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# A derivation of Judd-Ofelt theory by second quantization of configuration interaction

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ABSTRACT

A derivation of the equations in the Judd-Ofelt theory for quantifying the intensities of 4f-4f transitions based on the second quantization or occupation number representation is presented. This derivation is more concise and compact, emphasizing some approximations employed and aims at simplifying the comprehension of the theory. It is almost self-contained, with the properties and relationships pertaining to the second quantization approach being introduced, and it requires some basic understanding of quantum mechanics, particularly, of angular momentum techniques (e.g. 3-j symbols and Racah operators). It is expected that this derivation can be followed and comprehended by students, researchers, and enthusiasts, hopefully encouraging new implementations, applications, and developments involving the intensities of 4f-4f transitions.

## 1. Introduction

The technological, scientific, and geopolitical relevance of the rare-earth elements has increased significantly with each passing year [1,2]. Especially in the field of luminescence, their unique spectroscopic properties (e.g.: long excited state lifetime, narrow emission and absorption bands, weak interaction with the environment) make them unique in the periodic table [3].

For years, there was much discussion in the scientific community about the nature of their emissions, that is, it was known that 4f-4f transitions were forbidden by the electric dipole mechanism, but other explanations from time-dependent perturbation theory such as quadrupole or magnetic dipole transitions could not explain the observed intensities. It took until 1962 for Brian Judd and George S. Ofelt to independently state that the transitions are in fact electric dipole transitions, which happen at a much weaker intensity due to a parity breaking mechanism, which nowadays is just called the Judd-Ofelt theory [4,5].

However, for a scientist or student of the field, the reading of the original Judd and Ofelt papers is quite taxing and do not reach the same format of the expressions for the radiative rates and transition electric dipole that is most commonly used for nowadays applications of the theory. Therefore, we aim to propose a new way of reaching the expressions of Judd-Ofelt by means of second quantization of operators, first order time-independent perturbation theory, and angular momenta operator theory, which are topics commonly taught in graduate-level advanced quantum mechanics courses [6,7] and to whom graduate students can relate.

The derivations of the Judd-Ofelt theory available in the literature [4,5,8] employ the factorization of the wavefunction into a factor that is related to states of the lanthanide ion and another factor describing the states of the environment (e.g., ligands). In the present derivation, by employing the second quantization formalism, the separation between the states of the lanthanide and the ligands is performed at the operator level. Indeed, there is a set of creation and annihilation operators that act on the one-particle states of the lanthanide and another disjoint set that acts on the basis of the ligand states. This is a relevant novelty, because in addition to simplifying the derivation it makes the

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approximations more suitable to interpretation and amenable to corrections. This approach can also be applied and provide new insights into other relevant mechanisms for the 4f-4f transition intensities (e.g., dynamic-coupling [9–11]), as well as the models describing the non-radiative intramolecular energy transfer in lanthanide compounds and materials [12].

With the recent development of quantum computing, the interest in second quantization-based approaches was renewed because they are widely employed in the mapping of fermionic Hamiltonians (strings of creation and annihilation operators) to qubit Hamiltonians [13–15]. Thus, a derivation of the Judd-Ofelt theory based on second quantization should appeal to young researchers that might perform new improvements and implementations.

## 2. Second quantization approach in quantum mechanics

Second quantization or occupation number representation is a powerful formalism to develop quantum mechanics because it focuses on the operators, which become independent of the number of particles and most algebraic manipulations are reduced to commutations within a string of elementary operators [16,17]. This formalism introduces a complete set of one-particle states, which in electronic structure are the well-known spin-orbitals. This is a general formalism that describes both types of particles: bosons and fermions; however, the interest here is the electronic structure, so it will be limited to electrons. The general $N$-electron state is labeled by the eigenvalues of each electron, and the entire space is called a Fock space. The basis for this space is a distribution of electrons with the specified eigenvalues represented by the basis vector $|n_1, n_2, \ldots\rangle$, where $n_i$ is the number of electrons with eigenvalue $\varepsilon_i$ of the one-electron operators. The state with no particle is the vacuum state, which is denoted as $|0\rangle$, and the other states in the Fock space can be generated using *creation operators*. Hence, the creation operator $a_i^\dagger$ increases the number electrons in state $i$ by 1, or acting on the vacuum state will occupy spin-orbital $i$ expressed as: $a_i^\dagger|0\rangle = |n_i\ell_i m_{\ell_i} m_{s_i}\rangle$, and creates of an electron in the wavefunction specified by the quantum numbers of the state $i$, e.g., principal ($n$), orbital angular momentum ($\ell$) and its projection ($m_\ell$), and the projection of the spin ($m_s$) that can only have values of $\pm\frac{1}{2}$. The Hermitian conjugate (or adjunct) of the creation operator $a_i^\dagger$, denoted as $a_i$, removes or annihilates an electron from state $i$, thus called an *annihilation operator*, which changes the occupation of state $i$ by $-1$, leading to the reverse process of the creation, and for a normalized state can be expressed as:

$$1 = \langle i|i\rangle = \langle i|a_i^\dagger|0\rangle = \langle 0|a_i a_i^\dagger|0\rangle = \langle 0|a_i|i\rangle \leftrightarrow a_i|i\rangle = |0\rangle \tag{1}$$

Application of an annihilation operator $a_i$ to many-electrons state with an unoccupied spin-orbital $i$ yields zero: $a_i|n_1,\ldots,n_{i-1},n_{i+1},\ldots\rangle = 0$, whose Hermitian conjugate also yields $\langle\ldots,n_{i+1},n_{i-1},\ldots,n_1|a_i^\dagger = 0$, which are clearly valid for the vacuum state: $a_i|0\rangle = 0$ and $\langle 0|a_i^\dagger = 0$. This is an interesting result, because it allows for determining matrix elements by manipulating strings of creation and annihilation operators by bringing $a_i$ to act on the vacuum state or on the state with an unoccupied spin-orbital $i$.

The creation $a_i^\dagger$ and annihilation $a_i$ operators must satisfy the anti-commutation relations to be consistent with the antisymmetric properties of fermionic wavefunctions:

$$\{a_i^\dagger, a_j\} = a_i^\dagger a_j + a_j a_i^\dagger = \delta_{ij} \tag{2a}$$

and

$$\{a_i^\dagger, a_j^\dagger\} = a_i^\dagger a_j^\dagger + a_j^\dagger a_i^\dagger = \{a_i, a_j\} = a_i a_j + a_j a_i = 0 \tag{2b}$$

Any single-particle operator $\hat{o}(i)$ that acts on the vector space of particle-$i$ can be represented in second quantization as a linear combination of strings $a_\xi^\dagger a_\eta$ of creation and annihilation operators, where the complete operator $\hat{O}$ takes the following form:

$$\hat{O} = \sum_{i=1}^{N} \hat{o}(i) \rightarrow O = \sum_{\xi,\eta} o_{\xi\eta} a_\xi^\dagger a_\eta, \ \ o_{\xi\eta} = \langle\xi|o|\eta\rangle \tag{3}$$

where the Greek letters $\xi$ and $\eta$ represent the eigenstates of the system and $o_{\xi\eta}$ are the matrix elements of operator $\hat{o}$ represented in the single-particle basis. Within the second quantization, an important relationship can be derived [18] in which the sum over all possible angular momentum eigenstates of the same $n,\ell$ of the string $a_\xi^\dagger a_\eta$, with $(\xi,\eta)$ representing the $m_\ell$ and $m_s$ quantum numbers, is equivalent to the many-electron unitary tensor operator $U_q^{(k)}$, namely,

$$\sum_{\xi,\eta}(-1)^{s+m_s+m_{\ell_\xi}+\ell}(2\lambda+1)^{1/2}\begin{pmatrix} s & s & 0 \\ m_s & -m_s & 0 \end{pmatrix}\begin{pmatrix} \ell & \ell & \lambda \\ m_{\ell_\xi} & -m_{\ell_\eta} & \rho \end{pmatrix} a_\xi^\dagger a_\eta \stackrel{\text{def}}{=} (a^\dagger a)_{-\rho}^{(\lambda)}$$
$$= \left(\lambda+\frac{1}{2}\right)^{1/2} U_{-\rho}^{(\lambda)} = \frac{\sqrt{2\lambda+1}}{\sqrt{2}} U_{-\rho}^{(\lambda)} \tag{4}$$

where $s$ and $\ell$ are the usual spin and orbital angular momenta quantum numbers with $m_s$ and $m_\ell$ being their projections, whereas the quantities $\begin{pmatrix} a & b & c \\ d & e & f \end{pmatrix}$ are numerical coefficients called 3-j symbols that are related to the Clebsch-Gordan coefficients, but have more symmetrical properties [19]. This equation is what will enable to write the second quantization configuration interaction operator in terms of the unitary tensor operator $U$.

## 3. Configuration interaction caused by the ligand field

From the perturbation theory with a known unperturbed eigenstate in angular momentum representation, $|A\alpha\rangle$, and eigenvalue $E_{A\alpha}$, it is possible to express the first-order perturbed wavefunction as a configuration interaction-type *ansatz*, which is a function of the matrix elements involving the perturbation $V$ (e.g., the ligand field operator) [20]:

$$|A\alpha\rangle^{(1)} = |A\alpha\rangle + \sum_{B,\beta}\frac{\langle B\beta|V|A\alpha\rangle}{E_{A\alpha} - E_{B\beta}}|B\beta\rangle \tag{5}$$

where the eigenstate $|B\beta\rangle$ with eigenvalue $E_{B\beta}$ spans all other eigenstates of the system. For lanthanide ions, the labels $B$ and $\beta$ in the eigenstate $|B\beta\rangle$ denote configuration and the multiplet structure, respectively. For a given operator $T$ that is diagonal in the unperturbed eigenstates basis, i.e., $\langle A\alpha'|T|A\alpha\rangle = 0$, the perturbed matrix elements $\langle A\alpha'|T|A\alpha\rangle^{(1)} = T_{\alpha\alpha'}$ are then given at first order by:

$$T_{\alpha\alpha'} = \sum_{B,\beta}\frac{1}{E_{A\alpha} - E_{B\beta}}[\langle A\alpha'|V|B\beta\rangle\langle B\beta|T|A\alpha\rangle + \langle A\alpha'|T|B\beta\rangle\langle B\beta|V|A\alpha\rangle] \tag{6}$$

To obtain a workable form of these first-order perturbed matrix elements it is necessary to perform two approximations. The first one considers: $E_{A\alpha} - E_{B\beta} \approx E_A - E_B$ (analogous to the case of $|\Delta E(4f^N, 4f^{N-1}n\ell)| \approx |E_{4f} - E_{n\ell}|$ in Fig. 1), where the multiplet structures $E_{A\alpha}$ and $E_{B\beta}$ are approximated by the corresponding energy centroids (or barycenters) $E_A$ and $E_B$ for the A and B configurations. A second approximation consists in limiting the number of relevant contributions $B$ in the configuration interaction expansion.

For lanthanide ions, it is reasonable to consider only the $4f^{(n-1)}5d^1$ configuration, because the other excited configurations have a much greater energetic difference. Hence, for a given configuration $B$ (e.g., $4f^{(n-1)}5d^1$) for lanthanide ions, the effective matrix element takes the form:

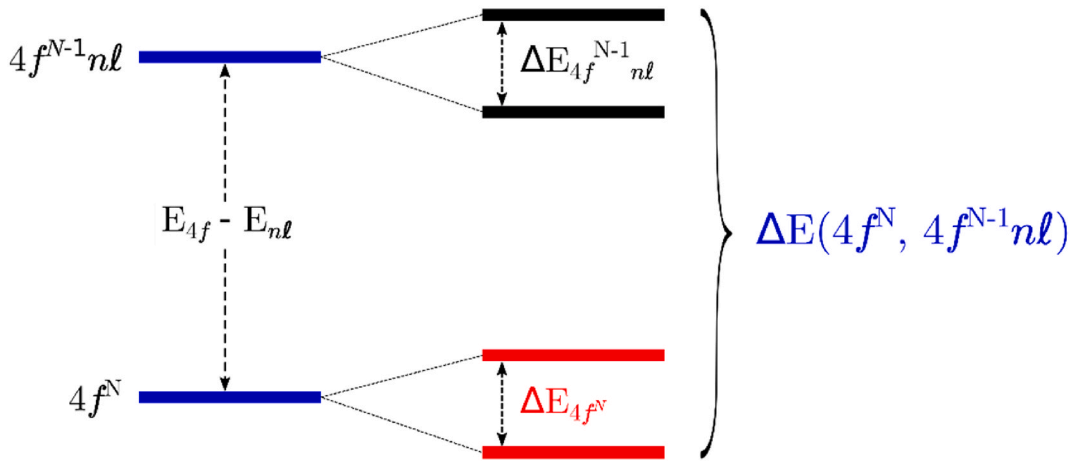


**Fig. 1.** Diagram showing the energy levels for the ground and excited states used in the Judd–Ofelt theory. Reproduced with permission from Ref. [21].

$$T_{\alpha\alpha'} = \frac{1}{E_A - E_B}\sum_{\beta}\langle A\alpha'|V|B\beta\rangle\langle B\beta|T|A\alpha\rangle + \langle A\alpha'|T|B\beta\rangle\langle B\beta|V|A\alpha\rangle \tag{7}$$

Notice that this expression is general and valid for any pair of operators $T$ and $V$. Because the $\alpha$- and $\beta$-state of interest involve orbital and spin angular momenta, it is convenient to let $T$ and $V$ be tensor operators of the form: $T_Q^{(K)}$ and $V_{Q'}^{(K')}$, where $K$ and $K'$ are their ranks, respectively, with $(2K+1)$- and $(2K'+1)$-components labeled by $Q$ and $Q'$. In addition, the unperturbed eigenstates $|B\beta\rangle$ form a complete set (or a basis), so, the closure relation (or the resolution of the identity): $\sum_{\beta}|B\beta\rangle\langle B\beta| = 1$ is satisfied. Thus, summation in Eq. (7) can be simplified as:

$$\begin{aligned}\sum_{\beta}\langle A\alpha'|V_{Q'}^{(K')}|B\beta\rangle\langle B\beta|T_Q^{(K)}|A\alpha\rangle &= \left(\langle A\alpha'|V_{Q'}^{(K')}\right)\sum_{\beta}|B\beta\rangle\langle B\beta|\left(T_Q^{(K)}|A\alpha\rangle\right)\\ &= \langle A\alpha'|V_{Q'}^{(K')}T_Q^{(K)}|A\alpha\rangle \equiv \langle A\alpha'|O|A\alpha\rangle\end{aligned} \tag{8}$$

which leads to the definition of an effective operator $O$ acting on the unperturbed wavefunctions, whose matrix elements are $\langle A\alpha'|O|A\alpha\rangle$. Thus, by evaluating the matrix element of the effective operator $O$, one can obtain the matrix elements $T_{\alpha\alpha'}$ in Eq. (7) from known matrix elements of the perturbation.

To take advantage of the second quantization formalism in deriving the expressions for the matrix elements of the effective operator $O$, it is convenient to define the second quantization operators $a_i$ as those acting on the $A$-configuration and $b_i$ acting on the $B$-configuration. It is important to notice that the Greek labels of the creation and annihilation operators represent single-electron quantum numbers ($m_\ell$, $s$, $m_s$), because $n$ and $\ell$ quantum numbers were already being specified by the $n\ell$-configurations $A$ and $B$. With these precautions, the operators $T_Q^{(K)}$ and $V_{Q'}^{(K')}$ in the effective operator $O$ can be represented in their single-electron second-quantized form as,

$$O = \sum_{\xi,\xi',\eta,\eta'}\langle n_A\ell_A\xi\left|v_{Q'}^{(K')}\right|n_B\ell_B\eta\rangle\langle n_B\ell_B\eta'\left|t_Q^{(K)}\right|n_A\ell_A\xi'\rangle a_\xi^\dagger b_\eta b_{\eta'}^\dagger a_{\xi'} \tag{9}$$

where $v_{Q'}^{(K')}$ and $t_Q^{(K)}$ are the one-electron operators that compose $V_{Q'}^{(K')}$ and $T_Q^{(K)}$ operators, respectively.

By using the anticommutation relation: $a_i^\dagger a_j = \delta_{ij} - a_j a_i^\dagger$, in Eq. (2a), the string of creation and annihilation operators can be expressed as

$$a_\xi^\dagger b_\eta b_{\eta'}^\dagger a_{\xi'} = a_\xi^\dagger\left(\delta_{\eta\eta'} - b_{\eta'}^\dagger b_\eta\right)a_{\xi'} = \delta_{\eta\eta'}a_\xi^\dagger a_{\xi'} - a_\xi^\dagger b_{\eta'}^\dagger b_\eta a_{\xi'} \tag{10}$$

So, the second term in Eq. (10): $-a_\xi^\dagger b_{\eta'}^\dagger b_\eta a_{\xi'}$, will always yield 0 (zero) when acting on $|A\alpha\rangle$ or $|B\beta\rangle$, because the wavefunctions representing the configurations $4f^n$ and $4f^{(n-1)}5d^1$ have no electrons for the $b_\eta$ or $a_{\xi'}$ operators to annihilate, respectively. As a result, the effective operator $O$ depends only on operators acting on the $A$-configuration, and depends only on the label $\eta$ due to the orthonormality $\delta_{\eta\eta'}$. Thus,

$$O = \sum_{\xi,\xi',\eta}\langle n_A\ell_A\xi\left|v_{Q'}^{(K')}\right|n_B\ell_B\eta\rangle\langle n_B\ell_B\eta\left|t_Q^{(K)}\right|n_A\ell_A\xi'\rangle a_\xi^\dagger a_{\xi'} \tag{11}$$

This simplification shows one of the advantages of employing the second quantization formalism. The factorization of the effective operator $O$ in terms of the matrix elements of one-electron irreducible tensor operators $v$ and $t$ is relevant because they can be expressed in terms of the *reduced matrix elements*, which are in fact merely a number, by the Wigner-Eckart theorem [22]. This theorem states that a matrix element $\langle\alpha jm\left|t_q^{(k)}\right|\alpha' j' m'\rangle$ of an irreducible tensor operator $t_q^{(k)}$ taken between two states labeled by angular momentum quantum numbers $j, m$ and $j', m'$, with additional quantum numbers $\alpha$ and $\alpha'$, can be expressed in terms of the reduced matrix element $\langle\alpha j\|t^{(k)}\|\alpha' j'\rangle$ as:

$$\langle\alpha jm\left|t_q^{(k)}\right|\alpha' j' m'\rangle = \frac{1}{(2j+1)^{1/2}}\langle j' km' q|j' kjm\rangle\langle\alpha j\|t^{(k)}\|\alpha' j'\rangle \tag{12a}$$

$$= (-1)^{j-m}\begin{pmatrix} j & k & j' \\ -m & q & m' \end{pmatrix}\langle\alpha j\|t^{(k)}\|\alpha' j'\rangle \tag{12b}$$

where $\langle j' km' q|j' kjm\rangle$ and $\begin{pmatrix} a & b & c \\ d & e & f \end{pmatrix}$ are the known Clebsch-Gordan coefficients and the 3-j symbols, respectively. As a result, the effective operator $O$ becomes:

$$O = \sum_{\xi,\xi',m_{\ell_\eta}}(-1)^{\ell_A+\ell_B-m_{\ell_\xi}-m_{\ell_\eta}}\begin{pmatrix} \ell_A & K' & \ell_B \\ -m_{\ell_\xi} & Q' & m_{\ell_\eta} \end{pmatrix}\begin{pmatrix} \ell_B & K & \ell_A \\ -m_{\ell_\eta} & Q & m_{\ell_{\xi'}} \end{pmatrix} \times\langle\ell_A\|v^{(K')}\|\ell_B\rangle\langle\ell_B\|t^{(K)}\|\ell_A\rangle a_\xi^\dagger a_{\xi'} \tag{13}$$

The 3-j symbols satisfy several relationships, in particular, that developed by Judd [22]:

$$\begin{aligned}&\sum_{m_{\ell_\eta}}(-1)^{K+\ell_A-Q+m_{\ell_\eta}}\begin{pmatrix} \ell_A & K' & \ell_B \\ -m_{\ell_\xi} & Q' & m_{\ell_\eta} \end{pmatrix}\begin{pmatrix} K & \ell_A & \ell_B \\ -Q & -m_{\ell_{\xi'}} & m_{\ell_\eta} \end{pmatrix}\\ &= \sum_{\lambda,\rho}(-1)^{\lambda+\rho}(2\lambda+1)\begin{Bmatrix} \ell_A & K' & \ell_B \\ K & \ell_A & \lambda \end{Bmatrix}\begin{pmatrix} K & K' & \lambda \\ Q & Q' & \rho \end{pmatrix}\begin{pmatrix} \ell_A & \ell_A & \lambda \\ -m_{\ell_\xi} & m_{\ell_{\xi'}} & -\rho \end{pmatrix}\end{aligned} \tag{14}$$

where $\begin{Bmatrix} a & b & c \\ d & e & f \end{Bmatrix}$ are 6-j symbols that arise when treating the coupling of three angular momenta [22]. Because this coupling can be performed between pairs of angular momenta it can be expressed as a linear combination of products of 3-j symbols. Hence, the summation over $m_{\ell_\eta}$ in Eq. (14) can be replaced by the summation over $(\lambda, \rho)$ that yields an intermediate form of the effective operator $O$:

$$O = \sum_{\xi,\xi',\lambda,\rho} (-1)^{\ell_A+\lambda+\rho-m_{\ell_\xi}} (2\lambda+1) \begin{pmatrix} \ell_A & \ell_A & \lambda \\ -m_{\ell_\xi} & m_{\ell_{\xi'}} & -\rho \end{pmatrix} \times \begin{Bmatrix} \ell_A & K' & \ell_B \\ K & \ell_A & \lambda \end{Bmatrix} \begin{pmatrix} K & K' & \lambda \\ Q & Q' & \rho \end{pmatrix} \langle \ell_A || v^{(K')} || \ell_B \rangle \langle \ell_B || t^{(K)} || \ell_A \rangle a^\dagger_\xi a_{\xi'} \tag{15}$$

which seems more complicated because of the increase in the number of summation indexes ($m_{\ell_\eta} \rightarrow \lambda, \rho$). However, it will be possible to collapse the summation over $\xi, \xi'$, by converting the effective operator $O$ into a single unitary tensor operator that operates on the electrons of the $A$-configuration. To accomplish this simplification, it is useful to employ the following property of the 3-j symbol [23]:

$$\begin{pmatrix} s & s & 0 \\ m_s & -m_s & 0 \end{pmatrix} = \frac{(-1)^{s-m_s}}{\sqrt{2s+1}} \tag{16}$$

So, by multiplying the right-side of Eq. (15) by $\left[(-1)^{s-m_s}/\sqrt{2}\right]\left[\sqrt{2}/(-1)^{s-m_s}\right]$, one obtains:

$$O = \sum_{\lambda,\rho} (-1)^{\lambda+\rho} \sqrt{2}\sqrt{2\lambda+1} \sum_{\xi,\xi'} (-1)^{-m_{\ell_\xi}-s+m_s+\ell_A} \sqrt{2\lambda+1} \times \begin{pmatrix} s & s & 0 \\ m_s & -m_s & 0 \end{pmatrix} \begin{pmatrix} \ell_A & \ell_A & \lambda \\ -m_{\ell_\xi} & m_{\ell_{\xi'}} & -\rho \end{pmatrix} a^\dagger_\xi a_{\xi'} \times \left[ \begin{Bmatrix} \ell_A & K' & \ell_B \\ K & \ell_A & \lambda \end{Bmatrix} \begin{pmatrix} K & K' & \lambda \\ Q & Q' & \rho \end{pmatrix} \langle \ell_A || v^{(K')} || \ell_B \rangle \langle \ell_B || t^{(K)} || \ell_A \rangle \right] \tag{17}$$

Notice that the summation over $\xi, \xi'$ can be replaced by $(a^\dagger a)^{(\lambda)}_{-\rho}$ according to Eq. (4), resulting in:

$$O = \sum_{\lambda,\rho} (-1)^{\lambda+\rho} \sqrt{2}\sqrt{2\lambda+1} \begin{Bmatrix} \ell_A & K' & \ell_B \\ K & \ell_A & \lambda \end{Bmatrix} \begin{pmatrix} K & K' & \lambda \\ Q & Q' & \rho \end{pmatrix} \times \langle \ell_A || v^{(K')} || \ell_B \rangle \langle \ell_B || t^{(K)} || \ell_A \rangle (a^\dagger a)^{(\lambda)}_{-\rho} \tag{18}$$

So, the effective operator can be finally written in terms of the unitary irreducible tensor operator $U^{(\lambda)}_{-\rho}$ defined in Eq. (4):

$$O = \sum_{\lambda,\rho} (-1)^{\lambda+\rho} (2\lambda+1) \begin{Bmatrix} \ell_A & K' & \ell_B \\ K & \ell_A & \lambda \end{Bmatrix} \begin{pmatrix} K & K' & \lambda \\ Q & Q' & \rho \end{pmatrix} \times \langle \ell_A || v^{(K')} || \ell_B \rangle \langle \ell_B || t^{(K)} || \ell_A \rangle U^{(\lambda)}_{-\rho} \tag{19}$$

To describe the 4f-4f transitions in lanthanides, the tensor operators $T^{(K)}_Q$ and $V^{(K')}_Q$ need to be specialized to represent the appropriate effects. For instance, the intensities of electronic transitions are proportional to the square modulus of the transition dipole moment [24], which immediately ascribes the tensor operator $T$ as the electric dipole operator, $\vec{\mu}$, which is a rank 1 tensor operator with the usual three components. Notice that as required in the development of Eq. (19), the matrix elements of $T = \vec{\mu}$ with respect to the unperturbed wavefunction are null: $\langle A\alpha' | T | A\alpha \rangle = 0$. The electric dipole operator can be converted into an irreducible tensorial form by transforming the position vector $\vec{r}_i$ of each particle in the system:

$$\vec{\mu} = -e\sum_i \vec{r}_i = -e\sum_{i,q} \left|\vec{r}_i\right| C^{(1)}_q \vec{e}^{\,*}_q \tag{20}$$

where $C^{(1)}_q$ is the Racah tensor operator (normalized spherical harmonic operator) and $\vec{e}^{\,*}_q$ is the complex conjugate of the spherical basis unit vectors.

In addition, these intensities are affected by the ligands, so the perturbation $V$ would be assigned as the ligand field Hamiltonian $H_{\text{LF}}$, which in its simplest form, is an electrostatic potential between the $j$-th ligand, represented by a charge $g_j$ at position $\vec{R}_j$, and each one of the 4f-electrons, as initially described by Bethe [25]:

$$H_{\text{LF}} = \sum_{i,j} \frac{g_j e^2}{\left|\vec{R}_j - \vec{r}_i\right|} \tag{21}$$

It will be further demonstrated that only odd-parity components of $H_{\text{LF}}$ contribute to the effective electric dipole. It has already been shown in several instances [26–28] that the ligand field Hamiltonian can expressed in terms of Racah operators $C^{(t)}_p$ of rank $t$ as:

$$H_{\text{LF}} = \sum_{t,p,i} \gamma^t_p r^t_i C^{(t)}_p(i) \tag{22}$$

with the quantity $\gamma^t_p$ encoding the symmetry of the ligands around the lanthanide ion. There are many crystal (ligand) field models for $\gamma^t_p$ [27, 29–32]. For instance, the point-charge electrostatic model (PCEM) describes this parameter as [25]:

$$\gamma^t_p = e^2\sqrt{\frac{4\pi}{2t+1}} \sum_j \frac{g_j}{R_j^{2t+1}} Y^{t^*}_p(\theta_j, \phi_j) \tag{23}$$

in this equation, $Y^{t^*}_p(\theta_j, \phi_j)$ is a spherical harmonic of rank $t$ acting on the angular coordinates of the $j$-th ligand. Inserting the expressions for the operators $T = \vec{\mu}$ and $V = H_{\text{LF}}$ in Eq. (19) and performing the summation in Eq (8), the effective perturbed electric dipole matrix element $\langle A\alpha' | \vec{\mu} | A\alpha \rangle^{(1)} = T_{\alpha\alpha'}$ in Eq. (7) for a 4f-4f transition can be expressed as:

$$T_{\alpha\alpha'} = -\frac{e}{E_A - E_B} \sum_{t,p,q} \sum_{\lambda,\rho} (-1)^{\lambda+\rho} (2\lambda+1) \Lambda^{t,\lambda}_{p,q,\rho} \gamma^t_p \langle A\alpha' | U^{(\lambda)}_{-\rho} | A\alpha \rangle \vec{e}^{\,*}_q \tag{24}$$

where

$$\Lambda^{t,\lambda}_{p,q,\rho} = \langle 4\text{f}|r^t|n\ell_B\rangle \langle n\ell_B|r|4\text{f}\rangle \langle \text{f}||C^{(t)}||\ell_B\rangle \langle \ell_B||C^{(1)}||\text{f}\rangle \begin{Bmatrix} \text{f} & t & \ell_B \\ 1 & \text{f} & \lambda \end{Bmatrix} \begin{pmatrix} 1 & t & \lambda \\ q & p & \rho \end{pmatrix} + \langle 4\text{f}|r|n\ell_B\rangle \langle n\ell_B|r^t|4\text{f}\rangle \langle \text{f}||C^{(1)}||\ell_B\rangle \langle \ell_B||C^{(t)}||\text{f}\rangle \begin{Bmatrix} \text{f} & 1 & \ell_B \\ t & \text{f} & \lambda \end{Bmatrix} \begin{pmatrix} t & 1 & \lambda \\ p & q & \rho \end{pmatrix} \tag{25}$$

For 4f-4f transitions in lanthanides, the angular momentum $\ell_A$ quantum number was replaced by $\ell_A = 3 \equiv \text{f}$, whereas the reduced matrix element $\langle \ell || C^{(k)} || \ell' \rangle$ are given by (see Eq. (1.57) on page 17 of reference [33]):

$$\langle \ell || C^{(k)} || \ell' \rangle = (-1)^{\ell} \sqrt{(2\ell+1)(2\ell'+1)} \begin{pmatrix} \ell & k & \ell' \\ 0 & 0 & 0 \end{pmatrix} \tag{26}$$

which is non-zero only when $\ell + k + \ell'$ is even due to the properties of the 3-j symbol [23,33]. This yields the first selection rule regarding the rank 1 reduced matrix element $\langle \ell || C^{(1)} || \ell' \rangle$: $\Delta\ell = \ell' - \ell = \pm 1$, also known as Laporte's rule. Therefore, in $\langle \ell_B || C^{(1)} || \text{f} \rangle$, $\ell_B$ must be 2 or 4, and for the electric dipole transition to be relaxed, the 4f configuration must interact with either the d or g excited configurations. The selection rules for higher rank reduced matrix elements $\langle \text{f} || C^{(t)} || \ell_B \rangle$ state that they will be non-zero if $3 + \ell_B + t$ is even, $5 + t$ or $7 + t$ must be even and, consequently, $t$ must be an odd integer.

Another identity involving the 3-j symbols is the exchange of two columns [23,33]:

$$(-1)^{a+b+c} \begin{pmatrix} a & b & c \\ d & e & f \end{pmatrix} = \begin{pmatrix} b & a & d \\ e & d & f \end{pmatrix} = \begin{pmatrix} c & b & a \\ f & e & d \end{pmatrix} = \begin{pmatrix} a & c & b \\ d & f & e \end{pmatrix} \tag{27}$$

So, the reduced matrix element in Eq. (26) satisfies: $\langle \ell' || C^{(k)} || \ell \rangle = (-1)^k \langle \ell || C^{(k)} || \ell' \rangle$, which together with the interchange of columns in the 3-j symbol can be used to reformulate the expression $\Lambda^{t,\lambda}_{p,q,\rho}$. To obtain a complete reformulation, some properties of the 6-j symbols are needed. For instance, 6-j symbols are invariant under (a) an interchange of columns, and (b) an interchange of any two numbers in the bottom row with the corresponding two numbers in the top row. Thus,

$$\begin{Bmatrix} \mathrm{f} & t & \ell_B \\ 1 & \mathrm{f} & \lambda \end{Bmatrix} \overset{(a)}{=} \begin{Bmatrix} t & \mathrm{f} & \ell_B \\ \mathrm{f} & 1 & \lambda \end{Bmatrix} \overset{(b)}{=} \begin{Bmatrix} \mathrm{f} & 1 & \ell_B \\ t & \mathrm{f} & \lambda \end{Bmatrix} \tag{28}$$

Combining the factors $(-1)^t$ and $(-1)^1$ from the transposition of the reduced matrix elements $\langle \mathrm{f}||C^{(t)}||\ell_B\rangle$ and $\langle \ell_B||C^{(1)}||\mathrm{f}\rangle$, respectively, with the factor $(-1)^{t+\lambda+1}$ from the interchange of columns of the 3-j symbol, yielding $(-1)^{2t+\lambda+2} = (-1)^\lambda$, the expression for $\Lambda^{t,\lambda}_{p,q,\rho}$ in Eq. (25) can be reformulated into:

$$\Lambda^{t,\lambda}_{p,q,\rho} = \langle 4\mathrm{f}|r|n\ell_B\rangle\langle n\ell_B|r^t|4\mathrm{f}\rangle\langle \mathrm{f}||C^{(1)}||\ell_B\rangle\langle \ell_B||C^{(t)}||\mathrm{f}\rangle \begin{Bmatrix} t & \mathrm{f} & \ell_B \\ \mathrm{f} & 1 & \lambda \end{Bmatrix} \begin{pmatrix} t & 1 & \lambda \\ p & q & \rho \end{pmatrix} \times \left[1+(-1)^\lambda\right] \tag{29}$$

which shows explicitly all the selections rules built into $\Lambda^{t,\lambda}_{p,q,\rho}$, namely, *i*) $\ell_B = \mathrm{d}$ or g from $\langle \mathrm{f}||C^{(1)}||\ell_B\rangle$, *ii*) $t$ must be an odd number from $\langle \ell_B||C^{(t)}||\mathrm{f}\rangle$, *iii*) $\lambda$ must be even from $1+(-1)^\lambda$, and *iv*) from the 6-j symbol, $0 \le \lambda \le 6\ (=\mathrm{f}+\mathrm{f})$ and $|\mathrm{f}-\ell_B| \le t \le \mathrm{f}+\ell_B$. So, the allowed values for the summations in Eq. (24) are $\lambda = 0, 2, 4, 6$ (the value 0 is excluded because the matrix elements are diagonal), and $t = 1, 3, 5, 7$, yielding the following form of the electric dipole matrix element:

$$T_{\alpha\alpha'} = -\frac{2e}{E_A - E_B}\sum_{t,p,q}\sum_{\lambda,\rho}(-1)^\rho(2\lambda+1)\langle 4\mathrm{f}|r|n\ell_B\rangle\langle n\ell_B|r^t|4\mathrm{f}\rangle \times \langle \mathrm{f}||C^{(1)}||\ell_B\rangle\langle \ell_B||C^{(t)}||\mathrm{f}\rangle \begin{Bmatrix} \mathrm{f} & 1 & \ell_B \\ t & \mathrm{f} & \lambda \end{Bmatrix} \begin{pmatrix} t & 1 & \lambda \\ p & q & \rho \end{pmatrix}\gamma^t_p\langle A\alpha'|U^{(\lambda)}_{-\rho}|A\alpha\rangle \vec{e}^{\,*}_q \tag{30}$$

Summing over all possible excited $B$-configurations, one reaches the final expression for the transition dipole moment for a 4f-4f transition:

$$\langle A\alpha'|\vec{\mu}|A\alpha\rangle = -e\sum_{t,p,q}\sum_{\lambda,\rho}(-1)^\rho(2\lambda+1)\begin{pmatrix} t & 1 & \lambda \\ p & q & \rho \end{pmatrix} B_{\lambda,t,p}\langle A\alpha'|U^{(\lambda)}_{-\rho}|A\alpha\rangle \vec{e}^{\,*}_q \tag{31}$$

where the parameter $B_{\lambda,t,p}$ encodes both the symmetry from $\gamma^t_p$ given in Eq. (23) and the configuration interaction between 4f and excited $n\ell$ configurations in $\Xi_{\lambda,t,p}$:

$$B_{\lambda,t,p} = \Xi_{\lambda,t,p}\gamma^t_p \tag{32}$$

with

$$\Xi_{\lambda,t,p} = \sum_{n,\ell}\frac{2}{E_{4\mathrm{f}} - E_{n\ell}}\langle 4\mathrm{f}|r|n\ell\rangle\langle n\ell|r^t|4\mathrm{f}\rangle\langle \mathrm{f}||C^{(1)}||\ell\rangle\langle \ell||C^{(t)}||\mathrm{f}\rangle\begin{Bmatrix} \mathrm{f} & 1 & \ell \\ t & \mathrm{f} & \lambda \end{Bmatrix} \tag{33}$$

With this expression, one can obtain, for instance, the radiative rate (or Einstein's spontaneous $A$ coefficient) for a 4f-4f transition in a vacuum. An additional simplification can be obtained by applying the Wigner-Eckart theorem to the operator $U^{(\lambda)}_{-\rho}$ and expressing its matrix element in terms of the reduced matrix element $\|U^{(\lambda)}\|$:

$$\langle A\alpha'|\vec{\mu}|A\alpha\rangle = -e\sum_{t,p,q}\sum_{\lambda,\rho}(-1)^\rho(2\lambda+1)\begin{pmatrix} t & 1 & \lambda \\ p & q & \rho \end{pmatrix} B_{\lambda,t,p} \times \begin{pmatrix} J_{\alpha'} & \lambda & J_\alpha \\ -M_{J_{\alpha'}} & -\rho & M_{J_\alpha} \end{pmatrix}\langle J_{\alpha'}||U^{(\lambda)}||J_\alpha\rangle \vec{e}^{\,*}_q \tag{34}$$

To find the total radiative rate between two $^{2S+1}L_J$ energy levels, one must sum over all possible $M_{J_{\alpha'}}$, $M_{J_\alpha}$ and divide by the degeneracy of the emitting level $|A\alpha\rangle$ $(2J_\alpha+1)$. This sum can be conceptually correct if all Stark levels of the emitting levels are equally populated. This can be considered valid at room temperature for ligand field splitting typically lower than 200 $\mathrm{cm}^{-1}$. It is also worth noting that the Judd-Ofelt theory considers that $J$ and $M_J$ are good quantum numbers, and that the theory does not account for individual intensities between Stark levels.

Taking the absolute square of the electric dipole moment in Eq. (34), one can use the orthogonality of Clebsch-Gordan coefficients to obtain:

$$|\langle A\alpha'|\vec{\mu}|A\alpha\rangle|^2 = \frac{e^2}{2J_\alpha+1}\sum_\lambda \Omega_\lambda\left|\langle J_{\alpha'}||U^{(\lambda)}||J_\alpha\rangle\right|^2 \tag{35}$$

where

$$\Omega_\lambda = (2\lambda+1)\sum_{t,p}\frac{|B_{\lambda,t,p}|^2}{(2t+1)} \tag{36}$$

are the so-called intensity parameters or Judd-Ofelt intensity parameter. The $(2\lambda+1)$ and $(2t+1)$ factors arise from the summation and orthogonalities properties of the 3-j symbols or the Clebsch-Gordan coefficients.

Equation (35) is the fundamental equation in the Judd-Ofelt theory, because it states that the intensities of the 4f-4f transitions can be split into two factors: a reduced matrix element $\langle J_{\alpha'}||U^{(\lambda)}||J_\alpha\rangle$ that depends only on the angular momentum quantum numbers of the initial and final states, and the intensity parameters $\Omega_\lambda$'s. The intensity parameter $\Omega_\lambda$ is independent of the transition, but it depends on the configuration interaction and, most of all, on the symmetry of the system. The matrix element $\langle J_{\alpha'}||U^{(\lambda)}||J_\alpha\rangle$ also introduces the selection rule for the angular momentum: $|J_{\alpha'} - J_\alpha| \le \lambda \le J_{\alpha'} + J_\alpha$, with $\lambda = 2, 4, 6$. Further contributions to the Judd-Ofelt theory consisted of easier calculations of the $B_{\lambda,t,p}$, such as the strategy developed by Malta by using Bebb and Gold [34,35] common energy denominator approximation, $E_{4\mathrm{f}} - E_{n\ell} \cong \langle\Delta E\rangle$, to close the summation on all possible configurations:

$$B_{\lambda,t,p} = \frac{2}{\langle\Delta E\rangle}\langle 4\mathrm{f}|r^{t+1}|4\mathrm{f}\rangle\theta_{\lambda,t}\,\gamma^t_p \tag{37}$$

where

$$\theta_{\lambda,t} = \langle \mathrm{f}||C^{(1)}||g\rangle\langle g||C^{(t)}||\mathrm{f}\rangle\begin{Bmatrix} \mathrm{f} & 1 & g \\ t & \mathrm{f} & \lambda \end{Bmatrix} + (1-2\delta_t)\langle \mathrm{f}||C^{(1)}||d\rangle\langle d||C^{(t)}||\mathrm{f}\rangle\begin{Bmatrix} \mathrm{f} & 1 & d \\ t & \mathrm{f} & \lambda \end{Bmatrix} \tag{38}$$

and

$$\delta_t = \frac{\sum_{n=3,4}\langle 4\mathrm{f}|r|n\mathrm{d}\rangle\langle n\mathrm{d}|r^t|4\mathrm{f}\rangle}{\langle 4\mathrm{f}|r^{t+1}|4\mathrm{f}\rangle} \tag{39}$$

The $\delta_t$ parameter encapsulates very high-energy core excitations, but its contributions to the overall calculation are lower, as shown through Hartree-Fock calculations [28]. The values for the $Eu^{3+}$ ions are: $\delta_1 = 0.539$, $\delta_3 = 0.223$, $\delta_5 = 0.082$, and $\delta_7 \approx 0$. With the final expression for the transition electric dipole moment, it is also possible to calculate the radiative rates, for example in a vacuum:

$$A_{\alpha'\alpha} = \frac{4\omega^3}{3c^3\hbar}|\langle A\alpha'|\vec{\mu}|A\alpha\rangle|^2 = \frac{4\omega^3e^2}{3c^3\hbar(2J_\alpha+1)}\sum_\lambda\Omega_\lambda\left|\langle J_{\alpha'}||U^{(\lambda)}||J_\alpha\rangle\right|^2 \tag{40}$$

It is noteworthy that the Judd-Ofelt mechanism for the relaxation of the electric dipole selection rule is not the only one at play for the 4f-4f transitions. The dynamic coupling between the incident electric field and the ligand polarizabilities was shown to yield radiative rates with the *exact* same form as Eqs. (35) and (36), so that both contributions to the $\Omega_\lambda$ cannot be experimentally distinguished.

## 4. Conclusions

By using the second-quantized operators, first order time-independent perturbation theory, and angular momenta operator theory, the equations of Judd-Ofelt theory for the (forced) electric dipole 4f-4f transition intensities were successfully derived in their modern form. An intermediate equation that combined several of these theoretical techniques was derived and explicitly encodes all the selection rules for these 4f-4f transitions Hopefully, this derivation should be more amenable for readers who are interested in the fundamentals of rare earth spectroscopy and could contribute to its further development.

## CRediT authorship contribution statement

**Lucca Blois:** Writing – review & editing, Writing – original draft, Validation, Methodology, Formal analysis, Conceptualization. **Ricardo L. Longo:** Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Formal analysis, Conceptualization. **Albano N. Carneiro Neto:** Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Formal analysis, Conceptualization. **Wagner M. Faustino:** Writing – review & editing, Writing – original draft, Validation. **Renaldo T. Moura:** Writing – review & editing, Writing – original draft, Validation. **Maria C.F.C. Felinto:** Writing – review & editing, Validation. **Hermi F. Brito:** Writing – review & editing, Writing – original draft, Visualization, Validation. **Oscar L. Malta:** Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Methodology, Formal analysis.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Data availability

No data was used for the research described in the article.

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