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Free ions Pr IV ($4f^2$) and Tm IV ($4f^{12}$): intermediate versus LS coupling scheme

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Abstract The intermediate and LS-coupling schemes for the free lanthanide ions Pr^{3+} and Tm^{3+} have been compared by the matrix elements of the tensor operator $\boldsymbol{U}^{(\boldsymbol{k})}$, k = 2, 4, 6. The necessary eigenvectors and eigenvalues have been computed with the aid of four parameters, F_2, F_4, F_6, and ζ_{4f}, known from free-ion spectra of the same ions. It has been found that both coupling types for each ion lead to close values of $|\boldsymbol{U}^{(\boldsymbol{k})}|^2$ only for transitions from the ground level to certain lower-lying energy levels within the $4f^N$ configuration.

Keywords Pr IV · Tm IV · Intermediate · LS · Coupling · $\boldsymbol{U}^{(\boldsymbol{k})}$ Matrix elements

1 Introduction

The term “free ion” has been often used in studies on trivalent lanthanides (Ln^{3+}) as an initial approximation or template in physical models applied to optical spectra, x-ray photoelectron spectra and magnetic properties of Ln^{3+} in condensed phase. In fact, states of Ln^{3+} ions free from environment have been observed only in the emission spectra by vaporizing lanthanide metals in an electric discharge [1]. Thus, free-ion fourth spectra (in atomic spectroscopy notation) of Pr IV [2,3], Nd IV [4], Er IV [5], Tm IV [6], and Yb IV [7] have been so far obtained. Other Ln IV free-ion spectra (Ln = Ce, Tb, Yb, and Lu), with sufficient number of $4f^N$-energy levels have been reported in a critical compilation earlier [8].

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The lowest electron configurations of the title free ions are as follows: $Pr^{3+} = [Xe]4f^2$ and $Tm^{3+} = [Xe]4f^{12}$. Both are complementary to the closed subshell $4f^{14}$ and each comprises 13 levels belonging to 7 multiplets: $^3F, ^3P, ^3H, ^2D, ^2G, ^2I$, and ^1S [9]. The first of the reports on Pr IV [2] contains matrix elements of electrostatic interaction E^k and constant of spin–orbit interaction $\zeta_4 f$ but does not include the position of the level $^1S_0$, while the content of the second one [3] is vice versa; 12 energy levels have identical positions in both studies.

The f $\leftrightarrow$ f transition probabilities can be presented either in the LS-coupling scheme that pertains to the non-relativistic Schrödinger equation or by the jj-coupling in the relativistic Dirac equation [10]. If the energy of electrostatic interaction becomes comparable with that of spin–orbit interaction, a transition takes place from LS- to jj-coupling scheme.

The intermediate coupling arises as a partial breakdown of the LS-coupling in the departure from the Landè interval rule: $\varepsilon(J) - \varepsilon(J-1) = \lambda\zeta_{4f} J$ [11]. In intermediate coupling, the actual wave function $|[SL]J\rangle$ is a linear combination of pure LS-functions $|SLJ\rangle$. The deviations from the LS-coupling are characterized by the magnitudes of the non-diagonal elements in the combined matrices of electrostatic and spin–orbit interactions.

As the matrix elements of the tensor operator $\boldsymbol{U}^{(\boldsymbol{k})}$ are important in the calculation of the crystal-field potential and the transition probabilities of lanthanide (3+) ions, it is worthy to be determined the dependence of their values on the coupling types.

The present study refers to a comparative analysis of $\boldsymbol{U}^{(\boldsymbol{k})}$ obtained in LS- and intermediate coupling basis of the free ions Pr IV($4f^2$) and Tm IV($4f^{12}$). To the best of our knowledge, such an analysis related to free lanthanide ions has not been reported yet.

2 Method

The f–f transitions arising by electric dipole mechanism are calculated according to the model of Judd–Ofelt [12,13]. The initial and the final states of a transition are usually designated as $\langle[SL]J|$ and $[S^I L^I]J^I\rangle$, respectively. The calculated oscillator strengths contain squared matrix elements of the tensor operator $\boldsymbol{U}^{(\boldsymbol{k})}$. These quantities are determined according to the Wigner–Eckart theorem as a product of 6j-symbols and doubly reduced matrix elements of the corresponding f^N configuration:

$$\left\langle f^n \alpha SLJ \left\| U^{(k)} \right\| f^n \alpha^I S^I L^I J^I \right\rangle = (-1)^{S+L'+J+k}\, \delta(S, S^I)[(2J+1)(2J^I+1)]^{1/2} x$$

$$\times \left\{ \begin{matrix} J & J^I & k \\ L^I & L & S \end{matrix} \right\} \left\langle f^n \alpha SL \left\| U^{(k)} \right\| f^n \alpha^I S^I L^I \right\rangle ; \left\{ \begin{matrix} a & b & c \\ d & e & f \end{matrix} \right\} \quad (1)$$

The 6j-symbol designates transformations between coupling schemes of three angular momenta and α is any quantum number not specifically stated. Eq. (1) applies also to the calculation of matrix elements of the crystal-field potential [9]. The matrix elements of the operator $\boldsymbol{U}^{(\boldsymbol{k})}$ in this work have been calculated by means of tabulated 6j-symbols [14,15] and doubly reduced matrix elements for the partially filled

f^2 that are also valid for the almost filled subshell f^{12} after transpondation. These for f^2 have been evaluated for each pair of multiplets [16]. The conditions for the δ-function and those of the triangle for each of the four triads must be satisfied, respectively:

$$\delta(S, S^{I}) = 1, \text{ for } S = S^{I}, \text{ or } \delta(S, S^{I}) = 0, \text{ for } S \neq S^{I}; \text{ (a e f), (c d e), (a b c), and (b d f).} \quad (2)$$

3 Results and discussion

3.1 Pr IV

The eigenvectors and eigenvalues of the free ion Pr IV ($4f^2$) in intermediate coupling have been computed with the following set of parameters of electrostatic interaction and constant of spin–orbit interaction (all in cm^{-1}): $F_2 = 322.09$, $F_4 = 51.558$, $F_6 = 5.1407$, and $\zeta_{4f} = 741$. The results are presented in Table 1.

The Slater parameters F_k have been derived from the matrix elements of electrostatic interaction E^k given for Pr IV in [2] by means of conversion formulae [9]. The r.m.s. deviation between the eigenvalues in this study and 12 energy levels in [2] is $\pm 84.3 cm^{-1}$. The resulting wave functions are listed in Table 1.

It is also seen from Tables 2 and 1 that the two coupling schemes lead to close values of $|\boldsymbol{U}^{(\boldsymbol{k})}|^2$ for the first five transitions located below 7,000 cm^{-1}. For the remaining higher-lying levels, there are differences between the squared matrix elements in the two coupling types except for three $|U^{(4)}|^2$ and one $|U^{(6)}|^2$ values. The magnitudes

Table 1 Eigenvectors and eigenvalues for wave functions of the free ion Pr IV in intermediate coupling

Level $^{2S+1}L_J$	Eigenvectors	Eigenvalues $\tilde{\nu}/cm^{-1}$
$\langle{}^3[H_4]\vert$	$0.987658 \langle{}^3H_4\vert + 0.154163 \langle{}^1G_4\vert - 0.0276832 \langle{}^3F_4\vert$	0
$\vert[{}^3H_5]\rangle$	$1.0000\vert{}^3H_5\rangle$	2,063.7
$\vert[{}^3H_6]\rangle$	$0.99863\vert{}^3H_6\rangle - 0.0523232\vert{}^1I_6\rangle$	4,239.1
$\vert[{}^3F_2]\rangle$	$0.989848\vert{}^3F_2\rangle + 0.141595\vert{}^1D_2\rangle - 0.0123077\vert{}^3P_2\rangle$	5,048.5
$\vert[{}^3F_3]\rangle$	$1.0000\vert{}^3F_3\rangle$	6,419.4
$\vert[{}^3F_4]\rangle$	$0.835956\vert{}^3F_4\rangle - 0.538178\vert{}^1G_4\rangle + 0.107435\vert{}^3H_4\rangle$	6,988.2
$\vert[{}^1G_4]\rangle$	$0.828612\vert{}^1G_4\rangle + 0.548098\vert{}^3F_4\rangle - 0.113975\vert{}^3H_4\rangle$	10,046.8
$\vert[{}^1D_2]\rangle$	$0.951389\vert{}^1D_2\rangle - 0.274586\vert{}^3P_2\rangle - 0.139508\vert{}^3F_2\rangle$	17,686.3
$\vert[{}^1I_6]\rangle$	$0.99863\vert{}^1I_6\rangle - 0.0523232\vert{}^3H_6\rangle$	21,607.8
$\vert[{}^3P_0]\rangle$	$0.996295\vert{}^3P_0\rangle + 0.0859959\vert{}^1S_0\rangle$	21,799.6
$\vert[{}^3P_1]\rangle$	$1.0000\vert{}^3P_1\rangle$	22,391.6
$\vert[{}^3P_2]\rangle$	$0.961484\vert{}^3P_2\rangle + 0.273515\vert{}^1D_2\rangle - 0.0271706\vert{}^3F_2\rangle$	23,579.8
$\vert[{}^1S_0]\rangle$	$0.996295\vert{}^1S_0\rangle - 0.0859959\vert{}^3P_0\rangle$	51,759.4

The wave functions of the ground level are designated as an initial or ⟨bra| state

Table 2 Squared matrix elements of the tensor operator $\boldsymbol{U}^{(\boldsymbol{k})}$ in intermediate (IM) and LS coupling schemes of Pr IV

Transition $^3H_4 \rightarrow$	$\lvert U^{(2)}\rvert^2$ IM	$\lvert U^{(4)}\rvert^2$ IM	$\lvert U^{(6)}\rvert^2$ IM	$\lvert U^{(2)}\rvert^2$ LS	$\lvert U^{(4)}\rvert^2$ LS	$\lvert U^{(6)}\rvert^2$ LS
$^3H_5$	0.3284	0.6112	1.8288	0.3219	0.6753	1.7515
$^3H_6$	0.0007	0.0905	0.5230	0.0056	0.0614	0.4683
$^3F_2$	1.4857	1.2104	0.3681	1.4966	1.2542	0.4242
$^3F_3$	0.1976	1.0464	2.0997	0.2095	1.0974	2.1212
$^3F_4$	0.0434	0.1083	1.2847	0.0082	0.1809	1.2727
$^1G_4$	0.0080	0.0522	0.1159	0	0	0
$^1D_2$	0.0003	0.0161	0.1138	0	0	0
$^3P_0$	0	0.5027	0	0	0.4762	0
$^3P_1$	0.0006	0.5340	0	0	0.5714	0
$^1I_6$	0.0077	0.0561	0.0386	0	0	0
$^3P_2$	0.00003	0.0948	0.4309	0	0.1212	0.5260
$^1S_0$	0	0.0031	0	0	0	0

of the non-zero matrix elements in the IM coupling depend on the products of the corresponding eigenvectors and on the doubly reduced matrix elements between pure LS-states.

3.2 Tm IV

The eigenvectors and eigenvalues of the free ion Tm IV ($4f^{12}$) in intermediate coupling have been computed with the following set of parameters of electrostatic interaction and constant of spin–orbit interaction (all in cm^{-1}) : $F_2 = 463.431, F_4 = 66.4215, F_6 = 6.9595$, and $\zeta_{4f} = 2640$. The results are presented in Table 3. The Slater parameters F_k have been obtained from parameters F^k for Tm IV in [6] by means of the coefficients D_k, k = 2, 4, 6 [17]:

$$F_k = F^k/D_k, D_2 = 225, D_4 = 1089, D_6 = 7361.64. \quad (3)$$

Only ten energy levels have been registered in the free-ion spectrum of Tm IV in [6]. The r.m.s. deviation between these experimental values and 10 eigenvalues in this study is $\pm 121.2\,cm^{-1}$. This value accounts mostly for the low number of compared energy levels.

The dominant components of the eigenfunctions determined from the free-ion spectrum of Tm IV [6] and those computed in this work are compared in Table 4.

The percentages of the leading components in Table 4 for Tm IV from experiment [6] and those obtained in this work in intermediate coupling coincide within ±0.5 % in 6 out of 10 wave functions; the deviations for the remaining vary from 3.3 to −2.8 %.

Table 3 Eigenvectors and eigenvalues for wave functions of the free ion Tm IV in intermediate coupling

Level$^{2S+1}L_J$	Eigenvectors	Eigenvalues $\tilde{\nu}$/cm^{-1}
$\langle[^3H_6]\vert$	$-0.9955\langle^3H_6\vert - 0.0947614\langle^1I_6\vert$	0
$\vert[^3F_4]\rangle$	$0.775846\vert^3F_4\rangle - 0.319846\vert^3H_4\rangle + 0.54384\vert^1G_4\rangle$	5,546.6
$\vert[^3H_5]\rangle$	$1.0000\vert^3H_5\rangle$	8,227.78
$\vert[^3H_4]\rangle$	$0.746321\vert^3H_4\rangle - 0.359855\vert^1G_4\rangle + 0.559919\vert^3F_4\rangle$	12,539.89
$\vert[^3F_3]\rangle$	$1.0000\vert^3F_3\rangle$	14,474.89
$\vert[^3F_2]\rangle$	$0.880565\vert^3F_2\rangle + 0.436652\vert^1D_2\rangle + 0.184231\vert^3]P_2\rangle$	15,087.73
$\vert[^1G_4]\rangle$	$0.758118\vert^1G_4\rangle - 0.290781\vert^3F_4\rangle + 0.583699\vert^3H_4\rangle$	20,990.58
$\vert[^1D_2]\rangle$	$0.673717\vert^1D_2\rangle - 0.581693\vert^3P_2\rangle - 0.455783\vert^3F_2\rangle$	28,412.38
$\vert[^1I_6]\rangle$	$0.9955\vert^1I_6\rangle - 0.0947614\vert^3H_6\rangle$	34,274.98
$\vert[^3P_0]\rangle$	$-0.972726\vert^3P_0\rangle + 0.231957\vert^1S_0\rangle$	34,740.95
$\vert[^3P_1]\rangle$	$1.0000\vert^3P_1\rangle$	36,520.18
$\vert[^3P_2]\rangle$	$0.79227\vert^3P_2\rangle + 0.596188\vert^1D_2\rangle - 0.129878\vert^3F_2\rangle$	38,852.78
$\vert[^1S_0]\rangle$	$-0.972726\vert^1S_0\rangle - 0.231957\vert^3P_0\rangle$	77,052.08

The wave functions of the ground level are designated as an initial or ⟨bra| state

Table 4 Leading eigenfunctions (in %) in certain free-ion levels of Tm IV ($4f^{12}$)

Eigenfunction	$^3H6$	$^3F_4$	$^3H_5$	$^3H_4$	$^3F_3$	$^3F_2$	$^1G_4$	$^1D_2$	$^1I_6$	$^3P_2$
From exp. [6]	99	62	100	59	100	78	57	43	99	60
This work	99.1	60.2	100	55.7	100	77.5	57.5	45.4	99.1	62.8

However, in the present study we deal with two more energy levels above the ground level, if compared to [6].

The matrix elements of the tensor operator $\boldsymbol{U}^{(k)}$ are presented in Tables 2 and 5 as squared because they have been used in such a form in their immediate application in the determination of transition intensities. For Pr IV,$|\boldsymbol{U}^{(k)}|^2$ include 17 zeros in the Russell-Saunders coupling but only 5 zeros in the IM coupling. For Tm IV,$|\boldsymbol{U}^{(k)}|^2$ in the LS-coupling contain 16 zeros and 6 zeros in the IM coupling. Each coupling scheme contains 36 matrix elements. There are differences for $|\boldsymbol{U}^{(k)}|^2$ of the transition $^3H_6 \rightarrow {}^3H_4$ of Tm IV in both coupling types.

For a given transition, the non-zero matrix elements in the IM coupling versus the corresponding zeros in the LS-coupling are exclusively due to contributions from those terms in the products of wave functions $\langle[^3H_4]|$ or $\langle[^3H_6]|$, respectively, and $|[S^I L^I]J^I\rangle$ that satisfy both the condition for the δ-function and the triangular conditions.

In order to express the above results in a condensed and indicative form, $|\boldsymbol{U}^{(k)}|^2$ for all transitions have been treated as coordinates of points ($|U^{(2)}|^{2,}|U^{(4)}|^2$, $|U^{(6)}|^2$). Thus, each transition is effectively presented by one point in a three dimensional space of the matrix elements of the tensor operator $\boldsymbol{U}^{(k)}$. Hence, each coupling scheme

Table 5 Squared matrix elements of the tensor operator $\boldsymbol{U}^{(\boldsymbol{k})}$ in intermediate (IM) and LS coupling schemes of Tm IV

Transition $^3H_6 \rightarrow$	$\lvert U^{(2)}\rvert^2$IM	$\lvert U^{(4)}\rvert^2$IM	$\lvert U^{(6)}\rvert^2$IM	$\lvert U^{(2)}\rvert^2$LS	$\lvert U^{(4)}\rvert^2$LS	$\lvert U^{(6)}\rvert^2$LS
$^3F_4$	1.4919	1.9811	0.6992	2.4762	2.6380	2.0606
$^3H_5$	0.3221	0.6940	1.9145	0.3250	0.7003	1.9318
$^3H_4$	0.8336	0.4518	1.8083	0.0056	0.0614	0.4683
$^3F_3$	2.1472	0.9489	2.5226	2.1667	0.9575	2.5455
$^3F_2$	0	0.2110	0.7303	0	0.0625	0.9091
$^1G_4$	0.1370	0.2608	0.0088	0	0	0
$^1D_2$	0	0.7026	0.5769	0	0	0
$^1I_6$	0.0008	0.0671	0.0321	0	0	0
$^3P_0$	0	0.5277	0.2161	0	0.5628	0.2143
$^3P_1$	0	1.2549	0.3716	0	1.2662	0.3750
$^3P_2$	0	1.0342	0.0155	0	1.6883	0.1705
$^1S_0$	0	0.0300	0.0312	0	0	0

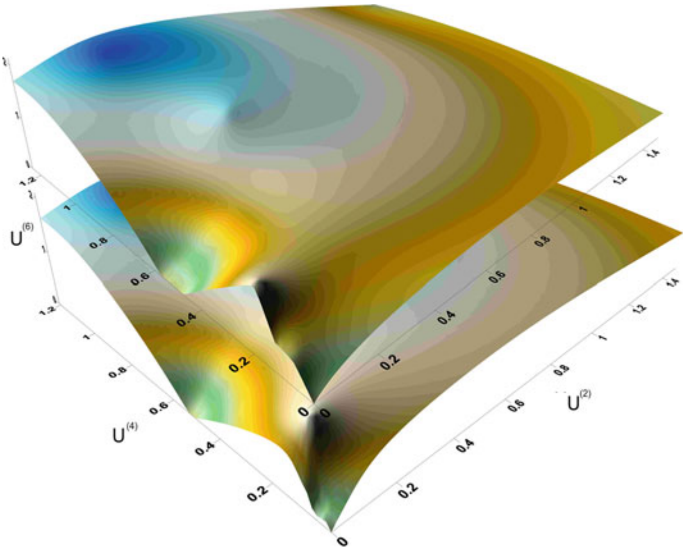

Fig. 1 Curved surfaces formed by the points of the squared matrix elements of the tensor operator $\boldsymbol{U}^{(\boldsymbol{k})}$ in IM and LS coupling of Pr IV

corresponds to a definite plane including the abovementioned number of f↔f transitions with certain close points of the alternative coupling scheme. This generalization has been visualized in Fig. 1 (the upper plane is formed by points in intermediate coupling for both figures) and Fig. 2.

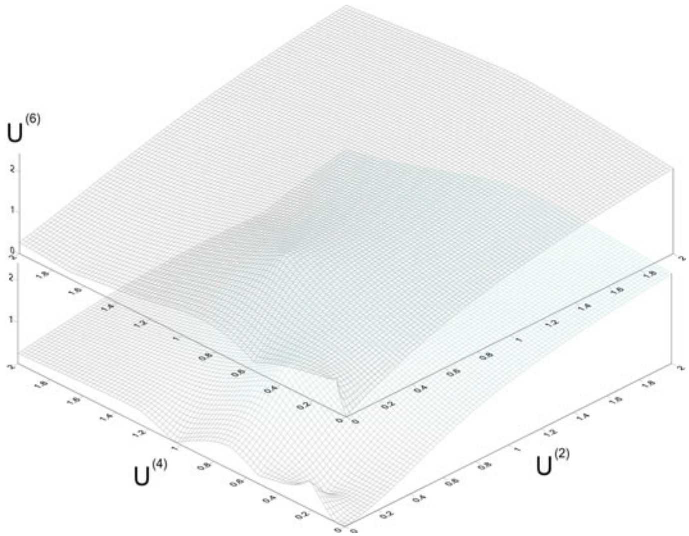

Fig. 2 Curved surfaces formed by the points of the squared matrix elements of the tensor operator $\boldsymbol{U}^{(\boldsymbol{k})}$ in IM and LS coupling of Tm IV

4 Conclusions

The squared matrix elements of the tensor operator $\boldsymbol{U}^{(\boldsymbol{k})}$ for the free ions Pr IV and Tm IV exhibit close values in both LS- and intermediate coupling types only for transitions from the respective ground levels $^3H_4$ and $^3H_6$ to the levels below 7,000 cm^{-1} for Pr IV and below 1,5000 cm^{-1} for Tm IV. In both cases, the relative proximity of the coupling schemes applies at most to five out of 12 4f-levels located above the ground level. The wave functions in the intermediate basis of the upper-lying levels contain admixtures from other levels, thus resulting in non-zero values of $|\boldsymbol{U}^{(\boldsymbol{k})}|^2$.

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