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Commentationes

The Non-Additive Ligand Field

An Operator and Parameter Symmetry-Analysis

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The semi-empirical ligand field is a perturbation operator whose consequences are taken to first order using a basis set of l functions. Since the basis spans an irreducible representation of the 3-dimensional rotation-inversion group R_{3i} it is useful to express the operator as a sum of components of irreducible tensor operators with respect to this group. If R_{3i} is reduced with respect to the molecular subgroup the electronic factor of each term in the sum must be totally symmetrical within this group. This choice of operator leads to the *crystal field parameterization* without implying an electrostatic model. Alternatively a shift operator within l space may be chosen as the essential part of the perturbation operator. This leads to the *ligand field parameterization.* Between the two parameterizations there exists a one to one relationship, whose coefficients are proportional to $3l$ symbols. This relationship is given together with a brief discussion of the reasons for the proposed parameterizations.

Key words: Ligand field parameterization – Crystal field parameterization

1. Introduction

The term ligand field leads conceptually to a model in which the role of the ligands is represented by a field i.e. a model in which the wave-functions associated with the ligands do not explicitly occur. This is not in disagreement with Orgel's original proposal [1] of using the name ligand field model, when conceptually it goes beyond the electrostatic model and includes such ideas as σ- and π-bonding. The reason for the lack of disagreement, which is buried in the principle of the perturbation method itself, is that the functions, with respect to order, are one step behind their corresponding energies. For the particular problem discussed here, d functions may, for example, be the zero order functions which are used to calculate the first order energies caused, at least partially, by metal-ligand bonding [2, 3].

When relative energies within a partially filled l shell are under consideration a semi-empirical model using a basis set of l orbitals is usually employed. This model will be reanalyzed in the present paper in terms of two symmetry parameterizations which are linearly related to each other. It will be discussed here without the assumption of the additivity of single ligand perturbation contributions. The discussion will be associated with an analysis of the form of the operators representing the ligand field i.e. an operator equivalent scheme [4].

* Dedicated to Hermann Hartmann who revived Bethe's crystal field model and was the first to realize its general applicability to describe d–d transitions.

2. Central Ion Functions and Projection Operators

Let $|\alpha lt\rangle$ be a real central ion function, normalized to unity. l is the azimuthal quantum number and t the particular component function within the set $|\alpha l\}$ containing $(2l+1)$ orthogonal functions whose further specification is given by α. The component functions will sometimes be denoted by u, v or w instead of t. The expression $|\alpha lu\rangle\langle\alpha lv|$ is a projection operator [5, Eq. (35)] which, for example, acts on a given function to its right by first multiplying this function by $\langle\alpha lv|$ and integrating over configuration space to give the fractional content – a number – of $\langle\alpha lv|$ in the given function, and then multiplying this number by $|\alpha lu\rangle$. In short, the projection operator takes the content of the normalized $|\alpha lv\rangle$ in the given function and transforms it into $|\alpha lu\rangle$. Such a projection operator is a shift operator within l space and for $u=v$ it is an idempotent which projects the content of $|\alpha lu\rangle$ out of the given function.

If the functions $|lt\rangle$ are written as solid harmonics in x, y, and z the operators $|lu\rangle\langle lv|$ may be written on the form $\mathfrak{M}_u^l\hat{\mathfrak{M}}_v^l$ where $\mathfrak{M}_u^l$ is a solid harmonic, normalized [5, Eq. (9)] to $4\pi/1\cdot 3\cdot\cdots(2l+1)$, and $\hat{\mathfrak{M}}_v^l$ is the differential operator obtained by the substitution $q\to\partial/\partial q$ $(q=x,y,z)$ in $\mathfrak{M}_v^l$. The direct product $|\alpha l\}\times\{\alpha l|$ represents the set of $(2l+1)^2$ projection operators which span the $(2l+1)^2$ dimensional reducible representation of the 3-dimensional rotation group which may be reduced into the direct sum

$$\mathrm{D}^{(l)}\times\mathrm{D}^{(l)}=\mathrm{D}^{(0)}+\mathrm{D}^{(1)}+\mathrm{D}^{(2)}+\cdots+\mathrm{D}^{(2l-1)}+\mathrm{D}^{(2l)} \tag{1}$$

where the terms with even superindices form the symmetrical part of the direct product [6, Eq. (28)]. $\mathrm{D}^{(2)}$ is the irreducible representation of dimension five spanned by the set $|\alpha d\}$. The sum $\Sigma_t|\alpha lt\rangle\langle\alpha lt|$ spans $\mathrm{D}^{(0)}$ and is the resolution of the identity within l space [5].

3. The Ligand Field Operators of the Most General Field Model, the Non-Additivity Model

The non-additive ligand field operator can be written as

$$\mathbf{V}=\sum_{t,w}\Delta_{tw}|\alpha lt\rangle\langle\alpha lw| \tag{2}$$

or, alternatively,

$$\bar{\mathbf{V}}=\sum_{t,w}\bar{\Delta}_{tw}|\alpha lt\rangle\langle\alpha lw| \tag{3}$$

where $\Delta_{tw}=\Delta_{wt}$ and $\bar{\Delta}_{tw}=\bar{\Delta}_{wt}$ are energy quantities transforming in such a way that $\mathbf{V}$ transforms as a scalar. The bar in Eq. (3) indicates that the number of parameters have been reduced by one relative to Eq. (2) by introducing the condition

$$\sum_t=\bar{\Delta}_{tt}=0 \tag{4}$$

where Eq. (4) expresses the barycenter or center of gravity rule. It is reasonable to require this rule be fulfilled because the semi-empirical ligand field model is only concerned with energy differences within the l shell. The parameter Δ_{tw} vanishes unless the operator $|\alpha lt\rangle\langle\alpha lw|$ contains terms which transform as the

totally symmetrical representation of the group G. The general matrix element has the form

$$\langle \alpha l u | \mathbf{V} | \alpha l v \rangle = \sum_{t,w} \Delta_{tw} \langle \alpha l u | \alpha l t \rangle \langle \alpha l w | \alpha l v \rangle = \Delta_{uv} . \tag{5}$$

We propose to call the parametrization associated with Eqs. (2)–(5) the *ligand field parametrization.*

When the system has no symmetry the number of independent parameters of the symmetric energy matrix, corresponding to Eq. (1) is [7]

$$[2l+1] + \tfrac{1}{2}[(2l+1)^2 - (2l+1)] = (2l+1)(l+1) . \tag{6}$$

There is an alternative way of enumerating the independent parameters and of parameterizing the ligand field in which the field is written as a sum of spherical irreducible tensor operators whose coefficients are energy quantities transforming also irreducibly so that $\mathbf{V}$ transforms as a scalar.

$$\mathbf{V} = \sum_{\substack{k,q \\ k \text{ even}}} \mathfrak{E}_q^k \mathfrak{U}_q^k \tag{7}$$

or, alternatively,

$$\bar{\mathbf{V}} = \sum_{\substack{k,q \\ k \text{ even}, k>0}} \mathfrak{E}_q^k \mathfrak{U}_q^k \tag{8}$$

where German gothic letters are used for irreducible tensorial quantities. The operators of Eqs. (7) and (8) are equal to those of Eqs. (2) and (3) and $\mathfrak{U}_q^k$ is the unit tensorial operator defined by its reduced elements [8, Eq. (67)]

$$\langle \alpha l \| \mathfrak{U}^k \| \alpha' l' \rangle = \delta(\alpha\alpha') \, \delta(ll') \, \delta(lkl') . \tag{9}$$

Where $\delta(lkl')$ expresses the triangular condition. In Eqs. (7) and (8) k must be even and maximally equal to $(2l)$ in order that $\mathfrak{U}_q^k$ shall span the symmetrical direct product of Eq. (1). The general matrix element of $\mathbf{V}$ of Eq. (7) is

$$\begin{aligned} \langle \alpha l u | \mathbf{V} | \alpha l v \rangle &= \sum_{\substack{k,q \\ k \text{ even}, 0 \leqq k \leqq 2l}} \langle \alpha l u | \mathfrak{E}_q^k \mathfrak{U}_q^k | \alpha l v \rangle \\ &= \sum_{\substack{k,q \\ k \text{ even}, 0 \leqq k \leqq 2l}} \mathfrak{E}_q^k \begin{pmatrix} l & k & l \\ u & q & v \end{pmatrix} . \end{aligned} \tag{10}$$

Again $\mathfrak{E}_q^k$ vanishes unless $\mathfrak{U}_q^k$ contains totally symmetrical terms under G which here and in the following is assumed to be simply reducible [6].

In Eq. (10) $\begin{pmatrix} l & k & l \\ u & q & v \end{pmatrix}$ are even $3l$ symbols corresponding to the Wigner $3j$ symbols and derivable from these [8]. Each one may also be derived as an integral [6] and this may be done by an integration by differentiation procedure [9, p. 108].

The general expression for the even $3l$ symbol is

$$\begin{pmatrix} l_1 & l_2 & l_3 \\ t_1 & t_2 & t_3 \end{pmatrix} = 2^{l_2}[(l_2+l_3-l_1)!\,(l_3+l_1-l_2)!\,(l_1+l_2-l_3)! \cdot (l_1+l_2+l_3+1)!]^{-\frac{1}{2}}\,[(l_2+l_3-l_1)/2]!\,[(l_1+l_2-l_3)/2]! \cdot \mathfrak{D}_{t_2}^{l_2} r^{l_3+l_1-l_2}[\mathfrak{H}_{t_3}^{l_3}\mathfrak{H}_{t_1}^{l_1}]\,. \tag{11}$$

Where $\mathfrak{H}_t^l$ is a solid harmonic expressed in the coordinates x, y, and z and normalized to $4\pi/(2l+1)$ and $\mathfrak{D}_t^l$ the corresponding differential operator obtained by the substitution $q \to \partial/\partial q$ $(q = x, y, z)$ into $\mathfrak{H}_t^l$. In Eq. (11) l_2 appears to play a unique role. However, the l's may be permuted in this formula.

At this stage we put in a remark which only has a peripheral relationship to the rest of this paper, but which nevertheless is necessary for understanding the discussion around Eq. (19). The $3l$ symbol of Eq. (11) may be called a 3Γ symbol of the 3-dimensional rotation group R_3 since l_1, l_2, and l_3 is a naming of three irreducible representations of R_3. 3Γ symbols have also been defined for the point groups [10] and redefined [6] with phases fixed by simple conventions relating them to corresponding $3l$ symbols through a lemma by Racah. For the pure rotation groups this *phase fixation* of the 3Γ symbols was established by defining standard spherical harmonic basis functions for the point groups using a "basic rule" [6, p. 210] and letting these standard functions define the sign of the 3Γ symbol through Eq. (11) and using a *positive* constant of renormalization to fulfill the condition

$$\sum_{\gamma_a \gamma_b \gamma_c} \begin{pmatrix} \Gamma_a & \Gamma_b & \Gamma_c \\ \gamma_a & \gamma_b & \gamma_c \end{pmatrix}^2 = 1\,. \tag{12}$$

This is the same as chosing the Racah lemma constant to be positive for the standard functions [6, p. 232].

The choice of standard functions thus defines the sign of the 3Γ symbols. This necessitates a distinction [6, p. 234] between standard functions and functions transforming in the standard way, i.e. transforming by identically the same matrices, because if non-standard functions, which do transform standard, had been used to define the 3Γ symbols, the same absolute values would have arisen, but, as a consequence of Racah's lemma, the signs would sometimes have been different.

We propose to call the parameterization associated with the Eqs. (7)–(10) *the crystal field parameterization* without thereby implying the electrostatic model. When the system has no symmetry all the terms in the expansion of Eq. (7) are nonvanishing and the number of independent parameters is

$$\sum_{k \text{ even},\, 0 \leq k \leq 2l} (2k+1) = (2l+1)(l+1) \tag{13}$$

i.e. the same number which results from counting the parameters in the ligand field parameterization of Eq. (6). A linear relationship between the A_{uv} parameters and the $\mathfrak{E}_q^k$ parameters is obtained by equating Eqs. (5) and (10)

$$A_{uv} = \sum_{k,q} \mathfrak{E}_q^k \begin{pmatrix} l & k & l \\ u & q & v \end{pmatrix} \tag{14}$$

and the reverse relationship by multiplying with $\begin{pmatrix} l & k' & l \\ u & q' & v \end{pmatrix}$ on either side of Eq. (14), and summing over u and v, using the orthogonality relations of the $3l$ symbols [8, Eq. (19a)]

$$\sum_{u,v} \Delta_{uv} \begin{pmatrix} l & k' & l \\ u & q' & v \end{pmatrix} = \sum_{k,q} \mathfrak{E}_q^k \sum_{u,v} \begin{pmatrix} l & k & l \\ u & q & v \end{pmatrix} \begin{pmatrix} l & k' & l \\ u & q' & v \end{pmatrix} = \frac{1}{2k'+1} \mathfrak{E}_{q'}^{k'} \tag{15}$$

or, changing back to unprimed indices

$$\mathfrak{E}_q^k = (2k+1) \sum_{u,v} \Delta_{uv} \begin{pmatrix} l & k & l \\ u & q & v \end{pmatrix}. \tag{16}$$

Associated with each of the parameters there is in both parameterization schemes a ligand field operator. The operator corresponding to Δ_{uv} is

$$\Delta_{uv}[|\alpha l u\rangle \langle \alpha l v| + |\alpha l v\rangle \langle \alpha l u|] \tag{17}$$

and that corresponding to $\mathfrak{E}_q^k$ is

$$\frac{1}{\sqrt{2k+1}} \mathfrak{E}_q^k [|\alpha l\} \times \{\alpha l|]_q^k = \mathfrak{E}_q^k \sum_{u,v} \begin{pmatrix} l & k & l \\ u & q & v \end{pmatrix} |\alpha l u\rangle \langle \alpha l v|. \tag{18}$$

4. Discussion

We have seen how the most general first order perturbation ligand field model, the non-additivity model, can be parameterized in two different ways. One of these may be said to be essentially founded upon the *basis functions* and called the *ligand field parameterization* and the other to be founded upon the *perturbation operator* and called the *crystal field parameterization.* There exists a one to one relationship between the two parameter sets and the coefficients in these relationships are proportional to the $3l$ symbols. It is parameters of the ligand field parameterization which are the chemically interesting ones because of their direct connection with the orbital energy concept of the model. The parameters of the crystal field parameterization may, however, when translated into the additivity model, reveal certain symmetry aspects of the model [11].

The two parameterization schemes and their relationships have been discussed previously for special examples [11] when the ligand field parameterization was called the orbital energy parameterization and the crystal field parameterization called the spherical harmonic parameterization.

The two parameterization schemes have also been demonstrated for the *additive ligand field* [9, 11], in which case the *ligand field parameterization* for linearly ligating ligands is identical to the e_σ, e_π, e_δ parameterization of the Angular Overlap Model when this is taken as a semi-empirical model.

The parameters $\mathfrak{E}_q^k$ of the crystal field parameterization of Eq. (10) were written E_q^k in Ref. [8] and called "reduced ligand field parameters" even though

they contain q. The reason for this choice of parameters rather than the reduced matrix elements of the molecular symmetry group G is rather trivial theoretically as can be seen by reference to the discussion around Eq. (12).

If the components of the irreducible representations of the 3-dimensional rotation-inversion group R_{3i} are chosen so as to transform irreducibly in a standard way within the sub-group G, i.e. if R_{3i} is reduced with respect to the group G, $\mathfrak{U}_q^k$ must transform as the unit representation Γ_1 of G and the general matrix element of $\mathbf{V}$ [compare Eq. (10)] has the form

$$\begin{aligned}
&\left\langle \alpha l c_a \Gamma_a \gamma_a \middle| \sum_{k c_1 \Gamma_1 \gamma_1} \mathfrak{E}^k_{c_1 \Gamma_1 \gamma_1} \mathfrak{U}^k_{c_1 \Gamma_1 \gamma_1} | \alpha l c_b \Gamma_b \gamma_b \right\rangle \\
&= \sum_{k c_1 \Gamma_1 \gamma_1} \mathfrak{E}^k_{c_1 \Gamma_1 \gamma_1} \begin{pmatrix} l & k & l \\ c_a \Gamma_a \gamma_a & c_1 \Gamma_1 \gamma_1 & c_b \Gamma_b \gamma_b \end{pmatrix} \\
&= \sum_{k c_1 \Gamma_1 \gamma_1} \mathfrak{E}^k_{c_1 \Gamma_1 \gamma_1} \langle l c_a \Gamma_a \| \mathfrak{U}^k_{c_1 \Gamma_1} \| l c_b \Gamma_b \rangle \begin{pmatrix} \Gamma_a & \Gamma_1 & \Gamma_b \\ \gamma_a & \gamma_1 & \gamma_b \end{pmatrix} \qquad (19) \\
&= \sum_{k c_1 \Gamma_1 \gamma_1} \mathfrak{E}^k_{c_1 \Gamma_1 \gamma_1} \langle l c_a \Gamma_a \| \mathfrak{U}^k_{c_1 \Gamma_1} \| l c_b \Gamma_b \rangle \frac{1}{\sqrt{[\Gamma_a]}} \delta(\Gamma_a \Gamma_b) \delta(\gamma_a \gamma_b) \\
&= \Delta_{(c_a \Gamma_a \gamma_a)(c_b \Gamma_b \gamma_b)} \delta(\Gamma_a \Gamma_b) \delta(\gamma_a \gamma_b) .
\end{aligned}$$

In Eqs. (19) and (20) irreducible representations written in square parenthesis represent their own dimension, the c labels refer to the situation when the same irreducible representation Γ arises more than once within l or k, and the symbols α, l, and k have the same meanings as in Eq. (10).

In Eq. (19) the Eq. (10) has first been used and the same conditions on k apply in the two equations. Then the Wigner-Eckart theorem for the group G has been used, resulting in the expression $\langle l c_a \Gamma_a \| \mathfrak{U}^k_{c_1 \Gamma_1} \| l c_b \Gamma_b \rangle$ which by Eq. (19) is a definition of the matrix element of the spherical irreducible unit operator reduced with respect to the components γ of the irreducible representations Γ of the group G [6, p. 203]. We know from the discussion around the Eq. (12) that this does not depend on α. It may be expressed as

$$\langle l c_a \Gamma_a \| \mathfrak{U}^k_{c_1 \Gamma_1} \| l c_b \Gamma_b \rangle = \sqrt{\frac{[\Gamma_a]}{[l]}} (k c_1 \Gamma_1 l c_b \Gamma_b | l c_a \Gamma_a) \qquad (20)$$

where the phase factor is plus one, because the $3l$ as well as the 3Γ symbols are even, and where $(k c_1 \Gamma_1 \; l c_b \Gamma_b | l c_a \Gamma_a)$ is a Racah lemma constant [6, Eq. (61)]. When the components u, v, and q of Eq. (10) are chosen as

$$u = c_a \Gamma_a \gamma_a ; \qquad v = c_b \Gamma_b \gamma_b, \quad \text{and} \quad q = c_1 \Gamma_1 \gamma_1 \qquad (22)$$

then the parameter $\Delta_{(c_a \Gamma_a \gamma_a)(c_b \Gamma_b \gamma_b)} \delta(\Gamma_a \Gamma_b) \delta(\gamma_a \gamma_b)$ in the last expression of Eq. (19) is identical to Δ_{uv} of Eq. (5).

In conclusion we note regarding Eq. (19) that the expression

$$\mathfrak{E}^k_{c_1 \Gamma_1 \gamma_1} \langle l c_a \Gamma_a \| \mathfrak{U}^k_{c_1 \Gamma_1} \| l c_b \Gamma_b \rangle = \mathfrak{E}^k_{c_1 \Gamma_1} \langle l c_a \Gamma_a \| \mathfrak{U}^k_{c_1 \Gamma_1} \| l c_b \Gamma_b \rangle \qquad (23)$$

which is the expression for a reduced matrix element within G, could equally well as $\mathfrak{E}^k_{c_1 \Gamma_1 \gamma_1}$ have been chosen as one of the independent ligand field parameters.

We have seen that our choice of ligand field parameters $\mathfrak{C}_q^k$ in the crystal field parameterization is a matter of convenience rather than necessity. On the other hand it has advantages of which we shall mention two. 1) Symmetry adaptation of $|lt\}$ is unnecessary which may be a useful freedom to have [12]. 2) $\mathfrak{U}_q^k$ may be symmetry adapted to a hierarchy of groups ordered according to decreasing symmetry. Thereby the barycenter rule may be made to apply at each stage [12–14] and, for example, such a concept as the cubic field becomes defined even in a tetragonal molecular system [12, 11].

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References

1. Orgel, L. E.: An introduction to transition-metal chemistry, p. 38. London: Methuen. New York: Wiley 1960
2. Schäffer, C. E., Jørgensen, C. K.: Mol. Phys. **9**, 401 (1965)
3. Schäffer, C. E.: Struct. Bonding **5**, 68 (1968)
4. Griffith, J. S.: J. Chem. Phys. **41**, 576 (1964)
5. Schäffer, C. E.: Intern. J. Quantum Chem. **5**, 379 (1971)
6. Harnung, S. E., Schäffer, C. E.: Struct. Bonding **12**, 201 (1972)
7. Griffith, J. S.: The theory of the transition-metal ions, p. 199. Cambridge: University Press 1961
8. Harnung, S. E., Schäffer, C. E.: Struct. Bonding **12**, 257 (1972)
9. Schäffer, C. E.: Struct. Bonding **14**, 69 (1973)
10. Griffith, J. S.: The irreducible tensor method for molecular symmetry groups. Prentice-Hall 1962
11. Schäffer, C. E.: in: Price, W. C., Chissick, S. S., Ravensdale, T. (Eds.): Wave mechanics – the first fifty years, Chapter XIV. London: Butterworths 1973
12. Schäffer, C. E.: Proc. Roy. Soc. London. A **297**, 96 (1967)
13. Kibler, M.: Intern. J. Quantum Chem. **3**, 795 (1969)
14. Soliverez, C. E.: Intern. J. Quantum Chem. **7**, 1139 (1973)

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