Coupling Schemes for Cubic Complexes

J. R. Perumareddi
Department of Chemistry, Florida Atlantic University, Boca Raton, Florida 33431

Z. Naturforsch. **40a,** 1133–1139 (1985); received July 16, 1985

In the presence of spin-orbit interaction, six coupling schemes are possible for cubic complexes. Five of these coupling schemes have been worked out although only three, called strong-field, weak-field and (j, j) coupling schemes, are well-known. We show the derivation of the sixth coupling scheme and review briefly the significance and utility of the six coupling schemes.

Introduction

When spin-orbit interaction is included, cubic complexes of d^n, $n = 2$ to 8, electronic configurations are characterized by three perturbations, the cubic ligand field potential $\mathscr{H}_1 = V_C^{LF}$, the interelectronic or Coulombic or electrostatic repulsion $\mathscr{H}_e = \sum_{j>i} e^2/r_{ij}$, and the spin-orbit interaction $\mathscr{H}_s = \sum_i \zeta(r_i)\, \boldsymbol{l}_i \boldsymbol{s}_i$. The ideal situation of obtaining energy levels is in a basis which diagonalizes all three perturbations simultaneously. Unfortunately it is not possible to find a basis which diagonalizes more than one perturbation *, hence the necessity for various coupling schemes. Starting with a basis in which one of the three perturbations is diagonal, two different coupling schemes should arise depending upon the sequence of the other two perturbations that will be carried out on the initial basis set. Thus a total of six coupling schemes, two for each case of the diagonalized perturbation, should be possible for cubic complexes. However, only one in each case of the diagonalized perturbation, known as strong-field, weak-field and (j, j) coupling schemes, which diagonalize cubic ligand field, electron repulsions and spin-orbit interaction, respectively, are well-known [1–16]. Two of the remaining three schemes have been worked out for d^2, d^8 electronic configurations [2, 17]. It is the purpose of this article to show the derivation of the sixth coupling scheme and review the significance and utility of all the six coupling schemes.

Naming of the Coupling Schemes

First we shall retain the names strong-field and weak-field coupling schemes for cases which diagonalize ligand field potential and inter-electronic repulsion, respectively. The third case of the coupling schemes that diagonalize spin-orbit interaction will be named, however, simply j. The two coupling schemes of each case are then called I and II. Thus, we have strong-field I and strong-field II, weak-field I and weak-field II, and j-I and j-II coupling schemes for cubic symmetries.

Using in general x^C (X^C for many electron) and γ^C (Γ^C for many electron) for the cubic representations without and with spin-orbit interaction, respectively, the coupling schemes can be given a representation notation*. The names of the coupling schemes and their representation notation along with the sequence of perturbations are summarized in Table 1. The strong-field I, weak-field II and j-II coupling schemes are the ones that are well-known. The strong-field I scheme originated with the development of the ligand field theory for many electron systems in the limit of zero spin-orbit interaction [18, 19]. Both the weak-field II and j-II coupling schemes, also known as the rare-earth and jj-coupling schemes, respectively, include ligand

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* Sometimes it is not possible to find a basis which diagonalizes even one perturbation completely. Thus, even though the interelectronic repulsion perturbation is completely diagonal for $d^{2,8}$ configuration it is not so for other configurations. We shall, however, in this report refer to the interelectronic repulsion perturbation as being diagonalized when it is applied first.

Reprint requests to Prof. J. R. Perumareddi, Department of Chemistry, Florida Atlantic University, Boca Raton/Florida 33431, USA.

* x^C represents either e_g or t_{2g} whereas X^C represents A_{1g}, A_{2g}, E_g, T_{1g} and T_{2g}. γ^C represents γ_j, $j = 7, 8$ whereas Γ^C represents Γ_j, $j = 1$ through 8.

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Table 1. Coupling schemes for cubic complexes.

Sequence of perturbations	Representation of coupling scheme		Name of coupling scheme
	Full form	Short form	
$\mathscr{H}_1, \mathscr{H}_e, \mathscr{H}_s$	$\{x^C x^C X^C \Gamma_j^C\}$	$\{x^C x^C\}$	Strong-field I
$\mathscr{H}_1, \mathscr{H}_s, \mathscr{H}_e$	$\{x^C \gamma^C \gamma^C \Gamma_j^C\}$	$\{x^C \gamma^C \gamma^C\}$	Strong-field II
$\mathscr{H}_e, \mathscr{H}_1, \mathscr{H}_s$	$\{SLX^C \Gamma_j^C\}$	$\{SLX^C\}$	Weak-field I
$\mathscr{H}_e, \mathscr{H}_s, \mathscr{H}_1$	$\{SLJ \Gamma_j^C\}$	$\{SLJ\}$	Weak-field II
$\mathscr{H}_s, \mathscr{H}_1, \mathscr{H}_e$	$\{j \gamma^C \gamma^C \Gamma_j^C\}$	$\{j \gamma^C \gamma^C\}$	j-I
$\mathscr{H}_s, \mathscr{H}_e, \mathscr{H}_1$	$\{jjJ \Gamma_j^C\}$	$\{jj\}$	j-II

field perturbation last on a many electron atomic problem which has already been worked out in considerable detail [20–25] before the advent of ligand field theory. The other two schemes that have been worked out are the strong-field II[2] and weak-field I[17] and that too for $d^{2,8}$ configurations only. To our knowledge, the j-I coupling scheme has not been carried out for any configuration. We will show the derivation of this scheme also.

Perturbations and Basis Functions

First perturbation and eigenfunctions

Since it is possible to find a basis set that diagonalizes the first perturbation, the basis functions of the first perturbation are also eigenfunctions.

The bases for the strong-field schemes are the well-known e_g and t_{2g} representations which we denote by x^C. They are also the cubic spherical harmonics (CSH) [26] of degree 2. Cubic spherical harmonics are the linear combinations of spherical harmonics of various orders of a given degree, $Y_l^{m_l}$ that form the bases for the representations of the cubic groups. These are given by Ballhausen [14], Griffith [15] and others.

It should be remembered that any state of orbital angular momentum L with its components M_L or of total angular momentum J with its components M_J will behave symmetry wise in the same fashion as a spherical harmonic $Y_l^{m_l}$, and hence, that in a ligand field a state of angular momentum L or total angular momentum J will split exactly as does the spherical harmonic $Y_l^{m_l}$. It should also be noted that whereas l and L can only be integers, J can be integer or half-integer. Thus, Griffith lists the CSH as $|JM\rangle$ and includes half-integral J values also. The linear combinations listed by these authors for T_1 and T_2 representations are imaginary. The imaginary combinations, however, can be combined further resulting in real functions. These CSH will become useful in other perturbations as will be described later.

The functions that diagonalize the interelectronic repulsion perturbation of the weak-field schemes are the $|SLM_S M_L\rangle$ functions which are obtained as the linear combinations of the single electron determinants or the microstates. The derivation of the eigenfunctions of the so called multiplets characterized by S and L involves the use of either the step-up and step-down operators also known as ladder operators (LO) or projection operators on the determinantal functions [20, 21]. For instance the eigenfunctions of the $d^{2,8}$ configurations are the $|SLM_S M_L\rangle$ functions of the multiplets ^3F, ^3P, ^1G, ^1D and ^1S.

The eigenfunctions of the j-coupling schemes that diagonalize the spin-orbit interaction perturbation are the $|j m_j\rangle$ functions formed from the one-electron $|l m_l s m_s\rangle$. Specifically for d-electrons, since $l=2$ with $m_l=\pm 2, \pm 1, 0$ and $s=1/2$ with $m_s=\pm 1/2$, we have possible j values 5/2 and 3/2, with corresponding m_j components of $\pm$ 5/2, $\pm$ 3/2, $\pm$ 1/2 and $\pm$ 3/2, $\pm$ 1/2, respectively. The $|j m_j\rangle$ eigenfunctions can be obtained by using ladder operators as follows. Starting with the (2^+) function which is $|5/2, 5/2\rangle$ all other functions of $j=5/2$ can be obtained by using ladder operators on $|5/2, 5/2\rangle$. The $|3/2, 3/2\rangle$ function is formed by orthogonality (with arbitrary phase) to the $|5/2, 3/2\rangle$ function. Application of ladder operators on $|5/2, 3/2\rangle$ will generate all other functions of $j=3/2$.

It should be realized that the formation of $|j m_j\rangle$ from $|l m_l s m_s\rangle$ functions represents coupling of two angular momenta l and s to obtain a third angular momentum j. This problem of adding angular momenta has been treated in general by Wigner, Racah and others. Thus, when two angular momenta j_1 and j_2 are added to give a resultant third angular momentum j, the coefficients in the expansion for $|j_1 j_2 j m\rangle$ in terms of linear combinations of

Table 2. First (or diagonalized) perturbation and basis functions.

Coupling scheme	First (diagonalized) perturbation	Basis functions (or eigenfunctions)	Derivation of basis functions
Strong-field I & II	$\mathscr{H}_{\mathrm{l}}$	x^{C}	CSH of $l=2$, $\langle l m_l \| x^{\mathrm{C}}\rangle$
Weak-field I & II	$\mathscr{H}_{\mathrm{e}}$	$\|SLM_S M_L\rangle$	LO on $\|m_{l_i} m_{s_i}\rangle$
j-I & J-II	$\mathscr{H}_{\mathrm{s}}$	$\|j m_j\rangle$	LO on $\|l m_l s m_s\rangle$ or WC, $\langle s l \| j m_j\rangle$

$|j_1 j_2 m_1 m_2\rangle$ are known as the Wigner coefficients (WC) [27] or Clebsch-Gordan or Vector coupling coefficients and are denoted by $\langle j_1 j_2 m_1 m_2 | j_1 j_2 j m\rangle$ or by one of ten different other notations [28]. Tables [16, 20, 21, 29] have been constructed to show the result of adding any, j_1 to $j_2=0$, 1/2, 1, 3/2, 2, 5/2... so that the coefficients can be conveniently evaluated. These vector coupling coefficients are related to Wigner's 3-j symbol the numerical values of which have also been tabulated [30]. The WC will become useful in other perturbations also. Table 2 summarises the first perturbation and the derivation of eigenfunctions.

Second and third perturbations and the corresponding eigenvectors

The second perturbation distinguishes each of the major coupling schemes into I and II. Although the perturbation operator cannot be diagonalized by any set of bases, the eigenvectors that are formed achieve considerable block diagonalization.

Strong-field I coupling scheme employs $\mathscr{H}_{\mathrm{e}}$ and $\mathscr{H}_{\mathrm{s}}$ as the second and third perturbations, respectively. The eigenvectors for the second perturbation are the appropriate bases for the irreducible representations of the cubic point groups, ${}^{(2S+1)}X_j^{\mathrm{C}}$ where $(2S+1)$ is the spin multiplicity and $X_j = \mathrm{A}_1$, A_2, E, T_1 and T_2. The formation of these ${}^{(2S+1)}X_j^{\mathrm{C}}$ basis vectors from x^{C}, x^{C} (two one-electron), or x^{C}, X^{C} (one-electron, many electron) or X^{C} and X^{C} (many electron, many electron) involves derivation [15, 16, 31, 2] and use of cubic coupling coefficients (CCC) which are also known as Clebsch-Gordan coefficients tabulated by Griffith [15] and others [16]. In order to form the eigenvectors for the third perturbation $\mathscr{H}_{\mathrm{s}}$ in this scheme, we again make use of the CCC, coupling the orbital representations X_j^{C} with the representations of the spin functions of spin-multiplicity $(2S+1)$. Recall that the spin functions S transform just as the orbital functions L in a ligand field of given symmetry. Thus the singlet spin function transforms as A_1, doublet as Γ_6, triplet as T_1, quartet as Γ_8, quintet as E and T_2, sextet as Γ_7 and Γ_8, and so on. Recall also that the bases for these spin representations are given by the CSH.

If $\mathscr{H}_{\mathrm{s}}$ precedes $\mathscr{H}_{\mathrm{e}}$, we have strong-field II coupling scheme. The eigenvectors for spin-orbit perturbation are obtained by coupling the doublet spin of the single electron, i.e., γ_6, with the orbital $\mathrm{e_g}$ representation resulting in $\gamma_8^{\mathrm{C}}(\mathrm{e_g})$ and with $\mathrm{t_{2g}}$ representation resulting in $\gamma_7^{\mathrm{C}}(\mathrm{t_{2g}})$ and $\gamma_8^{\mathrm{C}}(\mathrm{t_{2g}})$. The CCC that are needed here are between the double valued representation γ_6 and the single valued representations $\mathrm{e_g}$ and $\mathrm{t_{2g}}$. In order to carry out the $\mathscr{H}_{\mathrm{e}}$ perturbation to include electron repulsions, again CCC are used in the formation of eigenvectors. It should be noted that in the case of this coupling scheme (and also in j-I) there is a need for coupling coefficients among the double valued representations of the cubic group. We have derived these coefficients and listed them in Table 3.

The weak-field I and II coupling schemes employ $\mathscr{H}_{\mathrm{l}}$, $\mathscr{H}_{\mathrm{s}}$ and $\mathscr{H}_{\mathrm{s}}$, $\mathscr{H}_{\mathrm{l}}$ sequences of perturbations, respectively. In the weak-field I scheme, the $|SLM_S M_L\rangle$ functions with $M_s = S$ are first combined by using CSH to form the bases for the irreducible representations ${}^{(2S+1)}X_j^{\mathrm{C}}$ which are then transformed to Γ_j^{C} with the use of CCC [17]. In the weak-field II scheme, the $|SLM_S M_L\rangle$ functions are first transformed into $|JM_J\rangle$ functions by the use of WC and the $|JM_J\rangle$ functions are then converted to Γ_j^{C} using CSH.

The $\mathscr{H}_{\mathrm{l}}$, $\mathscr{H}_{\mathrm{e}}$ and $\mathscr{H}_{\mathrm{e}}$, $\mathscr{H}_{\mathrm{l}}$ sequences of perturbations, respectively, result in j-I and j-II coupling schemes. In the j-I scheme, the ligand field splits the $j=5/2$ level into $\gamma_7^{\mathrm{C}}({}^2\mathrm{D}_{5/2})$ and $\gamma_8^{\mathrm{C}}({}^2\mathrm{D}_{5/2})$ and it simply transforms the $j=3/2$ level as $\gamma_8^{\mathrm{C}}({}^2\mathrm{D}_{3/2})$ representation with an off-diagonal element of ligand field energy connecting the two γ_8^{C} levels. The bases for these representations are the CSH of $|j m_j\rangle$ of degrees 5/2 and 3/2. Including electrostatic energy among the γ_j^{C} levels involves the use of CCC to form the final Γ_j^{C} representations. In the j-II scheme the $|JM_J\rangle$ functions are formed first from the single-electron $|j m_j\rangle$ with the use of WC to

Table 3. Cubic coupling (or Clebsch-Gordan) coefficients, $\langle \Gamma_1 \gamma_1 \Gamma_2 \gamma_2 | \Gamma \gamma \rangle$ for double group representations in quadrate basis.

$\gamma_6 \times \gamma_6$

γ_1	γ_2 \ γ	Γ_1	Γ_4		
			a	b	c
a	a	0	0	$-i$	-1
	b	1	1	0	0
b	a	-1	1	0	0
	b	0	0	$-i$	1

× $1/\sqrt{2}$

$\gamma_7 \times \gamma_7$

γ_1	γ_2 \ γ	Γ_1	Γ_4		
			a	b	c
a	a	0	0	$-i$	-1
	b	1	1	0	0
b	a	-1	1	0	0
	b	0	0	$-i$	1

× $1/\sqrt{2}$

$\gamma_6 \times \gamma_7$

γ_1	γ_2 \ γ	Γ_2	Γ_5		
			a	b	c
a	a	0	0	$-i$	-1
	b	1	1	0	0
b	a	-1	1	0	0
	b	0	0	$-i$	1

× $1/\sqrt{2}$

$\gamma_7 \times \gamma_8$

γ_1	γ_2 \ γ	Γ_3		Γ_4			Γ_5		
		a	b	a	b	c	a	b	c
a	a	0	0	0	i	1	0	$i\sqrt{3}$	$-\sqrt{3}$
	b	2	0	2	0	0	0	0	0
	c	0	0	0	$-i\sqrt{3}$	$\sqrt{3}$	0	i	1
	d	0	-2	0	0	0	2	0	0
b	a	-2	0	2	0	0	0	0	0
	b	0	0	0	i	-1	0	$i\sqrt{3}$	$\sqrt{3}$
	c	0	2	0	0	0	2	0	0
	d	0	0	0	$-i\sqrt{3}$	$-\sqrt{3}$	0	i	-1

× $1/\sqrt{8}$

$\gamma_6 \times \gamma_8$

γ_1	γ_2 \ γ	Γ_3		Γ_4			Γ_5		
		a	b	a	b	c	a	b	c
a	a	0	0	0	$i\sqrt{3}$	$-\sqrt{3}$	0	i	1
	b	0	2	0	0	0	2	0	0
	c	0	0	0	i	1	0	$-i\sqrt{3}$	$\sqrt{3}$
	d	2	0	2	0	0	0	0	0
b	a	0	-2	0	0	0	2	0	0
	b	0	0	0	$i\sqrt{3}$	$\sqrt{3}$	0	i	-1
	c	-2	0	2	0	0	0	0	0
	d	0	0	0	i	-1	0	$-i\sqrt{3}$	$-\sqrt{3}$

× $1/\sqrt{8}$

$\gamma_8 \times \gamma_8$

γ_1	γ_2 \ γ	Γ_1	Γ_2	Γ_3		Γ_4^1			Γ_4^2			Γ_5^1			Γ_5^2		
				a	b	a	b	c	a	b	c	a	b	c	a	b	c
a	a	0	0	0	0	0	$-i2$	-2	0	i	1	0	0	0	0	$-i\sqrt{3}$	$\sqrt{3}$
	b	2	0	2	0	2	0	0	2	0	0	0	0	0	0	0	0
	c	0	0	0	0	0	0	0	0	$-\sqrt{3}$	$-\sqrt{3}$	0	$-i2$	-2	0	i	1
	d	0	2	0	2	0	0	0	0	0	0	2	0	0	2	0	0
b	a	-2	0	-2	0	2	0	0	2	0	0	0	0	0	0	0	0
	b	0	0	0	0	0	$-i2$	2	0	i	-1	0	0	0	0	$-i\sqrt{3}$	$-\sqrt{3}$
	c	0	-2	0	-2	0	0	0	0	0	0	2	0	0	2	0	0
	d	0	0	0	0	0	0	0	0	$i\sqrt{3}$	$\sqrt{3}$	0	$-i2$	2	0	i	-1
c	a	0	0	0	0	0	0	0	0	$i\sqrt{3}$	$-\sqrt{3}$	0	$i2$	2	0	i	1
	b	0	-2	0	2	0	0	0	0	0	0	-2	0	0	2	0	0
	c	0	0	0	0	0	$-i2$	-2	0	$-i$	-1	0	0	0	0	$i\sqrt{3}$	$-\sqrt{3}$
	d	2	0	-2	0	2	0	0	-2	0	0	0	0	0	0	0	0
d	a	0	2	0	-2	0	0	0	0	0	0	-2	0	0	2	0	0
	b	0	0	0	0	0	0	0	0	$i\sqrt{3}$	$\sqrt{3}$	0	$i2$	-2	0	i	-1
	c	-2	0	2	0	2	0	0	-2	0	0	0	0	0	0	0	0
	d	0	0	0	0	0	$-i2$	2	0	$-i$	1	0	0	0	0	$i\sqrt{3}$	$\sqrt{3}$

× 1/4

Table 4. Second perturbation and basis functions.

Coupling scheme	Second perturbation	Basis functions (or eigenvectors)	Derivation of basis functions
Strong-field I	$\mathscr{H}_{\mathrm{e}}$	$^{(2S+1)}X_j^{\mathrm{C}}$	CCC, $\langle x^{\mathrm{C}} x^{\mathrm{C}} \mid X^{\mathrm{C}} \rangle$
Strong-field II	$\mathscr{H}_{\mathrm{s}}$	γ_j^{C}	CCC, $^*\langle \gamma_{\mathrm{s}}^{\mathrm{C}} x^{\mathrm{C}} \mid \gamma^{\mathrm{C}} \rangle$
Weak-field I	$\mathscr{H}_{\mathrm{l}}$	$^{(2S+1)}X_j^{\mathrm{C}}$	CSH, $\langle LM_L \mid X_L^{\mathrm{C}} \rangle$
Weak-field II	$\mathscr{H}_{\mathrm{s}}$	$\mid JM_J \rangle$	WC, $\langle SL \mid JM_J \rangle$
j-I	$\mathscr{H}_{\mathrm{l}}$	γ_j^{C}	CSH, $\langle j m_j \mid \gamma^{\mathrm{C}} \rangle$
j-II	$\mathscr{H}_{\mathrm{e}}$	$\mid JM_j \rangle$	WC, $\langle jj \mid JM_J \rangle$

$^*\ \gamma_{\mathrm{s}}^{\mathrm{C}} \equiv \gamma_6^{\mathrm{C}}$

Table 5. Third perturbation and basis functions.

Coupling scheme	Third perturbation	Basis functions (or eigenvectors)	Derivation of basis functions
Strong-field I	$\mathscr{H}_{\mathrm{s}}$	Γ_j^{C}	CCC, $^*\langle X^{\mathrm{C}} X_S^{\mathrm{C}} \mid \Gamma_j^{\mathrm{C}} \rangle$
Strong-field II	$\mathscr{H}_{\mathrm{e}}$	Γ_j^{C}	CCC, $\langle \gamma^{\mathrm{C}} \gamma^{\mathrm{C}} \mid \Gamma_j^{\mathrm{C}} \rangle$
Weak-field I	$\mathscr{H}_{\mathrm{s}}$	Γ_j^{C}	CCC, $^*\langle X_L^{\mathrm{C}} X_S^{\mathrm{C}} \mid \Gamma_j^{\mathrm{C}} \rangle$
Weak-field II	$\mathscr{H}_{\mathrm{l}}$	Γ_j^{C}	CSH, $\langle JM_J \mid \Gamma_j^{\mathrm{C}} \rangle$
j-I	$\mathscr{H}_{\mathrm{e}}$	Γ_j^{C}	CCC, $\langle \gamma^{\mathrm{C}} \gamma^{\mathrm{C}} \mid \Gamma_j^{\mathrm{C}} \rangle$
j-II	$\mathscr{H}_{\mathrm{l}}$	Γ_j^{C}	CSH, $\langle JM_J \mid \Gamma_j^{\mathrm{C}} \rangle$

$^*\ X_S^{\mathrm{C}}$ or Γ_S^{C}

take into account the electrostatic energy, and then the $\mid JM_j \rangle$ functions are transformed into Γ_j^{C} eigenvectors by using CSH to take into account the ligand field perturbation. Tables 4 and 5 summarize the second and third perturbations and the required eigenvectors and their derivation.

Parameters and Energy Matrices

It is well-known that the cubic ligand field perturbation gives rise to the Dq parameter, the electron repulsion perturbation to the A, B, C parameters and the spin-orbit interaction to the one-electron ζ parameter. Thus, the Dq parameter is diagonalized in the strong-field schemes, the A, B, C parameters in the weak-field schemes and the ζ parameter in the j-schemes.

We present the j-I energy matrices for d^2 configuration in Table 6. These matrices have been derived here for the first time. The strong-field I and weak-field II matrices were derived by Liehr and Ballhausen [1]. The strong-field II and j-II matrices were derived by the author [2, *]. The weak-field I matrices were derived by Perumareddi and Collins [17].

Review of the Coupling Schemes

We may always use any coupling scheme for any ion, provided we are prepared to take into account complete configuration interaction, since any coupling scheme will give the same eigenvalues for a given set of parameters. This is so because any two coupling schemes are after all connected by a unitary transformation [1, 2, 17, 31]. However, there is a reason why one should choose a particular coupling scheme for a problem at hand. If a given perturbation is less dominant, then a coupling scheme in which that perturbation is applied last will result in the following advantages. First, there will be less mixing of eigenvectors, i.e., the eigenfunctions will be purer. Second, a simple version of the coupling scheme in which not all basic states are taken into account may become applicable. Third, in the limit of approximation in which that perturbation can be neglected, the resulting eigenvectors are the correct labels of energy levels for the ion.

Spin-orbit interaction never dominates the other two energies for ions of the three transition-series so that the coupling schemes in which that perturbation is included last are the most useful ones for these ions. Thus, the strong-field I and the weak-field I are the most appropriate coupling schemes for a large number of compounds of the ions of the transition series. Between these two coupling schemes, strong-field I becomes more useful in a generalized ligand-field theory where a more general form for the electrostatic interaction and spin-orbit interaction energy is used resulting in more independent parameters than just the spherical A, B, C and ζ parameters [15, 31].

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[*] The matrices of s.f.II and j-II schemes were actually derived for quadrate ligand fields with the quadrate ligand field component as the last perturbation. The cubic matrices in the limit of zero axial ligand field can be extracted from them by setting the axial ligand field parameters Ds, Dt equal to zero.

Table 6. d^2 cubic energy matrices in $\{j\,\gamma^C\gamma^C\Gamma_j^C\}$ representation.

Γ_1

$\gamma_8(^2D_{3/2})^2$	$\gamma_8(^2D_{3/2})\,\gamma_8(^2D_{5/2})$	$\gamma_7(^2D_{5/2})^2$	$\gamma_8(^2D_{5/2})^2$
$-3\zeta+7(7B+2C)/5$	$-4\sqrt{3}\,Dq$	$7\sqrt{2}(B+C)/5$	$14(B+C)/5$
	$-\zeta/2+2Dq+8(B+C)/5$	$4\sqrt{6}(6B+C)/15$	$-4\sqrt{3}\,Dq-4\sqrt{3}(6B+C)/15$
		$2\zeta-8Dq+5C/3$	$\sqrt{2}(84B+19C)/15$
			$2\zeta+4Dq+4(21B+11C)/15$

Γ_2

$\gamma_8(^2D_{3/2})\,\gamma_8(^2D_{5/2})$
$-\zeta/2+2Dq-8B$

Γ_3

$\gamma_8(^2D_{3/2})^2$	$\gamma_8(^2D_{3/2})\,\gamma_7(^2D_{5/2})$	$\gamma_8(^2D_{3/2})\,\gamma_8(^2D_{5/2})$	$\gamma_7(^2D_{5/2})\,\gamma_8(^2D_{5/2})$	$\gamma_8(^2D_{5/2})^2$
$-3\zeta-7(21B-2C)/25$	$-2\sqrt{30}\,(7B+C)/25$	$-4\sqrt{3}\,Dq-4\sqrt{3}(7B+C)/25$	$2\sqrt{5}(B-2C)/25$	$-8(B-2C)/25$
	$-\zeta/2-4Dq+2(17B+14C)/35$	$-\sqrt{10}\,(3B+4C)/25$	$-2\sqrt{6}\,Dq+4\sqrt{6}\,C/15$	$4\sqrt{30}\,(18B-C)/75$
		$-\zeta/2+2Dq+2(17B+16C)/25$	$-8\sqrt{15}\,(12B+C)/75$	$-4\sqrt{3}\,Dq+4\sqrt{3}(6B-7C)/75$
			$2\zeta-2Dq-4B+8C/15$	$-8\sqrt{5}(4B+C)/75$
				$2\zeta+4Dq-2(18B-31C)/75$

Γ_4

$\gamma_8(^2D_{3/2})\,\gamma_7(^2D_{5/2})$	$[\gamma_8(^2D_{3/2})\,\gamma_8(^2D_{5/2})]^2$	$[\gamma_8(^2D_{3/2})\,\gamma_8(^2D_{5/2})]^1$	$\gamma_7(^2D_{5/2})\,\gamma_8(^2D_{5/2})$
$-\zeta/2-4Dq-(21B-4C)/15$	$2\sqrt{10}\,(27B+2C)/30$	$-4\sqrt{10}\,(9B-C)/30$	$-2\sqrt{6}\,Dq-4\sqrt{6}(6B+C)/30$
	$-\zeta/2+2Dq-2B+2C/3$	$2C/3$	$-2(6B+C)/\sqrt{15}$
		$-\zeta/2+2Dq+4B+2C/3$	$-2(6B+C)/\sqrt{15}$
			$2\zeta-2Dq-4(7B-C)/5$

Γ_5

$\gamma_8(^2D_{3/2})^2$	$\gamma_8(^2D_{3/2})\,\gamma_7(^2D_{5/2})$	$[\gamma_8(^2D_{3/2})\,\gamma_8(^2D_{5/2})]^1$	$[\gamma_8(^2D_{3/2})\,\gamma_8(^2D_{5/2})]^2$	$\gamma_7(^2D_{5/2})\,\gamma_8(^2D_{5/2})$	$\gamma_8(^2D_{5/2})^2$
$-3\zeta-7(21B-2C)/25$	$-2\sqrt{30}\,(7B+C)/75$	$-4\sqrt{3}\,Dq+8\sqrt{3}(7B+C)/75$	$4\sqrt{3}(7B+C)/15$	$4\sqrt{5}(B-2C)/25$	$2(B-2C)/25$
	$-\zeta/2-4Dq-(17B-16C)/15$	$-14\sqrt{10}\,(7B+C)/75$	$\sqrt{10}\,(5B+2C)/15$	$-2\sqrt{6}\,Dq-2\sqrt{6}(2B-C)/15$	$-8\sqrt{30}\,(7B+C)/75$
		$-\zeta/2+2Dq-2(194B-13C)/75$	$2(8B-C)/15$	$2\sqrt{15}\,(14B-3C)/75$	$-4\sqrt{3}\,Dq+4\sqrt{3}(26B+3C)/75$
			$-\zeta/2+2Dq+2(B+C)/3$	$2(10B-C)/\sqrt{15}$	$-4\sqrt{3}(2B+C)/15$
				$2\zeta-2Dq+2(6B+7C)/15$	$4\sqrt{5}(12B+C)/75$
					$2\zeta+4Dq-4(99B-8C)/75$

Electrostatic and spin-orbit energies dominate the ligand field energy for rare-earth ions and sometimes for f-electron configurations of actinide ions so that the weak-field II or the rare-earth coupling scheme is the most appropriate for these cases.

As we pointed out earlier, even though it is recognized that it is the weak-field I coupling scheme of the two weak-field schemes that is more appropriate to the study of the ions of the first transition series [15], all the weak-field calculations that have been carried out so far, for the d-electron configurations are using the rare-earth coupling scheme [1, 5, 6, 8, 9, 11 – 13]. The only exception is that of $d^{2,8}$ electron configuration carried out by us [17].

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