Irreducible tensor method and its application

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Abstract – The irreducible tensor method is extended from continuous group
to the system with point group symmetry. Especially, the V-coupling
coefficient from SO(3) to octahedral group is introduced for simplifying
the calculation of matrix elements. As an application, the analysis of
the spectra of praseodymium penta phosphate is presented.

INTRODUCTION

In this paper, an attempt has been made to extend the irreducible tensor method to molecular
system (ref. 1-8). In order to make sufficient use of the generalized Wigner-Eckart
theorem in evaluating matrix element, the interactions in molecules are formulated in
terms of irreducible tensor set which is associated with a group chain leading from
continuous group to point group. Especially, the V-coupling coefficients from SO(3)
to point group O (ref. 6-8) is factorized from the reduced matrix element to make a
simplification of matrix element calculation. As an application, the analysis of the
spectra of praseodymium penta phosphate is presented.

IRREDUCIBLE TENSOR METHOD FOR MOLECULAR SYSTEM

Let us consider a system with octahedral symmetry. For configuration $(a_2 t_1 t_2)^n$
characterized by the irreducible representation a_2, t_1 and t_2 of octahedral group O,
several group chains stemmed from Lie algebra have been introduced in the treatment of
many electron system (ref. 3-13). In this paper, we only consider one of them

$$SO(28) \supset SU^Q(2) \times \left\{ Sp(14) \supset SU^S(2) \times [SO(7) \supset G_2 \supset SO(3)] \right\} \qquad (1)$$

This group chain is an extension of the well-known one, due to Racah (ref. 5),
adapting the octahedral symmetry in quasispin (Q) scheme. When the Russell-Saunders
coupling (SxL→J) is considered, a subgroup $SO_J(3)$ can be introduced in the group
chain (1) by writing

$$SO(28) \supset SU^Q(2) \times \left\{ Sp(14) \supset SU^S(2) \times [SO(7) \supset G_2 \supset SO(3)] \supset SO_J(3) \supset O \right\} \qquad (2)$$

This group chain is suitable for the treatment of an rare-earth ion in the environment
of ligand field with octahedral symmetry. If the field is of low symmetry, a subgroup
D of the octahedral group can be further introduced in chain (2) in the following manner

$$O \supset D \qquad (3)$$

Accordingly, an irreducible tensor set can be built up, by means of bi-coupling technique

$$W^{q\ t}_{\eta\ \tau}(SLJ) \qquad (4)$$

where the superscript t, which is an irreducible representation of group O, arises from
the decomposition of J which is the result of Russell-Saunders coupling, i.e. SxL→J→t,
and where q denotes the irreducible representation of quasispin group $SU^Q(2)$, and   and
signify the components of q and t, respectively. Furthermore, the group theoretical
classification of the irreducible tensors is listed in Table 1. Alternatively, another
irreducible tensor set associated with quadruple-coupling can be constructed as

$$K^{q\ t}_{\eta\ \tau}(SLJ) \qquad (5)$$

For brevity, the classification of them is omitted.

In SLJt scheme, the interaction in ligand field theory such as the ligand field

interaction H_c, the relativistic effect H_r, and the electron repulsion interaction H_e can be expressed in terms of the irreducible tensor $W^q{}^t$ and $K^q{}^t$ in the forms

$$H_c = \sum_K B(0KK)W_0^1{}^{A_1}_a(0KK) \tag{6}$$

$$H_r = \sum_{K,K'} B(1KK')W_0^1{}^{A_1}_a(1KK') \tag{7}$$

$$H_e = \sum_p D(pp0) \sum_X (-1)^X (2X+1)^{\frac{1}{2}} \begin{pmatrix} 1 & 1 & X \\ 0 & 0 & 0 \end{pmatrix} K_0^X{}^{A_1}_a(000) \tag{8}$$

Note that the spin-orbital interaction H_s

$$H_s = B(110)W_0^1{}^{A_1}_a(110) \tag{9}$$

is included in the relativistic effect H_r. The coefficients $B(0KK)$, $B(1KK')$ and $D(pp0)$ in Eqs.(6), (7) and (8) can be evaluated by means of quantum chemistry calculation or they can be taken as parameters to fit experimental data.

For simplicity, we only discuss the matrix element of ligand field interaction H_c. Application of generalized Wigner-Eckart theorem to the matrix element of H_c in SLJt scheme gives

$$\langle f^n \alpha SLJt\tau| H_c | f^n \alpha'S'L'J't'\tau'\rangle = \delta_{SS'} \delta_{tt'}\delta_{\tau\tau'} \sum_K B(0KK)[(2J+1)\cdot$$

$$\cdot(2J'+1)/((2S+1)\lambda(t))]^{\frac{1}{2}} \begin{Bmatrix} L & L' & K \\ J' & J & S \end{Bmatrix} V\begin{pmatrix} J & J' & K \\ t & t' & A_1 \end{pmatrix} (-1)^{Q-M_Q} \begin{pmatrix} Q & 1 & Q' \\ -M_Q & 0 & M'_Q \end{pmatrix} \cdot$$

$$\cdot\langle \alpha SL || W^1(0K) || \alpha'S'L'\rangle \tag{10}$$

It is especially noteworthy that the V-coupling coefficients from SO(3) to group O,

$$V\begin{pmatrix} J & J' & K \\ t & t' & A_1 \end{pmatrix} \tag{11}$$

defined by Tang (ref. 6-8), play an important role in the evaluation of matrix elements, as they can bridge the gap between the continuous group and the point group. For practical calculation of the rare-earth complexes, the numerial values of the V-coupling coefficients from SO(3) to group O in the range j=1/2 to j=25/2 have been evaluated (ref. 10). From Eq.(10), we see that the reduced matrix element introduced by Racah can be further splitted into the product of the 3-j symbol of quasispin group $SU^Q(2)$ and the reduced matrix element of $W^1(0K)$ which is independent of the number of electrons. As the V-coupling coefficients from SO(3) to group and the 3-j symbol of quasispin $SU^Q(2)$ are introduced, they will make a simplification of the matrix element calculation.

TABLE 1. The group theoretical classification of $W^q{}^t$(SLJ)

	SO(28)	$SU^Q(2)$	Sp(14)	$SU^S(2)$	SO(7)	G_2	SO(3)	$SO_J(3)$
$W^{0A_1}(000)$	(00...0)	0	[00...0]	0	(000)	(00)	0	0
$W^0{}^t(101)$	(110...0)	0	[20...0]	1	(000)	(00)	0	1
$W^0{}^t(033)$	(110...0)	0	[20...0]	0	(110)	(10)	3	3
$W^0{}^t(0LL)$	(110...0)	0	[20...0]	0	(110)	(11)	1	1
							5	5
$W^0{}^t(1LJ)$	(110...0)	0	[20...0]	1	(200)	(20)	2, 4, 6	J
$W^{1A_1}(000)$	(110...0)	1	[00...0]	0	(000)	(00)	0	0
$W^1{}^t(0LL)$	(110...0)	1	[110...0]	0	(200)	(20)	2, 4, 6	J
$W^1{}^t(1LJ)$	(110...0)	1	[110...0]	1	(110)	(11)	1, 5	J
$W^1{}^t(13J)$	(110...0)	1	[110...0]	1	(110)	(10)	3	J

SPECTRA OF PRASEODYMIUM PENTA PHOSPHATE

The symmetry of crystal structure of praseodymium penta phosphate is of the distorted C_{4v}. Since C_{4v} is equivalent to D_4, the matrix in Eq.(10) can be modified by means of the V-coupling coefficients from octahedral group to group D_4 to adapt the lower symmetry of praseodymium penta phosphate. As a direct result, there are eighteen parameters with lower symmetry which can be used to fit the experimental data provided by one of the auther B.Y. Bai to give,

for the ligand field interaction,

B(022E)=-164, B(044A$_1$)=-104, B(044E)=-404, B(066A$_1$)=-414, B(066E)=-314;

for the spin-orbital interaction,

B(110A$_1$)=-3485;

for the relativistic effect,

B(112E)=-44, B(132E)=-59, B(134A$_1$)=-29, B(134E)=-124, B(154A$_1$)=-9, B(154E)=-94,

B(156A$_1$)=-39, B(156E)=56;

for the electron repulsion interaction,

D(000A$_1$)=0, D(220A$_1$)=29030, D(440A$_1$)=11040, D(660A$_1$)=8820.

THe result of theoretical calculation and the experimental data of fluoresent spectra are listed in Table 2. The root-mean-square deviation is 34 cm^{-1}.

TABLE 2. The splitting of terms of ^3H_J, ^3F_J, ^1G_J, ^1D_J, ^3P_J, ^1I_J and ^1S_J for Pr^{3+} in the field of $P_5O_{14}^{3-}$ with C_{4v} symmetry

Terms	Expt. (cm^{-1})	Calc. (cm^{-1})	Irr.[a]	Terms	Expt. (cm^{-1})	Calc. (cm^{-1})	Irr.[a]
$^3H_4$	0	0	A$_1$			4750	B$_1$
	20	17	E			4793	E
	48	46	A$_2$	$^3F_2$	5053	5032	A$_1$
	99	64	A$_1$		5081	5050	E
	154	143	B$_2$		5111	5132	B$_1$
	256	258	E		5216	5185	B$_2$
	526	520	B$_1$	$^3F_3$	6427	6382	E
$^3H_5$	2139	2156	E		6449	6445	B$_2$
	2170	2186	A$_2$		6456	6472	A$_2$
	2179	2223	E		6481	6514	E
	2218	2242	B$_1$		6497	6545	B$_1$
	2229	2249	A$_1$	$^3F_4$	6849	6801	A$_1$
	2286	2304	A$_2$		6853	6852	B$_2$
	2382	2469	E		6861	6879	E
	2640	2535	B$_2$		6869	6906	A$_2$
$^3H_6$	4326	4270	E		6997	7008	A$_1$
	4338	4343	B$_2$		7030	7040	B$_1$
	4367	4382	B$_1$		7098	7093	E
	4385	4392	A$_1$	$^1G_4$		9648	A$_1$
	4412	4433	E			9794	B$_2$
	4528	4480	B$_2$			9858	E
	4584	4579	A$_2$			9873	A$_2$
		4592	A$_1$			9888	B$_1$

TABLE 2.   (Continued from previous page)

Term	Energy	Irrep[a]	Term	Energy	Irrep[a]
$^1D_2$	10181	E		21008	B_2
	10224	A_1		21021	A_2
	17278	E		21033	B_1
	17295	B_1		21127	E
	17335	A_1		21386	E
	17473	B_2		21397	B_2
$^3P_0$	21048	A_1	$^3P_2$	21448	A_1
$^3P_1$	21642	E		22895	E
	21738	A_2		22924	A_1
$^1I_6$	20954	E		22939	B_1
	20978	A_1		23077	B_2
	21000	B_1	$^1S_0$	49644	A_1
RMSD[b] 34					

[a]Irreducible representation of C_{4v}.

[b]The root-mean-square deviation is abbreviated as RMSD.

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