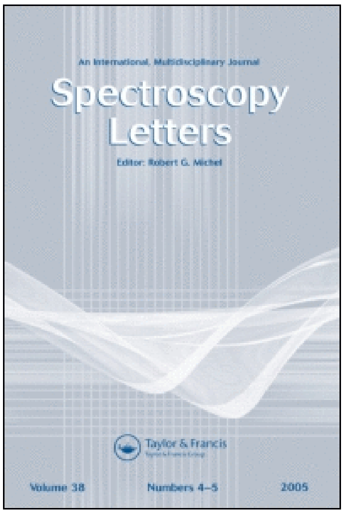

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Hyperfine-Induced *f*↔*f* Transitions: Effective Operator Formulation

Lidia Smentek[a,b]; A. Kdziorski[b]
[a] Department of Chemistry, Vanderbilt University, Nashville, Tennessee, USA [b] Department of Physics, Nicolaus Copernicus University, Toruń, Poland

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Hyperfine-Induced $f \leftrightarrow f$ Transitions: Effective Operator Formulation

Lidia Smentek
Department of Chemistry, Vanderbilt University, Nashville, Tennessee
USA and Department of Physics, Nicolaus Copernicus University, Toruń,
Poland

A. Kędziorski
Department of Physics, Nicolaus Copernicus University, Toruń, Poland

Abstract: The direct perturbing influence of the nuclear magnetic and electric multipole hyperfine interactions upon the amplitude of the $f \leftrightarrow f$ electric dipole transitions is analyzed. In this approach, the role of the forcing mechanism is played by an interaction other than the crystal field potential, which is the origin of all existing theoretical models. In particular, new effective operators of the second order that result from the electric dipole hyperfine interactions and compete with the standard Judd–Ofelt terms are introduced. In addition, the tensorial structure of the third-order effective operators that contribute to the transition amplitude is discussed, and attention is directed to the possibility and necessity of the introduction of a new parameterization scheme of *f*-spectra that would be applicable for the description of the hypersensitivity and such transitions that are highly forbidden by the standard selection rules.

Keywords: Double perturbation theory, effective operators, forced electric dipole transitions, hyperfine interactions, Judd–Ofelt theory, rare earth ions, spectroscopy

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Address correspondence to Lidia Smentek, Department of Chemistry, Vanderbilt University, Nashville, Tennessee 37235, USA. E-mail: smentek1@aol.com

INTRODUCTION

In 1962, Wybourne[1] suggested that the highly forbidden electric dipole $f \leftrightarrow f$ transitions in crystals might become possible as a result of hyperfine interactions. It took more than 20 years to verify this hypothesis when Popova with her collaborators observed the effects of the interaction of the nuclear magnetic dipole and electric quadrupole moments in the case of the lanthanides in crystals.[2–8]

The problem to describe these subtle properties of the atomic structure of the lanthanides is as difficult and complex as the Hamiltonian, which, in a symbolic way, consists of several terms

$$H = H_0 + H_{corr} + H_{so} + H_{CF} + H_{hfs} + H_{EM} + \dots,$$

where H_0 denotes the part of interactions that is described within the central field potential approximation (in practice usually chosen as the Hartree–Fock model). The remaining symbols represent interactions that are possibly the most important in the description of any many electron system, namely

The noncentral part of Coulomb interaction that is responsible for the electron correlation effects,
Spin-orbit interaction,
The crystal field potential that represents the electrostatic interactions between the lanthanide ion and its environment,
Nuclear magnetic hyperfine interactions,
Electric multipole hyperfine interactions.

The ellipsis in Eq. (1) denotes that the presented list is not complete, and other mechanisms may be also important for better understanding of the $f \leftrightarrow f$ transitions.

In order to include various physical interactions in the theoretical description of a system, the standard procedure requires diagonalization of the matrix of all elements of the Hamiltonian that are evaluated with the basis functions, starting with those obtained for H_0. In order to make the calculations possible in practice, very often the radial integrals of the matrix elements are treated as adjustable parameters while only the angular parts are evaluated directly. This type of calculations was performed by Wells et al. in the analysis of Zeeman and hyperfine infrared spectra of Pr^{3+} ion in the hosts of C_{4v} symmetry.[9] The same procedure has been recently applied by Guillot-Noël et al.[10] to analyze magnetic interactions in the lanthanides in the $Y_3Al_5O_{12}$. As a result of such a procedure, the optimal values of the energy and the functions associated with each energy state are obtained.

The physical reality of each system predicts the order in which the operators in H above should be included in the calculations. At the same time, the kind of interactions included in the calculations defines the coupling scheme in which the wave functions are constructed. This is a consequence of the fact that each distinct term added to the Hamiltonian changes its commutation relations with the symmetry operations. Similarly as it is in the case of the spherical symmetry of free atoms, whose Hamiltonian has to commute with the angular momentum operators that are the generators of the rotational symmetry. This requirement must be satisfied at each point of analysis, and as a consequence the energy levels are described by the symmetry adapted wave functions. This means that for any many-electron system, the wave function has to be not only antisymmetric, but its symmetry is also defined by the transformation properties under the symmetry operations.

In all cases, when the wave functions of the energy states are known, it is possible to describe the *properties* of a system, because they are determined by expectation values of appropriate operators. It should be realized however, that such a theoretical description of the properties of a system is precise within the accuracy of the energy calculations. However, a question arises whether the accuracy of the energy calculations is good enough also for evaluation of the transition amplitude, for example. It is well-known, and very well numerically documented, that double-excited configurations play a dominant role in the description of the energy when the model is extended beyond the single configuration approximations and the interactions between various excitations are included via CI (configuration interaction), MCHF (multi configuration Hartee–Fock), or MBPT (many body perturbation theory) methods. At the same time, the results of numerical analysis of spectroscopic properties of the lanthanides in crystals demonstrated that the major contributions to the transition amplitude originate from the perturbing influence of single excited configurations while the doubly excitations are negligible.

It is possible to approach the theoretical description of the properties of a system from a different perspective and modify the functions by such aspects (components) that are possibly unimportant for the energy evaluation but are crucial for the spectroscopic properties. This approach is applied in the current investigation, which is devoted to the electric dipole $f \leftrightarrow f$ transitions and to their new physical origin, which is attributed to the hyperfine interactions.

THEORETICAL BACKGROUND

Although the electronic structure of the lanthanides is complex, due to its special properties, it is possible to regard the additional terms in the Hamiltonian presented above as perturbations. Furthermore, instead of the parts of physical interactions that contribute to the energy (and therefore their impact is included in the wave functions obtained from the energy criterion), it is possible to take into account those components that affect directly the $f \leftrightarrow f$ transition amplitude. This means that the functions that are the solutions of the zero-order eigenvalue problem are improved by the corrections representing a part of particular physical mechanism, which does not contribute to the energy, but modifies the transition amplitude. In order to avoid the potential danger of including the same physical effect twice, it is important to partition the whole space spanned by the solutions obtained for H_0.

The Hamiltonian for which the perturbation approach is applied here has the following form

$$H = H_0 + \lambda_1 V_{corr} + \lambda_2 V_{so} + \lambda_3 V_{CF} + \lambda_4 V_{hfs} + \lambda_5 V_{EM}, \tag{1}$$

where each perturbation (note the change of symbols and the presence of the perturbation parameters) is limited to the intershell interactions. This means that if the states of the $4f^N$ configuration span the subspace P, the remaining part, Q, is associated with the states of all excited configurations, and each perturbation is built of two terms, $V \equiv PVQ + QVP$. The presence of P and Q in each perturbing operator limits the interactions via V to those between the ground and excited configurations (while PVP possibly contribute to the energy).

In the case of the description of electric dipole $f \leftrightarrow f$ transitions, the crystal field potential, V_{CF}, plays a crucial role. The solutions of the zero-order Hamiltonian defined within the free ionic system approximation are of the same parity, and therefore the transitions between such energy levels are parity forbidden. The odd part of $V_{CF} \equiv P\ V_{CF}Q + Q\ V_{CF}P$, which does not contribute to the energy within the single configuration approximation, admixes to the functions of the $4f^N$ configuration components of opposite parity. In this sense, the crystal field potential is the forcing mechanism of electric dipole transitions, which actually result from the breaking of the spherical symmetry of the lanthanide ion assumed at the zero-order level of the calculations. These corrections to the wave functions determine the second-order contributions to the transition amplitude. They define the basic concept of the Judd–Ofelt theory,[11,12] which is the origin of all theoretical models of *f*-electron spectra, including the effectively relativistic approach.[13,14]

The energy of a many electron system is sensitive to the electron correlation effects that are described by the noncentral part of the Coulomb interaction. Therefore, the results of the calculations performed within the central field approximation have to be corrected by the impact due to these effects. The same sensitivity is observed in the case of the transition amplitude that is evaluated within the Judd–Ofelt theory, which is in fact based on the single configuration approximation. In this particular case, the perturbing influence of the electron correlation effects upon the transition amplitude has to be taken into account together with the crystal field potential. The double perturbation approach formulated for such a Hamiltonian results in third-order contributions to the transition amplitude. All aspects of this model have been analyzed in detail previously.[15] The main conclusions derived from the results of the *ab initio*–type numerical analysis performed for ions across the lanthanide series have demonstrated that electron correlation effects have to be taken into account in any reliable theoretical model of direct calculations of the transition amplitude. Although the selection rules remain the same as for the second-order Judd—Ofelt theory, the third-order electron correlation contributions are at least of the same magnitude, and for some cases even greater, as the standard second order ones.

The analysis devoted to the importance of the spin-orbit interactions began in 1982 with a paper by Judd and Pooler[16] devoted to the amplitude of the two photon $f \leftrightarrow f$ transitions. This aspect of the $f \leftrightarrow f$ transition theory was also addressed by Downer and Burdick,[17,18] discussed in the terms of the perturbed functions approach in Ref. 19, and finally analyzed within the effectively relativistic approach to the description of electric dipole transitions.[13,14]

Two remaining perturbing operators in Eq. (1), V_{hfs} and V_{EM}, are new and their influence upon the transition amplitude is the main subject of the current analysis. The investigation presented here provides the answer to the search for such contributions to the amplitude that relax the strict selection rules of all the previous formulations and make a theoretical description of the unusual transitions possible. This analysis concerns not so strongly the possibility of the direct evaluation of the transition amplitude but is rather devoted to the formulation of a new parameterization scheme of f-spectra that is applicable also to unusual transitions as, for example, $0 \leftrightarrow 0$ and $0 \leftrightarrow 1$ observed in Eu^{3+} in various materials.

PERTURBATION APPROACH

In this particular application, the analysis of the hyperfine interactions upon the transition amplitude is based on double perturbation theory defined for the Hamiltonian, which contains two perturbing operators,

$$H = H_0 + \lambda(PV_{CF}Q + QV_{CF}P) + \mu(PVQ + QVP), \tag{2}$$

where P, as above, is spanned by the eigenfunctions of H_0 obtained for the electron configuration $4f^N$, $Q = 1 - P$, and it is associated with the singly excited configurations $4f^{N-1}n'\ell'$ (all the operators regarded here are single particle objects, and therefore the doubly excited configurations do not contribute). The crystal field potential is defined in the terms of spherical tensors as follows,

$$V_{CF} = \sum_{tp} B_p^t \sum_i r_i^t C_p^{(t)}(\vartheta_i \varphi_i), \tag{3}$$

with structural parameters (crystal field parameters) B_p^t. The second perturbation V denotes either the nuclear magnetic hyperfine interaction, V_{hfs}, or the electric hyperfine multipole interactions, V_{EM}.

The perturbing operators in Eq. (2) represent the intershell interactions, because only the matrix elements between the functions belonging to P and Q are nonzero. Limiting the expansion of the wave functions to the first-order corrections in both perturbations, the transition amplitude defined up to the third-order consists of the following additive terms

$$\Gamma = \lambda\left\{\left\langle\Psi_f^0|D_\rho^{(1)}|\Psi_i^{10}\right\rangle + \left\langle\Psi_f^{10}|D_\rho^{(1)}|\Psi_i^0\right\rangle\right\} + \mu\left\{\left\langle\Psi_f^0|D_\rho^{(1)}|\Psi_i^{01}\right\rangle + \left\langle\Psi_f^{01}|D_\rho^{(1)}|\Psi_i^0\right\rangle\right\} + \lambda\mu\left\{\left\langle\Psi_f^{10}|D_\rho^{(1)}|\Psi_i^{01}\right\rangle + \left\langle\Psi_f^{01}|D_\rho^{(1)}|\Psi_i^{10}\right\rangle\right\}, \quad (4)$$

where $D_\rho^{(1)}$ is the electric dipole radiation operator, and it is defined by a spherical tensor in the following way

$$D_\rho^{(1)} = \sum_i r_i C_\rho^{(1)}(\vartheta_i \varphi_i). \quad (5)$$

The third-order contributions that originate from the perturbing operators $QV_{CF}Q$ and QVQ, and which consequently are determined by the matrix elements of the type $\langle\Psi^{11}|D_\rho^{(1)}|\Psi^0\rangle$, are not included in Eq. (4). The discussion here is devoted mainly to the intershell terms that form the basic concept of the standard Judd–Ofelt theory. Indeed, here the aim of the perturbation approach is also to admix new components to the wave functions of the ground configuration via a certain physical mechanism. The particular contributions that are omitted in Eq. (4), those generated by Ψ^{11}, as seen in the above matrix element, describe the interactions within the space associated with the excited configurations. They obviously improve the description of the states of the excited configurations, but this aspect is not of primary interest in the current discussion. However, for the completeness of the presentation, their tensorial structure is also introduced at the end of this paper.

In order to evaluate the second- and third-order contributions to the transition amplitude listed in Eq. (4), the first-order corrections to the wave functions have to be constructed. The procedure is standard for the Rayleigh–Schrödinger perturbation theory. The first-order corrections that originate from crystal field potential V_{CF} are defined as linear combinations of zero order functions,

$$\Psi_i^{(10)} = \sum_{k\neq i}{}' \frac{\left\langle\Psi_k^0|QV_{cryst}P|\Psi_i^0\right\rangle}{E_i^0 - E_k^0}\Psi_k^0. \quad (6)$$

The terms associated with the perturbing parameter λ in Eq. (4) are the contributions to the transition amplitude of the second order, and they originate from the perturbing influence of the crystal field potential. They are determined by the matrix elements with the corrections defined in Eq. (6), and they define the standard Judd–Ofelt theory of $f \leftrightarrow f$ electric dipole transitions. From the whole expansion of the crystal field potential in Eq. (3), only the interactions via its odd part are effective in forcing the electric dipole transitions. When, following Judd and Ofelt, it is assumed that the energy levels of distinct configurations might be regarded as degenerate in relation to the large energy distance between the ground configuration $4f^N$ and all the excited ones, it is possible to perform *the partial closure* and derive the transition amplitude in its effective operator form

$$\Gamma_{J-O} = 2 \sum_{t,p}^{odd} B_p^t \sum_{\lambda\mu}^{even} \sum_{\ell'}^{even} (-1)^q [\lambda]^{1/2} \begin{pmatrix} t & 1 & \lambda \\ p & \rho & -\mu \end{pmatrix} A_t^\lambda(\ell') R_{JO}^t(\ell') \left\langle 4f^N \Psi_f^0 | U_\mu^{(\lambda)} | 4f^N \Psi_i^0 \right\rangle, \tag{7}$$

where the angular term is defined as

$$A_t^\lambda(\ell') = [\lambda]^{1/2} \begin{Bmatrix} t & \lambda & 1 \\ f & \ell' & f \end{Bmatrix} \left\langle f \| C^{(1)} \| \ell' \right\rangle \left\langle \ell' \| C^{(t)} \| f \right\rangle, \tag{8}$$

and the radial integrals are expressed in the terms of the perturbed functions[20] in the following way

$$R_{JO}^t(\ell') = \left\langle \varrho^t(4f \longrightarrow \ell') | r | 4f \right\rangle, \tag{9}$$

where $|4f\rangle \equiv P_{4f}$ and $\varrho^t(4f \rightarrow \ell') \equiv \varrho^t(r;\, 4f \rightarrow \ell')$.

Note that due to the perturbed function approach, the sum of the original Judd–Ofelt radial integrals over the complete radial basis sets of one electron excited functions of ℓ' symmetry is replaced by a single integral with new functions that contain this very troublesome summation inside their definition (see Ref. 20). The Judd–Ofelt effective operators are presented here because they define the background for all comparisons and form the language for investigations that are devoted to the selection rules and parametrization schemes of f-spectra.

The second-order contributions to the transition amplitude that are proportional to the perturbing parameter μ are determined by the first-order corrections Ψ^{01}, which are due to the perturbation V. Furthermore, these contributions do not vanish only if Ψ^{01} is of an opposite parity to the parity of Ψ^0. Indeed, this particular first-order correction to the wave function is defined by an analog of Eq. (6) with the crystal field potential replaced by V. This implies that the perturbation V from Eq. (2) has to have nonvanishing matrix elements with the functions of the opposite parities. From among both perturbing operators, V_{hfs} and V_{EM}, this parity condition is satisfied only for the odd part of the electric multipole hyperfine interactions. Thus, for the first time in the theory of $f \leftrightarrow f$ transitions in crystals there are nonzero second-order contributions that are of a new origin and which compete at the same order of analysis with the standard Judd–Ofelt terms. These new terms originate from the electric dipole hyperfine interactions. At the same time their presence indicates that there are nonzero contributions to the amplitude of parity forbidden electric dipole transitions in the case of free atomic/ionic systems. In this particular case, it is concluded that such transitions originate from the distortion of the spherical symmetry of the nucleus that is perturbed by the surrounding electrons. Thus the interactions via V_{EM} represent the mechanism that forces the electric dipole $f \leftrightarrow f$ transitions in spherical systems and also those of lower symmetry.

The terms in Eq. (4) that are proportional to $\lambda\mu$ are of the third order, and in general they consist of two triple products of the matrix elements that differ from each other by the order of appropriate operators, namely

$$
{}^{3}\Gamma_{V}(inter) = \sum_{Xx}\sum_{Yy}\left\{ \frac{\left\langle \Psi_f^0 | PVQ | Yy \right\rangle \left\langle Yy | D_\rho^{(1)} | Xx \right\rangle \left\langle Xx | QV_{CF}P | \Psi_i^0 \right\rangle}{(E_i^0 - E_{Xx}^0)(E_f^0 - E_{Yy}^0)} \right.
$$

$$
\left. + \frac{\left\langle \Psi_f^0 | PV_{CF}Q | Xx \right\rangle \left\langle Xx | D_\rho^{(1)} | Yy \right\rangle \left\langle Yy | QVP | \Psi_i^0 \right\rangle}{(E_f^0 - E_{Xx}^0)(E_i^0 - E_{Yy}^0)} \right\}, \tag{10}
$$

where, as mentioned above, following the concept of the standard Judd–Ofelt theory, the crystal field potential still plays a special, but no longer unique, role of a mechanism which forces the electric dipole $f \leftrightarrow f$ transitions.

NUCLEAR MAGNETIC HYPERFINE INTERACTIONS

The interaction between the nuclear magnetic moment and the magnetic field generated at the nucleus by each electron in an open shell of a symmetry other than s is represented by the operator

$$
V_{hfs} = \mathcal{A} r^{-3}\left(L^{(1)} - \sqrt{15}\left\langle \ell \| C^{(2)} \| \ell' \right\rangle W^{(12)1}(s\ell, s\ell')\right) \cdot I^{(1)}, \tag{11}
$$

where the numerical factor contains

$$
\mathcal{A} = 2\beta\beta_N g_I \tag{12}
$$

and $W^{(12)1}$ is the double tensor operator with an even rank in the orbital part. In the analysis presented here, the wave functions of the $4f^N$ are expressed in the intermediate coupling scheme, and with the angular nuclear momenta uncoupled. As a result the matrix elements of V_{hfs} are determined by the product of an electronic part and a part associated with the nuclear magnetic moment. The latter may be taken as diagonal in the nuclear spin, because the nuclear levels are usually well separated in comparison with the electronic states.

As seen in Eq. (11), there are two separate terms of V_{hfs} that are distinguished by their tensorial structures, namely the orbital magnetic terms that represent the orbital moment at the nucleus caused by the electrons of the open shell,

$$
h_{hfs}^{1} = r^{-3}\sum_{q} L_q^{(1)}, \tag{13}
$$

and the spin dipolar interaction between the nucleus and the spin of the open shell electrons,

$$h^2_{hfs} = r^{-3}\left\langle \ell \| C^{(2)} \| \ell' \right\rangle W^{(12)1}(\ell\ell'). \tag{14}$$

The parity requirements eliminate the second-order contributions that originate from the magnetic hyperfine interactions, and all terms associated with μ in Eq. (5) vanish. Therefore in the particular case of these interactions the first nonvanishing contributions to the transition amplitude are of the third order. This means that no competition for the Judd–Ofelt effective operators arises from the interactions via V_{hfs}.

The evaluation of the matrix elements of the first part of the hyperfine interactions requires special attention. The operator $L^{(1)}$ has nonzero matrix elements only for the states of the same configuration, as in the case of the orbital part of the magnetic dipole operator. However, because in h^1_{hfs} this angular momentum operator is multiplied by the radial part, it is possible to evaluate its off-diagonal elements. This is possible in the case of two configurations that differ from each other only by the principal quantum numbers of two occupied one electron states (which are of the same symmetry determined by the same angular momentum quantum numbers). In the particular case of the $4f^N$ configuration, the nonzero impact caused by the perturbing influence of single excitations $4f^{N-1}n'f$, for all $n' \geq 5$ taken into account via h^1_{hfs} is expected.

In the terms of unit tensor operators, h^1_{hfs} is defined in the following way,

$$h^1_{hfs} \Rightarrow \left\langle 4f|r^{-3}|n'f\right\rangle \left\langle f\|\ell^{(1)}\|f\right\rangle u^{(1)}_q(nf, n'f), \tag{15}$$

and the third-order correction, its electronic part, is determined by the operator that results from the contraction of operators in the sequence

$$\left\langle 4f^N\Psi_f|u^{(1)}_q(4f, n''f)u^{(1)}_\rho(n''f, n'\ell')u^{(t)}_p(n'\ell', 4f)|4f^N\Psi_i\right\rangle. \tag{16}$$

In addition to the sequence of operators in Eq. (16), there is an additional term contributing to the transition amplitude, which is defined by a similar triple product of matrix elements but with the positions of $u^{(1)}_q$ and $u^{(t)}_p$ interchanged.

Adopting the assumption of the Judd–Ofelt theory about the relative degeneracy of the energy levels of various configurations, it is possible to perform the partial closure over all the quantum numbers that identify the energy states except the principal quantum numbers of the one electron excited states. This means that the creation and annihilation operators representing appropriate tensor operators are contracted to result in the effective operator that acts within the $4f^N$ configuration.

Taking into account both terms of the third order, the contribution to the transition amplitude is determined by the effective operator

$$
\begin{aligned}
&{}^{3}\Gamma_{h^{1}_{hfs}}(h^{1}DV_{CF}+V_{CF}Dh^{1})\\
&\quad=\sum_{kq}\sum_{tp}(-1)^{q}B^{t}_{p}\sum_{\ell'}^{even}\langle\varrho^{t}(4f\longrightarrow\ell')|r|\varrho^{-3}(4f\longrightarrow f)\rangle\\
&\qquad\sqrt{\ell(\ell+1)(2\ell+1)}\langle\ell\|C^{(t)}\|\ell'\rangle\langle\ell'\|C^{(1)}\|\ell\rangle\\
&\qquad\sum_{\lambda\mu}(-1)^{\lambda+p}[\lambda]\Big(X^{1t1}_{qp\rho}(\lambda\mu;\,\ell'\ell)+X^{t11}_{pq\rho}(\lambda\mu;\,\ell'\ell)\Big)U^{(\lambda)}_{\mu}(\ell\ell),
\end{aligned}
\tag{17}
$$

where ρ denotes the components of the electric dipole radiation operator (the polarization), and in the particular case of $n\ell^{N}\equiv 4f^{N}$, the numerical factor in front of the reduced matrix elements of spherical tensors has the value of $2\sqrt{21}$. In general the collection of angular momentum coupling coefficients is defined as follows,

$$
\begin{aligned}
X^{k_1k_2k_3}_{q_1q_2q_3}(\lambda\mu;\,\ell'\ell'')=&\sum_{x\sigma}[x]\begin{pmatrix}k_1 & k_3 & x\\ q_1 & q_3 & -\sigma\end{pmatrix}\begin{pmatrix}x & k_2 & \lambda\\ \sigma & q_2 & -\mu\end{pmatrix}\\
&\begin{Bmatrix}k_3 & x & k_1\\ \ell & \ell' & \ell''\end{Bmatrix}\begin{Bmatrix}k_2 & \lambda & x\\ \ell & \ell'' & \ell\end{Bmatrix}.
\end{aligned}
\tag{18}
$$

Using the standard rules of coupling and recoupling of the angular momenta, it is straightforward to express the coefficients collected in Eq. (18) by the following expression

$$
\begin{aligned}
X^{k_1k_2k_3}_{q_1q_2q_3}(\lambda\mu;\,\ell'\ell'')=&(-1)^{k_2+q_2+k_3+q_3}\sum_{y\eta}[y]\begin{pmatrix}k_1 & k_2 & y\\ q_1 & q_2 & \eta\end{pmatrix}\\
&\begin{Bmatrix}k_2 & \ell'' & \ell\\ k_1 & \ell' & \ell\\ y & k_3 & \lambda\end{Bmatrix}.
\end{aligned}
\tag{19}
$$

It is seen, however, that this manipulation does not introduce noticeable simplification of the expression. Instead of the summation over x in Eq. (18), now there is a summation over all possibilities of y that are determined by the triangular conditions of the $3-j$ and $9\text{–}j$ symbols.

It is interesting to note that the radial integrals of Eq. (17) are determined by the perturbed functions that have already been introduced previously. Indeed, ϱ^{t} is the function of the Judd–Ofelt theory (see the radial integral in Eq. (9), and ϱ^{-3} was introduced when the perturbing influence of the spin-orbit interaction upon the transition amplitude was analyzed. At the same time, the tensorial structure of the effective operators in Eq. (17) demonstrates that these third-order contributions contain the odd part of the crystal field potential, similarly as the second-order Judd–Ofelt terms. Indeed, if ℓ' is even, it follows from the reduced matrix elements of the spherical tensors that the rank of the crystal field potential operators t is limited to its odd values.

The third-order terms arising from the second part of V_{hfs} are determined also by two triple products of the matrix elements, namely

$$V_{CF}D^{(1)}h^2_{hfs} \text{ and } h^2_{hfs}D^{(1)}V_{CF}. \tag{20}$$

For example, in the case of the first sequence of operators

$$^3\Gamma_{h^2_{hfs}}(VDh^2) = \langle 4f^N\Psi_f|V_{CF}|Xx\rangle\langle Xx|D^{(1)}|Yy\rangle\langle Yy|h^2_{hfs}|4f^N\Psi_i\rangle, \tag{21}$$

where X and Y denote the singly excited configurations of appropriate parity, the third order expression contains:

Radial integrals with the energy denominators,

$$\sum_{n'}\sum_{n''}\langle 4f|r^t|n'\ell'\rangle\langle n'\ell'|r^1|n''\ell''\rangle\langle n''\ell''|r^{-3}|4f\rangle/\Delta E_{n'\ell'}\Delta E_{n''\ell''}, \tag{22}$$

Angular factors,

$$C^t(\ell'\ell'') = \langle f\|C^{(t)}\|\ell'\rangle\,\langle \ell'\|C^{(1)}\|\ell''\rangle\langle \ell''\|C^{(2)}\|f\rangle, \tag{23}$$

And finally, the intershell unit tensor operators that have to be contracted to give an effective operator that acts within the $4f^N$ shell,

$$\langle 4f^N\Psi_f|w^{(0t)t}(4f, n'\ell')w^{(01)1}(n'\ell', n''\ell'')w^{(12)1}(n''\ell'', 4f)|4f^N\Psi_i\rangle, \tag{24}$$

where the spin in the arguments of the double tensor operators is omitted because it is obvious that in general, they act within the spin orbital space.

For the second term of Eq. (20), the order of operators is different, and one may expect a different final effective operator as a result of different coupling schemes applied in both cases. The coupling of the operators in Eq. (24) (or contraction, if each tensor operator is interpreted as a pair of creation and annihilation operators) is performed in the accordance with the general commutation relation of double tensor operators presented in Eq. (6) of Ref. 13. The final result is of the following form

$$\begin{aligned}
&^3\Gamma_{h^2_{hfs}}(h^2DV + VDh^2)\\
&\quad= \sqrt{3}\sum_{\ell'}\sum_{\ell''}\sum_{tp}^{odd}B^t_p\Big\langle \varrho^t(4f \longrightarrow \ell')|r|\varrho^{-3}(4f \longrightarrow \ell'')\Big\rangle C^t(\ell'\ell'')\\
&\sum_q(-1)^q\sum_y\sum_{\lambda,\mu}[y][\lambda]^{1/2}\sum_{x,\sigma}(-1)^x[x]\begin{pmatrix} t & 1 & x\\ p & \rho & -\sigma\end{pmatrix}\begin{pmatrix} x & 1 & \lambda\\ \sigma & q & -\mu\end{pmatrix}\\
&\big[(-1)^{\lambda+y+1}A^{\lambda ty}_x(\ell\ell'\ell'') + B^{\lambda ty}_x(\ell\ell'\ell'')\big]W^{(1y)\lambda}_\mu(s\ell, s\ell),
\end{aligned} \tag{25}$$

where C^t is defined in Eq. (23), and as expected, there are two different angular factors resulting from each coupling scheme, namely

$$A_x^{\lambda t y}(\ell\ell'\ell'') = \sum_z [z] \begin{Bmatrix} 1 & z & 2 \\ \ell & \ell'' & \ell' \end{Bmatrix} \begin{Bmatrix} t & y & z \\ \ell & \ell' & \ell \end{Bmatrix} \begin{Bmatrix} 1 & z & 2 \\ \lambda & y & 1 \\ x & t & 1 \end{Bmatrix}, \qquad (26)$$

which, in fact, after performing the summation is expressed by $12-j$ symbol

$$= (-1)^y \left\{ \begin{array}{cccccccc} \ell'' & & 2 & & 1 & & t & \\ & \ell & & 1 & & x & & \ell' \\ \ell & & y & & \lambda & & 1 & \end{array} \right\}.$$

The second angular factor is defined as follows,

$$B_x^{\lambda t y}(\ell\ell'\ell'') = \begin{Bmatrix} 1 & x & t \\ \ell & \ell' & \ell'' \end{Bmatrix} \begin{Bmatrix} 2 & y & x \\ \ell & \ell'' & \ell \end{Bmatrix} \begin{Bmatrix} 2 & 1 & 1 \\ \lambda & y & x \end{Bmatrix}. \qquad (27)$$

However, when the $3-j$ symbols in Eq. (25) and $B_x^{\lambda t y}(\ell\ell'\ell'')$ are summed over x, and σ, instead of all those terms dependent on x, similarly as in the previous case, the $12-j$ symbol is obtained. Thus the whole angular part of this effective operator has the form

$$-\sum_{z,\zeta} [z](-1)^{z+y+p+\lambda-\mu} \begin{pmatrix} t & 1 & z \\ p & q & -\zeta \end{pmatrix} \begin{pmatrix} z & 1 & \lambda \\ \zeta & \rho & -\mu \end{pmatrix}$$
$$\left\{ \begin{array}{cccccccc} 1 & & t & & \ell & & y & \\ & z & & \ell' & & \ell & & 1 \\ \lambda & & 1 & & \ell'' & & 2 & \end{array} \right\}.$$

Note the interchange of the components q and ρ in the $3-j$ symbols in comparison with those in Eq. (25). The symmetry properties of the $12-j$ symbols[21] indicate that these two coefficients are the same, and therefore finally the third-order effective operator originated from the interactions h_{hfs}^2 has a much simpler form

$${}^3\Gamma_{h_{hfs}^2}(h^2DV + VDh^2) = \sqrt{3} \sum_{\ell'} \sum_{\ell''} \sum_{tp}^{odd} B_p^t \langle \varrho^t(4f \longrightarrow \ell')|r|\varrho^{-3}(4f \longrightarrow \ell'')\rangle$$
$$C^t(\ell'\ell'') \sum_q (-1)^q \sum_y \sum_{\lambda,\mu} [y][\lambda]^{1/2} \sum_{x,\sigma} (-1)^{x+\lambda+1}[x]$$
$$\left[\begin{pmatrix} t & 1 & x \\ p & \rho & -\sigma \end{pmatrix} \begin{pmatrix} x & 1 & \lambda \\ \sigma & q & -\mu \end{pmatrix} + (-1)^{y+1} \begin{pmatrix} t & 1 & x \\ p & q & -\sigma \end{pmatrix} \begin{pmatrix} x & 1 & \lambda \\ \sigma & \rho & -\mu \end{pmatrix} \right]$$
$$\left\{ \begin{array}{cccccccc} \ell'' & & 2 & & 1 & & t & \\ & \ell & & 1 & & x & & \ell' \\ \ell & & y & & \lambda & & 1 & \end{array} \right\} W_\mu^{(1y)\lambda}(s\ell, s\ell). \qquad (28)$$

If $\rho = q$ (the components of the electric dipole radiation operator, which determines the polarization is equal to the component of the magnetic nuclear hyperfine interaction), the third-order contribution vanishes unless y is *odd*. The same condition has to be satisfied for $\rho \neq q$, because the four possibilities of the products of the $3-j$ symbols for $\rho, q = \pm 1$ have the same values but differ by signs in pairs. Thus, the intershell contribution due to h_{hfs}^2 has the final form

$$
\begin{aligned}
&{}^3\Gamma_{h_{hfs}^2}(h^2DV + VDh^2) = 2\sqrt{3}\sum_{\ell'}\sum_{\ell''}\sum_{tp}^{odd} B_p^t \langle \varrho^t(4f \longrightarrow \ell')|r|\varrho^{-3}(4f \longrightarrow \ell'')\rangle \\
&C^t(\ell'\ell'')\sum_q(-1)^q \sum_y^{odd}\sum_{\lambda,\mu}^{even}[y][\lambda]^{1/2}\sum_{x,\sigma}(-1)^{x+1}[x] \\
&\begin{pmatrix} t & 1 & x \\ p & \rho & -\sigma \end{pmatrix}\begin{pmatrix} x & 1 & \lambda \\ \sigma & q & -\mu \end{pmatrix}\left\{\begin{array}{ccccccccc} \ell'' & & 2 & & 1 & & t & & \\ & \ell & & 1 & & x & & \ell' & \\ \ell & & y & & \lambda & & 1 & & \end{array}\right\} \\
&W_{\mu}^{(1y)\lambda}(s\ell, s\ell)
\end{aligned}
\tag{29}
$$

with $\ell \equiv f\,(=3)$ for the lanthanides.

At the same time, if $y = odd$ and the Hermiticity of the double tensor operators is required (especially in the case when they contribute to the line strength rather than to the transition amplitude), this limitation implies that the final rank $\lambda = even$. This means that the terms associated with the scalar double tensor operator, for $\lambda = 0$, which requires $y = 1$, exist. This particular case creates the possibility for a non-relativistic description of highly forbidden transitions $0 \rightarrow 0$ observed in Eu^{3+} ion in various materials. This aspect of new selection rules that are introduced to the theory via the nuclear magnetic hyperfine interactions is of special importance for investigations devoted to the new parameterization schemes of f-spectra. Indeed, there is a search for such physical mechanisms that are important not only in the sense of the magnitude of the modification of the transition amplitude they cause, but also because of their role in relaxing the standard selection rules. At the same time, this detailed analysis provides deeper insight into the nature of the $f \leftrightarrow f$ transitions. Indeed, already at this point it is possible to conclude that the unusual $0 \leftrightarrow 0$ transitions, whose description and reproduction by the theory for many years is a challenge for many researchers, belong to the group of the hyperfine induced transitions in the *strict* sense of this categorization.

The parity requirements for the nonvanishing reduced matrix elements of the spherical tensors in C^t defined in Eq. (23) indicate that ℓ'' is odd. This means that ℓ' has to be even, which leads to the conclusion that t in the expansion of the crystal field potential is odd. In summary, it is seen from Eq. (29) that the third-order nuclear magnetic hyperfine terms include the interactions between the configurations $4f^N–4f^{N-1}n'd$; $n'g$ via the odd part of V_{CF}, and $4f^N–4f^{N-1}n''p$; $n''f$ via h^2_{hfs}. These contributions are defined for all the values of the principal quantum numbers of excited one electron functions, including the continuum part of the set for a given symmetry. Indeed, because the radial integrals of Eq. (29) are defined in the terms of the perturbed functions, the complete radial basis sets of one electron excited states are taken into account. In fact, it is interesting to note that the perturbed functions in Eq. (29) again are not new in the intensity theory, because ϱ^t is the function that defines the Judd–Ofelt radial integral in Eq. (9), and as mentioned before, ϱ^{-3} has been introduced previously in the discussion of the perturbing influence of the spin-orbit interaction upon the transition amplitude. Note also that the radial integral of the effective operator in Eq. (17) is a particular case of the radial term of Eq. (29) for $\ell'' \equiv f$.

The effective operators contributing to the transition amplitude defined in Eq. (29) are new. They are expressed by double tensor operators that act within the spin-orbital space and therefore are beyond the framework of the standard formulation of Judd and Ofelt. In fact, they are of the same nature as the effectively relativistic effective operators introduced into the $f \leftrightarrow f$ transition theory in Ref. 13. Thus, it is concluded that only the one-particle relativistic parameterization scheme of f-spectra, which is based on the double tensor operators, includes the subtle nuclear magnetic hyperfine interactions when the fitting procedure is applied. Consequently, it is possible now to understand better the problems with the reproduction of some transitions within the standard parameterization, which while working very well for the majority of cases, is unable to describe all observations. The details of new parameterization scheme of the f-spectra are beyond the scope of the current investigations, and they are discussed in a separate analysis which is in preparation.

ELECTRIC MULTIPOLE HYPERFINE INTERACTIONS

The distortion from the spherical symmetry of a nucleus with the spin $I > 0$ is described by the electrostatic interactions between the electron and nucleon charge densities, which, in the terms of the multipole expansion, have the following tensorial form,

$$V_{EM} = \sum_k \frac{r_n^k}{r_e^{k+1}} \left(C_e^{(k)} \cdot C_n^{(k)} \right). \tag{30}$$

For energy considerations, especially those performed within the single configuration approximation, k in the expansion above is even, and the remaining contributions for k odd vanish. In the current discussion the intershell electric multipole hyperfine interactions are analyzed, and therefore it is possible that for k odd in Eq. (30) there are nonzero contributions to the transition amplitude. The analysis becomes simpler by separating the nuclear and electronic coordinates and by expressing the wave functions in the scheme of the uncoupled electron angular and nuclear spin momenta. As a consequence, it is possible to define the nuclear multipole moments in a general way as matrix elements

$$M_q^k(I) = \left\langle I | r_n^k C_{q,n}^{(k)} | I \right\rangle, \tag{31}$$

and focus on the electron part of the new term contributing to the transition amplitude.

The possibility of $k = odd$ in the expansion of the V_{EM} is utilized here to derive new contributions to the transition amplitude that are of the second order and that compete with the standard Judd–Ofelt terms, as mentioned above. The second-order terms proportional to μ in Eq. (5) with $V \equiv V_{\mathrm{EM}}$ for $k = odd$ (in particular $k = 1$ for the dipole interactions) satisfy the parity requirements for the nonvanishing matrix elements of electric dipole transition operator. This is due to the fact that the first-order correction Ψ^{01} originating from the odd part of V_{EM} is of opposite parity in relation to the parity of the energy states of $4f^N$.

For the first time then, it is possible to analyze the second-order terms contributing to the transition amplitude that are of different physical origin from the crystal field potential. Within the framework of the basic assumptions and approximations of the standard Judd–Ofelt theory, it is straightforward to find that these new one-particle effective operators have the following form

$$\begin{aligned} {}^2\Gamma_{EM} = 2(-1)^{\rho} \sum_{k,q}^{odd} M_q^k(I) \sum_{\ell'}^{even} \sum_{\lambda}^{even} [\lambda]^{1/2} \begin{pmatrix} 1 & k & \lambda \\ \rho & q & -(\rho+q) \end{pmatrix} \\ A_k^{\lambda}(\ell') R_{JO}^{-k-1}(\ell') \left\langle 4f^N \Psi_f^0 | U_{\mu}^{(\lambda)}(\ell\ell) | 4f^N \Psi_i^0 \right\rangle \end{aligned} \tag{32}$$

where the angular factors are defined by Eq. (8), and the radial integral is presented in Eq. (9).

The similarity of these effective operators to those of the standard Judd–Ofelt theory from Eq. (7) is striking. There are the same angular factors, the same radial integrals, the same even-rank unit tensor operators U. Only the physical origin in both cases is different. Although the odd rank crystal field parameters B_p^t of Eq. (7) are replaced in Eq. (32) by the matrix element of nuclear dipole moment M_q^1, the selection rules for the nonvanishing contributions are the same in both cases.

The second-order Judd–Ofelt effective operators represent the electrostatic interactions caused by the distortion of the spherical symmetry of a free ion by its environment represented by the crystal field potential. Here, the new second-order terms originate from the electrostatic interactions that are the consequence of the distortion of a spherical symmetry of a nucleus caused by its closest environment created by the surrounding electrons. It is possible then to conclude, that in addition to the crystal field potential, also the electric dipole hyperfine interactions are the forcing mechanism of electric dipole the $f \leftrightarrow f$ transitions. In both cases, the distortion of the spherical symmetry plays a crucial role in the theoretical description of the observed spectroscopic properties of *f*-electron systems.

Because λ in Eq. (32) is even, the perturbing influence of the electric hyperfine interactions upon the amplitude of the $f \leftrightarrow f$ transitions is included by the standard Judd–Ofelt intensity parameters Ω_λ when they are determined through the fitting procedure. Especially in the case for $\lambda = 2$ it is interesting to note that the new terms introduced here contribute to the effective operators associated with $U^{(2)}$; this is the very term that determines the amplitude of the hypersensitive transitions. The hypersensitivity of some electric dipole transitions to the environment is manifested by unusual changes of the values of the intensity parameters, usually Ω_2, observed for various systems. This suggests that within the standard approach, the hypersensitivity is reproduced theoretically by the terms that are associated with the rank $t = 1$ of the crystal field potential. However, the unexpected values of Ω_2, that for some cases are even negative, which is in contradiction to their definition, are also observed in the case of systems with symmetry without the terms with $t = 1$ in the expansion of the crystal field potential. The new terms defined in Eq. (32) are independent of the crystallographic symmetry of the system, and therefore they do contribute to the transition amplitude, in particular to its part associated with $U^{(2)}$, regardless of it.

Thus, it is concluded that the electric dipole hyperfine interactions are responsible for the hypersensitivity of some electric dipole transitions observed in various materials. Obviously, it is impossible to establish the relative importance of these new contributions without numerical calculations. However, for all the cases for which the crystal field potential does not contain the terms with $t = 1$, the new effective operators of Eq. (32), for $k = 1$, are the only contributions to the transition amplitude dominated by $U^{(2)}$.

The third-order contributions originating from the interplay of the crystal field potential and electric multipole hyperfine interactions have a standard tensorial structure, namely

$$
\begin{aligned}
&{}^3\Gamma_{EM}(V_{EM}DV_{CF} + V_{CF}DV_{EM}) \\
&\quad = \sum_{kq}\sum_{tp}(-1)^q B^t_p M^k_q(I) \sum_{\ell'\ell''}\Big\langle \varrho^{-k-1}(4f \longrightarrow \ell')|r|\varrho^t(4f \longrightarrow \ell'')\Big\rangle \\
&\qquad \langle \ell \| C^{(k)} \| \ell' \rangle \langle \ell' \| C^{(1)} \| \ell'' \rangle \langle \ell'' \| C^{(t)} \| \ell \rangle \\
&\qquad \sum_{\lambda\mu}(-1)^{\lambda+p}[\lambda]\Big(X^{kt1}_{qp\rho}(\lambda\mu;\, \ell'\ell'') + (-1)^{k-p} X^{tk1}_{pq\rho}(\lambda\mu;\, \ell''\ell')\Big) U^{(\lambda)}_\mu(\ell\ell),
\end{aligned}
\qquad (33)
$$

where the collection of angular momentum coupling coefficients for each sequence of operators is defined by Eq. (18) (or by Eq. (19), because they are the same factors as in the case of the effective operators caused by h^1_{hfs}.

The effective operators defined in Eq. (33) contain the impact of both parts of the crystal field potential, even and odd, which is assisted by dipole and quadrupole hyperfine interactions, respectively. From the reduced matrix elements of the spherical tensors in Eq. (33), it is apparent that the parity of t is opposite to the parity of k. This makes it possible for the first time to evaluate directly the contributions to the transition amplitude caused by the terms for $t = even$. Because the even part of the crystal field potential contributes to the energy, in most cases it is straightforward to determine the even rank crystal field parameters applying the fitting procedure (assuming that the experimental data are rich enough to perform reproduction of the measurements). The values of such parameters are then used to evaluate, in accordance with Eq. (33), a particular part of the transition amplitude. Unfortunately, such a direct calculation of the transition amplitude is impossible in the case for the odd rank crystal field parameters, because they do not contribute to the energy. Therefore, in order to compare various contributions with $t = odd$ in Eq. (33), the numerical analysis is based on the discussion of the magnitude of crystal-structure-independent terms.

At the same time, there are no limitations or any requirements for the parity of the final rank of the effective operator λ in Eq. (33). This means that there are contributions associated with the even ranks 2, 4, 6, as in the standard formulation of the Judd–Ofelt theory, and in addition, there are terms with $\lambda = odd$. These latter are beyond the standard selection rules, and their presence gives the first chance for a direct theoretical description of the unusual transitions such as the transition $0 \leftrightarrow 1$ observed in Eu^{+3} ion in various hosts.

INTRA-Q-SHELL INTERACTIONS

The intra-Q-shell interactions via any perturbing operator are beyond the concept of admixing to the wave functions of the ground configuration new components that contribute to the transition amplitude, as utilized in the standard Judd–Ofelt theory. For the completeness of the presentation, however, the remaining third-order terms caused by the intra-Q-shell interactions are introduced here. They are determined by the matrix elements that contain the first-order corrections to the wave functions that are due to both perturbations taken into account simultaneously,

$$\lambda\mu\left(\left\langle\Psi^0_f|D^{(1)}|\Psi^{(11)}_i\right\rangle + \left\langle\Psi^{(11)}_f|D^{(1)}|\Psi^0_i\right\rangle\right). \tag{34}$$

$\Psi^{(11)}_i$ is the correction to the wave function of the lowest order among those that are quintessential for the double perturbation theory. As a consequence of the equation that this function has to satisfy, its definition contains the first-order corrections associated with λ and μ separately,

$$\Psi_i^{(11)} = \sum_{Yy} \left\{ \frac{\left\langle Yy | V_{CF} | \Psi_i^{(01)} \right\rangle}{(E_i^0 - E_{Yy}^0)} + \frac{\left\langle Yy | V | \Psi_i^{(10)} \right\rangle}{(E_i^0 - E_{Yy}^0)} \right\} |Yy\rangle, \tag{35}$$

where $\Psi_i^{(10)}$ is defined in Eq. (6), and $\Psi_i^{(01)}$ is expressed in the same manner, but with V_{CF} replaced by the second perturbation operator.

The intra-Q-shell interactions taken into account at the third order are determined by the perturbing expression

$$\begin{aligned} {}^3\Gamma_V = \sum_{Xx} \sum_{Yy} & \left\{ \frac{\left\langle 4f^N \Psi_f^0 | D^{(1)} | Yy \right\rangle \left\langle Yy | QVQ | Xx \right\rangle \left\langle Xx | V_{CF} | 4f^N \Psi_i^0 \right\rangle}{(E_i^0 - E_{Yy}^0)(E_i^0 - E_{Xx}^0)} \right. \\ & \left. + \frac{\left\langle 4f^N \Psi_f^0 | V_{CF} | Xx \right\rangle \left\langle Xx | QVQ | Yy \right\rangle \left\langle Yy | D^{(1)} | 4f^N \Psi_i^0 \right\rangle}{(E_f^0 - E_{Yy}^0)(E_f^0 - E_{Xx}^0)} \right\}, \end{aligned} \tag{36}$$

where, as before, a specific choice of the second perturbation V has to be made.

In the case of the intra-Q-shell interactions via h_{hfs}^1, using the same definition and adopting the same contraction rules as previously, the effective operator is simplified to the form

$$\begin{aligned} & {}^3\Gamma_{h_{hfs}^1}(Dh^1 V_{CF} + V_{CF} h^1 D) = \sum_{tp} B_p^t \sum_{\ell'}^{even} \sum_{\ell''} \delta(\ell'', \ell') \\ & \left\langle \varrho^t(4f \longrightarrow \ell') | r | \varrho^{-3}(4f \longrightarrow \ell') \right\rangle \\ & \sqrt{\ell'(\ell'+1)(2\ell'+1)} \langle \ell \| C^{(t)} \| \ell' \rangle \langle \ell' \| C^{(1)} \| \ell \rangle \\ & \sum_{\lambda\mu} (-1)^{\lambda+\rho} [\lambda] \left(X_{p\rho q}^{t11}(\lambda\mu; \ell'\ell') + X_{\rho pq}^{1t1}(\lambda\mu; \ell'\ell') \right) U_\mu^{(\lambda)}(\ell\ell). \end{aligned} \tag{37}$$

These are the third-order contributions that originate from the off-diagonal configuration interaction between $4f^{N-1}n'\ell'$ and $4f^{N-1}n''\ell'$ for $\ell' = even$ ($\equiv d,g$) and for $n' \neq n''$. The diagonal terms, for $n' = n''$ are more complex and in order to derive their effective operator version some additional approximations, have to be introduced. With the assistance of further approximations, it is also possible to include the whole impact of the nuclear magnetic hyperfine interactions and use the measured value of the magnetic hyperfine structure constant. However, such an approach would not provide new information about the nature and sensitivity of the $f \leftrightarrow f$ transitions to these subtle interactions.

Inserting h_{hfs}^2 into Eq. (36) results in new effective operators of the third-order. In this particular case, all the operators in Eq. (36) have to be expressed by the double tensor operators, as in the case of the intershell interactions. For example, for the sequence of the matrix elements Vh^2D, the final effective operator has the form, which is very similar to the intershell interactions defined in Eq. (29), namely

$$
\begin{aligned}
&{}^3\Gamma_{h^2_{hfs}}(h^2DV + VDh^2) = \frac{1}{2}\sqrt{3}\sum_{\ell'}\sum_{\ell''}\sum_{tp}^{odd} B^t_p \\
&\left\langle \varrho^t(4f \longrightarrow \ell')|r^{-3}|\varrho^1(4f \longrightarrow \ell'')\right\rangle \\
&\left\langle \ell \| C^{(t)} \| \ell' \right\rangle \left\langle \ell' \| C^{(2)} \| \ell'' \right\rangle \left\langle \ell'' \| C^{(1)} \| \ell \right\rangle \\
&\sum_q \sum_y^{odd} \sum_{\lambda,\mu}^{even} [y][\lambda]^{1/2} \sum_{x,\sigma} (-1)^{x+y+t+\lambda-\mu}[x] \\
&\begin{pmatrix} 1 & 1 & x \\ \rho & q & -\sigma \end{pmatrix} \begin{pmatrix} t & x & \lambda \\ p & \sigma & -\mu r \end{pmatrix} \left\{ \begin{array}{cccccccc} \ell & & y & & 1 & & 2 & \\ & \ell & & \lambda & & 1 & & \ell'' \\ \ell' & & t & & x & & 1 & \end{array} \right\} \\
&W^{(1y)\lambda}_{\mu}(s\ell, s\ell)
\end{aligned} \tag{38}
$$

As seen from this example, the effective operators that represent the intrashell interactions have a similar tensorial structure to those that include the intershell interactions. In general, it is concluded that taking formally all possible sequences of operators in triple products of matrix elements (without their physical meaning), the final structure of the derived effective operators contain all permutations of the indices that identify the angular coefficients. This is exactly what is observed when comparing the structures of the intra- and intershell interactions taken into consideration via nuclear magnetic interactions V_{hfs}. The same conclusion is derived from the analysis of the effective operators with the intrashell interactions included via the electric multipole hyperfine interactions V_{EM}. Indeed, the set of the effective operators presented in Eq. (33) is completed by the additional objects associated with the unit tensor operator $U^{(\lambda)}$ multiplied by the radial integrals with all possible assignments of the ranks of the perturbed functions and powers of the radial coordinate. The angular factors of these operators are determined by $X^{k_1k_2k_2}_{q_1q_2q_3}$ defined in Eq. (18) (or Eq. (19)), for all assignments of $(k_1, k_2, k_3) = (k, t, 1)$, with the adjusted order of their components q, p, ρ.

Thus, in general the intrashell interactions do not provide effective operators that would change the selection rules for the nonvanishing contributions to the transition amplitude established at the third-order analysis of the objects representing the intershell interactions of various physical origins.

CONCLUSIONS

To summarize this general analysis devoted to new contributions to the transition amplitude that are caused by the hyperfine interactions, it is useful to look at the presented effective operators in a general way, as at objects that all are defined within the spin-orbital space. To transform an orbital tensor operator to such a form, it is enough to remember that each unit tensor operator $u^{(k)}$ within the accuracy of factor of $\sqrt{2}$ may be replaced by a double tensor operator $w^{(0k)k}$, which acts as a scalar within the spin space (with a rank $\kappa = 0$), and an original tensor of rank k in the orbital part.

Thus

1. $W^{(0\lambda)\lambda}$ with $\lambda = even$ represent all the physical mechanisms that are described by the standard parameterization based on the Judd–Ofelt theory implemented by the third-order electron correlation contributions; as demonstrated here, these effective operators contain in addition to the crystal field potential and electron correlation also the impact of electric multipole (dipole and quadrupole in particular) hyperfine interactions determined by Eq. (32), at the second-, and by Eq. (33) at the third-order;
2. $W^{(0\lambda)\lambda}$ with $\lambda = odd$ introduced in Eq. (24) represent third-order terms that originate from the electric multipole hyperfine interactions; they are beyond the standard parameterization scheme;
3. $W^{(1k)\lambda}$ with $\lambda = even$ and *odd* represent all interactions within the spin-orbital space, and in particular they include the nuclear magnetic hyperfine interactions that are represented by the third-order effective operators defined in Eq. (29); these terms are also beyond the standard parameterization scheme.

Inspection of the tensorial structure of all effective operators presented here does not provide any information about their relative importance in the description of the electric dipole transitions. There is neither *a priori* information nor rules established how to measure the importance of certain expressions. In each case, the numerical calculations have to be performed for a given system to verify the hierarchy of various effects. Because the contributions to the transition amplitude are discussed here and not the corrections to the energy, it is even impossible to expect that for example the third-order terms should be smaller than those of the second order. Obviously, this would be the case for the energy and its convergent series of corrections, assuming that the partitioning of the Hamiltonian is properly performed.

The results of the current discussion demonstrate that there is a physical evidence for the validity of the scheme of parameterization of *f*-spectra extended to the form introduced within the relativistic approach in Refs. 13

and 14. Thus it is suggested that the standard intensity parameters Ω_λ of the Judd–Ofelt scheme

$$S_{f\leftarrow i} = \sum_{\lambda=2,4,6} \Omega_\lambda |\langle \Psi_f \| U^{(\lambda)} \| \Psi_i \rangle|^2$$

are replaced by the set of new parameters

$$S_{f\leftarrow i} = \sum_{\lambda} \sum_{\kappa k} \Omega_\lambda^{\kappa k} |\langle \Psi_f | W^{(\kappa k)\lambda} | \Psi_i \rangle|^2$$

There is a demand for such a modification of the standard scheme, and the best examples of this are the difficulties in the description of the unusual transitions $0 \leftrightarrow 0$ and $0 \leftrightarrow 1$ observed in Eu^{+3} ion. In the particular case of these transitions, it is not only important to be able to describe them theoretically because of purely scientific challenge of basic research. The demand for new parameterization that is also applicable for these particular transitions is reinforced by their importance when used as spectroscopic tools for the structural recognition of various isomers of tissue selective organic chelates, as described for example in Ref. 22.

Of special importance for the understanding of the nature of the $f \leftrightarrow f$ transitions is the conclusion that the primacy of the crystal field potential as the forcing mechanism of the standard Judd–Ofelt theory is terminated by the presence of a new physical mechanism, which directly contributes to the transition amplitude at the second order. As mentioned above, V_{EM} for $k = odd$ in its multipole expansion of Eq. (30) takes over the role that is played by the odd part of the crystal field in the standard model and gives rise to a new approach for the theoretical description of the spectroscopic properties of the lanthanides in crystals. As a consequence, those transitions regarded as forced by the crystal field are in their nature induced by hyperfine interactions. This conclusion has a serious impact also upon the description of the parity forbidden electric dipole transitions in free atomic/ionic systems. The distortion of the spherical symmetry of the nucleus by the surrounding electrons of the open shell gives rise to new (and the only) contributions to the transition amplitude of a free system; in such cases, the important role of these interactions cannot be overestimated. Only for ions in crystals when the second order contributions of two various origins compete is a numerical analysis necessary to find their relative importance.

Unfortunately, it is impossible to estimate the relative magnitude of various contributions via the inspection of their tensorial structure, as there is no *a priori* information available about the hierarchy of various terms contributing to the transition amplitude. In the case of the analysis of energy, and its calculation, it is expected that, if the Hamiltonian is properly partitioned, the energy corrections of various orders form a convergent series. This means that obviously the third-order corrections to the energy are smaller than the second-order terms, for example. The situation is different in the case of the so-called properties where, not the corrections (that are reserved for the energy only), but the contributions of various orders are analyzed. The results of *ab initio* calculations performed for the lanthanide series demonstrate that the third-order contributions to the transition amplitude that originate from the correlation effects are larger (for some ions—even several times) than the second-order Judd–Ofelt terms. Thus in order to find the relative importance of various terms contributing to the transition amplitude, direct calculations have to be performed (not semiempirical!). Inspection of various terms presented here shows that such a numerical procedure requires special programs (the radial integrals have to be calculated, and not treated as parameters), knowledge of the crystal structure of the materials (and unfortunately the odd rank crystal field parameters are unknown, and it is impossible to evaluate them even through the fitting procedure); such a task requires additional approximations and an extended scheme of numerical analysis.

The numerical illustration of conclusions presented here is in preparation.

As demonstrated, the hyperfine interactions indeed induce the electric dipole $f \leftrightarrow f$ transitions as predicted by Wybourne in 1962. It must be admitted that, as mentioned at the beginning of this discussion, it took more than 20 years to observe this property experimentally by Popova and her collaborators, and it took more than 40 years to verify it theoretically. In fact, not the lack of interest but the complexity of both experimental and theoretical investigations were the reasons that the field developed in a way that so much time separated the distinct steps of its advancements.

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