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Relativistic f ↔ f transitions in crystal fields

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Abstract. A relativistic model of f ↔ f transitions based on the transformation of all intershell tensor operators to effective relativistic double tensor operators is developed. The transition amplitude is expressed in terms of effective operators acting within the f^N shell due to a *partial closure* performed upon the relativistic intershell operators. The final expression is discussed in the light of its reduction to the non-relativistic case that describes f ↔ f transitions in the language of the standard Judd–Ofelt theory.

1. Introduction

The first successful theoretical treatment of the transition probabilities of the f ↔ f transitions so characteristic of the lanthanides and actinides in solid and liquid environments was developed, independently, almost 40 years ago by Judd [1] and Ofelt [2], forming what has been commonly known as the Judd–Ofelt theory of intensities. For general details see [3] and references therein. The Judd–Ofelt theory, and its various extensions, is couched in the language of the LS-coupling basis, in which the various radial integrals are independent of the one-electron total angular momentum quantum number j, characteristic of the jj-coupling basis. The LS-basis is natural in the non-relativistic Schrodinger equation whereas the jj-basis is natural for the relativistic Dirac equation. In the latter basis the radial integrals depend explicitly on the large and small components arising from solutions of the Dirac equation and are dependent not only on the one-electron orbital quantum number ℓ but also on j.

The Judd–Ofelt theory can also be viewed as an effective operator theory [4, 5]. In this paper we formulate a relativistic effective operator theory of f ↔ f transitions based upon extensions of the original proposal of Sandars and Beck [6] for calculating relativistic effects in many-electron hyperfine structure through the introduction of the concept of an LS-coupled relativistic state. By a means of an effective Hamiltonian acting on these states the relativistic problem was turned into a non-relativistic one that could be solved more easily. It was found that the adaption of their approach to crystal field theory led to a relativistic mechanism of particular significance for half-filled shell ions [7, 8]. Here the problem is complicated by the need to consider matrix elements coupling different electron configurations. In some respects it is like producing a relativistic form of configuration interaction in a crystal field [9] except that one of the operators is the electric dipole operator.

While the existence of relativistic effects is beyond dispute the assessment of their relevance to actual spectra requires quantitative evaluation and to date there has been no such determination. This assessment involves two distinct problems: firstly, the determination

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of the form of the relativistic effective operators expressed in terms of tensor operators and relativistic radial integrals in an appropriate perturbative structure, and secondly, quantitative evaluation of the radial integrals and tensor operator matrix elements for specific systems. In this paper we present a solution to the first problem with the hope that it will eventually lead to the solution of the second problem. The key result, equation (12), should form the basis for that solution. Already one can see from that result that relativistic effects introduce new effective operators that go beyond those normally associated with the Judd–Ofelt model of f $\leftrightarrow$ f transitions in crystal fields.

Angular momentum theory plays a key role in much of this paper and, in general, the notation developed by Judd [10] and Edmonds [11] is adopted.

2. Relativistic effective operators

Following the proposal of Sandars and Beck [6] for finding effective relativistic tensor operators, each of the spherical tensors expressed in terms of unit tensor operators, together with a certain radial integral, is replaced by the double tensor operator in the following way:

$$\langle n\ell|r^x|n'\ell'\rangle\langle\ell\|C^{(x)}\|\ell'\rangle u^{(x)}_{\varrho}(\ell,\ell')$$
$$\Rightarrow \sum_{\kappa_1 k_1}\sum_{i_1,i_2}^{2}\beta^{x\ell'\ell}_{\kappa_1 k_1}(j_{i_1}j'_{i_2})R^x(j_{i_1}j'_{i_2})\langle j_{i_1}\|C^{(x)}\|j'_{i_2}\rangle w^{(\kappa_1 k_1)x}_{\varrho}(s\ell,s\ell'), \tag{1}$$

where $j_\pm \equiv \ell \pm 1/2$ is numbered by $i_1 = 1, 2$ and, in the general case, $j'_\pm \equiv \ell' \pm 1/2$ is numbered independently by $i_2 = 1, 2$; the ranks κ_1 and k_1 are limited by the triangular conditions for the non-vanishing 9-j symbol of the angular factor

$$\beta^{x\ell'\ell}_{\kappa_1 k_1}(j_{i_1}j'_{i_2}) = (-1)^{\kappa_1+k_1+x}[j_{i_1}, j'_{i_2}]^{1/2}\begin{Bmatrix}\ell' & \ell & k_1\\ s & s & \kappa_1\\ j'_{i_2} & j_{i_1} & x\end{Bmatrix}. \tag{2}$$

The radial integrals contain the *large* and *small* components [12], and they are defined as follows:

$$R^x(j_{i_1}, j'_{i_2}) = \langle P^{j_{i_1}}|r^x|P^{j'_{i_2}}\rangle + \langle Q^{j_{i_1}}|r^x|Q^{j'_{i_2}}\rangle. \tag{3}$$

The reduced matrix element of the spherical tensor in equation (1) is the generalization of the intrashell case presented in [7], namely

$$\langle j_{i_1}\|C^{(x)}\|j'_{i_2}\rangle = (-1)^{j_{i_1}+1/2}[j_{i_1}, j'_{i_2}]^{1/2}\varepsilon(\ell+x+\ell')\begin{pmatrix} j_{i_1} & x & j'_{i_2}\\ \frac{1}{2} & 0 & -\frac{1}{2}\end{pmatrix}. \tag{4}$$

The parity requirement $\varepsilon(\ell + x + \ell')$, that is equal 1 when $\ell + x + \ell'$ is even and 0 otherwise, represents the triangular condition for the non-vanishing 3-j symbol in the reduced matrix element on the left-hand side of equation (1).

The double intershell operator $w^{(\kappa_1 k_1)x}_{\varrho}(s\ell, s\ell')$ is a unit tensor operator, and it is defined by its reduced matrix element

$$\langle s\ell''\|w^{(\kappa_1 k_1)}(s\ell,s\ell')\|s\ell'''\rangle = \delta(\ell'',\ell)\delta(\ell',\ell'''). \tag{5}$$

In table 1 the possible ranks of the relativistic effective double tensor operators are presented. In general, there are two separate cases for each of the two possible ranks $\kappa_1 = 0, 1$. Namely, for $\kappa_1 = 1$, the parity of $\kappa_1 + k_1 + x$ is distinguished since the even parity of this sum of operator ranks guarantees the Hermiticity of the operator (see [6]).

Table 1. Tensor operator ranks.

x	$\kappa_1 + k_1 + x =$ even	$\kappa_1 + k_1 + x =$ odd
1	(01)1 (10)1 (12)1	(11)1
2	(02)2 (11)2 (13)2	(12)2
3	(03)3 (12)3 (14)3	(13)3
4	(04)4 (13)4 (15)4	(14)4
5	(05)5 (14)5 (16)5	(15)5
6	(06)6 (15)6 (17)6	(16)6
7	(07)7 (16)7 (18)7	(17)7

3. Coupling of intershell double tensor operators

Double tensor operators act within the spin and orbital spaces simultaneously, and in the case of intershell objects the rule of their coupling has the form

$$w_{\rho}^{(\kappa_1 k_1)x}(s\ell, s\ell')w_{\eta}^{(\kappa_2 k_2)y}(s\ell', s\ell) = \sum_{z\zeta}\sum_{\kappa_3 k_3}(-1)^{x-y-\zeta+\kappa_3+k_3+2s}[z, x, y]^{1/2}[\kappa_3, k_3]\begin{pmatrix} x & y & z \\ \varrho & \eta & -\zeta \end{pmatrix} \times \begin{Bmatrix} \kappa_2 & \kappa_3 & \kappa_1 \\ \frac{1}{2} & \frac{1}{2} & \frac{1}{2} \end{Bmatrix}\begin{Bmatrix} k_2 & k_3 & k_1 \\ \ell & \ell' & \ell \end{Bmatrix}\begin{Bmatrix} \kappa_1 & k_1 & x \\ \kappa_2 & k_2 & y \\ \kappa_3 & k_3 & z \end{Bmatrix} w_{\zeta}^{(\kappa_3 k_3)z}(\ell\ell). \tag{6}$$

It is seen that the rule of coupling of two double intershell tensor operators in equation (6) is the generalization of the well known commutator presented in [10] for the intrashell objects. Indeed, only the expression in equation (6) remains from the whole commutator since, for the product of two operators with reversed order, the resultant tensor operator, $w_{\zeta}^{(\kappa_3 k_3)z}(\ell'\ell')$, has vanishing matrix element among the states of f^N configuration. This is clearly seen when all tensor operators are translated into the language of second quantization.

The tensor operator on the right-hand side of equation (6), acting within the f^N shell, is the effective operator. This means that equation (6) is very useful for performing the so-called *partial closure* in the derivation of the transition amplitude. The ranks of the final effective operator $w_{\zeta}^{(\kappa_3 k_3)}(\ell\ell)$ are determined from the triangular conditions for the non-vanishing coupling coefficients in equation (6).

4. Relativistic amplitude of f $\leftrightarrow$ f transitions

The intensity of f $\leftrightarrow$ f transitions in rare earth doped materials is described in the standard way by the model that is based on the perturbation expansion performed for the Hamiltonian

$$H = H_0 + \lambda V_{\mathrm{CF}} \tag{7}$$

where H_0 represents the zeroth-order Hamiltonian, and V_{CF} is the crystal field potential that perturbs the free-system approximation. The perturbing operator in equation (7) is defined in such a way that it mixes into the states of f^N configurations new components of opposite parity, namely

$$V_{\mathrm{CF}} \equiv PV_{\mathrm{CF}}Q + QV_{\mathrm{CF}}P \tag{8}$$

where Q projects onto the orthogonal complement of P.

Due to the parity requirements the first-order contributions to the transition amplitude of electric dipole transition vanish. The first non-zero terms are of second order, and they have

the form of products of the matrix elements,

$$\Gamma^2_\lambda = \sum_{Xx}\{\langle\Psi^0_f|D^{(k)}_q|Xx\rangle\langle Xx|QV_{\rm CF}P|\Psi^0_i\rangle/(E^0_i - E^0_{Xx}) + \langle\Psi^0_f|PV_{\rm CF}Q|Xx\rangle\langle Xx|D^{(k)}_q|\Psi^0_i\rangle/(E^0_f - E^0_{Xx})\} \tag{9}$$

where Xx represent the states of intermediate excited configuration X that has the opposite parity to the parity of f^N. In terms of the unit tensor operators the electric dipole radiation operator has the form

$$PD^{(k)}_q Q = \sum_i \langle\ell|r^k_i|\ell'\rangle\langle\ell\|C^{(k)}_i\|\ell'\rangle u^{(k)}_{q,i}(\ell,\ell') \qquad (k=1) \tag{10}$$

with the crystal field potential

$$QV_{\rm CF}P = \sum_{t,p}^{\rm all} B^t_p \sum_i^N \langle\ell'|r^t_i|\ell\rangle\langle\ell'\|C^{(t)}_i\|\ell\rangle u^{(t)}_{p,i}(\ell',\ell) \tag{11}$$

where B^t_p are the so-called crystal field parameters.

In order to formulate the relativistic model of $\mathrm{f}\leftrightarrow\mathrm{f}$ transitions the procedure presented in equation (1) has to be used, and the coupling of double tensor operators has to be performed in accordance with equation (6). Taking into account the two terms that determine the transition amplitude at the second order (equation (9)), the relativistic effective operators have the form

$$\begin{aligned}\{DV+VD\}^R = \sqrt{3}\sum_{tp} B^t_p[t]^{1/2} &\sum_{\kappa_1=0,1}\sum_{k_1\leqslant|\kappa_1-1|}^{\kappa_1+1}\sum_{\kappa_2=0,1}\sum_{k_2\leqslant|\kappa_2-t|}^{\kappa_2+t}\sum_{\ell'}\varepsilon(\ell+1+\ell')\\ &\times\varepsilon(\ell+t+\ell')\mathcal{A}^{\kappa_1\kappa_2}_{k_1k_2}(t\ell')\\ &\times\sum_{\kappa_3=0,1}\sum_{k_3\leqslant|t-1|}^{t+1} a\sum_{k\leqslant|\kappa_3-k_3|}^{\kappa_3+k_3}[k]^{1/2}\sum_q(-1)^{\kappa_3+k_3+t-q}[\kappa_3,k_3]\\ &\times\begin{pmatrix}1 & t & k\\ \varrho & p & -q\end{pmatrix}\begin{Bmatrix}\kappa_2 & \kappa_3 & \kappa_1\\ \frac12 & \frac12 & \frac12\end{Bmatrix}\\ &\times\begin{Bmatrix}k_2 & k_3 & k_1\\ \ell & \ell' & \ell\end{Bmatrix}\begin{Bmatrix}\kappa_1 & k_1 & 1\\ \kappa_2 & k_2 & t\\ \kappa_3 & k_3 & k\end{Bmatrix}W^{(\kappa_3k_3)k}_q(\ell\ell)\end{aligned} \tag{12}$$

where $\mathcal{A}^{\kappa_1\kappa_2}_{k_1k_2}(t\ell')$ is defined by the angular and radial terms in the following way:

$$\begin{aligned}\mathcal{A}^{\kappa_1\kappa_2}_{k_1k_2}(t\ell') = \sum_{i_1,i_2}^{2}&\beta^{1\ell'\ell}_{\kappa_1k_1}(j_{i_1}j'_{i_2})\beta^{t\ell\ell'}_{\kappa_2k_2}(j'_{i_2}j_{i_1})R^1(j_{i_1}j'_{i_2})R^t(j'_{i_2}j_{i_1})\\ &\times\langle j_{i_1}\|C^{(1)}\|j'_{i_2}\rangle\langle j'_{i_2}\|C^{(t)}\|j_{i_1}\rangle\end{aligned} \tag{13}$$

and i_1 and i_2 number $j_\pm$ and $j'_\pm$; the angular factors and the radial integrals are defined by equations (2) and (3). In addition, the factor a in equation (12) is equal to 2 when the parity of appropriate ranks of operators is the same; otherwise it vanishes, namely,

$$a = \begin{cases}2 & \text{if}\quad p(\kappa_1+k_1+1+\kappa_2+k_2+t) = p(\kappa_3+k_3)\\ 0 & \text{otherwise.}\end{cases} \tag{14}$$

The expression in equation (12) determines the amplitude of the $\mathrm{f}\leftrightarrow\mathrm{f}$ transition defined at the second order of perturbation expansion with the inclusion of the relativistic effects. The tensor operators $W^{(\kappa_3k_3)k}_q(\ell\ell)$, as double tensor operators, act within the spin and orbital spaces; they include in an *effective* way the relativistic effects and, as objects acting within the $4\mathrm{f}^N$ shell, they are *effective* operators. Summarizing, the operators that determine the transition amplitude are *doubly effective double tensor operators*.

5. Discussion

The effective operators defined in equation (12) generalize the standard Judd–Ofelt effective operators, and the reduction to the non-relativistic case is easily seen when all the ranks of operators acting within the spin space are equal to zero. Indeed, setting $\kappa_1 = \kappa_2 = \kappa_3 = 0$ results in $k_1 = 1$, $k_2 = t$ and $k_3 = k$. In such a situation, the rank of the effective unit tensor operator is even, the spin-dependent 6-j symbol in equation (12) is a number, 9-j is reduced to a number and the remaining 6-j has the form

$$\begin{Bmatrix} t & k & 1 \\ \ell & \ell' & \ell \end{Bmatrix} \tag{15}$$

which, together with the 3-j symbol, gives exactly the angular part of standard Judd–Ofelt effective operators. The contributions that are represented by the terms with $\kappa_1, \kappa_2, \kappa_3 = 1$ describe the effects that are new in the spectroscopy of rare earth ions in crystals. The model of $f \leftrightarrow f$ transitions introduced here gives for the first time the opportunity to establish, already at the second order, the importance of relativistic effects in relation to the standard Judd–Ofelt terms. Indeed, even purely crystal field effects are described here in the language of the relativistic approach.

There is no *a priori* information on the relative magnitude of various terms contributing to the transition amplitude, and therefore to establish the hierarchy of important terms an extensive numerical analysis is required; work along this line is in progress.

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