Judd-Ofelt theory in a new light on its (almost) 40^{th} anniversary

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Abstract. The standard Judd-Ofelt theory of one photon electric dipole transitions in f^N systems is discussed in the language of the one particle parametrization scheme. An overview of various physical mechanisms that contribute to the Judd-Ofelt intensity parameters is performed. The analysis of the morphology of these parameters is based on the static model of their original derivation, dynamic model, electron correlation third order approach, spin orbit interaction influence, and an exotic perturbation caused by a specific mass shift. As a new aspect of the investigations on the physical nature of $f \longleftrightarrow f$ transitions, a transformation of the Judd-Ofelt effective operators to their relativistic version is presented. In this approach the transition amplitude is expressed by the effective double tensor operators, acting within the $4f^N$ shell, and effectively representing relativistic contributions. In particular, the relativistic form of the crystal field potential is employed, and in addition, the interactions through the crystal field potential within the spin-orbital space are included.

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1. Introduction

It is a common opinion that the task of reproduction of spectra of rare earth doped materials is reduced to the problem of adjusting at most three intensity parameters in accordance with the following expression

$$S_{f\longleftarrow i} = \sum_{\lambda=2,4,6} \Omega_\lambda \mid \langle \Psi_f \mid\mid U^{(\lambda)} \mid\mid \Psi_i \rangle \mid ^2 \tag{1}$$

For the vast majority of researchers that are involved in the spectroscopy of rare earth ions this technical point of view very often defines the well-known Judd-Ofelt theory [1,2]; for some of them however, the Judd-Ofelt theory has a broader interpretation.

Without the definition of the physical model that characterizes the Judd Ofelt theory, expression Eq. (1) is an algebraic scheme of the parametrization of the spectrum. ¿From such a point of view, there is no reason to limit the terms in the summation to just those with even ranks. Actually, treating the expression in Eq. (1) in a formal way, it is possible to introduce in an *ad hoc* way completely new terms for λ odd without giving them any physical explanation. However it should be realized that such a technical improvement of the fitting procedure (more degrees of freedom, better adjustment) loses its identity as an extension of the original Judd Ofelt theory as introduced by its authors in 1962.

When the parameters Ω_λ in Eq. (1) are determined in a semiempirical way, and the intensities are reproduced, one may conclude that the one particle parametrization scheme applied for the spectrum works well; and this is the success of the Judd-Ofelt theory.

The aim of this presentation is to answer the question about the physical mechanisms that contribute to the intensity parameters which are determined from Eq. (1) in a semiempirical way. The present discussion demonstrates the generality and universality of the Judd-Ofelt theory which, in fact, goes far beyond the initial limitations of its original derivation.

2. Non-relativistic approach

2.1. Second order effective operators

The transition amplitude defined within the standard Judd-Ofelt theory, based on the static model, is determined by matrix elements of the effective operators

$$\begin{aligned}\Omega_\lambda \ : \quad T_{J-O} \ &= 2 \sum_{t,p}^{odd} B_p^t \sum_{\lambda,q}^{even} \sum_{\ell'}^{even} (-1)^q [\lambda]^{1/2} \begin{pmatrix} t & 1 & \lambda \\ p & \rho & -q \end{pmatrix} A_t^\lambda(\ell') \\ &\langle \varrho^1(4f \longrightarrow \ell') \mid r^t \mid 4f \rangle \, \langle 4f^N \, \Psi_f^0 \mid \ U_q^{(\lambda)} \ \mid 4f^N \, \Psi_i^0 \rangle \end{aligned} \tag{2}$$

where B_p^t are the crystal field parameters, and the angular term has the form

$$A_t^{\lambda}(\ell') \;=\; [\lambda]^{1/2} \begin{Bmatrix} t & \lambda & 1 \\ f & \ell' & f \end{Bmatrix} \langle f\|C^{(1)}\|\ell'\rangle \, \langle \ell'\|C^{(t)}\|f\rangle \tag{3}$$

The radial integral in Eq. (2) contains the perturbed function $\varrho^1(4f \longrightarrow \ell')$ [3] that represents the perturbing influence of all single excitations from the $4f$ shell to one electron states of ℓ' symmetry.

When the mutual interaction between the lanthanide ion and the ligands is taken into account, a part of intensity parameters is interpreted as the terms that represent the so-called dynamic coupling mechanism [4],

$$\Omega_\lambda \;:\; T_{dyn} = A^L_{\lambda+1}\, \alpha_\lambda(L) \langle 4f \mid r^\lambda \mid 4f\rangle \langle f \mid\mid C^{(\lambda)} \mid\mid f\rangle \, U_q^\lambda \tag{4}$$

where $A^L_{\lambda+1}$ is a structural parameter, and $\alpha_\lambda(L)$ is related to the frequency dependent polarizability of the ligand (see [5]).

2.2. Third order effective operators

The original model of Judd and Ofelt is based on the single configuration approximation. When the effects of electron correlation are taken into account at the third order, the transition amplitude in general is determined by the following effective operators

$$\begin{aligned} \Omega_\lambda \;:\; {}^1\Gamma \approx \sum_{tp}^{odd} \Big\{ \sum_{\lambda}^{even} \{ (T_{J-O} \;+\; {}^1T_{stat.corr.}) \,+ \\ \delta(t, \lambda+1)(T_{dyn} \;+\; {}^1T_{dyn.corr.}) \} \; U^{(\lambda)}(ff) \end{aligned} \tag{5}$$

where ${}^1T_{stat.corr.}$ and ${}^1T_{dyn.corr.}$ are the third order terms that represent the impact of electron correlation, and they originate from the static and dynamic models.

The results of a numerical analysis demonstrated that the major part of electron correlation effects is represented by third order one-particle effective operators [5]. The angular part of these effective operators is the same as in the case of standard Judd-Ofelt term in Eq. (2), while the radial parts are different. For example, the static part of the transition amplitude defined up to the third order has the form

$$\Omega_\lambda \;:\; {}^1T^{\lambda t}_{stat} = \sum_{\ell'}^{even} [R^t_{JO}(\ell') - R^t_{HF}(\ell' f) + \frac{(N-1)}{2} R^0_t(\ell' f)] A^\lambda_t(\ell') \tag{6}$$

The radial terms in Eq. (6) have the following interpretation:

$R^t_{JO}(\ell')$ represents the standard Judd-Ofelt theory (see Eq. (2)),

$R^t_{HF}(\ell' f) =< \rho^1(4f \rightarrow \ell')|r^t|\rho_{HF}(4f \rightarrow f) > \;+\; < \rho^t(4f \rightarrow \ell')|r^1|\rho_{HF}(4f \rightarrow f) >$, and these terms are associated with the third-order effective operators arising from the Hartree-Fock potential,

$R^0_t(\ell' f) =< \rho^0(4f \to f)|r^1|\rho^t((4f \to \ell') > \; + \; < \rho^0(4f \to f)|r^t|\rho^1((4f \to \ell') >$, and these terms are also of third-order but they are caused by the Coulomb operator.

The perturbed functions $\rho^t(4f \to \ell')$, $\rho_{HF}(4f \to f)$ and $\rho^s(4f \to \ell'')$ contain the first order corrections due to the perturbing influence of single excitations from the $4f$ shell to all (discrete and continuum) states of ℓ', f and ℓ'' symmetry [3].

As an example of an exotic interaction, the mass specific shift is regarded as perturbation affecting the transition amplitude [6]. In this particular case the third order effective operators are also one particle object, and therefore one may conclude that they contribute to the intensity parameters evaluated from Eq. (1),

$$\begin{aligned}\Omega_\lambda \; : \quad {}^1T_{mass} \; &= \; \frac{1}{2}\sum_{\lambda,q}^{all}(-1)^{\lambda-q}[\lambda]^{1/2}\sum_{t,p}^{odd}B^t_p\sum_{\ell'}^{even}\begin{pmatrix}1 & t & \lambda\\ \rho & p & -q\end{pmatrix}A^\lambda_t(\ell') \\ &\quad (\varepsilon_\lambda+\varepsilon^*_\lambda)\,\mathcal{T}^{\mathcal{P}(\lambda)t}_{mass}(\ell')\;U^{(\lambda)}_q(ff) \qquad (7)\end{aligned}$$

where ε_λ and ε^*_λ select even and odd values of λ, and $\mathcal{P}(\lambda)$ determines the parity of λ. It is interesting to note that also in this particular case the angular part of the effective operator is the same as for the standard Judd-Ofelt term (Eq. (2)) The radial term

$$\mathcal{T}^{\mathcal{P}(\lambda)t}_{mass}(\ell') \; = \; -\frac{N}{3M}\left[(-1)^\lambda \; + \; \delta(t,1)\right] R^{\mathcal{P}(\lambda)t}_{mass}(\ell') \qquad (8)$$

is an appropriate combination of the following radial integrals [6],

$$\begin{aligned}R^1_1(\ell') \; &= \; \langle\varrho^1(4f \longrightarrow \ell')\,|\frac{\delta}{\delta r}\,|4f\rangle \\ R^1_2(\ell') \; &= \; \langle\varrho^1(4f \longrightarrow \ell')\,|\frac{1}{r}\,|4f\rangle, \qquad (9)\end{aligned}$$

where the perturbed functions are the same as in the radial integrals of the standard Judd-Ofelt theory.

Due to the asymmetry of the reduced matrix elements of $\bigtriangledown^{*(1)}$ that defines the specific mass shift operator, the sum of the radial integrals does not vanish for λ odd, and therefore also the odd rank unit tensor operators associated with ϵ^*_λ in Eq. (7) contribute to the intensity parameters. This means that, in the nomenclature of the semiempirical approach, the standard parametrization scheme of the Judd Ofelt theory is extended now by additional parameters that are associated with the odd rank unit tensor operators. As a consequence, the expression in Eq. (1) should be enriched by the terms for $\lambda = odd$.

3. Relativistic contributions

An alternative approach to the description of $f \longleftrightarrow f$ transitions is defined within the relativistic framework where the relativistic crystal field potential is taken as a perturbing operator, and relativistic version of the electric dipole radiation operator is used for the evaluation of the transition amplitude. In such a way the second order transition amplitude is determined by the matrix elements of double but still one-particle effective operators of the form [7],

$$\begin{aligned}\Omega_\lambda \ : \quad T^{rel} &= \sqrt{3} \sum_{tp} B_p^t \, [t]^{1/2} \sum_{\kappa_1=0,1} \sum_{k_1 \leq |\kappa_1-1|}^{\kappa_1+1} \sum_{\kappa_2=0,1} \sum_{k_2 \leq |\kappa_2-t|}^{\kappa_2+t} \\ &\sum_{\ell'} \varepsilon(f+1+\ell')\varepsilon(f+t+\ell') \ \mathcal{A}_{k_1k_2}^{\kappa_1\kappa_2}(t\ell') \\ &\sum_{\kappa_3=0,1} \sum_{k_3 \leq |t-1|}^{t+1} a \sum_{\lambda \leq |\kappa_3-k_3|}^{\kappa_3+k_3} [\lambda]^{1/2} \sum_q (-1)^{\kappa_3+k_3+t-q} \, [\kappa_3, k_3] \\ &\begin{pmatrix} 1 & t & \lambda \\ \varrho & p & -q \end{pmatrix} \begin{Bmatrix} \kappa_2 & \kappa_3 & \kappa_1 \\ \frac{1}{2} & \frac{1}{2} & \frac{1}{2} \end{Bmatrix} \begin{Bmatrix} k_2 & k_3 & k_1 \\ f & \ell' & f \end{Bmatrix} \\ &\begin{Bmatrix} \kappa_1 & k_1 & 1 \\ \kappa_2 & k_2 & t \\ \kappa_3 & k_3 & \lambda \end{Bmatrix} W_q^{(\kappa_3 k_3)\lambda}(ff)\end{aligned} \tag{10}$$

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

$$\begin{aligned}\mathcal{A}_{k_1k_2}^{\kappa_1\kappa_2}(t\ell') \ &= \sum_{i_1,i_2}^{2} \ \beta_{\kappa_1k_1}^{1\ell' f}(j_{i_1}j'_{i_2})\beta_{\kappa_2k_2}^{tf\ell'}(j'_{i_2}j_{i_1}) \\ &R^1(j_{i_1}j'_{i_2}) \ R^t(j'_{i_2}j_{i_1}) \ \langle j_{i_1}||C^{(1)}||j'_{i_2}\rangle \ \langle j'_{i_2}||C^{(t)}||j_{i_1}\rangle\end{aligned} \tag{11}$$

and i_1 and i_2 number $j_\pm$ and $j'_\pm$. The factor a in Eq. (10) is equal 2 when the parity of appropriate ranks of operators is the same, otherwise it vanishes. The angular factors have the form

$$\beta_{\kappa_1k_1}^{x\ell'\ell}(j_{i_1}j'_{i_2}) \ = \ (-1)^{\kappa_1+k_1+x} \, [j_{i_1}, j'_{i_2}]^{1/2} \begin{Bmatrix} \ell' & \ell & k_1 \\ s & s & \kappa_1 \\ j'_{i_2} & j_{i_1} & x \end{Bmatrix}, \tag{12}$$

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

$$R^x(j_{i_1}, j'_{i_2}) \ = \ \langle P^{j_{i_1}}|r^x|P^{j'_{i_2}}\rangle \ + \ \langle Q^{j_{i_1}}|r^x|Q^{j'_{i_2}}\rangle, \tag{13}$$

The reduced matrix element of the spherical tensor in Eq. (11) is a generalization of the intra-shell case introduced by Wybourne [8], namely

$$\langle j_{i_1}||C^{(x)}||j'_{i_2}\rangle \ = \ (-1)^{j_{i_1}+1/2} \, [j_{i_1}, j'_{i_2}]^{1/2} \, \varepsilon(\ell+x+\ell') \begin{pmatrix} j_{i_1} & x & j'_{i_2} \\ -\frac{1}{2} & 0 & \frac{1}{2} \end{pmatrix}. \tag{14}$$

The double tensor operator $W^{(\kappa_3 k_3)\lambda}(ff)$ acts within the spin-orbital space. It should be mentioned that a particular part of Eq. (10) associated with W^{11} (spin-orbit interaction) has been previously included at the third order [9], while here it is taken into account already at the second order. In addition, for $\kappa_3 = 0$ in Eq. (10) the expression is reduced to the standard effective operator of Judd and Ofelt.

Finally it should be concluded that T^{rel} gives a new picture of the Judd-Ofelt theory, and its relativistic origin sheds a new light onto theoretical description of $f \longleftrightarrow f$ transitions.

4. Summary

The short review presented here demonstrates that the intensity parameters Ω_λ of the Judd-Ofelt theory are indeed more general than one might expect from their original derivation.

The list of physical mechanisms discussed here contains:

1. crystal field influence based on the static model at second order,
2. crystal field influence based on the dynamic model at the second order,
3. electron correlation effects at the third order, and based on the static and dynamic models,
4. spin-orbit interaction at the third order,
5. mass polarization shift at the third order,

and finally

6. relativistic effects

Do the results of *ab initio* calculations performed within the above scheme give agreement with experiment, and do the contributions caused by these mechanisms reproduce the values of Ω_λ determined from the fitting procedure?

Obviously the above list of physical mechanisms is not complete yet, and there are still some other mechanisms that have to be at least verified. At the same time however, Judd-Ofelt theory, traditionally understood as a single particle parametrization scheme, covers all aspects of these problematic questions.

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