

A New Weak-Field Coupling Scheme for Cubic Complexes

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In the presence of spin-orbit interaction, in addition to the well-known weak-field coupling scheme for cubic complexes in which the ligand field perturbation is applied last, we show that it is possible to devise a second weak-field coupling scheme in which the spin-orbit perturbation is applied last by constructing the corresponding energy matrices for $d^{2,8}$ electronic configurations. We also show that for the parameters applicable to actual experimental systems, the new weak-field coupling scheme yields purer eigenfunctions than the well-known weak-field coupling scheme.

Key words: Cubic complexes, weak-field coupling scheme for \sim

1. Introduction

In the absence of spin-orbit perturbation, the coupling scheme for cubic transition-metal complexes in which the ligand field perturbation is carried out after the perturbation due to interelectronic repulsions is known as the weak-field coupling scheme. Defining the scheme in which the perturbation due to interelectronic repulsions is applied first as a weak-field coupling scheme then, two weak-field coupling schemes should be possible for cubic complexes in the presence of spin-orbit interaction, depending upon the sequence of perturbations of the ligand field potential and spin-orbit interaction. Only one of these, the one in which spin-orbit perturbation precedes that of ligand field has been worked out for all the d^n , $n = 2$ to 8, electronic configurations so far [1–4]. It is possible, however, to devise in general the second weak-field coupling scheme also in which the ligand field perturbation precedes that due to spin-orbit interaction. We show the derivation of this new scheme by constructing the energy matrices for $d^{2,8}$ electronic configurations. We find that the new weak-field scheme presented here is more appropriate not only to systems with minor spin-orbit interaction such as the $3d$ transition-

metal complexes but to other systems in which the spin-orbit interaction can be dominant as well.

2. Theory

Representing the perturbations due to electron repulsions, cubic ligand field potential and spin-orbit interaction as $\sum_{j>i} e^2/r_{ij}$, V_C^{LF} and $\zeta(r_i)\mathbf{l}_i \cdot \mathbf{s}_i$, respectively, the well-known weak-field scheme which employs the sequence of perturbations $\sum_{j>i} e^2/r_{ij} > \zeta(r_i)\mathbf{l}_i \cdot \mathbf{s}_i > V_C^{LF}$ will be designated $\{LSJ\Gamma_j^{\mathcal{O}}\}$ representation and the new scheme employing the sequence of perturbations $\sum_{i>j} e^2/r_{ij} > V_C^{LF} > \zeta(r_i)\mathbf{l}_i \cdot \mathbf{s}_i$ will be designated $\{LSX^{\mathcal{O}}\Gamma_j^{\mathcal{O}}\}$ representation¹.

There are obvious reasons for the use of the sequence of perturbations $\sum_{j>i} e^2/r_{ij} > \zeta(r_i)\mathbf{l}_i \cdot \mathbf{s}_i > V_C^{LF}$. The (LSJ) spin-orbital levels of the Russell-Saunders (or LS) terms become the basis for the ligand field perturbation and thus the electron repulsion and the spin-orbit energy terms are same as those of the atomic problem which are either known or can be calculated easily by the well-known methods [5]. Thus by connecting the spherical $\{JM_J\}$ representation to the cubic $\{\Gamma_j^{\mathcal{O}}\}$ representation, the matrix elements which need to be explicitly computed in this basis are those involving the ligand field potential V_C^{LF} .

2.1. The New Weak-Field Coupling Scheme

The second weak-field coupling scheme possible is with the $\sum_{j>i} e^2/r_{ij} > V_C^{LF} > \zeta(r_i)\mathbf{l}_i \cdot \mathbf{s}_i$ sequence of perturbations. The (LS) terms resulting from electron repulsions perturbation of a given electronic configuration are still the basis functions in this scheme to start with. These terms, however, will be split first into the cubic (XS) levels by the ligand field perturbation which are then split into the final cubic $\Gamma_j^{\mathcal{O}}$ levels by spin-orbit perturbation. The connection of the atomic $\{LM_L\}$ representation to the cubic $\{X^{\mathcal{O}}\}$ representation is exactly same as the $\{JM_J\}$ - $\{\Gamma_j^{\mathcal{O}}\}$ connection mentioned above, where the $\{JM_J\}$ representation is replaced by $\{LM_L\}$ representation. This part of the coupling scheme is, of course, well known because it is same as the weak-field scheme in the absence of spin-orbit perturbation.

The connection of the cubic $^{(2S+1)}X(LS)$ levels to the $\Gamma_j^{\mathcal{O}}$ representation is carried out as follows. Using the symmetry transformation properties of the spin (S) and coordinate (X) functions, these functions are made to combine in exactly the same way as in the strong field approach [6] to form the $\Gamma_j^{\mathcal{O}}$ representations. The coefficients in the connection thus become the well-known cubic coupling coefficients (or Clebsch-Gordon coefficients), $\langle \Gamma_j^{\mathcal{O}} | X_L^{\mathcal{O}}(LM_L)X_S^{\mathcal{O}}(SM_S) \rangle$.

The two coupling schemes are related by the unitary transformation

$$\langle \langle \Gamma_j^{\mathcal{O}} | X_L^{\mathcal{O}}(LM_L)X_S^{\mathcal{O}}(SM_S) \rangle | \langle \Gamma_j^{\mathcal{O}} | JM_J \rangle \rangle$$

where

$$|JM_J\rangle \equiv |LSJM_J\rangle$$

¹ We shall use the $\Gamma_j^{\mathcal{O}}$, $j = 1$ to 8, notation for cubic representations including coordinate and spin space and the $X^{\mathcal{O}}$, $X = A_1, A_2, E, T_1, T_2$ notation for cubic representations of coordinate space only.

and the $|LSJM_J\rangle$ functions are given by an expansion of $|LM_L SM_S\rangle$ functions in terms of the Wigner coefficients or the 3- j symbols

$$\langle LSJM_J | LM_L SM_S \rangle, \text{ i.e.}$$

$$\langle LSJM_J | LM_L SM_S \rangle = (-1)^{S-L-M_J} \sum_{M_L M_S} (2J+1)^{1/2} \begin{pmatrix} L & S & J \\ M_L & M_S & -M_J \end{pmatrix}.$$

The mixing of a given Γ_j^{\square} wave function from one scheme to the other will take place only if it arises out of different J levels of a certain (LS) term. If an (LS) term does not give rise to the same Γ_j^{\square} level from its different J values, the wave functions of the Γ_j^{\square} levels arising out of that term will be same in both the coupling schemes, i.e. the wave functions in the two schemes are related at most by a phase factor. It is obvious that in the case of the singlet spin functions (i.e. $S = 0$), the 1X and the Γ representations become identical.

The explicit formation of the wave functions in the $\{LSX^{\square}\Gamma_j^{\square}\}$ scheme can be carried out either directly or indirectly. In the direct formation, first the cubic coordinate functions ${}^{(2S+1)}X(LS)$ are obtained with the use of the $|LM_L SM_S\rangle$ functions with $M_S = S$. These coordinate functions are then combined with the many-electron spin functions to form the final Γ_j^{\square} levels. While combining, of course, the spins of the individual electrons have to be suppressed from the $|LM_L SM_S\rangle$ functions. The indirect procedure of obtaining the wave functions involves the application of the unitary transformation on the wave functions of the $\{LSJM_J\}$ scheme.

2.2. Application to $d^{2,8}$ Electronic Configurations

The d^2 and d^8 electronic configurations perturbed by the electron repulsions give rise to the terms 3F , 3P , 1G , 1D and 1S . The splittings of these terms in the two weak-field coupling schemes and the correlation of energy levels in the two schemes are shown in Fig. 1. The wave function of any Γ_j^{\square} level generated by the terms 1G , 1D , 1S and 3P is same in both the coupling schemes. Similarly Γ_2 level will have the same wave function whether it is produced from 3F_3 or ${}^3F({}^3T_{2g})$. This is also true for the Γ_1 level of 3F_4 and ${}^3F({}^3T_{1g})$. The only levels that scramble on going from one scheme to the other are the two Γ_3 , two Γ_4 and three Γ_5 , all produced by 3F . The unitary transformations connecting the two schemes for these scrambled Γ_j^{\square} levels are as follows.

Γ_3	3F_2	3F_4	Γ_4	3F_3	3F_4
${}^3T_{1g}({}^3F)$	$\sqrt{9/14}$	$-\sqrt{5/14}$	${}^3T_{1g}({}^3F)$	$i\sqrt{3/8}$	$-\sqrt{5/8}$
${}^3T_{2g}({}^3F)$	$-\sqrt{5/14}$	$-\sqrt{9/14}$	${}^3T_{2g}({}^3F)$	$-i\sqrt{5/8}$	$-\sqrt{3/8}$
Γ_5	3F_3	3F_4	3F_2		
${}^3A_{2g}({}^3F)$	$i/\sqrt{3}$	$\sqrt{3/7}$	$-\sqrt{5/21}$		
${}^3T_{1g}({}^3F)$	$-i\sqrt{5/8}$	$\sqrt{5/56}$	$-\sqrt{2/7}$		
${}^3T_{2g}({}^3F)$	$-i/\sqrt{24}$	$\sqrt{27/56}$	$\sqrt{10/21}$		

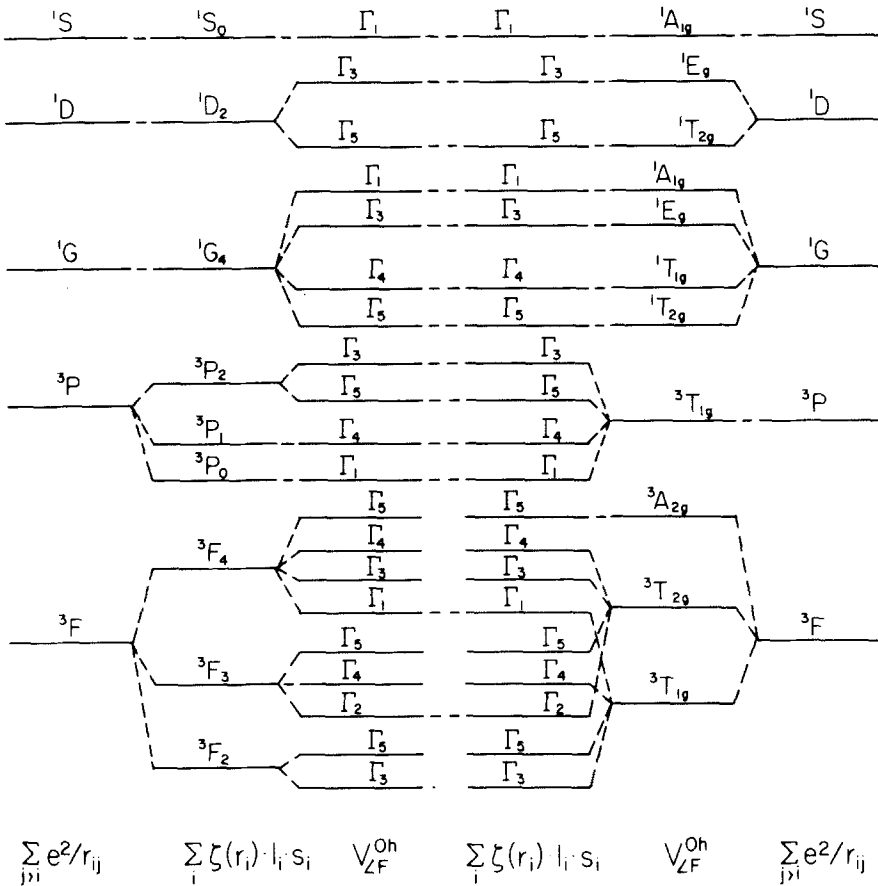


Fig. 1. Correlation of $d^{2,8}$ cubic energy levels in the two weak-field coupling schemes. The unconnected levels are the ones that are scrambled between the two schemes

The $\Gamma_3, \Gamma_4, \Gamma_5$ energy matrices of the d^2 configuration in the new coupling scheme, $\{LSX^O\Gamma_f^O\}$, are given in Table 1. The corresponding matrices in the $\{LSJ\Gamma_f^O\}$ scheme are well known [1]. The Γ_1 energy matrix as well as the Γ_2 matrix will be same in both the schemes because there is no mixing of levels from one scheme to the other in these representations. It is only the Γ_3, Γ_4 and Γ_5 matrices that will be different between the two schemes. In the case of these matrices also, in a given Γ_j matrix, that part of the matrix involving levels which are related only by a phase factor in the two coupling schemes will be same. It is the diagonal and the off-diagonal elements of levels that are scrambled on going from one scheme to the other that will be different in the two schemes. In addition, the off-diagonal elements between scrambled and unscrambled levels will also be different. Thus, for these scrambled levels the Dq parameter is diagonalized in the $\{LSX^O\Gamma_f^O\}$ representation, whereas the spin-orbit ζ parameter is diagonalized in the $\{LSJ\Gamma_f^O\}$ representation.

2.3. Advantages of the $\{LSX^O\Gamma_f^O\}$ Coupling Scheme

An obvious advantage of the new weak-field coupling scheme is in the use of its levels in the limit of zero spin-orbit interaction. In this limit, the levels of this

Table 1. d^2 Cubic energy matrices in $\{LSX^{\circ}\Gamma^{\circ}\}$ representation

Γ_3						
${}^3T_{1g}({}^3F)$	${}^3T_{2g}({}^3F)$	${}^3T_{1g}({}^3P)$	${}^1E_g({}^1D)$	${}^1E_g({}^1G)$		
$A - 8B - 6Dq - 3\zeta/4$	$3\sqrt{5}\zeta/4$ $A - 8B + 2Dq + \zeta/4$	$-4Dq$ 0 $A + 7B + \zeta/2$	$-3\sqrt{6}\zeta/\sqrt{35}$ $\sqrt{42}\zeta/7$ $\sqrt{21}\zeta/\sqrt{10}$ $A - 3B + 2C + 24Dq/7$	$-\sqrt{5}\zeta/\sqrt{14}$ $-3\zeta/\sqrt{14}$ 0 $-40\sqrt{3}Dq/7$ $A + 4B + 2C + 4Dq/7$		
Γ_4						
${}^3T_{1g}({}^3F)$	${}^3T_{2g}({}^3F)$	${}^3T_{1g}({}^3P)$	${}^1T_{1g}({}^1G)$			
$A - 8B - 6Dq + 3\zeta/4$	$\sqrt{15}\zeta/4$ $A - 8B + 2Dq + \zeta/4$	$-4Dq$ 0 $A + 7B - \zeta/2$	$-\sqrt{5}\zeta/\sqrt{8}$ $-\sqrt{3}\zeta/\sqrt{8}$ 0 $A + 4B + 2C + 2Dq$			
Γ_5						
${}^3T_{1g}({}^3F)$	${}^3T_{2g}({}^3F)$	${}^3A_{2g}({}^3F)$	${}^3T_{1g}({}^3P)$	${}^1T_{2g}({}^1D)$	${}^1T_{2g}({}^1G)$	
$A - 8B - 6Dq - 3\zeta/4$	$\sqrt{15}\zeta/4$ $A - 8B + 2Dq - \zeta/4$	0 $\sqrt{2}\zeta$ $A - 8B + 12Dq$	$-4Dq$ 0 $A + 7B + \zeta/2$	$2\sqrt{6}\zeta/\sqrt{35}$ $-2\sqrt{2}\zeta/\sqrt{7}$ $2\zeta/\sqrt{7}$ $\sqrt{21}\zeta/\sqrt{10}$ $A - 3B + 2C - 16Dq/7$	$\sqrt{5}\zeta/\sqrt{56}$ $3\sqrt{3}\zeta/\sqrt{56}$ $\sqrt{3}\zeta/\sqrt{7}$ 0 $20\sqrt{3}Dq/7$ $A - 4B + 2C - 26Dq/7$	

Table 2. Purities of eigenfunctions

ζ, cm^{-1}	$\{LSX^2\Gamma^0\}$ Representation				$\{LSJ^2\Gamma^0\}$ Representation											
	Γ_3		Γ_4		Γ_5		Γ_3		Γ_4		Γ_5		Aver- age			
	${}^3T_{1g}$ (3F)	${}^3T_{2g}$ (3F)	${}^3T_{1g}$ (3F)	${}^3T_{2g}$ (3F)	${}^3T_{1g}$ (3F)	${}^3T_{2g}$ (3F)	${}^3A_{2g}$ (3F)	Aver- age	3F_2	3F_4	3F_3	3F_2		3F_4		
0	80.0	100.0	80.0	100.0	80.0	100.0	100.0	91.4	51.4	64.3	62.5	50.0	47.6	50.0	42.9	52.7
-550	73.6	94.4	81.3	99.2	77.2	98.7	99.4	89.1	59.4	70.6	54.5	43.8	46.6	45.9	49.8	52.9
-1250	59.0	85.8	80.3	95.9	72.1	93.9	97.1	83.4	60.8	71.2	49.5	56.0	44.2	39.9	58.1	54.2
-2000	44.7	80.1	76.4	89.9	65.9	86.4	93.4	76.7	56.0	71.1	60.8	66.2	36.8	40.9	65.6	56.8
-3000	28.3	75.5	69.5	80.5	57.7	74.7	87.9	67.7	44.2	71.2	72.3	76.0	40.4	31.4	73.4	58.4
-4000	46.3	72.5	62.9	72.0	49.7	62.4	82.5	64.0	49.3	71.3	79.8	81.8	42.2	32.6	78.9	62.3
(a) d^8 Configuration: $Dq = -1000 \text{ cm}^{-1}, B = 800 \text{ cm}^{-1}, C/B = 4$																
0	90.4	100.0	90.4	100.0	90.4	100.0	100.0	95.9	58.1	64.3	62.5	56.5	47.6	56.5	42.9	55.5
210	90.6	99.9	90.2	100.0	90.6	99.8	99.9	95.9	60.0	65.6	61.7	55.3	48.1	56.2	44.3	55.9
1250	89.6	97.7	88.8	98.8	89.5	95.0	97.1	93.8	68.0	70.7	57.5	49.5	48.9	53.1	50.4	56.9
2000	87.8	94.3	87.5	96.9	87.0	88.8	93.4	90.8	72.3	72.4	54.5	45.4	48.6	49.5	53.6	56.6
(b) d^2 Configuration: $Dq = 1800 \text{ cm}^{-1}, B = 600 \text{ cm}^{-1}, C/B = 4$																

scheme become the proper eigenfunctions while the levels of the $\{LSJ\}$ scheme are completely scrambled. In other words, the $|LSX^c\rangle$ functions are the proper labels of energy levels in the absence of spin-orbit interaction. As we will show below the eigenfunctions of the $\{LSX^c\Gamma_f^c\}$ scheme remain purer even in the presence of the spin-orbit interaction.

The scrambling of eigenvectors from one scheme to the other affects the purities of eigenfunctions of only these levels. The purities of eigenfunctions of levels involving eigenvectors that are related only by a phase factor in the two schemes will not be different. Hence in comparing the purities of eigenfunctions of the two schemes we are only interested in those eigenvectors that mix on going from one scheme to the other.

The eigenvector components of the eigenfunctions obtained for d^2 and d^8 electronic configurations using V^{+3} and Ni^{+2} ions as examples are presented in Table 2. The values used for Dq , B and C parameters are those of the aquo complexes. The ζ values of 210 and -550 cm^{-1} correspond to the average values found for the complexes of Vanadium(III) and Nickel(II), respectively. For these values of ζ and in the limit of zero spin-orbit interaction the $\{LSX^c\Gamma_f^c\}$ representation yields eigenfunctions of much greater purity than the $\{LSJ\Gamma_f^c\}$ representation. In the case of d^2 configuration, even for increased values of ζ up to 2000 cm^{-1} , the $|LSX^c\Gamma_f^c\rangle$ levels remain of much higher purity. For d^8 configuration, it is at a ζ value of -4000 cm^{-1} , the $|LSX^c\Gamma_f^c\rangle$ levels become of similar purity as the $|LSJ\Gamma_f^c\rangle$ levels. It should be noted that the levels at increased ζ values have been obtained at the same Dq value. An increase in Dq value which is applicable to the elements of $4d$ and $5d$ transition series should give rise to a better purity in $\{LSX^c\Gamma_f^c\}$ representation as can be seen from a comparison of the $|LSX^c\Gamma_f^c\rangle$ levels for the d^2 and d^8 cases of $\pm 2000\text{ cm}^{-1}$ ζ value. Thus, we conclude the new weak-field coupling scheme presented here is the more appropriate scheme than the well-known weak-field coupling scheme of cubic complexes, not only for the weak-field complexes of $3d$ series but for the weak-field complexes of $4d$ and $5d$ series as well.

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