (\sqrt{3}/2)(x^2 - y^2), \qquad (1)$$

$$|dt_2\xi\rangle = \sqrt{3}yz; \; |dt_2\eta\rangle = \sqrt{3}zx; \; |dt_2\zeta\rangle = \sqrt{3}xy. \qquad (2)$$

The *de*(*O*) set of orbitals of a central ion have the right symmetry to participate in forming σ bonds (but not π bonds) with six ligands placed on the Cartesian axes, while the $dt_2(O)$ set of orbitals may form π bonds (but not σ bonds). Both *de*(*O*) and $dt_2(O)$ may form δ bonds, but in each case only single δ bonds (δc and δs, respectively[10]). Those δ orbitals on the ligands which have their nodal planes coinciding with the Cartesian planes *XY*, *YZ* and *ZX* may interact with the $dt_2(O)$ orbitals, and the orthogonal δ orbitals may interact with the *de*(*O*) orbitals.

In addition to being used as basis functions for the discussion of atomic ligand field theory the real *d* orbitals of Eqs.(1) and (2) are used to generate real standard irreducible representations of the octahedral rotation group *O*. So $\{e\theta\ e\varepsilon\}$ or, for short $\{\theta\ \varepsilon\}$, means a function basis which transforms under the symmetry operators of *O* by the same matrices as does the basis $\{de\theta\ de\varepsilon\}$. *It is important to note that such a* $\{\theta\ \varepsilon\}$ *basis may be constructed from any set of molecular orbitals transforming as* *e*(*O*); θ and ε are thus not necessarily *d* functions.

Further, in a hierarchy of ligand fields of octahedral, tetragonal and orthorhombic symmetry, *the orthorhombic field having its twofold axes coincide with the fourfold axes of the octahedron,* the octahedrally assigned orbital energy levels may split according to the schemes of Eqs.(3) and (4):

$$\begin{aligned} \theta &= e(O)a_1(D_4)a(D_2), \\ \varepsilon &= e(O)b_1(D_4)a(D_2); \end{aligned} \tag{3}$$

$$\begin{aligned} \xi &= t_2(O)e(D_4)b_3(D_2), \\ \eta &= t_2(O)e(D_4)b_2(D_2), \\ \zeta &= t_2(O)b_2(D_4)b_1(D_2). \end{aligned} \tag{4}$$

It is seen from these schemes that the *e*(*O*) set and the $t_2(O)$ set do not give rise to any common irreducible representation in D_4 or D_2. In a ligand field context, this means that even for these lower symmetries, no mixing can take place between the orbitals classified in the group *O* as *e* and t_2, respectively, or in other words, any orbital eigenstate has a pure *e*(*O*) or $t_2(O)$ parentage.

II. MOLECULAR LIGAND FIELD THEORY WITH AN *e*(*O*) BASIS

1. Orthonormal Function Basis

For a space $V^{e(O)}$ associated with the irreducible representation e of the octahedral rotation group an orthonormal basis $\{\theta\ \varepsilon\}$ may be chosen. The orthonormality is expressible in bracket notation as in Eqs.(5)–(8) and, alternatively, in the form of the self-overlap (or metric) matrix (9). Such a matrix is always the unit matrix for an orthonormal basis:

$$\langle\theta|\theta\rangle = 1, \tag{5}$$

$$\langle\theta|\varepsilon\rangle = 0, \tag{6}$$

$$\langle\varepsilon|\theta\rangle = 0, \tag{7}$$

$$\langle\varepsilon|\varepsilon\rangle = 1, \tag{8}$$

$$\begin{array}{c|cc} & |\theta\rangle & |\varepsilon\rangle \\ \hline \langle\theta| & 1 & 0 \\ \langle\varepsilon| & 0 & 1 \end{array} . \tag{9}$$

The symbols θ and ε indicate that the transformation properties of the ordered set $\{\theta\ \varepsilon\}$ under the generators $\hat{C}_3^{x=y=z}$ and $\hat{C}_4^{Z}$ of the group O are identical to those of the set $\{de\theta\ de\varepsilon\}$ (Ref. 4, p. 390). This is expressed in Eqs.(10)–(13):

$$|\theta'\rangle \equiv \hat{C}_3^{x=y=z}|\theta\rangle = -\tfrac{1}{2}|\theta\rangle + (\sqrt{3}/2)|\varepsilon\rangle, \tag{10}$$

$$|\varepsilon'\rangle \equiv \hat{C}_3^{x=y=z}|\varepsilon\rangle = -(\sqrt{3}/2)|\theta\rangle - \tfrac{1}{2}|\varepsilon\rangle, \tag{11}$$

$$|\theta'''\rangle \equiv \hat{C}_4^{Z}|\theta\rangle = |\theta\rangle, \tag{12}$$

$$|\varepsilon'''\rangle \equiv \hat{C}_4^{Z}|\varepsilon\rangle = -|\varepsilon\rangle. \tag{13}$$

Again, the same information is given in matrix form in Eqs.(14) and (15):

$$[|\theta'\rangle|\varepsilon'\rangle] = \hat{C}_3^{x=y=z}[|\theta\rangle|\varepsilon\rangle] = [|\theta\rangle|\varepsilon\rangle]\begin{bmatrix} -\dfrac{1}{2} & -\dfrac{\sqrt{3}}{2} \\ \dfrac{\sqrt{3}}{2} & -\dfrac{1}{2} \end{bmatrix}, \tag{14}$$

$$[|\theta'''\rangle|\varepsilon'''\rangle] = \hat{C}_4^Z\,[|\theta\rangle|\varepsilon\rangle] = [|\theta\rangle|\varepsilon\rangle]\begin{bmatrix}1 & 0\\ 0 & -1\end{bmatrix} \tag{15}$$

The orthogonal irreducible matrix representation of O defined by Eqs.(14) and (15) was taken as the *standard* form of $e(O)$ that was used in generating *phase-fixed* coupling coefficients (Section II.5) for the group O (see Ref. 11, p. 239 and Tables 8 and 19). Expressions (16) and (17) contain the representation matrices, in the $\{\theta\ \varepsilon\}$ basis, of the group generators selected:

$$\begin{array}{c|cc} \hat{C}_3^{x=y=z} & |\theta\rangle & |\varepsilon\rangle \\ \hline \langle\theta| & -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \langle\varepsilon| & \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{array}, \tag{16}$$

$$\begin{array}{c|cc} \hat{C}_4^Z & |\theta\rangle & |\varepsilon\rangle \\ \hline \langle\theta| & 1 & 0 \\ \langle\varepsilon| & 0 & -1 \end{array}. \tag{17}$$

A third interpretation of the same information is given in (18) and (19), where the rotated bases $\{\theta'\ \varepsilon'\}$ and $\{\theta'''\ \varepsilon'''\}$ of Eqs.(10)–(13) have been used to conceive the matrices as *overlap matrices:*

$$\begin{array}{c|cc} & |\theta'\rangle & |\varepsilon'\rangle \\ \hline \langle\theta| & -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \langle\varepsilon| & \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{array}, \tag{18}$$

$$\begin{array}{c|cc} & |\theta'''\rangle & |\varepsilon'''\rangle \\ \hline \langle\theta| & 1 & 0 \\ \langle\varepsilon| & 0 & -1 \end{array}. \tag{19}$$

We shall later need the basis defined by Eq.(20):

$$[|\theta''\rangle|\varepsilon''\rangle] \equiv \hat{C}_3^{x=y=z}[|\theta'\rangle|\varepsilon'\rangle]. \tag{20}$$

The orthogonality of the overlap matrices, i.e., the property that their rows are orthonormal (as are their columns), makes it possible to interpret the individual matrix elements in terms of their squares. For example, it is meaningful from the first column of the matrix (18) to say that $|\theta'\rangle$ contains 25% of $|\theta\rangle$ and 75% of $|\varepsilon\rangle$.

2. Orthonormal Operator Basis

Once a basis has been chosen for the space $V^{e(O)}$—for example, the $\{\theta\ \varepsilon\}$ basis—all operators acting within this space can be written as linear combinations of the ket–bra operators of Eqs.(21)–(24):

$$\hat{S}_{\theta\theta} = |\theta\rangle\langle\theta|, \tag{21}$$

$$\hat{S}_{\theta\varepsilon} = |\theta\rangle\langle\varepsilon|, \tag{22}$$

$$\hat{S}_{\varepsilon\theta} = |\varepsilon\rangle\langle\theta|, \tag{23}$$

$$\hat{S}_{\varepsilon\varepsilon} = |\varepsilon\rangle\langle\varepsilon|. \tag{24}$$

Such operators are well known in mathematics and physics and have recently been discussed also in theoretical chemistry.[12–15] We have used these operators or similar ones in a ligand field context before.[1,5,16] The ket–bra operators may be defined by their matrices (25)–(28):

$$\begin{array}{c|cc} \hat{S}_{\theta\theta} & |\theta\rangle & |\varepsilon\rangle \\ \hline \langle\theta| & 1 & 0 \\ \langle\varepsilon| & 0 & 0 \end{array}, \tag{25}$$

$$\begin{array}{c|cc} \hat{S}_{\theta\varepsilon} & |\theta\rangle & |\varepsilon\rangle \\ \hline \langle\theta| & 0 & 1 \\ \langle\varepsilon| & 0 & 0 \end{array}, \tag{26}$$

$$\begin{array}{c|cc} \hat{S}_{\varepsilon\theta} & |\theta\rangle & |\varepsilon\rangle \\ \hline \langle\theta| & 0 & 0 \\ \langle\varepsilon| & 1 & 0 \end{array}, \tag{27}$$

$$\begin{array}{c|cc} \hat{S}_{\varepsilon\varepsilon} & |\theta\rangle & |\varepsilon\rangle \\ \hline \langle\theta| & 0 & 0 \\ \langle\varepsilon| & 0 & 1 \end{array}. \tag{28}$$

An important property of an operator defined in a given space is its trace. The trace of an operator is by definition the sum of the diagonal elements of one of its matrices (this quantity is independent of the basis). The two operators $\hat{S}_{\theta\theta}$ and $\hat{S}_{\varepsilon\varepsilon}$ have a trace of unity and are called "idempotents" because they are equal to their own squares. This latter property is shown for $\hat{S}_{\theta\theta}$ in Eq.(29), where the fact that $\langle\theta|\theta\rangle = 1$ [Eq.(5)] has been used:

$$\hat{S}^2_{\theta\theta} = \hat{S}_{\theta\theta}\,\hat{S}_{\theta\theta} = |\theta\rangle\langle\theta|\theta\rangle\langle\theta| = |\theta\rangle\langle\theta| = \hat{S}_{\theta\theta}. \tag{29}$$

Suppose more generally that $\hat{A}$ and $\hat{B}$ are operators acting on the same space. The trace of the operator $\hat{A}^\dagger\hat{B}$, where $\hat{A}^\dagger$ is the Hermitian conjugate (adjoint) of $\hat{A}$, has been called the "overlap"[1] between the operators $\hat{A}$ and $\hat{B}$, and this definition does indeed introduce a scalar product between operators. In Eq.(30), where the asterisk means complex conjugation, it is shown that this overlap is the sum of the diagonal elements of the matrix $\mathbb{A}^\dagger\mathbb{B}$, where $\mathbb{A}$ and $\mathbb{B}$ are matrix representations of $\hat{A}$ and $\hat{B}$, using the same orthonormal basis. The overlap is independent of the basis.

$$\langle\hat{A}|\hat{B}\rangle \equiv \mathrm{Tr}(\hat{A}^\dagger\hat{B}) = \mathrm{Tr}(\mathbb{A}^\dagger\mathbb{B}) = \sum_{i,\,j}\mathbb{A}^\dagger_{ji}\,\mathbb{B}_{ij} = \sum_{i,\,j}\mathbb{A}^*_{ij}\,\mathbb{B}_{ij}. \tag{30}$$

For the set of four operators of Eqs.(21)–(24), the orthonormality conditions of Eq.(31) are valid, or in other words these operators have an overlap of unity with themselves and one of zero with each other:

$$\begin{aligned}\langle\hat{S}_{t_3t_4}|\hat{S}_{t_1t_2}\rangle &= \mathrm{Tr}(\hat{S}^\dagger_{t_3t_4}\,\hat{S}_{t_1t_2}) = \mathrm{Tr}(|t_4\rangle\langle t_3|t_1\rangle\langle t_2|)\\ &= \delta_{t_3t_1}\,\mathrm{Tr}(|t_4\rangle\langle t_2|) = \delta_{t_3t_1}\,\delta_{t_4t_2},\\ &t_1,t_2,t_3,t_4 \in \{\theta,\ \varepsilon\}.\end{aligned} \tag{31}$$

This normalization means that for each of the operators *the sum of the squares of its matrix elements is equal to one*. In the angular overlap model of the ligand field this is true also for the operators representing the angular factor of the ligand field arising from individual linearly ligating ligands.[16] In the next subsection we will by analogy use our present four operators to formulate the symmetry part of the ligand field. We shall call the operators $\hat{S}_{\alpha\beta}$ of Eqs.(21)–(24) the "basic unit (i.e., normalized) operators" of the space $V^{e(O)}$ with the basis $\{\theta\ \varepsilon\}$.

3. The Ligand Field in Terms of the Basic Unit Operators

We continue with our example of two orbitals which span the irreducible representation e of the octahedral rotation group and transform as θ and ε as defined in Eqs.(14) and (15). We assume that a ligand field $\hat{W}$ of arbitrary symmetry acts on this basis set and that the matrix of $\hat{W}$ is as given in Expression (32). The four elements of this matrix are ligand field parameters and thus have the dimension of energy; they are distinguished from the corresponding operators by not carrying the caret overhead.

$$\begin{array}{c|cc} \hat{W} & |\theta\rangle & |\varepsilon\rangle \\ \hline \langle\theta| & S_{\theta\theta} & S_{\theta\varepsilon} \\ \langle\varepsilon| & S_{\varepsilon\theta} & S_{\varepsilon\varepsilon} \end{array}\ , \tag{32}$$

$$\hat{W} = |\theta\rangle\langle\theta|S_{\theta\theta} + |\theta\rangle\langle\varepsilon|S_{\theta\varepsilon} + |\varepsilon\rangle\langle\theta|S_{\varepsilon\theta} + |\varepsilon\rangle\langle\varepsilon|S_{\varepsilon\varepsilon}. \tag{33}$$

An alternative way of writing Eq.(32) is Eq.(33), as one may verify by showing that the operator expression (33) leads back to the energy matrix (32). For example, for $\langle\theta|\hat{W}|\varepsilon\rangle$ three of the four terms of (33) vanish and we are left with the second term in agreement with (32). Explicit calculations of the first and the second terms [Eqs.(34) and (35)] illustrate this:

$$\langle\theta|\theta\rangle\langle\theta|S_{\theta\theta}|\varepsilon\rangle = S_{\theta\theta}\langle\theta|\theta\rangle\langle\theta|\varepsilon\rangle = 0, \tag{34}$$

$$\langle\theta|\theta\rangle\langle\varepsilon|S_{\theta\varepsilon}|\varepsilon\rangle = S_{\theta\varepsilon}\langle\theta|\theta\rangle\langle\varepsilon|\varepsilon\rangle = S_{\theta\varepsilon}. \tag{35}$$

Having verified Eq.(33), we rewrite it in Eq.(36) in the notation of Eqs.(21)–(24) and thereby emphasize its symmetric form:

$$\begin{aligned} \hat{W} &= \hat{S}_{\theta\theta}\, S_{\theta\theta} + \hat{S}_{\theta\varepsilon}\, S_{\theta\varepsilon} + \hat{S}_{\varepsilon\theta}\, S_{\varepsilon\theta} + \hat{S}_{\varepsilon\varepsilon}\, S_{\varepsilon\varepsilon} \\ &= \sum_{\alpha,\beta\,\in\,\{\theta,\varepsilon\}} \hat{S}_{\alpha\beta}\, S_{\alpha\beta} = \hat{\mathbb{S}}\, \mathbb{S}^T \end{aligned} \tag{36}$$

The information given with the summation sign means that α and β independently run over the set $\{\theta,\varepsilon\}$. The last expression of (36) is a matrix formulation in which $\hat{\mathbb{S}}$ is a row matrix containing the operators and $\mathbb{S}$ is the corresponding matrix of the energy parameters, T meaning transposition so that $\mathbb{S}^T$ is a column matrix. An orthonormal basis change within the $V^{e(O)}$ space, i.e., the formation of an orthonormal set of linear combinations of θ and ε, which of course does not change $\hat{W}$, does not change the *form* of $\hat{W}$ either. By introducing, for example, θ' and ε' of Eqs.(10) and (11) we can write Eq.(37):

$$\hat{W} = \hat{S}_{\theta'\theta'}\, S_{\theta'\theta'} + \hat{S}_{\theta'\varepsilon'}\, S_{\theta'\varepsilon'} + \hat{S}_{\varepsilon'\theta'}\, S_{\varepsilon'\theta'} + \hat{S}_{\varepsilon'\varepsilon'}\, S_{\varepsilon'\varepsilon'}. \tag{37}$$

We see that the ligand field operator may be viewed[17] as a *vector* in the four-dimensional space spanned by the orthonormal operator basis consisting of the operators $\hat{S}_{\alpha\beta}$. The parameters $S_{\alpha\beta}$ are the vector components and we shall refer to these as the "basic ligand field parameters." As we shall see in Section II.4, the number of *independent* parameters is, however, only three in a ligand field context.

4. The Ligand Field in Terms of Unit Irreducible Tensor Operators

The preceding section showed how the ligand field is parametrized in the basic scheme, where the values of the parameters $S_{\alpha\alpha}$ can directly be associated with the energies of the $|\theta\rangle$ or $|\varepsilon\rangle$ functions as long as the nondiagonal parameters are vanishing. However, the values of the basic parameters do not give any immediate indication of the symmetry of the ligand field. In order to achieve this we shall transform Eq.(36) into a form where each term corresponds to a particular symmetry in a hierarchy of groups.

The basic unit operators $\hat{S}_{\theta\theta}$ and $\hat{S}_{\varepsilon\varepsilon}$ are diagonal, have real matrix elements and are thereby Hermitian. The operators $\hat{S}_{\theta\varepsilon}$ and $\hat{S}_{\varepsilon\theta}$ are mutually Hermitian conjugates (adjoints) of each other. Because of this relationship it is useful to form the linear combinations of these two operators given in Eqs.(38) and (39). The operator in Eq.(38) is Hermitian and symmetric to subscript permutation, while that in Eq.(39) is anti-Hermitian and antisymmetric:

$$\hat{N}^{e}_{\varepsilon} = -(\sqrt{2}/2)(\hat{S}_{\theta\varepsilon} + \hat{S}_{\varepsilon\theta}), \tag{38}$$

$$\hat{N}^{a_2}_{\omega} = -(\sqrt{2}/2)(\hat{S}_{\theta\varepsilon} - \hat{S}_{\varepsilon\theta}). \tag{39}$$

The new operators formed here by arguments of permutational symmetry are, incidentally, irreducible tensor operators of the octahedral rotation group. The operator in Eq.(38) transforms as the ε component of $e(O)$, while that in Eq.(39) transforms as the one-dimensional irreducible representation $a_2(O)$, which has been given the (trivial) component specification ω.

The two factors $-\sqrt{2}/2$, whose sign will be explained in Section II.5, ensure that the operators are normalized in the sense of Eq.(31).

The operators of Eqs.(38) and (39) will be called "unit irreducible tensor operators." $\hat{N}^e_\varepsilon$ and $\hat{N}^{a_2}_\omega$ are traceless and mutually orthogonal. They are furthermore both orthogonal to $\hat{S}_{\theta\theta}$ and $\hat{S}_{\varepsilon\varepsilon}$. Rewriting $\hat{W}$ in terms of these irreducible tensor operators combined with $\hat{S}_{\theta\theta}$ and $\hat{S}_{\varepsilon\varepsilon}$ we obtain Eq.(40), where the new parameters N^e_ε and $N^{a_2}_\omega$ are given in Eqs.(41) and (42):

$$\hat{W} = \hat{S}_{\theta\theta}\, S_{\theta\theta} + \hat{S}_{\varepsilon\varepsilon}\, S_{\varepsilon\varepsilon} + \hat{N}^e_\varepsilon\, N^e_\varepsilon + \hat{N}^{a_2}_\omega\, N^{a_2}_\omega, \tag{40}$$

$$N^e_\varepsilon = -(\sqrt{2}/2)(S_{\theta\varepsilon} + S_{\varepsilon\theta}), \tag{41}$$

$$N^{a_2}_\omega = -(\sqrt{2}/2)(S_{\theta\varepsilon} - S_{\varepsilon\theta}). \tag{42}$$

It is a general result that the expressions for corresponding operators and parameters resulting from orthogonal transformations are identical [Ref. 1, Eq.(30)]; this is illustrated by comparing Eqs.(38) and (39) with (41) and (42), respectively.

That the sum of the two last terms of Eq.(40) is in fact equal to the sum of the two middle terms of Eq.(36) can be seen from Eq.(43), where Eqs.(38), (39), (41) and (42) have been inserted into the last two terms of Eq.(40):

$$\begin{aligned} \hat{N}^e_\varepsilon\, N^e_\varepsilon + \hat{N}^{a_2}_\omega\, N^{a_2}_\omega &= (\sqrt{2}/2)(\hat{S}_{\theta\varepsilon} + \hat{S}_{\varepsilon\theta})(\sqrt{2}/2)(S_{\theta\varepsilon} + S_{\varepsilon\theta}) \\ &+ (\sqrt{2}/2)(\hat{S}_{\theta\varepsilon} - \hat{S}_{\varepsilon\theta})(\sqrt{2}/2)(S_{\theta\varepsilon} - S_{\varepsilon\theta}) = \hat{S}_{\theta\varepsilon}\, S_{\theta\varepsilon} + \hat{S}_{\varepsilon\theta}\, S_{\varepsilon\theta}. \end{aligned} \tag{43}$$

The requirement that $\hat{W}$ be a ligand field Hamiltonian operator imposes the restriction that the matrix for $\hat{W}$ be real,[18] and thus symmetric, in the $\{\theta\ \varepsilon\}$ basis. Of the four operators appearing in Eq.(40), only $\hat{N}^{a_2}_\omega$ is not symmetric. The matrix for the last term of Eq.(40), given explicitly in (44), is only symmetric when the parameter $N^{a_2}_\omega$ is equal to zero:

$$\begin{array}{cc} \hat{N}^{a_2}_\omega N^{a_2}_\omega & \begin{array}{cc} |\theta\rangle & \quad |\varepsilon\rangle \end{array} \\ \begin{array}{c} \langle\theta| \\[2ex] \langle\varepsilon| \end{array} & \begin{bmatrix} 0 & -\dfrac{\sqrt{2}}{2} \\[2ex] +\dfrac{\sqrt{2}}{2} & 0 \end{bmatrix} N^{a_2}_\omega \end{array} \tag{44}$$

So our operator $\hat{W}$ has, because of the fact that it is a ligand field Hamiltonian operator, only three independent components, which, for example, may be chosen as $\hat{S}_{\theta\theta}S_{\theta\theta}$, $\hat{S}_{\varepsilon\varepsilon}S_{\varepsilon\varepsilon}$ and $\hat{N}^{e}_{\varepsilon}N^{e}_{\varepsilon}$. The restriction arising from the requirement of a symmetric energy matrix can be particularly clearly understood by reference to the basic ligand field parameters of (32). Here $S_{\theta\varepsilon}$ must be equal to $S_{\varepsilon\theta}$, which according to Eq.(42) means that $N^{a_2}_{\omega}$ is equal to zero.

We are now left with three terms in Eq.(40). Of these, only one corresponds to a particular symmetry species, namely, the ε component of the irreducible representation $e(O)$. As we shall see later, this term may represent an orthorhombic ligand field component for which the three twofold axes coincide with the three mutually perpendicular fourfold axes of the octahedron. We now aim to transform the two first terms of $\hat{W}$ into two new terms involving octahedral irreducible tensor operators. It will become evident that these terms can be chosen to have cubic and tetragonal symmetry, respectively.

An operator of cubic symmetry within $V^{e(O)}$ must (by Schur's lemma) be proportional to the unit operator on $V^{e(O)}$, which may be written in terms of our basic operators as $\hat{S}_{\theta\theta} + \hat{S}_{\varepsilon\varepsilon}$. Normalizing to unity we arrive at the operator (45) to which we shall associate the parameter (46):

$$\hat{N}^{a_1}_{\iota} = (\sqrt{2}/2)(\hat{S}_{\theta\theta} + \hat{S}_{\varepsilon\varepsilon}), \tag{45}$$

$$N^{a_1}_{\iota} = (\sqrt{2}/2)(S_{\theta\theta} + S_{\varepsilon\varepsilon}). \tag{46}$$

The notation reflects the fact that $\hat{N}^{a_1}_{\iota}$ transforms as the irreducible representation $a_1(O)$, which we have given here the component designation ι.

The octahedral ligand field component $\hat{V}(O)$ may now be written as in Eq.(47) with the matrix (48):

$$\hat{V}(O) = \hat{N}^{a_1}_{\iota}\, N^{a_1}_{\iota} = (\sqrt{2}/2)(\hat{S}_{\theta\theta} + \hat{S}_{\varepsilon\varepsilon})\, N^{a_1}_{\iota}, \tag{47}$$

$$\begin{array}{c|cc} \hat{V}(O) & |\theta\rangle & |\varepsilon\rangle \\ \hline \langle\theta| & \frac{\sqrt{2}}{2} & 0 \\ \langle\varepsilon| & 0 & \frac{\sqrt{2}}{2} \end{array} \; N^{a_1}_{\iota}. \tag{48}$$

The matrix (48) demonstrates the degeneracy of the two e orbitals. We see that their common eigenvalue is $(1/2)(S_{\theta\theta} + S_{\varepsilon\varepsilon})$ so that their cubic energy is the mean value of their energies under the total operator $\hat{W}$ [Eq.(32)].

We next consider the ligand field component $\hat{V}(D_4)$ of tetragonal symmetry and observe from Eq.(3) that the irreducible representation $e(O)$ is reducible in D_4 with the two irreducible components given in Eq.(49):

$$e(O) = a_1(D_4) \oplus b_1(D_4). \tag{49}$$

This equation implies that a tetragonal field will split the $e(O)$ set of orbitals into an $a_1(D_4)$ and a $b_1(D_4)$ eigenfunction. We further observe [Eq.(3)] that $|\theta\rangle$ in fact transforms as $a_1(D_4)$ and that $|\varepsilon\rangle$ transforms as $b_1(D_4)$. The splitting $S_{\theta\theta} - S_{\varepsilon\varepsilon}$ corresponds to the normalized operator of Eq.(50) whose corresponding parameter is given in (51):

$$\hat{N}^e_\theta = (\sqrt{2}/2)(\hat{S}_{\theta\theta} - \hat{S}_{\varepsilon\varepsilon}), \tag{50}$$

$$N^e_\theta = (\sqrt{2}/2)(S_{\theta\theta} - S_{\varepsilon\varepsilon}). \tag{51}$$

As mentioned above, the θ component of $e(O)$ is totally symmetric in D_4 and the operator $\hat{N}^e_\theta$ is the unit irreducible tensor operator which together with the tetragonal empirical parameter N^e_θ makes up the tetragonal ligand field component $\hat{V}(D_4)$ [Eq.(52)]. The matrix of $\hat{V}(D_4)$, which is given in (53), shows by comparison with (51) that the energies of $|\theta\rangle$ and $|\varepsilon\rangle$ are $\frac{1}{2}(S_{\theta\theta} - S_{\varepsilon\varepsilon})$ and $-\frac{1}{2}(S_{\theta\theta} - S_{\varepsilon\varepsilon})$, respectively, so that their energy difference is $S_{\theta\theta} - S_{\varepsilon\varepsilon}$.

$$\hat{V}(D_4) = \hat{N}^e_\theta N^e_\theta = (\sqrt{2}/2)\,(\hat{S}_{\theta\theta} - \hat{S}_{\varepsilon\varepsilon})\,N^e_\theta, \tag{52}$$

$$\begin{array}{ccc} \hat{V}(D_4) & |\theta\rangle & |\varepsilon\rangle \\ \langle\theta| & \left[\begin{matrix} \dfrac{\sqrt{2}}{2} \\ \\ 0 \end{matrix}\right. & \left.\begin{matrix} 0 \\ \\ -\dfrac{\sqrt{2}}{2} \end{matrix}\right] \\ \langle\varepsilon| & & \end{array} N^e_\theta. \tag{53}$$

In orthorhombic symmetry both $e(O)$ components are totally symmetric [see Eq.(3)] and thus the orthorhombic ligand field component

$\hat{V}(D_2)$ will have a nondiagonal element connecting θ and ε. A consequence of the existence of this nondiagonal element is that the separation of the two eigenvalues of (32) will be greater than the absolute value, $|S_{\theta\theta} - S_{\varepsilon\varepsilon}|$, of the difference between diagonal elements, and the associated eigenstates will be two (mutually orthogonal) mixtures of $|\theta\rangle$ and $|\varepsilon\rangle$. Referring to the irreducible tensor operator scheme, this orthorhombic term is the third term of Eq.(40) and its matrix is given in Expression (54) referring to the operator expression of Eq.(38) and the associated energy parameter expression of Eq.(41):

$$\begin{array}{c|cc} \hat{V}(D_2) & |\theta\rangle & |\varepsilon\rangle \\ \hline \langle\theta| & 0 & -\dfrac{\sqrt{2}}{2} \\ \langle\varepsilon| & -\dfrac{\sqrt{2}}{2} & 0 \end{array} \; N_\varepsilon^e. \tag{54}$$

We have now exhausted the space of the four operators [Eqs.(21)–(24)] of our basic scheme and described it in terms of irreducible tensor operators. These operators span the space $V^{e(O)} \otimes \bar{V}^{e(O)}$ which carries the tensor product representation $e \otimes \bar{e}$ given in Eq.(55).[17] It should be remembered that the e term in the product space can be expressed as a sum of a θ term and an ε term.

$$e \otimes \bar{e} = a_1 \oplus e \oplus a_2. \tag{55}$$

It is a general property of non-totally symmetric operators[19] that their traces are zero; they are said to be traceless. In ligand field theory, only traceless operators correspond to observables. In our particular case the parameter $N_\iota^{a_1}$, which formally appears in the expression for the ligand field, only represents an absoluteness of the energy scale and thus cannot be observed. It is a characteristic of ligand field theory that only parameters expressing energy *differences* are extractable from experimental data interpreted with the models.

We finally write our ligand field operator $\hat{W}$ in the unit irreducible tensor operator scheme in Eq.(56) which is an alternative to the expression of Eq.(36):

$$\begin{aligned} \hat{W} = \hat{W}(D_2) &= \hat{V}(O) + \hat{V}(D_4) + \hat{V}(D_2) \\ &= \hat{N}_\iota^{a_1} N_\iota^{a_1} + \hat{N}_\theta^e N_\theta^e + \hat{N}_\varepsilon^e N_\varepsilon^e = \hat{\mathbb{N}}\mathbb{N}^T. \end{aligned} \tag{56}$$

We notice that the total operator $\hat{W} = \hat{W}(D_2)$ has the symmetry of its lowest symmetry component $\hat{V}(D_2)$. Further, no matter how low the actual symmetry of our molecular system it is a consequence of our assumptions about our function space—namely, that it transforms as $e(O)$—that the lowest symmetry term of our model Hamiltonian will be totally symmetric in the group D_2 when analyzed in the hierarchy $O \supset D_4 \supset D_2$.

5. Clebsch–Gordan Coefficients Relating the Two Operator Schemes

The relation between the basic unit operators of Eqs.(21)–(24) and the unit irreducible tensor operators of Eqs.(38), (39), (45) and (50) can be expressed by the operator overlap matrix (57) which is orthogonal:

$$\begin{array}{c} \\ \hat{S}_{\theta\theta} \\ \\ \hat{S}_{\theta\varepsilon} \\ \\ \hat{S}_{\varepsilon\theta} \\ \\ \hat{S}_{\varepsilon\varepsilon} \end{array} \begin{array}{c} \begin{array}{cccc} \hat{N}^{a_1}_{\iota} & \hat{N}^{e}_{\theta} & \hat{N}^{e}_{\varepsilon} & \hat{N}^{a_2}_{\omega} \end{array} \\ \begin{bmatrix} \frac{\sqrt{2}}{2} & \frac{\sqrt{2}}{2} & 0 & 0 \\ 0 & 0 & -\frac{\sqrt{2}}{2} & -\frac{\sqrt{2}}{2} \\ 0 & 0 & -\frac{\sqrt{2}}{2} & \frac{\sqrt{2}}{2} \\ \frac{\sqrt{2}}{2} & -\frac{\sqrt{2}}{2} & 0 & 0 \end{bmatrix} \end{array} . \tag{57}$$

The elements[1] of the matrix (57) are the so-called Clebsch–Gordan coefficients associated with the tensor product of Eq.(55). The element $\langle \hat{S}_{\theta\varepsilon} | \hat{N}^{e}_{\varepsilon} \rangle$, for example, is the coefficient normally written as $\langle E\theta\ E\varepsilon | E\varepsilon \rangle$ [the complex conjugation present in Eq.(55) may be dropped because the irreducible representation E is chosen here in a real matrix form]. The signs are chosen in agreement with the phase fixations made elsewhere (Ref. 11, Table 19).

The orthogonality of the matrix (57) makes it meaningful to make statements like the following: Each of the operators $\hat{S}_{\theta\theta}$ and $\hat{S}_{\varepsilon\varepsilon}$ has 50% cubic and 50% tetragonal character.

6. Coordinate Frame Dependence of the Tetragonal and Orthorhombic Ligand Field Components

There exists to our knowledge no orthorhombic complex from whose spectrum tetragonal and orthorhombic ligand field parameters have been directly determined. However, for the purpose of illustrating the formalism of the present paper one may establish a plausible set of such parameters for the $e(O)$ orbitals of the hypothetical orthorhombic complex *trans,trans,trans*-$[CrBr_2Cl_2F_2]^{3-}$ on the basis of the angular overlap model parameters previously obtained[20] for the series of complexes *trans*-$[Cr(NH_3)_4X_2]^+$, X = Br, Cl, F.

In doing this we shall for the moment assume our functions $|\theta\rangle$ and $|\varepsilon\rangle$ to be d functions and apply the angular overlap model, as was done in the analysis[20] of the tetragonal complexes. Further, we shall assume the AOM parameters of Ref. 20 to be transferable to the mixed hexahalido complex. We write in Eq.(58) the one-electron energy difference $S_{\theta\theta} - S_{\varepsilon\varepsilon}$ for *trans*-$[Cr(NH_3)_4X_2]^+$ in the AOM notation without defining this notation here.

$$
\begin{aligned}
(S_{\theta\theta} - S_{\varepsilon\varepsilon})_{trans\text{-}[Cr(NH_3)_4X_2]^+} &= 2e'_{\sigma X} - 2e'_{\sigma NH_3} \\
&= (2/3)(\Delta'_{\sigma X} - \Delta'_{\sigma NH_3}).
\end{aligned}
\tag{58}
$$

In Eq.(59) the corresponding quantity for the *trans,trans,trans*-dibromodichlorodifluorochromate(III) complex, the Z axis being chosen along the F–Cr–F direction, has been given:

$$
\begin{aligned}
&(S_{\theta\theta} - S_{\varepsilon\varepsilon})_{trans,trans,trans\text{-}[CrBr_2Cl_2F_2]^{3-}} \\
&\qquad = (1/3)(2\Delta'_{\sigma F} - \Delta'_{\sigma Cl} - \Delta'_{\sigma Br}).
\end{aligned}
\tag{59}
$$

We note that while θ and ε in Eq.(58) represent eigenfunctions because the orthorhombic field is vanishing, this is not so in Eq.(59). In this case there will be a nondiagonal element connecting θ and ε, which represents the orthorhombic ligand field component arising from the difference between the field attributed to Cl^- and Br^-. The expression for this nondiagonal element is given in Eq.(60) when the two chlorines are on the X axis:

$$S_{\theta\varepsilon} = S_{\varepsilon\theta} = -(\sqrt{3}/6)(\Delta'_{\sigma Cl} - \Delta'_{\sigma Br}). \tag{60}$$

From Eqs.(59) and (60), N_θ^ε and $N_\varepsilon^\varepsilon$ can be obtained using Eqs.(41) and (51), respectively (Table I). Note that the discussion to follow

TABLE I

$\Delta'_{\sigma F} = 22.2$ kK	$\Delta'_{\sigma Cl} = 16.6$ kK	$\Delta'_{\sigma Br} = 14.8$ kK
(a)	(b)	(c)
$N^e_\theta = 3.1$ kK	$N^e_{\theta'} = -0.9$ kK	$N^e_{\theta''} = -2.2$ kK
$N^e_\varepsilon = 0.7$ kK	$N^e_{\varepsilon'} = -3.0$ kK	$N^e_{\varepsilon''} = 2.3$ kK
$\alpha = 0.993$	$\alpha' = 0.598$	$\alpha'' = -0.395$
$\beta = -0.117$	$\beta' = 0.801$	$\beta'' = 0.919$

(1 kK = 1000 cm^{-1})

Angular overlap model σ parameters[20] $\Delta'_{\sigma X}$ (X = F, Cl, Br) and tetragonal and orthorhombic parameters for the ligand field components acting on the *e* orbitals of the complex *trans,trans,trans*-$[\text{CrBr}_2\text{Cl}_2\text{F}_2]^{3-}$. The three columns correspond to the choices of tetragonal axis in Figures 1a, 1b and 1c, respectively. The α,β sets are eigenvector components of the upper eigenvalue. Using the orthogonality property of eigenvectors and assuming them to be normalized, components corresponding to the lower eigenvalue can easily be found. In the double primed frame, for example, eigenvectors associated with the upper and lower eigenstates are $\alpha''|\theta''\rangle + \beta''|\varepsilon''\rangle$ and $\beta''|\theta''\rangle - \alpha''|\varepsilon''\rangle$, respectively. The upper one contains $(\beta'')^2 = 84\%$ of $|\varepsilon''\rangle$, while the lower one contains the remaining $(\alpha'')^2 = 16\%$ of $|\varepsilon''\rangle$. It should be noted that the priming of $\Delta'_{\sigma X}$ has to do with the zero point of energy for $\Delta_{\sigma X}$ (cf. Note 7 and Ref. 20) and has nothing to do with the primed coordinate frame of column b of this table.

applies in general, irrespective of the assumptions made in calculating the parameter values used to illustrate it.

We shall study first the conceptual consequences of choosing the Z axis along the three mathematically equivalent, natural directions in the mixed halido complex and see that we can obtain a quantitative measure of such terms as compressed or elongated tetragonality or rhombicity.

In Figure 1 the complex has been drawn in three different Cartesian frames, unprimed, primed and doubly primed, corresponding to the bases $\{\theta\ \varepsilon\}$, $\{\theta'\ \varepsilon'\}$, and $\{\theta''\ \varepsilon''\}$ whose relationships are given in Eqs.(10), (11) and (20).

The tetragonal and orthorhombic parameters for the primed and double-primed bases can be obtained from Eqs.(61) and (62) (Table I):

$$[N^e_{\theta'}\ N^e_{\varepsilon'}] = [N^e_\theta\ N^e_\varepsilon]\begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix}, \qquad (61)$$

$$[N^e_{\theta''}\ N^e_{\varepsilon''}] = [N^e_{\theta'}\ N^e_{\varepsilon'}]\begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix}. \qquad (62)$$

It is a consequence of the fact that the different parametrizations are connected by orthogonal transformations, that the sum of the squares

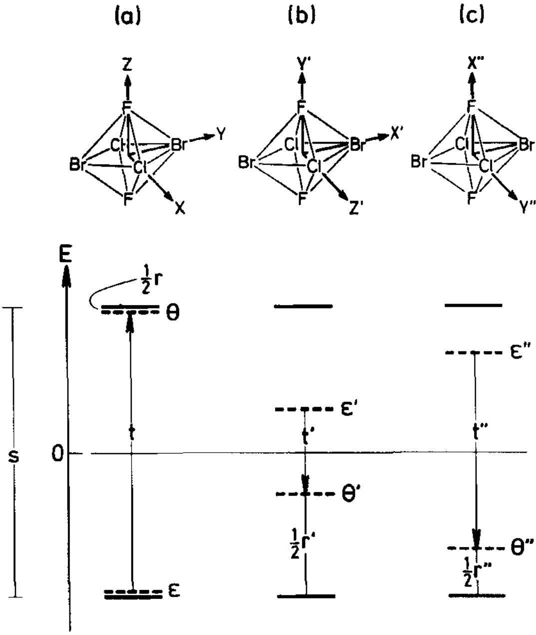

FIGURE 1 From experimental single ligand parameters of the *trans*-tetraamminedihalidochromium(III) complexes, empirical ligand field parameters for *trans,trans,trans*-$[CrBr_2Cl_2F_2]^{3-}$ can be obtained. Using these parameters, the splitting s of the $e(O)$ orbital level [Eq.(67)] can be calculated and is here indicated to the left of the vertical energy axis. This splitting is in principle directly observable. It can be analyzed as a sum of the absolute value of a tetragonal splitting t, whose sign is defined in Eq.(68), and an orthorhombic splitting r [Eq.(69)]. There are three mathematically equivalent ways of performing this decomposition, according to which twofold axis of the molecule is chosen as the tetragonal axis. These are illustrated in (a), (b) and (c) where the common total splitting s appears as the energy difference between heavy horizontal lines. The tetragonal splittings t, t', and t'' are represented by arrows to indicate their sign; the orthorhombic splittings are $r = s - |t|$, etc. The whole situation can be discussed in detail in terms of tetragonal and orthorhombic compressions and elongations .

of the parameters is an invariant of the system as expressed in Eq.(63); indeed, each of the three sums in Eq.(63) is equal to $\langle\hat{\overline{W}}(D_2)|\hat{\overline{W}}(D_2)\rangle$, where $\hat{\overline{W}}(D_2) = \hat{V}(D_4) + \hat{V}(D_2) = \hat{V}'(D_4) + \hat{V}'(D_2) = \hat{V}''(D_4) + \hat{V}''(D_2)$ [cf. the definition of operator overlap in Eq.(30)]:

$$(N^e_\theta)^2 + (N^e_\varepsilon)^2 = (N^e_{\theta'})^2 + (N^e_{\varepsilon'})^2 = (N^e_{\theta''})^2 + (N^e_{\varepsilon''})^2. \qquad (63)$$

Because $\hat{V}(D_4)$ and $\hat{V}(D_2)$ form an orthogonal operator set so that Eq.(64) is valid, this square sum is also the sum of the squares of the matrix elements of $\hat{V}(D_4)$ plus the sum of the squares of those of $\hat{V}(D_2)$.

$$\langle\hat{\overline{W}}(D_2)|\hat{\overline{W}}(D_2)\rangle = \langle\hat{V}(D_4)|\hat{V}(D_4)\rangle + \langle\hat{V}(D_2)|\hat{V}(D_2)\rangle. \qquad (64)$$

The bar over the W indicates that the barycenter rule applies within our function space $V^{e(O)}$, i.e., that $\hat{\overline{W}}(D_2)$ is traceless. For our particular example the square sum is given in Eq.(65):

$$(N^e_\theta)^2 + (N^e_\varepsilon)^2 = 10.0\ (\mathrm{kK})^2. \qquad (65)$$

The *total splitting* s of the $e(O)$ level arising from the combined effect of the tetragonal and orthorhombic field components, taken here to be a nonnegative quantity, may be obtained by the following argument. If the elements of the diagonal matrix resulting from a diagonalization of $\hat{\overline{W}}(D_2)$ are d and $-d$, so that $s = 2|d|$, then we have Eq.(66) and thus Eq.(67), because both sides in Eq.(66) are equal to $\langle\hat{\overline{W}}(D_2)|\hat{\overline{W}}(D_2)\rangle$:

$$d^2 + (-d)^2 = (N^e_\theta)^2 + (N^e_\varepsilon)^2, \qquad (66)$$

$$s = \sqrt{2}\,\sqrt{(N^e_\theta)^2 + (N^e_\varepsilon)^2}. \qquad (67)$$

The total splitting s, which in principle can be directly observed, is of course independent of the choice of coordinate frame; this is borne out by Eq.(63) and also illustrated in Figures 1a, 1b and 1c.

It is of interest to view the total splitting as a sum of a tetragonal and an orthorhombic part. In agreement with Expression (53) we shall define in each of the three cases the *tetragonal splitting t* as the difference between the expectation values of $\hat{V}(D_4)$ for the θ and the ε function. This is equal to the same quantity for $\hat{W}(D_2)$ of Eq.(56), since the expectation values of $\hat{V}(O)$ are the same for both $e(O)$ functions and $\hat{V}(D_2)$ has only vanishing matrix elements in the diagonal. For the primed system, for example, we have Eq.(68):

$$\begin{aligned} t' &\equiv \langle\theta'|\hat{V}'(D_4)|\theta'\rangle - \langle\varepsilon'|\hat{V}'(D_4)|\varepsilon'\rangle \\ &= \langle\theta'|\hat{W}(D_2)|\theta'\rangle - \langle\varepsilon'|\hat{W}(D_2)|\varepsilon'\rangle \\ &= \langle\theta'|\hat{\overline{W}}(D_2)|\theta'\rangle - \langle\varepsilon'|\hat{\overline{W}}(D_2)|\varepsilon'\rangle \\ &= \sqrt{2}\,N^{e}_{\theta'}. \end{aligned} \tag{68}$$

Defined in this way, the tetragonal splitting has the same sign as the corresponding parameter N^{e}_{θ}. The absolute value of t is less than or equal to the total splitting s.

The "orthorhombic splitting" r will then be defined as the difference between the total splitting s and the absolute value $|t|$ of the tetragonal splitting. For the primed coordinate system the expression for the orthorhombic splitting r' is given in Eq.(69). As a consequence of this definition the orthorhombic splitting is always a non-negative quantity.

$$r' \equiv s - |t'| = \sqrt{2}\,\sqrt{(N^{e}_{\theta'})^2 + (N^{e}_{\varepsilon'})^2} - \sqrt{2}\,|N^{e}_{\theta'}|. \tag{69}$$

Equation (68) shows for t' the relationship between the tetragonal splitting and the tetragonal parameter. An analogous relationship between the total splitting s and the "root-sum-square parameter" $\sqrt{(N^{e}_{\theta})^2 + (N^{e}_{\varepsilon})^2}$ is seen in Eq.(67). It is a consequence of these two equations that the orthorhombic splitting r depends on both N^{e}_{θ} and N^{e}_{ε}. The difference in the relationship between the splitting and parameter for the tetragonal and the orthorhombic components of the ligand field is caused by the fact that the former is diagonal and the latter nondiagonal in our basis, which is symmetry adapted to the hierarchy $O \supset D_4 \supset D_2$ [Eq.(3)]. The splitting effect of $\hat{V}(D_2)$ therefore depends on the difference between the diagonal elements, which is equal to t and therefore, according to Eq.(68), depends on N^{e}_{θ}.

The specification of the total splitting s does not, of course, give as much information as the specification of both N^{e}_{θ} and N^{e}_{ε}. The piece of information lost concerns eigenvectors, or equivalently, the signs and relative magnitudes of the tetragonal and orthorhombic field components (that is, of their associated parameters, N^{e}_{θ} and N^{e}_{ε}).[21] From a symmetry point of view, there are three equally acceptable resolutions of s, represented itself by the length of the vector OP of Figure 2. These resolutions, which refer to our unprimed, primed and double-primed coordinate systems of Figure 1, are also illustrated in Figure 2.

Note from the eigenvectors of Table I that the eigenstates of the total field $\hat{\overline{W}}(D_2)$ resemble those of $\hat{V}(D_4)$ much more than those of $\hat{V}'(D_4)$

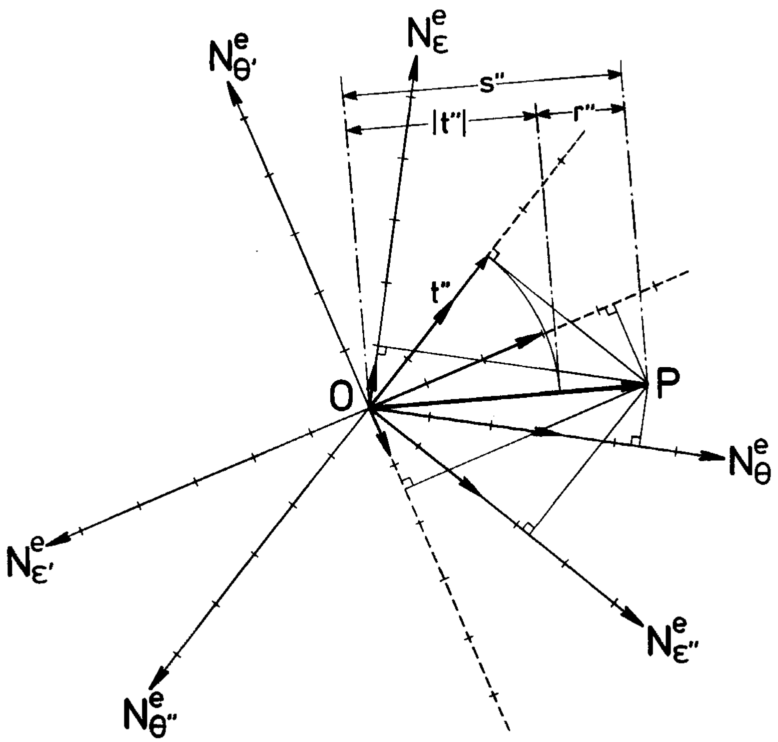

FIGURE 2 In *trans,trans,trans*-$[CrBr_2Cl_2F_2]^{3-}$ a parametrization of the ligand field in terms of a tetragonal and an orthorhombic empirical parameter can be chosen in three ways, using either of the parameter sets $\{N^e_\theta, N^e_\varepsilon\}$, $\{N^e_{\theta'}, N^e_{\varepsilon'}\}$, or $\{N^e_{\theta''}, N^e_{\varepsilon''}\}$ depending on whether F–Cr–F, Cl–Cr–Cl, or Br–Cr–Br, respectively, is chosen as the tetragonal axis (cf. Figure 1). The three parameter sets are related (Eqs.(61) and (62)). The splitting situation is represented by the two-dimensional vector *OP*. The length of this vector is the total splitting *s* of the e(*O*) orbital level, i.e, the value of the splitting caused by the combined action of the tetragonal and orthorhombic field components. The direction of the vector represents information about its decomposition into a tetragonal part *t* whose magnitude and sign is defined according to Eq.(68) and a corresponding orthorhombic part *r* (Eq.(69)) which is always non-negative. This is illustrated explicitly for the double primed coordinate frame, where the longer vector on the negative part of the $N^e_{\theta''}$ axis represents t''. The coordinates of *OP* can be given in either of the three rectangular coordinate systems which are rotated by 120° relative to each other. A given such coordinate is equal to the parameter in question (given with sign, as a vector), multiplied by $\sqrt{2}$ [cf. Table 1 and Eq.(68)]. Thus, a coordinate referring to an N^e_θ axis is equal to the tetragonal splitting (with sign) of the frame in question, but a coordinate referring to an N^e_ε axis is not equal to the orthorhombic splitting which is rather obtained as $|OP|$ minus the absolute value of the tetragonal splitting.

and $\hat{V}''(D_4)$. Having $\hat{V}(D_4)$ as the tetragonal field component corresponds to a situation where the two F^- ligands rather than two Cl^- or two Br^- ligands determine the tetragonal axis. This choice of tetragonal axis is, of course, also the natural one from a chemical point of view, since the two heavy halide ligands in all chemical respects resemble each other more than each of them resembles fluoride.

We next come to the question of the possible interpretation of the *signs* of the tetragonal and orthorhombic parameters. We recall that in an LCAO-molecular-orbital interpretation of ligand field theory for complexes of a d^q configuration, the *e* orbitals are σ-antibonding orbitals whose bonding counterparts are mainly ligand in character. Since the trace of the operator $\hat{N}^e_\theta$ is zero, the tetragonal field component has the effect of increasing (or decreasing) the energy of $|\theta\rangle$ by the same amount as it decreases (increases) that of $|\varepsilon\rangle$. This just expresses the fact that the cubic field component remains unchanged upon addition of the tetragonal one. Thus, for example, a decrease of the distances to the Z-axis ligands associated with the tetragonal field component must be accompanied by a certain increase of the distances in the XY plane. Such a compression along the Z axis does not influence the energy of $|\varepsilon\rangle$ since $|\varepsilon\rangle$ is of $b_1(D_4)$ symmetry [Eq.(3)] and no linear combinations of ligand σ or π orbitals situated on the Z axis can achieve this symmetry; thus only the expansion in the XY plane affects $|\varepsilon\rangle$ and, accordingly, its energy decreases. By the above barycenter argument, $|\theta\rangle$ rises in energy by the same amount. Referring to Eq.(53) we see that the resulting situation, by our sign convention for N^e_θ, corresponds to N^e_θ positive. Conversely, an elongation along the Z axis (together with corresponding compressions along the X and Y axes) corresponds to N^e_θ negative. The meaning of the sign of N^e_ε is perhaps less obvious; however, if we transform a parameter set $(N^e_\theta, N^e_\varepsilon)$ with $N^e_\theta = 0$ and N^e_ε positive by the matrices of Eqs.(61) and (62) we obtain a positive $N^e_{\theta'}$ value and a negative $N^e_{\theta''}$ value, showing that N^e_ε positive indicates compression along the Z' axis, which is the unprimed X axis, and elongation along the Z'' axis, which is the unprimed Y axis.

In a *given* coordinate frame, distortions associated with N^e_θ (i.e., compression along the Z axis and concomitant elongations along the X and Y axes or vice versa) will be called "tetragonal" distortions and those associated with N^e_ε (i.e., compression along the X axis and corresponding elongation along the Y axis or vice versa) will be called "orthorhombic" distortions.

Using compression and elongation in this "parametric" sense (rather than in an immediate geometric sense), we may now discuss our hexahalido complex of Figures 1a, 1b and 1c on the basis of the parameter values of Table I. In the unprimed frame the system is described as a tetragonally compressed system which has a quite small orthorhombic compression along the X axis (and elongation along the Y axis). In the primed frame the system is tetragonally elongated, and in addition orthorhombically elongated along the X' axis. Finally, in the doubly primed frame it is even more tetragonally elongated but orthorhombically compressed along the X'' axis.

The discussion of the tetragonality and the orthorhombicity can be made quantitative. The fact that Eq.(63) is valid makes it immediately possible to compare the size of the tetragonal and orthorhombic field components by using the squares of their parameters as a measure. For example, it would be a perfectly well defined quantitative statement to say that a system is $\{(N^e_\theta)^2/[(N^e_\theta)^2 + (N^e_\varepsilon)^2]\} \times 100\%$ tetragonal and $\{(N^e_\varepsilon)^2/[(N^e_\theta)^2 + (N^e_\varepsilon)^2]\} \times 100\%$ orthorhombic, and for the preferred choice of tetragonal axis, that of Figure 1a, the rhombicity is accordingly 5%. We remark that the comparison of field components and total fields in terms of squared parameters is related to splittings as follows. The sum of the squared deviations from the barycenter energy is equal to $(N^e_\theta)^2$ for the tetragonal field and equal to $(N^e_\theta)^2 + (N^e_\varepsilon)^2$ for the total field.

It is interesting to approach the freedom of choice of coordinate frames by studying the case where N^e_θ is equal to zero, i.e., 100% rhombicity in the unprimed frame. Using Eqs.(61) and (62), we find Eqs.(70), which imply Eqs.(71), showing that the 100% rhombicity situation in the unprimed frame is a situation with 75% tetragonality in each of the other two frames:

$$-\frac{N^e_{\theta'}}{N^e_{\varepsilon'}} = \frac{N^e_{\theta''}}{N^e_{\varepsilon''}} = \sqrt{3}, \qquad (70)$$

$$\frac{(N^e_{\theta'})^2}{(N^e_{\theta'})^2 + (N^e_{\varepsilon'})^2} = \frac{(N^e_{\theta''})^2}{(N^e_{\theta''})^2 + (N^e_{\varepsilon''})^2} = \frac{3}{4}. \qquad (71)$$

In fact, it can be seen from Eqs.(61) and (62)—most easily by inspecting the geometric disposition of the vectors $(N^e_\theta, N^e_\varepsilon)$, $(N^e_{\theta'}, N^e_{\varepsilon'})$ and $(N^e_{\theta''}, N^e_{\varepsilon''})$ in the plane—that there will always be at least one tetragonality greater than or equal to 75%, and that if one of the frames gives >75% tetragonality the other two will both give <75% tetragonality (the sum of the tetragonalities is always 3/2). *It is therefore not only possible to* *choose the frame giving the highest tetragonality in a unique way* (except for the maximal rhombicity situation); *one also knows with that choice that the tetragonality exceeds 75%.*

Before leaving the discussion regarding the choice of the tetragonal axis it is interesting to note that although this is probably new in a ligand field context, it is well known and very similar in a spin-Hamiltonian context. The spin-Hamiltonian for a system with $S > \frac{1}{2}$ is conventionally written as in Eq.(72):

$$\hat{H} = D\left[\hat{S}_z^2 - \frac{1}{3}\hat{S}^2\right] + E[\hat{S}_x^2 - \hat{S}_y^2], \tag{72}$$

$$\begin{aligned}\hat{H} &= \frac{2}{3}D\left[\hat{S}_z^2 - \frac{1}{2}\hat{S}_x^2 - \frac{1}{2}\hat{S}_y^2\right] + \frac{2}{3}\sqrt{3}\,E\left[\frac{\sqrt{3}}{2}(\hat{S}_x^2 - \hat{S}_y^2)\right]\\ &= \frac{1}{\sqrt{n}}\left\{\left[\hat{S}_z^2 - \frac{1}{2}\hat{S}_x^2 - \frac{1}{2}\hat{S}_y^2\right]N_\theta^e + \left[\frac{\sqrt{3}}{2}(\hat{S}_x^2 - \hat{S}_y^2)\right]N_\varepsilon^e\right\}.\end{aligned} \tag{73}$$

In Eq.(73), the operator parts have been *normalized*[22] to unity by multiplication with the factor $1/\sqrt{n}$. With respect to symmetry, N_θ^e and N_ε^e have the same meaning as in the rest of this paper. The ratio $N_\theta^e/N_\varepsilon^e$ corresponds to $D/(E\sqrt{3})$ and referring to Eq.(70), the ratio conditions of (74) are just those used[23,24] when communicating zero-field splitting data in EPR spectroscopy.

$$\begin{aligned}|N_\theta^e/N_\varepsilon^e| &> \sqrt{3},\\ |D/E| &> 3.\end{aligned} \tag{74}$$

III. ATOMIC LIGAND FIELD THEORY USING A REAL d BASIS

1. Molecular and Atomic Bases

If we extend the space $V^{e(O)}$ by adding a space $V^{t_2(O)}$, thus going from a two-dimensional to a five-dimensional space, the number of linearly independent operators acting within this new space is 25. One may choose four linearly independent operators acting within $V^{e(O)}$, for example, the ones defined in Eqs.(21)–(24), and nine linearly independent operators among those which act exclusively within $V^{t_2(O)}$. Operators of these two types may be called[1] "in-space" operators of the group O. The 12-dimensional orthogonal complement to the 13-dimensional subspace of in-space operators consists of "cross-space" operators[1] of O connecting $V^{e(O)}$ and $V^{t_2(O)}$ by mapping e functions onto t_2 functions and vice versa, but having only zero matrix elements within each of the spaces $V^{e(O)}$ and $V^{t_2(O)}$.

If we make the particular assumption that our new function space $V^{e(O)} \oplus V^{t_2(O)}$ is spanned by a set of d orbitals, then all operators of the d space are in-space operators of R_3. If we choose the five real d orbitals given in Eqs.(1) and (2) then our previous discussion of the space $V^{e(O)}$, its operator bases and their ligand field implications is still valid, except that all the statements are now concerned with a subspace $V^{d(R_3)e(O)}$ of the space $V^{d(R_3)}$ and the operators of Eqs.(21)–(24) are now $\hat{S}_{d\theta d\theta}$, $\hat{S}_{d\varepsilon d\theta}$, $\hat{S}_{d\theta d\varepsilon}$ and $\hat{S}_{d\varepsilon d\varepsilon}$, which still make up an orthonormal set. This latter setup is of the type we call "a molecular scheme for atomic ligand field theory." Such a scheme will be discussed in the rest of Section III.

2. The Ligand Field Components Acting Within the *de* Subspace

Supposing our basis for the d space consists of the real functions given in Eqs.(1) and (2), we may easily obtain "molecular scheme irreducible tensor operators" acting within the *de* subspace. Because the *de* functions of Eq.(1) transform by the same representation matrices in O as the general e functions discussed in Section II, all the results from Section II are transferable to our *de* subspace. [The difference between the general e functions of molecular ligand field theory and the *de* functions of atomic ligand field theory is that the former may be functions with no or only partial d character (e.g., molecular orbitals), whereas the latter, like atomic d orbitals, by definition transform as $d(R_3)$.] The irreducible tensor operators acting within the *de* subspace are given in Eqs.(75)–(78):

$$\hat{N}_{\iota}^{dede|a_1} = \sum_{\gamma_1,\gamma_2} \langle E\gamma_1 E\gamma_2 | A_1\iota\rangle \, \hat{S}_{de\gamma_1 de\gamma_2} = \frac{\sqrt{2}}{2}(\hat{S}_{d\theta d\theta} + \hat{S}_{d\varepsilon d\varepsilon}), \tag{75}$$

$$\hat{N}_{\omega}^{dede|a_2} = \sum_{\gamma_1,\gamma_2} \langle E\gamma_1 E\gamma_2 | A_2\omega\rangle \, \hat{S}_{de\gamma_1 de\gamma_2} = -\frac{\sqrt{2}}{2}(\hat{S}_{d\theta d\varepsilon} - \hat{S}_{d\varepsilon d\theta}), \tag{76}$$

$$\hat{N}_{\theta}^{dede|e} = \sum_{\gamma_1,\gamma_2} \langle E\gamma_1 E\gamma_2 | E\theta\rangle \, \hat{S}_{de\gamma_1 de\gamma_2} = \frac{\sqrt{2}}{2}(\hat{S}_{d\theta d\theta} - \hat{S}_{d\varepsilon d\varepsilon}), \tag{77}$$

$$\hat{N}_{\varepsilon}^{dede|e} = \sum_{\gamma_1,\gamma_2} \langle E\gamma_1 E\gamma_2 | E\varepsilon\rangle \, \hat{S}_{de\gamma_1 de\gamma_2} = -\frac{\sqrt{2}}{2}(\hat{S}_{d\theta d\varepsilon} + \hat{S}_{d\varepsilon d\theta}). \tag{78}$$

To the left in these equations we have—in order to be able to convey information about the space upon which the operators act—introduced a self-explanatory notation which is more elaborate than that used in Section II.4. The middle expressions in Eqs.(75)–(78) remind us of the connection in terms of Clebsch–Gordan coefficients mentioned in Section II.5 between the irreducible tensor operators and the basic operators. In the notation of Ref. 1, the irreducible tensor operators are $\hat{N}_{\iota}^{dede|a_1} = [|de\} \otimes \{de|]_{\iota}^{a_1}$, etc.

3. Outline of the Ligand Field Components Acting within the dt_2 Subspace

We shall not write explicitly all nine operators which act within $V^{d(R_3)t_2(O)}$ and correspond to those of Eqs.(75)–(78) for $V^{d(R_3)e(O)}$. The former operators can be classified as one operator of $\hat{N}^{a_1}$ type, two operators of $\hat{N}^{e}$ type, three of $\hat{N}^{t_1}$ type and three of $\hat{N}^{t_2}$ type.

The totally symmetrical operator of the group O acting within the dt_2 subspace is given in Eq.(79):

$$\hat{N}_{\iota}^{dt_2dt_2|a_1} = (\sqrt{3}/3)(\hat{S}_{d\xi d\xi} + \hat{S}_{d\eta d\eta} + \hat{S}_{d\zeta d\zeta}). \tag{79}$$

This operator has a nonvanishing trace and therefore does not correspond to an observable within the dt_2 subspace.

The $\hat{N}^{e}$-type operators are defined in Eqs.(80) and (81), where again Clebsch–Gordan coefficients from Ref. 11 have been used:

$$\hat{N}_{\theta}^{dt_2dt_2|e} = -(\sqrt{6}/6)(2\hat{S}_{d\zeta d\zeta} - \hat{S}_{d\xi d\xi} - \hat{S}_{d\eta d\eta}), \tag{80}$$

$$\hat{N}_{\varepsilon}^{dt_2dt_2|e} = (\sqrt{2}/2)(\hat{S}_{d\eta d\eta} - \hat{S}_{d\xi d\xi}). \tag{81}$$

These two operators represent in the dt_2 subspace the tetragonal field component ($\hat{N}_{\theta}^{dt_2dt_2|e}$) and the orthorhombic field component ($\hat{N}_{\varepsilon}^{dt_2dt_2|e}$). The corresponding parameters have, as usual, similar expressions. We point out that all the results from Section II which relate only to the symmetries of the operators (i.e., not to the space on which they act) are applicable for the dt_2 space, too.

Using the angular overlap model and the parameter values from Ref. 20, we can calculate the tetragonal and orthorhombic parameters for the dt_2 subspace of the mixed hexahalido complex discussed in Section II.6. These parameter sets are given in Table II for the three coordinate frames of Figure 1.

In the total d space there are thus two sets of $\hat{N}^{e}$-type operators: one for the de subspace and one for the dt_2 subspace. This means that there

TABLE II

$\Delta'_{\pi F} = 6.8$ kK	$\Delta'_{\pi Cl} = 3.5$ kK	$\Delta'_{\pi Br} = 2.5$ kK	
	(a)	(b)	(c)
$N_{\theta}^{dt_2dt_2\|e}$	1.6 kK	−0.5 kK	−1.1 kK
$N_{\varepsilon}^{dt_2dt_2\|e}$	0.4 kK	−1.5 kK	1.2 kK

Angular overlap model π parameters[20] $\Delta'_{\pi X}$ (X = F, Cl, Br) and tetragonal and orthorhombic parameters for the ligand field components acting on the dt_2 orbitals of *trans,trans,trans*-$[CrBr_2Cl_2F_2]^{3-}$. The three columns correspond to the three different tetragonal axes of Figure 1. The eigenvectors are trivial because $dt_2\xi$, $dt_2\eta$, and $dt_2\zeta$ do not mix in orthorhombic symmetry [Eq.(4)].

are two independent sets of low symmetry operators for which the preferred tetragonal axes (cf. Section II.6) may be different. In other words, it may well turn out that a choice of axis for which $(N_{\theta}^{dede|e})^2 > 3\,(N_{\varepsilon}^{dede|e})^2$ will not imply the corresponding inequality for the $N^{dt_2dt_2|e}$ parameters.[25] In such a case a new convention about the choice of tetragonal axis would be necessary. This could, for example, be based upon the condition that $(N_{\tilde{\theta}}^{dede|e})^2 + (N_{\tilde{\theta}}^{dt_2dt_2|e})^2$ be maximal, where $\tilde{\theta}$ refers to one of the three choices of axis, unprimed, primed or double-primed.

4. The Observable Cubic Field

Within the *de* and dt_2 subspaces the totally symmetric operators of $\hat{N}^{a_1}$ type do not correspond to observables. The octahedral field component is, however, observable in the total *d* space. Any operator within the total *d* space which is of octahedral symmetry is clearly of the form (82) with suitable coefficients a_e and a_{t_2}:

$$\hat{T} = a_e\,\hat{N}_{\iota}^{dede|a_1} + a_{t_2}\,\hat{N}_{\iota}^{dt_2dt_2|a_1}. \tag{82}$$

The combined requirements of barycentering of $\hat{T}$, i.e., the condition that $\mathrm{Tr}(\hat{T}) = 0$ (which is here equivalent[19] to demanding that $\hat{T}$ contains no spherically symmetric part), and unit normalization within the *d* space, i.e., $\langle\hat{T}|\hat{T}\rangle = 1$, now lead to the conditions $|a_e| = \sqrt{3/5}$ and $a_{t_2} = -a_e\sqrt{2/3}$ on the coefficients in (82). Choosing a_e positive we arrive at the operator in Eq.(83):

$$\begin{aligned}\hat{N}_{a_1\iota}^{dd|g} &= \sqrt{\frac{3}{5}}\,\hat{N}_{\iota}^{dede|a_1} - \sqrt{\frac{2}{5}}\,\hat{N}_{\iota}^{dt_2dt_2|a_1}\\ &= \sqrt{\frac{3}{10}}\,(\hat{S}_{d\theta d\theta} + \hat{S}_{d\varepsilon d\varepsilon}) - \sqrt{\frac{2}{15}}\,(\hat{S}_{d\xi d\xi} + \hat{S}_{d\eta d\eta} + \hat{S}_{d\zeta d\zeta}).\end{aligned} \tag{83}$$

The notation $\hat{N}^{dd|g}_{a_1\iota}$ reflects the fact that this operator actually belongs to the atomic scheme[26]; it is equal to $[|d\} \otimes \{d|]^{g}_{a_1\iota}$ in the alternative notation,[1] and its construction from the basic operators $\hat{S}_{d\gamma_1 d\gamma_2}$ involves octahedrally adapted *spherical* coupling coefficients of the type $\langle 2\,\Gamma(O)\gamma_1\; 2\,\Gamma(O)\gamma_2|4A_1\iota\rangle$. The matrix of $\hat{N}^{dd|g}_{a_1\iota}$ is given in (84) and that of the related operator $\hat{Q}_\Delta = \sqrt{(6/5)}\,\hat{N}^{dd|g}_{a_1\iota}$ in (85):

$$
\begin{array}{c|cc|ccc|}
\hat{N}^{dd|g}_{a_1\iota} & |de\theta\rangle & |de\varepsilon\rangle & |dt_2\xi\rangle & |dt_2\eta\rangle & |dt_2\zeta\rangle \\
\langle de\theta| & \sqrt{\frac{3}{10}} & 0 & & & \\
\langle de\varepsilon| & 0 & \sqrt{\frac{3}{10}} & & \mathbb{O} & \\
\hline
\langle dt_2\xi| & & & -\sqrt{\frac{2}{15}} & 0 & 0 \\
\langle dt_2\eta| & & \mathbb{O} & 0 & -\sqrt{\frac{2}{15}} & 0 \\
\langle dt_2\zeta| & & & 0 & 0 & -\sqrt{\frac{2}{15}}
\end{array}, \qquad (84)
$$

$$
\begin{array}{c|cc|ccc|}
\hat{Q}_\Delta & |de\theta\rangle & |de\varepsilon\rangle & |dt_2\xi\rangle & dt_2\eta\rangle & |dt_2\zeta\rangle \\
\langle de\theta| & \frac{3}{5} & 0 & & & \\
\langle de\varepsilon| & 0 & \frac{3}{5} & & \mathbb{O} & \\
\hline
\langle dt_2\xi| & & & -\frac{2}{5} & 0 & 0 \\
\langle dt_2\eta| & & \mathbb{O} & 0 & -\frac{2}{5} & 0 \\
\langle dt_2\zeta| & & & 0 & 0 & -\frac{2}{5}
\end{array} \qquad (85)
$$

It is seen that a ligand field operator $\hat{V}(O)$ of octahedral symmetry *acting in the d space* may be written as in Eq.(86):

$$\hat{V}(O) = \hat{Q}_{\Delta}\Delta = \hat{N}_{a_{1\iota}}^{dd|g} N_{a_{1\iota}}^{dd|g}. \quad (86)$$

Here the first expression involves the well known spectrochemical parameter Δ, which is equal to the energy difference between the *de* orbitals and the dt_2 orbitals in a cubic ligand field, and the second expression uses the energy parameter $N_{a_{1\iota}}^{dd|g} = \sqrt{(6/5)}\,\Delta$ associated with the normalized operator of Eq.(83). The value of the cubic parameter is independent of whether the primed, the unprimed or the double-primed coordinate system of Figure 1 is used.

5. Magnitude of the Cubic Ligand Field Component Compared with Low Symmetry Components

We now give another illustration of how the use of orthonormal operators in formulating ligand field theory makes it possible to compare different terms of the ligand field expansion. Again, the comparison is based upon squares of the empirical parameters.

Returning to our example from Section II.6, we shall need the value of the normalized cubic parameter $N_{a_{1\iota}}^{dd|g}$. Using the AOM parameter values of Tables I and II, we first calculate in Eq.(87) the value of its unnormalized equivalent Δ_{av}:

$$\begin{aligned}\Delta_{av} &= (1/3)(\Delta_{\mathrm{Br}} + \Delta_{\mathrm{Cl}} + \Delta_{\mathrm{F}})\\ &= (1/3)[(\Delta'_{\sigma\mathrm{Br}} - \Delta'_{\pi\mathrm{Br}}) + (\Delta'_{\sigma\mathrm{Cl}} - \Delta'_{\pi\mathrm{Cl}}) + (\Delta'_{\sigma\mathrm{F}} - \Delta'_{\pi\mathrm{F}})] \quad (87)\\ &= (1/3)[(14.8 - 2.5) + (16.6 - 3.5) + (22.2 - 6.8)]\mathrm{kK}\\ &= 13.6\ \mathrm{kK}.\end{aligned}$$

In Eq.(88) the value of the normalized parameter is given together with its square:

$$N_{a_{1\iota}}^{dd|g} = \sqrt{(6/5)}\,\Delta_{av} = 14.9\ \mathrm{kK};\ (N_{a_{1\iota}}^{dd|g})^2 = 222.0\ (\mathrm{kK})^2. \quad (88)$$

Since the operators $\hat{N}_{a_{1\iota}}^{dd|g}$, $\hat{N}_{\theta}^{dede|e}$, $\hat{N}_{\varepsilon}^{dede|e}$, $\hat{N}_{\theta}^{dt_2dt_2|e}$ and $\hat{N}_{\varepsilon}^{dt_2dt_2|e}$ are all normalized to unity within the *d* set, it is possible to make a statement analogous to that relating the low symmetry orthorhombic field component to the total field within the e(O) space in Section II.6.

In Eq.(89) the squared magnitude of the total field has been calculated as the sum of the squares of the parameters corresponding to its components:

$$(N^{dd|g}_{a_1\iota})^2 + (N^{dede|e}_{\theta})^2 + (N^{dede|e}_{\varepsilon})^2 + (N^{dt_2dt_2|e}_{\theta})^2 + (N^{dt_2dt_2|e}_{\varepsilon})^2 = 234.8\ (\mathrm{kK})^2. \quad (89)$$

This sum of squares is invariant to basis transformations in the d space and thus, in particular, to the choice of coordinate system among those of Figure 1. Furthermore, it is equal to the sum of the squares of the energy deviations of the five d functions from their barycenter. In Eq.(90) the magnitudes (in the squares) of the field components in the unprimed coordinate frame have been compared to the total field:

$$\begin{aligned}(N^{dd|g}_{a_1\iota})^2/234.8 &= 94.6\%,\\ (N^{dede|e}_{\theta})^2/234.8 &= 4.1\%,\\ (N^{dede|e}_{\varepsilon})^2/234.8 &= 0.2\%,\\ (N^{dt_2dt_2|e}_{\theta})^2/234.8 &= 1.1\%,\\ (N^{dt_2dt_2|e}_{\varepsilon})^2/234.8 &= 0.1\%.\end{aligned} \quad (90)$$

We see that the cubic field component is by far the most dominant. The tetragonal components are also seen to be much larger than the orthorhombic ones, and both of these component types are larger within the *de* subspace than within the dt_2 subspace.

The total splitting situation for *trans,trans,trans*-$[\mathrm{CrBr_2Cl_2F_2}]^{3-}$ is shown in Figure 3 for the preferred choice of tetragonal axis (Figure 1a). The cubic field component splits the d orbital set into a *de* set and a dt_2 set. The low symmetry splitting within an $e(O)$ level was thoroughly discussed in Section II.6. For the dt_2 level the effect of the tetragonal field component is to split it into an $e(D_4)$ and a $b_2(D_4)$ level, and the orthorhombic field component then further splits the $e(D_4)$ level into two states. In contrast to the basis $\{de\theta\ de\varepsilon\}$ the basis $\{dt_2\xi\ dt_2\eta\ dt_2\zeta\}$ is by symmetry [Eq.(4)] automatically an eigenbasis in an orthorhombic ligand field.

IV. CONCLUSION

The one-electron part of ligand field theory has been under discussion using the orthonormal operators formalism.[1] It is, however, one of the important features of ligand field theory that it includes consideration

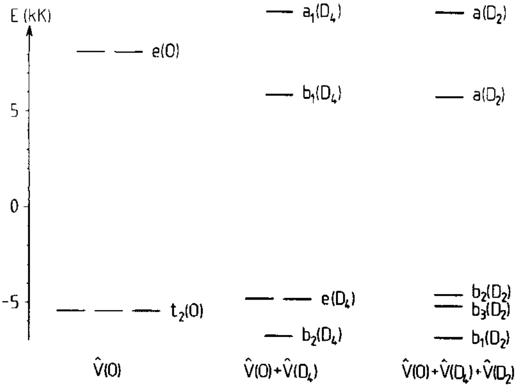

FIGURE 3 The ligand field situation for the orthorhombic complex *trans,trans,trans*-$[CrBr_2Cl_2F_2]^{3-}$ analyzed in the hierarchy $O \supset D_4 \supset D_2$. The tetragonal axis has been chosen along the F–Cr–F direction which is the preferred axis in both the *de* and the dt_2 subspace. The coordinate frame is thus that of Figure 1a. The choice of coordinate frame affects the positions of the energy levels in the column $\hat{V}(O) + \hat{V}(D_4)$, but not the two other columns because both the cubic field component $\hat{V}(O)$ and the total field are independent of the coordinate frame. The positions of the energy levels are calculated on the basis of the normalized parameters of Eq.(88), Table Ia and Table IIa. The effect of the cubic ligand field component is to split the *d* orbitals into two subsets: *de* and dt_2. These are again themselves split by the tetragonal field components of which there are two: one for the *de* subset (corresponding to the operator $\hat{N}_\theta^{dede|e}$) and one for the dt_2 subset (corresponding to the operator $\hat{N}_\theta^{dt_2dt_2|e}$). The splitting of the *e*(*O*) level by $\hat{N}_\theta^{dede|e}$ is what in Section II we called the tetragonal splitting *t*. In the total field of D_2 symmetry the θ and ε functions mix. This mixing causes the energy levels to repel. For our preferred choice of coordinate frame this orthorhombic effect is, as intended, very small. The orthorhombic ligand field component acting in the dt_2 subspace splits the $e(D_4)$ level into a $b_2(D_2)$ and a $b_3(D_2)$ level. Here in contrast to the situation in the *de* subspace, there is no mixing of basis functions because the three $t_2(O)$ functions transform according to different irreducible representations of D_2 [Eq.(4)].

of the interelectronic repulsion. This can of course be accounted for in the conventional way, even when the ligand field is handled by the use of orthonormal operators. Alternatively, a formalism using orthonormal operators can also be used for the interelectronic repulsion.

From the point of view of deriving repulsion parameters from experiment, atomic ligand field theory is the only feasible proposition since it is already the case in octahedral symmetry that nine independent repulsion parameters are allowed[4] in molecular ligand field theory. One way to try to circumvent this dilemma is to use *atomic ligand field theory,* whereby only two repulsion parameters are needed, and use a *molecular scheme* to describe the ligand field. This is what is invariably done when using the angular overlap model.[6,20,27]

The symmetry foundation of the orthonormal operators formalism makes it applicable beyond the one-electron case. For example, most of what has been said in Section II of this Comment about an $e(O)$ orbital set also applies to any ${}^{2S+1}E$ term of a polyelectron system in octahedral symmetry. One might say that the formalism can also be used *locally,* i.e., within one term of a composite term system. The values of the tetragonal and orthorhombic symmetry parameters for such a term will, however, be functions not only of the tetragonal and orthorhombic one-electron ligand field parameters but also of the cubic parameter and of the interelectronic repulsion parameters.

Formulating ligand field theory in terms of orthonormal operators provides an account of the number of symmetry-independent empirical parameters and definitions which specify the parameters with respect to *magnitude* as well as *sign.* These two properties were also characteristic of previous treatments.[3,6] The use of orthonormal[28] operators has the additional advantage that it allows a quantitative comparison of the splitting effects of the different terms which arise when the field is analyzed with respect to a symmetry hierarchy, for example, $O \supset D_4 \supset D_2$.

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6. C. E. Schäffer, in *Wave Mechanics—The First Fifty Years.* edited by W. C. Price, S. S. Chissick, and T. Ravensdale (Butterworths, London, 1973), Chap. 12.
7. The angular overlap model, when applied to linearly ligating ligands, associates with a given central-ion-to-ligand system, Cr–F say, a set of empirical parameters e_σ, e_π, and e_δ, and is then symmetry-based in the sense that the d orbitals associated with these energies are the $d\sigma$, $d\pi$, and $d\delta$ orbitals labeled by irreducible representations of the group $C_{\infty v}$ of Cr–F. Often e_δ is put equal to zero. This is equivalent to

introducing the new parameters $e'_\sigma = e_\sigma - e_\delta$ and $e'_\pi = e_\pi - e_\delta$. However, the subscripts of e'_σ and e'_π have thereby strictly speaking lost their symmetry meaning.

8. A ligand field model may also be based upon a reducible space. If, for example, an *s* set and a *d* set of functions are combined, it is based upon a reducible space $V^{s(R_3)} \oplus V^{d(R_3)}$.
9. What in this Comment has been called a "molecular scheme" was in Ref. 6 called an "orbital energy parametrization scheme" and in Ref. 5, a "ligand field parametrization scheme". The "atomic scheme" in this Comment was called the "spherical harmonic scheme" and the "crystal field parametrization scheme", respectively.
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17. The ligand field operator may further be looked upon as a *tensor* in the following way: as indicated by Eqs.(21)–(24), there is a natural isomorphic relationship between the four-dimensional operator space just mentioned and the direct or *tensor* product space $V^{e(O)} \otimes \overline{V^{e(O)}}$ where $\overline{V^{e(O)}}$ is the space spanned by the bras $\langle\theta|$ and $\langle\varepsilon|$, just as $V^{e(O)}$ is spanned by the kets $|\theta\rangle$ and $|\varepsilon\rangle$ ($\overline{V^{e(O)}}$ is sometimes said to be complex conjugate to $V^{e(O)}$). Thus, $\hat{W}$ is a mixed tensor of rank (or degree) 2 on a two-dimensional space ("mixed" because of the complex conjugation on just one factor in the above tensor product and "of rank 2" because there are two factors in the tensor product). It therefore has $2 \times 2 = 4$ components. The tensor components are the parameters $S_{\alpha\beta}$.
18. The reality restriction is in fact a somewhat delicate question from the point of view of what we have here called molecular ligand field theory (see Introduction and Section III.1). Atomic ligand field theory *may* be based on explicitly defined real functions within a Hilbert space where the Hamiltonian is composed of terms which are either just multiplication operators (potentials) or second-order differential operators (kinetic energy). In such a situation the Hamiltonian can only have real matrix elements in the basis chosen. The real basis functions generate real matrix representations when acted upon by the usual, explicitly defined rotation operators; thus, for example, the set $\{de\theta, de\varepsilon\}$ mentioned in connection with Eqs.(10)–(13) generates the real form of $e(O)$ defined by Eqs.(14) and (15). The property of the Hamiltonian having real matrix elements is then taken over in the molecular theory when using basis sets generating real matrix representations. Not all consequences of this have been satisfactorily investigated.
19. Operators transforming according to different irreducible representations can easily be seen to be mutually orthogonal with respect to the operator scalar product defined in Eq.(30). Thus, if $\hat{A}$ is an operator containing no totally symmetric terms, we have, since the identity operator $\hat{1}$ *is* totally symmetric, $0 = \langle\hat{1}|\hat{A}\rangle = \mathrm{Tr}(\hat{A})$, i.e., $\hat{A}$ is traceless.
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21. Determination of N^e_θ and N^e_ε using a purely symmetry-based nonadditive field model is a complicated problem in practice, but can in principle be carried out by performing a sufficient number of suitable experiments (for example, spectra of oriented crystals).

22. The factor of normalization depends on the dimension of the space, i.e., on the value of the effective spin S. As the matrix of $\hat{S}_z^2 - (1/3)\hat{S}^2$ is diagonal in the $|S\, M_S\rangle$ basis, the sum of its elements squared is given by the expression

$$n = \sum_{M_S=-S}^{S} [M_S^2 - (1/3)S(S+1)]^2,$$

where M_S is the eigenvalue of the operator $\hat{S}_z$. The factor of normalization for $(\sqrt{3}/2)\,[\hat{S}_x^2 - \hat{S}_y^2]$ is the same as for $\hat{S}_z^2 - \frac{1}{2}\hat{S}_y^2 - \frac{1}{2}\hat{S}_x^2$ owing to the relation between these two operators by an orthogonal transformation [cf. the relation of $de\theta = z^2 - \frac{1}{2}y^2 - \frac{1}{2}x^2$ and $de\varepsilon = (\sqrt{3}/2)(x^2 - y^2)$ in Eqs.(10) and (11)].

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24. C. P. Poole and H. A. Farach, J. Chem. Phys. **61**, 2220–2221 (1974).

25. For *trans,trans,trans*-$[CrBr_2Cl_2F_2]^{3-}$ the two preferred choices of tetragonal axis are the same, namely the F–Cr–F axis. The complex *trans,trans,trans*-$[CrBr_2F_2(NH_3)_2]^-$ may exemplify a different situation. In this complex the preferred tetragonal axis in the de subspace is Br–Cr–Br while it is F–Cr–F in the dt_2 subspace. This emerges from a calculation of the normalized parameters based on the AOM parameters of Ref. 20, Table IV.

26. The two operators appearing on the right-hand side of Eq.(82) are those of $a_1(O)$ symmetry in the molecular scheme. They can be transformed into those of $a_1(O)$ symmetry in the atomic scheme by using the orthogonal Racah lemma matrix $\{dd|a_1\}$ described in Ref. 1. Thereby the operator $N_{a_1\iota}^{dd|g}$, mentioned in the main text, arises together with the spherically symmetric operator $N_{a_1\iota}^{dd|s}$ which is unobservable within the d space. Similar transformations from the molecular scheme to the atomic one can be made for the operators of $e(O)$ symmetry using the Racah lemma matrix $\{dd|e\}$ for the θ component as well as the ε component.

27. C. E. Schäffer, Proc. R. Soc. London Ser. A **297**, 96–133 (1967).

28. There are other ways of normalizing operators than the one used here. For example, Racah's unit operators $\hat{U}_q^k$ and $\hat{V}_q^k$ are within an l space, for $0 \leqq k \leqq 2l$, normalized to $1/(2k+1)$ (see Ref. 11, p. 243). An alternative way of stating this is to note that our normalized operators $\hat{N}_q^k$ have reduced matrix elements of $\sqrt{2k+1}$. Using this fact and Eq. 61 of Ref. 29, one obtains the relationship $E_q^k = N_q^k \sqrt{2k+1}$ between the reduced ligand field parameters and the parameters of the orthonormal operators scheme. The relationship[6] between the parameters E_q^k and the parameters I_q^k, which correspond to the operators being multiplicative and expressed by spherical harmonics[3] normalized over the unit sphere to $4\pi/(2k+1)$, is $E_q^k = I_q^k \langle l \| \hat{C}_q^k \| l \rangle$, where $\langle l \| \hat{C}_q^k \| l \rangle$ is given by Eqs.(41) and (21) of Ref. 29.

29. S. E. Harnung and C. E. Schäffer, Struc. Bond. **12**, 257–295 (1972).