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# Relativistic $f \longleftrightarrow f$ transitions in crystal fields: II. Beyond the single-configuration approximation

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**Abstract**

A relativistic model of $f \longleftrightarrow f$ transitions introduced previously is completed here by the third-order contributions caused by electron correlation. The approach is based on the transformation of all tensor operators to their relativistic effective form; the final effective operators that act within the $4f$ shell are derived by means of the so-called *partial closure*. The tensorial structure of the new effective operators, that are in general two-particle objects, is discussed and their reduced form is analysed in the light of the standard single-particle parametrization scheme of $f \longleftrightarrow f$ transition spectra.

## 1. Introduction

In the previous paper [1] (hereinafter denoted by I) a relativistic model of $f \longleftrightarrow f$ transitions in rare earth ions in crystals was introduced. The approach was based on the transformation of all inter-shell tensor operators to their effective relativistic form by means of the transformation [2]

$$\langle n\ell|r^x|n'\ell'\rangle\langle\ell||C^{(x)}||\ell'\rangle u^{(x)}_{\varrho}(\ell,\ell') \sim \sum_{\kappa_1,k_1} \mathcal{A}R^x w^{(\kappa_1 k_1)x}_{\varrho}(s\ell, s\ell') \tag{1}$$

where $\mathcal{A}$ denotes, in a symbolic way, a coefficient that is responsible for such replacement, $R^x$ contains the *large* and *small* components of the appropriate wavefunctions and $w$ is the double-unit-tensor operator acting within the spin-orbital space (for details see equation (1) in I).

Each operator of the third-order terms contributing to the transition amplitude has to be transformed following the procedure described in I.

From the analysis presented in I it was concluded that the translation of the standard Judd–Ofelt theory does not change the parametrization of $f \longleftrightarrow f$ spectra, and still, even in the language of the relativistic approach, it is based on the one-particle scheme. However, due to the fact that the unit-tensor operators of the Judd–Ofelt approach are replaced by the double-unit-tensor operators, the traditional Judd–Ofelt parameters $\Omega_\lambda$ are substituted by an object that possesses an internal structure, ${}^2\Omega_{(\kappa_3 k_3)\lambda}$, where the superscript shows that the approach in

  

I includes the terms of second order. Thus, within the relativistic approach, of second order, the line strength of the $f \longleftrightarrow f$ transition is determined by the reduced matrix element of a $W$ operator weighted by the newly defined parameters,

$$\mathcal{S}_{f\leftarrow i} = \sum_{\lambda}^{\text{all}} \left| \sum_{\kappa_3 k_3} {}^2\Omega_{(\kappa_3 k_3)\lambda} \langle \Psi_f || W^{(\kappa_3 k_3)\lambda} || \Psi_i \rangle \right|^2 \tag{2}$$

where $\lambda$ is even or odd; the latter terms are new in comparison to the standard non-relativistic Judd–Ofelt approach, and they create a possibility of a better description of difficult cases, and make the theoretical description of transitions such as $0 \longleftrightarrow 1$ possible.

It is seen from equation (2) that the number of parameters is increased, and instead of at most three standard Judd–Ofelt parameters $\Omega_\lambda$ for $\lambda = 2, 4$ and 6 in the present approach, there are 24 parameters in total, among which 12 are associated with even $\lambda$ (see table 1 in I).

The aim of the present investigation is to introduce the third-order contributions to the transition amplitude that represent the perturbing influence of electron correlation effects. In such a way the single-configuration approximation of the second-order relativistic approach presented in I is broken, and additional effective operators contributing to the transition amplitude are introduced. This extension of the model of the theoretical description of $f \longleftrightarrow f$ transitions is motivated by numerical evidence of the very strong impact of electron correlation that has been observed in the case of the non-relativistic third-order model.

## 2. Third-order approach

The third-order terms contributing to the transition amplitude have the general form of a triple product of matrix elements, that differ from each other by the sequence of various operators, for example

$$\Gamma^3_{\text{VDV}} = \sum_{Xx} \sum_{Bb} \langle \Psi^0_f | P V_{\text{corr}} Q | Bb \rangle \langle Bb | D^{(1)}_\varrho | Xx \rangle \langle Xx | Q V_{\text{CF}} P | \Psi^0_i \rangle / (E^0_i - E^0_{Bb})(E^0_i - E^0_{Xx}) \tag{3}$$

where $V_{\text{corr}}$ represents the non-central part of the Coulomb interaction operator that is included in the Hamiltonian as a second perturbing operator, in addition to $V_{\text{CF}}$; $Bb$ and $Xx$ denote the states of excited configurations $B$ and $X$ that are of the same and opposite parity to the parity of $4f^N$. The counterpart terms for the expression defined in equation (3) are a triple product of matrix elements with the positions of $V_{\text{corr}}$ and $V_{\text{CF}}$ interchanged. In order to complete the list of all third-order terms contributing to the transition amplitude, the terms arising from the corrections $\Psi^{11}$, in the matrix elements with $\Psi^0$, also should be taken into account (see equation (25) in [3]).

## 3. Relativistic effective operators

The operators in equation (3) (as well as in the other perturbing expressions for the third-order contributions) have to be replaced by their relativistic effective form [1, 2], and partial closure has to be performed. As a result, in the particular case of the term defined in equation (3), the effective operator that is associated with the Coulomb potential has the form (without the energy denominators),

$$T^{\text{rel}}_{\text{corr}} = \sqrt{3} \sum_{tp} B^t_p [t]^{1/2} \sum_{s} \sum_{\ell',\ell''} \varepsilon_s \varepsilon^*_t \varepsilon_{\ell'} \varepsilon^*_{\ell''} \sum_{\kappa_1,k_1} \sum_{\kappa_2,k_2} \sum_{\kappa_3,k_3} \sum_{\kappa_4,k_4} \mathcal{A}^{\kappa_1\kappa_2\kappa_3\kappa_4}_{k_1k_2k_3k_4}(st\ell''\ell')$$

$$\times \sum_{\lambda,q} (-1)^{t-q} [s,\lambda]^{\frac{1}{2}} \begin{pmatrix} 1 & t & \lambda \\ \varrho & p & -q \end{pmatrix} \sum_{\kappa_5 k_5} [\kappa_5, k_5]$$
$$\times \begin{Bmatrix} \kappa_2 & \kappa_5 & \kappa_1 \\ \frac{1}{2} & \frac{1}{2} & \frac{1}{2} \end{Bmatrix} \begin{Bmatrix} k_2 & k_5 & k_1 \\ \ell'' & \ell' & f \end{Bmatrix} \begin{Bmatrix} \kappa_1 & k_1 & 1 \\ \kappa_2 & k_2 & t \\ \kappa_5 & k_5 & \lambda \end{Bmatrix}$$
$$\times \sum_{x} (-1)^{x+\lambda} [x]^{\frac{1}{2}} \sum_{\kappa_6 k_6} (-1)^{\kappa_6+k_6+1} [\kappa_6, k_6]$$
$$\times \begin{Bmatrix} \kappa_5 & \kappa_6 & \kappa_4 \\ \frac{1}{2} & \frac{1}{2} & \frac{1}{2} \end{Bmatrix} \begin{Bmatrix} k_5 & k_6 & k_4 \\ f & \ell'' & f \end{Bmatrix} \begin{Bmatrix} \kappa_4 & k_4 & s \\ \kappa_5 & k_5 & \lambda \\ \kappa_6 & k_6 & x \end{Bmatrix}$$
$$\times \sum_{i<j} [w_i^{(\kappa_3 k_3)s}(ff) \times w_j^{(\kappa_6 k_6)x}(ff)]^{(\lambda)} \tag{4}$$

where $\mathcal{A}^{\kappa_1\kappa_2\kappa_3\kappa_4}_{k_1k_2k_3k_4}(st\ell''\ell')$ is defined by the angular and radial terms in the following way:

$$\mathcal{A}^{\kappa_1\kappa_2\kappa_3\kappa_4}_{k_1k_2k_3k_4}(st\ell''\ell') = \sum_{i_1,i_2}^{2} \sum_{i_3,i_4}^{2} \beta^{sff}_{\kappa_3 k_3}(j_{i_3} j_{i_3}) \beta^{s\ell'' f}_{\kappa_4 k_4}(j_{i_1} j''_{i_4}) \beta^{1\ell'\ell''}_{\kappa_1 k_1}(j''_{i_4} j'_{i_2}) \beta^{tf\ell'}_{\kappa_2 k_2}(j'_{i_2} j_{i_1})$$
$$\times R^s(j_{i_3} j_{i_1} j_{i_3} j''_{i_2}) R^1(j''_{i_4} j'_{i_2}) R^t(j'_{i_2} j_{i_1})$$
$$\times \langle j_{i_3} || C^{(s)} || j_{i_3} \rangle \langle j_{i_1} || C^{(s)} || j''_{i_4} \rangle \langle j''_{i_4} || C^{(1)} || j'_{i_2} \rangle \langle j'_{i_2} || C^{(t)} || j_{i_1} \rangle \tag{5}$$

and $i_1$, $i_2$, $i_3$ and $i_4$ number $j_\pm$ and $j'_\pm$. This factor describes the transformation of the initial operators to their relativistic effective form, and each pair of $\kappa k$ is associated with one of them. Indeed, at third order there are four operators in total, since the contribution is expressed by a triple product of matrix elements, and one of them contains the Coulomb interaction potential that is a scalar product of two spherical tensors.

The angular terms $\beta$ originate from the transformation from $LS$ coupling to $jj$ coupling that is required for all relativistic investigations; this part of the procedure is reflected by the structure of the 9-$j$ symbol in the definition of $\beta$, namely,

$$\beta^{x\ell'\ell}_{\kappa_1 k_1}(j_{i_1} j'_{i_2}) = (-1)^{\kappa_1+k_1+x} [j_{i_1}, j'_{i_2}]^{1/2} \begin{Bmatrix} \ell' & \ell & k_1 \\ s & s & \kappa_1 \\ j'_{i_2} & j_{i_1} & x \end{Bmatrix}. \tag{6}$$

In fact the whole procedure associated with the transformation of each operator to its relativistic form is described by the indices of $\beta$. Namely, the inter-shell operator of rank $x$ is replaced by a tensor operator with ranks $\kappa_1 k_1$ (that are coupled together to $x$). Furthermore, the initial operator acts between shells $\ell$ and $\ell'$, while after the transformation the resulting operator is still an inter-shell object, but it acts between the shells defined within the $jj$ coupling scheme.

The radial integrals contain the *large* and *small* components, and they are defined by equation (3) of I. The reduced matrix element of the spherical tensor evaluated with the functions defined within the $jj$ coupling is presented in equation (4) of I.

It is seen from equation (4) that the third-order relativistic contributions that involve the perturbing influence of the Coulomb interaction are associated with two particle operators acting within the spin–orbital space. In the non-relativistic electron correlation approach the third-order operators are expressed by the tensorial product of unit-tensor operators $U$ while here, since the active space is extended by spin, there is a tensorial product of double-tensor operators. In fact, the operators in equation (4) are *doubly effective*, since the first step of the translation of intensity theory to the language of relativity is to construct the operators that are relativistic in an effective way (factor $\mathcal{A}$, in equation (1)). The next step is to perform the so-called *partial closure* to obtain the effective operators in the sense of their action within

the space spanned by the wavefunctions of $4f^N$ configuration (the 6-$j$ and 9-$j$ symbols in equation (4)).

When certain ranks in the effective operators in equation (4) are set to zero, the third-order contributions to the transition amplitude are determined by the one-particle double-tensor operators similarly as in the case of the second-order terms. For example, with $\kappa_6 = k_6 = 0$ $T^{\rm rel}_{\rm corr}$ has the form

$$T^{\rm rel}_{\rm corr}(x=0) \Longrightarrow \frac{\sqrt{3}}{\sqrt{2}[\ell]^{1/2}} \sum_{tp} B^t_p [t]^{1/2} \sum_{\lambda,q}^{\rm even} [\lambda]^{1/2} (-1)^{t-q} \sum_{\ell',\ell''} \varepsilon^*_t \varepsilon_{\ell'} \varepsilon^*_{\ell''}$$
$$\times \sum_{\kappa_1,k_1} \sum_{\kappa_2,k_2} \sum_{\kappa_3,k_3} \sum_{\kappa_4,k_4} \mathcal{A}^{\kappa_1\kappa_2\kappa_3\kappa_4}_{k_1k_2k_3k_4}(\lambda t \ell'' \ell') \begin{pmatrix} 1 & t & \lambda \\ \varrho & p & -q \end{pmatrix}$$
$$\times \begin{Bmatrix} \kappa_2 & \kappa_4 & \kappa_1 \\ \frac{1}{2} & \frac{1}{2} & \frac{1}{2} \end{Bmatrix} \begin{Bmatrix} k_2 & k_4 & k_1 \\ \ell'' & \ell' & f \end{Bmatrix} \begin{Bmatrix} \kappa_1 & k_1 & 1 \\ \kappa_2 & k_2 & t \\ \kappa_4 & k_4 & \lambda \end{Bmatrix} W^{(\kappa_3 k_3)\lambda}(ff). \tag{7}$$

The effective operators in equation (7) have a structure similar to the relativistic version of the second-order contributions defined by equation (12) in I. The only difference between the two expressions lies in the replacement of $\mathcal{A}^{\kappa_1\kappa_2}_{k_1k_2}$ in equation (12) of I by $\mathcal{A}^{\kappa_1\kappa_2\kappa_3\kappa_4}_{k_1k_2k_3k_4}$. This modification is obviously caused by the fact that at the third order there are four initial operators to be coupled together, and for each one there is a pair of new ranks ($\kappa k$) introduced (two spherical tensors form the definition of Coulomb interaction, crystal field potential and electric dipole radiation operator); at the same time at the second order there are only two operators that have to be transformed to their relativistic forms, and therefore there are two sets of new ranks.

There is another origin of the one-particle effective operators contributing to the transition amplitude at the third order. When in equation (3) the Hartree–Fock potential for $V_{\rm corr}$ is inserted (in accordance with the definition of the electron correlation operator), then the effective operator has the form

$$T^{\rm rel}_{\rm HF} = \sqrt{3} \sum_{tp} B^t_p [t]^{1/2} \sum_{\ell',\ell''} \delta(\ell'', f) \varepsilon^*_t \varepsilon_{\ell'} \sum_{\kappa_1,k_1} \sum_{\kappa_2,k_2} \sum_{\kappa_3,k_3} \delta(\kappa_1, k_1) \mathcal{A}^{\kappa_1\kappa_2\kappa_3}_{k_1k_2k_3}(0 t \ell'' \ell')$$
$$\times \sum_{\lambda,q}^{all} (-1)^{t-q} [\lambda]^{\frac{1}{2}} [k_1]^{-\frac{1}{2}} \begin{pmatrix} 1 & t & \lambda \\ \varrho & p & -q \end{pmatrix} \sum_{\kappa_5 k_5} [\kappa_5, k_5]$$
$$\times \begin{Bmatrix} \kappa_2 & \kappa_5 & \kappa_1 \\ \frac{1}{2} & \frac{1}{2} & \frac{1}{2} \end{Bmatrix} \begin{Bmatrix} k_2 & k_5 & k_1 \\ f & \ell'' & \ell' \end{Bmatrix} \begin{Bmatrix} \kappa_2 & k_2 & 1 \\ k_5 & \kappa_5 & k_1 \end{Bmatrix}$$
$$\times \sum_{\kappa_6 k_6} (-1)^{\kappa_6+k_6+k_5} [\kappa_6, k_6] \begin{Bmatrix} \kappa_3 & \kappa_6 & \kappa_5 \\ \frac{1}{2} & \frac{1}{2} & \frac{1}{2} \end{Bmatrix} \begin{Bmatrix} k_3 & k_6 & k_5 \\ f & \ell' & f \end{Bmatrix}$$
$$\times \begin{Bmatrix} \kappa_5 & k_5 & 1 \\ \kappa_3 & k_3 & t \\ \kappa_6 & k_6 & \lambda \end{Bmatrix} W^{(\kappa_6 k_6)\lambda}(ff) \tag{8}$$

where $\delta(\ell'', f)$ results from the fact that the Hartree–Fock potential is associated with the spherical tensor of rank zero; $\delta(\kappa_3, k_3)$ is also a result of the latter, that is taken into account for the reduction of $\beta$ (defined in equation (6)) associated with the transformation of the Hartree–Fock potential to its relativistic form. In addition, the third 6-$j$ symbol in equation (8) results from the reduction of the 9-$j$ coefficient that originates from the coupling of the zero-order double-tensor operator (it represents the Hartree–Fock potential) with the relativistic electric dipole radiation operator.

The transformation factor in this particular case, where there are three operators under consideration, has a general form

$$\mathcal{A}^{\kappa_1\kappa_2\kappa_3}_{k_1k_2k_3}(xt\ell''\ell') = \sum_{i_1,i_2,i_3}^{2} \beta^{x\ell''f}_{\kappa_3k_3}(j_{i_1}j''_{i_3})\beta^{1\ell'\ell''}_{\kappa_1k_1}(j''_{i_3}j'_{i_2})\beta^{tf\ell'}_{\kappa_2k_2}(j'_{i_2}j_{i_1})$$
$$\times R^{\mathrm{HF}}(j_{i_1}j''_{i_3})R^{1}(j''_{i_3}j'_{i_2})R^{t}(j'_{i_2}j_{i_1})$$
$$\times \langle j_{i_1}||C^{(x)}||j''_{i_3}\rangle\langle j''_{i_3}||C^{(1)}||j'_{i_2}\rangle\langle j'_{i_2}||C^{(t)}||j_{i_1}\rangle. \tag{9}$$

It is interesting to mention that when the appropriate ranks associated with the spin part of each operator are set to zero, the effective operators are reduced to their non-relativistic form analysed previously. This property demonstrates that the approach presented here is well defined and the expressions discussed originate from a well established background.

## 4. Discussion

In the present discussion the standard non-relativistic parametrization of the $4f^N$ ion spectrum is replaced by a more general expression that represents the interactions within the spin–orbital space, namely

$$\mathcal{S}_{f\leftarrow i} = \sum_{\lambda}\left|\sum_{\kappa_3k_3}\Omega_{(\kappa_3k_3)\lambda}\langle\Psi_f||W^{(\kappa_3k_3)\lambda}||\Psi_i\rangle\right|^2.$$

The parameters $\Omega_{(\kappa_3k_3)\lambda}$ contain, in addition to second-order terms that represent the interaction via the crystal field potential, ${}^2\Omega_{(\kappa_3k_3)\lambda}$ from equation (2), also the third-order contributions caused by electron correlation, ${}^3\Omega_{(\kappa_3k_3)\lambda}$. The number of parameters that contain electron correlation effects is the same as at the second order, since no new objects of unusual tensorial structure are obtained at the third order. This conclusion is based on the assumption that the third-order contributions associated with the two-particle operators, similarly to the case of non-relativistic approach, are relatively unimportant. However, in order to consider this assumption as a justified approximation, the relative magnitudes of the various terms have to be evaluated numerically. Finally, it should be pointed out that the selection rules for the non-vanishing matrix elements that contribute to the transition amplitude are the same at the second and third order, but at the same time they are different from those of the non-relativistic model. The main difference is caused by the fact that, in general, the final ranks, $\lambda$, of the effective operators may have both even *and* odd values.

Due to the change of the selection rules it is possible now to describe theoretically such transitions that are forbidden by a standard non-relativistic approach. Indeed, due to the selection rules for the non-vanishing matrix element of unit-tensor operator $U$, the amplitude of the transition $0 \longrightarrow 0$ defined within the standard Judd–Ofelt theory vanishes. In the language of the relativistic approach, and in accordance with equation (2), the amplitude of this transition is determined by the following expression:

$$\mathcal{T}_{0\longrightarrow 0} = \Omega_{(11)0}\langle 0||W^{(11)0}||0\rangle.$$

The operator in the above matrix element represents the spin–orbit interaction. It should be noted, however, that the amplitude of this unusual transition does not vanish only for such symmetries for which in the expansion of the crystal field potential the term with the rank $t = 1$ exists. In fact, this is the case of $C_{2v}$ symmetry, and the most interesting electric dipole transitions $0 \longrightarrow 0$ are observed in $Eu$ in the host of this very symmetry.

The other special transition $0 \longrightarrow 1$ is not allowed by the required parity of ranks of effective operators in the standard Judd–Ofelt theory. In the present approach, the transition amplitude is determined by three components, namely,

$$\mathcal{T}_{0\longrightarrow 1} = \Omega_{(01)1}\langle 1||W^{(01)1}||0\rangle + \Omega_{(10)1}\langle 1||W^{(10)1}||0\rangle + \Omega_{(11)1}\langle 1||W^{(11)1}||0\rangle.$$

Inspection of the expressions for the third-order contributions shows that the Coulomb interaction potential does not contribute to the transition amplitude of this transition since only the even-rank effective operators are defined in equation (7). At the same time the effective operators associated with the Hartree–Fock potential, as defined by equation (8), do contribute to the transition amplitude of the $0 \longrightarrow 1$ transition.

In order to relate the newly introduced parameters to those of the standard Judd–Ofelt approach, it is convenient to define the ratio of reduced matrix elements (introduced in [4])

$$X^{(\kappa t)k}(\Psi, \Psi') = \langle \ell^N[\alpha SL]J||W^{(\kappa t)k}||\ell^N[\alpha' S'L']J'\rangle / \langle \ell^N[\alpha SL]J||U^{(k)}||\ell^N[\alpha' S'L']J'\rangle$$

for all the reduced matrix elements of $U \neq 0$. In such a way the basic expression of the Judd–Ofelt theory

$$\mathcal{S}_{f\leftarrow i} = \sum_{\lambda} \Omega_{\lambda} |\langle \Psi_f||U^{\lambda}||\Psi_i\rangle|^2$$

where $\Omega_\lambda$ represents various interactions within the orbital space [5], is generalized in the following way:

$$\mathcal{S}^{\mathrm{rel}}_{f\leftarrow i} = \sum_{\lambda} \Omega^{\mathrm{rel}}_{\lambda}(\Psi_f \Psi_i) |\langle \Psi_f||U^{\lambda}||\Psi_i\rangle|^2$$

where

$$\Omega^{\mathrm{rel}}_{\lambda}(\Psi_f \Psi_i) = \left( \sum_{\kappa_3 k_3} \Omega_{(\kappa_3 k_3)\lambda} X^{(\kappa_3 k_3)\lambda}(\Psi_f, \Psi_i) \right)^2.$$

The parameters $\Omega^{\mathrm{rel}}_{\lambda}(\Psi_f \Psi_i)$ are new objects and they depend on the states involved in the described process. In this sense the universality of the non-relativistic parametrization scheme is lost when the relativistic effects are included. However, it is demonstrated here that the $f \longleftrightarrow f$ spectra are still parametrized within the single-particle scheme.

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