

Matrix elements for configuration d^4s in a weak octahedral field using Racah methods

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Abstract—The general formula for matrix elements of configuration $d^n s$ in a weak crystalline field have been derived by means of Racah algebra. These have been explicitly applied to the case of $d^4 s$. The tabulated reduced matrix elements should be of assistance in the analysis of spectra of $d^4 s$, and perhaps d^5 , complexes having cubic or near-cubic symmetry.

1. INTRODUCTION

IN interpreting the spectra of some tetrahedral complexes of Co^{2+} (ground configuration d^7), STONEMAN [1] suggested that some terms arising from the $d^6 s$ configuration might play an important role in the ordering of energy levels. Although the lowest terms of the $d^6 s$ configuration observed in the spectrum of the ion Co^{2+} is over twice as high as any of the observed terms of d^7 , it can be argued that the presence of the ligands reduces the effective charge of the transition metal ion. Thus, the situation for Co^{2+} might well resemble that in the free ion Fe^+ . Indeed, if the atomic spectra of the isoelectronic sequence Mn, Fe^+ , and Co^{2+} are examined more closely, it is found that each has a different ground configuration, $d^5 s^2$, $d^6 s$, and d^7 respectively.

An analogous situation has been observed in some simpler transition metal systems. In a recent review article [2], DUNN gave the following account of the ScO spectrum. Sc^{2+} has the ground state electronic configuration $3d^1(^2D)$. Its first two excited states are $4s^1(^2S, \sim 24,000 \text{ cm}^{-1})$ and $4p^1(^2P, \sim 62,000 \text{ cm}^{-1})$. Recall that a perturbing negative charge will partially resolve the degeneracy of the d orbitals, viz. $d(\delta) < d(\pi) < d(\sigma)$, δ and π orbitals being doubly degenerate. A similar ligand will split the p orbitals into $p(\pi) < p(\sigma)$. On the basis of such a splitting pattern, it might be supposed that the lowest state of Sc^{2+} in the field of a negative charge would be $d(\delta^1)$, with diatomic ground term $^2\Delta$. However, the observed energy levels of ScO consist of a $^2\Sigma$ ground state, a $^2\Pi$, first excited state and a higher-lying $^2\Sigma$ state. This dilemma can be resolved by applying the argument given in the preceding paragraph. Indeed, as Dunn points out, both Ca^+ and K, isoelectronic with Sc^{2+} , have $4s^1(^2S)$ ground states, which in the field of a negatively charged ligand, give rise to a $^2\Sigma$ ground term. Moreover, since the $4p(^2P)$ level has dropped from $62,000 \text{ cm}^{-1}$ above the ground state in Sc^+ , to only $\sim 20,000 \text{ cm}^{-1}$ in Ca^+ and $\sim 15,000 \text{ cm}^{-1}$ in K, the $^2\Pi$, and $^2\Sigma$ excited states of the ScO spectrum can be attributed to ligand-field splitting of this atomic 2P term.

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[2] T. M. DUNN, Coordination compounds. *Physical Chemistry, An Advanced Treatise* (Edited by H. EYRING, D. HENDERSON and W. JOST), Vol. 5. Academic Press (1968).

A similar situation is thought to prevail in the case of the (nearly) tetrahedral complex FeCl_4 . The visible spectrum [3] can not be readily interpreted within the domain of the d^5 configuration. Even though the isoelectronic ions Cr^+ , Mn^{2+} , and Fe^{3+} have the same $d^5, {}^6S$ ground term, the ordering of the excited terms for these ions is vastly different. Thus, the first two excited terms for Cr^+ arise from the d^4s configuration, while the first few excited terms for Mn^{2+} and Fe^{3+} are from the d^5 configuration. By the preceding arguments, the situation in the Fe^{3+} complex may well resemble that in Cr^+ . The object of this paper is, accordingly, to calculate the ordering of crystal field levels for terms arising from a d^4s configuration.

2. METHOD AND RESULTS

For the case of a transition metal ion embedded in a weak octahedral crystalline field, the spin-orbit coupling and crystal field interactions can be treated as perturbation terms. It is convenient to employ the $|SLJM\rangle$ representation [4]. The perturbation Hamiltonian can be written

$$\mathcal{H}' = \zeta_{nl} \sum_i \mathbf{s}_i \cdot \mathbf{l}_i + 14Dq\pi^{1/2} \sum_i \{Y_{40}(\theta_i, \varphi_i) + (\frac{5}{14})^{1/2} [Y_{44}(\theta_i, \varphi_i) + Y_{4-4}(\theta_i, \varphi_i)]\}, \quad (1)$$

where ζ_{nl} is the one-electron spin-orbit coupling parameter and Dq , the usual crystal field parameter.

A general method for calculating matrix elements of the spin-orbit interaction for configuration $d^n s$, based on irreducible tensor-operator techniques, has been given by TREES [6]. The matrices for $d^4 s$ have also been calculated by BOZMAN and TREES [7].

Matrix elements of the weak crystalline field can also be calculated by means of Racah algebra. Applying the Wigner-Eckart theorem, the matrix elements

$$\langle d^n(v'S'L')sS_1'L'J'M' | V_p^k | d^n(vSL)sS_1LJM \rangle$$

where

$$V_p^k = \sum_{i=1}^{n+1} Y_{kp}(\theta_i, \varphi_i)$$

and v is the seniority number defined by Racah, have the following form:

$$\begin{aligned} & \langle d^n(v'S'L')sS_1'L'J'M' | V_p^k | d^n(vSL)sS_1LJM \rangle \\ & = (2J' + 1)^{-1/2} \langle JMkp | J'M' \rangle \langle d^n(v'S'L')sS_1'L'J' \| V^k \| d^n(vSL)sS_1LJ \rangle \end{aligned} \quad (2)$$

Since the potential acts only on the orbital part of the eigenfunction, the double-barred

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matrix elements in (2) can be reduced using equation (44b) of Ref. [8]:

$$\begin{aligned} &\langle d^n(v'S'L')_s S_1' L' J' \| V^k \| d^n(vSL)_s S_1 L J \rangle \\ &= \delta_{s_1 s_1'} (-1)^{S_1' + k - L' - J} [(2J + 1)(2J' + 1)]^{1/2} W(L' J' L J; S_1 k) \\ &\quad \cdot \langle d^n(v'S'L')_s S_1' L' \| V^k \| d^n(vSL)_s S_1 L \rangle. \end{aligned} \quad (3)$$

The double-barred matrix elements on the right hand side of (3) can be further reduced using the same formula:

$$\begin{aligned} &\langle d^n(v'S'L')_s S_1' L' \| V^k \| d^n(vSL)_s S_1 L \rangle \\ &= (-1)^{L' + k - L} [(2L + 1)(2L' + 1)]^{1/2} W(L' L' L L; 0k) \\ &\quad \cdot \langle d^n v' S' L' \| \sum_{i=1}^n Y_{kp}(\theta_i \varphi_i) \| d^n v S L \rangle. \end{aligned} \quad (4)$$

The Racah coefficient $W(L' L' L L; 0k)$, which can be evaluated directly, is given by

$$W(L' L' L L; 0k) = (-1)^{L+L-k} [(2L + 1)(2L' + 1)]^{-1/2}. \quad (5)$$

Combining equations (2-5), the matrix elements can be expressed

$$\begin{aligned} &\langle d^n(v'S'L')_s S_1' L' J' M' | V_p^k | d^n(vSL)_s S_1 L J M \rangle \\ &= (-1)^{S_1' + L + k - J} (2J + 1)^{1/2} W(L' J' L J; S_1 k) \langle J M k p | J' M' \rangle \\ &\quad \cdot \langle d^n v' S' L' \| \sum_{i=1}^n Y_k(\theta_i \varphi_i) \| d^n v S L \rangle. \end{aligned} \quad (6)$$

The reduced matrix elements $\langle d^n v' S' L' \| \sum_{i=1}^n Y_k(\theta_i \varphi_i) \| d^n v S L \rangle$ can be calculated by a method based on coefficients of fractional parentage. Explicit formulas are given by BRINK and SATCHLER [9].

As pointed out by FINKELSTEIN and VAN VLECK [10], it is convenient to use basis functions which diagonalize the octahedral potential apart from elements non-diagonal in J . Such functions are classified according to their cubic representation Γ rather than according to M . The transformation matrices $\langle J \Gamma | J M \rangle$ for $J = \frac{1}{2}$ to $J = 4\frac{1}{2}$ are tabulated in GRIFFITH's book [11]. The matrices for $J = 5\frac{1}{2}$ and $6\frac{1}{2}$ are reported in Ref. [12].

The matrix elements $\langle d^4(v'S'L')_s S_1' L' J' \Gamma_i | V_{oct} | d^4(vSL)_s S_1 L J | \Gamma_i \rangle$ where v_{oct} is the octahedral field potential and $i = 6, 7, 8$, can, in this way, be calculated. The only quantities in equation (6) which are not readily available in the literature are $\langle d^4 v' S' L' \| Y_4 \| d^4 v S L \rangle$. The non-vanishing elements of this matrix are listed in Table 1.

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Table 1*. Non-vanishing reduced matrix elements
 $\sqrt{(\pi)} \langle v'S'L' \parallel Y_4 \parallel vSL \rangle$

$v'S'L'$	vSL	$\sqrt{(\pi)} \langle v'S'L' \parallel Y_4 \parallel vSL \rangle$
5_4D	5_4D	$-3(14)^{1/2}/14$
4_2H	4_2H	$(26)^{1/2}/7$
3_2H	3_2G	$-(78)^{1/2}/28$
3_2H	3_2F	$(26)^{1/2}/7$
4_2H	4_2F	$3(26)^{1/2}/28$
3_2H	3_2D	$(5)^{1/2}/7$
4_2H	3_2P	$-(14)^{1/2}/7$
4_2H	4_2P	$1/7$
3_2G	3_2G	$-3(2002)^{1/2}/196$
3_2G	3_2F	$-2(66)^{1/2}/21$
3_2G	3_2F	$-(66)^{1/2}/84$
3_2G	3_2D	$(1155)^{1/2}/98$
3_2G	3_2P	$(21)^{1/2}/21$
4_2G	3_2P	$-17(6)^{1/2}/84$
3_2F	3_2F	$-(22)^{1/2}/14$
3_2F	3_2D	$10(7)^{1/2}/49$
3_2F	3_2P	$-1/7$
3_2F	3_2P	$5(14)^{1/2}/49$
3_2F	3_2F	$3(22)^{1/2}/28$
3_2F	3_2D	$15(7)^{1/2}/98$
3_2F	3_2P	$5/7$
3_2F	3_2P	$-(14)^{1/2}/196$
3_2D	3_2D	$-11(14)^{1/2}/98$
1_4I	1_4I	$2(1309)^{1/2}/77$
1_4I	1_2G	$5(2)^{1/2}/7$
1_4I	1_2G	$-25(22)^{1/2}/308$
1_4I	1_4F	$-(2)^{1/2}/4$
1_4I	1_2D	$-(10)^{1/2}/7$
1_4I	1_2D	$(5)^{1/2}/7$
1_2G	1_2G	$(2002)^{1/2}/294$
1_2G	1_2G	$-10(182)^{1/2}/147$
1_2G	1_2D	$5(77)^{1/2}/147$
1_2G	1_4D	$5(154)^{1/2}/147$
1_2G	1_2S	$(21)^{1/2}/7$
1_2G	1_4S	$5/21$
1_4G	1_2G	$17(2002)^{1/2}/6468$
1_4G	1_4F	$-15(2)^{1/2}/28$
1_4G	1_2D	$5(7)^{1/2}/147$
1_4G	1_4D	$-65(14)^{1/2}/588$
1_4G	1_2S	$2(11)^{1/2}/21$
1_4F	1_4F	$-(22)^{1/2}/28$
1_4F	1_2D	$(35)^{1/2}/7$
1_4F	1_4D	$(70)^{1/2}/196$
1_2D	1_2D	$2(14)^{1/2}/49$
1_2D	1_4D	$10(7)^{1/2}/49$
1_4D	1_4D	$-8(14)^{1/2}/49$

* The values here are calculated using formulas (4.17) and (5.21) of Ref. [9].

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