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Are the odd-rank crystal field parameters independent quantities?

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Abstract

The relation between various odd-rank crystal field parameters is discussed in the context of the theoretical description of the spectroscopic properties of rare earth ions in crystals.

Keywords: Odd-rank crystal field parameters; Rare earth ions

The intensity of electric dipole one photon transitions between the energy levels of the $4f^N$ configuration of rare earth ions in crystals is traditionally analyzed by means of Judd Ofelt theory [1,2]. In this theory the transition amplitude is determined by second order terms which include the perturbing influence of excited configurations taken into account via the odd part of the crystal field potential. In terms of effective operators the line strength of the one photon electric dipole transition is defined by the expression

$$S_{f\to i} = \sum_\lambda \Omega_\lambda |\langle 4f^N \Psi_f | U^{(\lambda)} | 4f^N \Psi_i \rangle|^2 \tag{1}$$

where Ω_λ are the so-called Judd Ofelt parameters which are usually determined through a fitting procedure. It is also possible, however, to evaluate them directly. The angular factors contributing to Ω evaluated once might be used for any ion of the lanthanide series, since they are independent of the electronic structure of the investigated system. It is also easy to evaluate the radial integrals, and when the perturbed function approach is applied they are evaluated for the complete radial basis sets of one electron states of a given symmetry. There is a problem, however, with the crystal field parameters with odd ranks which when squared contribute to Ω.

In terms of tensor operators the crystal field potential is defined as a one particle operator

$$V_{CF} = \sum_{kq} B^k_q \sum_i r^k_i C^{(k)}_q (\theta_i \phi_i) \tag{2}$$

The structural factors B^k_q are called the crystal field parameters, and they describe the environment of the rare earth ion, including its symmetry. In practice, the crystal field parameters are usually determined from a fitting procedure applied for the reproduction of the observed energies. Indeed, all attempts made to calculate them directly have failed since the model of the most important physical interactions which have to be taken into account for a proper description is not as yet well defined [3,4]. In this sense, as the name ‘‘parameters’’ implies, B^k_q in Eq. (12) represent the numbers which are determined from a fitting procedure. This means that the definition of the crystal field potential here is general, and it goes beyond the stereotype of the traditional interpretation based on the point charge approximation of the electrostatic model.

In general, the summation in Eq. (2) includes the terms up to infinity. However, in practice the triangular conditions for the non-vanishing matrix elements of spherical tensors limit the expansion to the terms with rank not greater than 6 for the rare earth ions. In addition, only the even-rank terms contribute to the energy, while the odd-rank terms contribute to the intensity of electric dipole f↔f transitions. This means that the even-rank crystal parameters might be determined through the reproduction of the measured energy of the levels of the $4f^N$ configuration. Actually, the measured energies of the states of a system which contain a rare earth ion in a crystal, E_i, $i = 1,2,\ldots,l$, are, in general, expressed by linear combinations of unknown even-rank crystal field parameters

$$a_{i1} B^{k_1}_{q_1} + a_{i2} B^{k_2}_{q_2} + \cdots + a_{il} B^{k_l}_{q_l} = E_i \quad \text{for } i = 1,2,\ldots,r, \text{ and } l \le r \tag{3}$$

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where the coefficients are evaluated with approximate functions and within a certain approximation; some of them vanish due to the symmetry of the states taken into account. In this sense the values of even-rank crystal field parameters are related to each other. It should be realized that Eq. (3) demonstrates a linear combination of appropriate structural parameters, and this is not a linear combination of various terms of the multipole expansion. Indeed, at the point of applying the fitting procedure there is no other interpretation of B^k_q other than the fact that these are the structural parameters. The values of crystal field parameters obtained from the fitting procedure involve the impact due to all physical interactions which might be represented by one particle operators (see, for example, the papers of Newman where the necessity of the two particle parametrization scheme is introduced). The fitting procedure applied for finding the crystal field parameters of even rank is very illustratively described in the PhD Thesis of Hölsä [5], where the adjusted values are compared to those evaluated directly within the point charge model.

The situation is much more complicated in the case of the odd-rank crystal field parameters which do not contribute to the energy. Indeed, these parameters, the knowledge of which is crucial for the evaluation of the transition intensities, cannot be determined in a semi-empirical way.

The main aim of the present discussion is to derive a relationship between various crystal field parameters of odd rank. At the same time it is believed that the present discussion helps to cover an existing gap in theoretical analysis as noted in, and used here as an example, Hölsä's thesis written in 1983.

Indeed, his results of direct calculations of even-rank parameters are compared to values obtained from the fitting procedure. Unfortunately, the odd-rank parameters evaluated directly could not be compared 15 years ago and still cannot be compared to the so-called ‘‘experimental’’ values since the latter are unknown as there is no fitting procedure for this case established.

The standard Judd Ofelt theory and all the third order models discussed in the literature are based on the length form of the electric dipole radiation operator, which in terms of tensor operators, has the form

$$D^{(1)}_{\varrho} = \sum_i r_i C^{(1)}_{\varrho}(\theta_i \phi_i) \qquad (4)$$

For many electron systems the momentum operator is no longer equivalent to the velocity operator when its hamiltonian contains the non-local potential such as, for example, in the case of the standard Hartree–Fock method [6]. Indeed,

$$[\boldsymbol{r},h_0] = \frac{i\hbar}{\mu}\boldsymbol{p} + [\boldsymbol{r},V(\boldsymbol{rr}')]$$

where h_0 is the hamiltonian of Hartree–Fock model and V is its potential which includes the exchange potential; the latter is obviously represented by a non-local operator. Using the solutions of h_0

$$h_0\Psi_k = E_k\Psi_k,\ k = 1,2,\ldots$$

the above relation is written in terms of matrix elements in the following way:

$$(E_i - E_{\mathrm{f}})\langle\Psi_{\mathrm{f}}|\boldsymbol{r}|\Psi_i\rangle = \langle\Psi_{\mathrm{f}}|\nabla|\Psi_i\rangle + \langle\Psi_{\mathrm{f}}|[\boldsymbol{r},V(\boldsymbol{r},\boldsymbol{r}')]|\Psi_i\rangle \qquad (5)$$

The left-hand side of Eq. (5) determines the transition amplitude defined with the length form of the electric dipole radiation operator. This is the amplitude of a transition which originates from the state Ψ_i and terminates in the state Ψ_{f} of the $4\mathrm{f}^N$ configuration. The first element on the right-hand side of the equality represents the transition amplitude which is defined with the velocity form of the radiation operator. The last term on the right-hand side of Eq. (5) is caused by the non-local character of the potential. Note that this additional matrix element vanishes if the potential is local, and consequently there is an equivalence of the length and velocity formulas of the electric dipole radiation operator. It should be mentioned that the equality between the length and velocity forms of the transition amplitude is very often used as a criterion of the quality of the wavefunctions used for the analysis. It is seen from Eq. (5), however, that it is possible to analyze the quality of the functions only if the additional term is included, otherwise any discrepancy between both forms of the radiation operator determines the measure of the non-locality of the potential which is present in the hamiltonian.

The equivalence in Eq. (5) plays a crucial role in the present discussion. It should be realized, however, that within the free ionic system approximation and the single configuration approximation applied for the description of the electronic structure of rare earth ion crystals the matrix elements in Eq. (5) vanish due to the parity requirements. Therefore, the spectroscopic properties of these systems are described within the perturbation theory applied, in the simplest approach, for the following hamiltonian:

$$H = h_0 + \lambda V^{\mathrm{odd}}_{\mathrm{CF}} \qquad (6)$$

where the perturbation is defined in the following way:

$$V^{\mathrm{odd}}_{\mathrm{CF}} \equiv QV^{\mathrm{odd}}_{\mathrm{CF}}P + PV^{\mathrm{odd}}_{\mathrm{CF}}Q \qquad (7)$$

and P is the projection operator onto the space spanned by the solutions of h_0, and Q is its orthogonal complement. Due to the definition of the perturbation operator in Eq. (7), the zeroth order energy of the states of the $4\mathrm{f}^N$ configuration is not changed when the hamiltonian H is introduced. At the same time, the wavefunctions are improved by new components which represent the perturbing influence of the crystal field potential. In general, each wavefunction is expressed by a power series in λ, namely

$$\Psi = \sum_m \lambda^m \Psi^{(m)} \qquad (8)$$

where the distinct corrections to the wavefunctions have to satisfy the appropriate equations. Consequently, each function involved in the matrix elements of the equivalence in Eq. (5) has to be expanded in accordance with Eq. (8)

$$(E_i - E_\mathrm{f})\left\langle \sum_m \lambda^m \Psi_\mathrm{f}^{(m)} | \boldsymbol{r} | \sum_n \lambda^n \Psi_i^{(n)} \right\rangle$$
$$= \left\langle \sum_m \lambda^m \Psi_\mathrm{f}^{(m)} | \nabla | \sum_n \lambda^n \Psi_i^{(n)} \right\rangle$$
$$+ \left\langle \sum_m \lambda^m \Psi_\mathrm{f}^{(m)} | [\boldsymbol{r}, V(\boldsymbol{r},\boldsymbol{r}')] | \sum_n \lambda^n \Psi_i^{(n)} \right\rangle \tag{9}$$

The equality in Eq. (9) is exact since the exact expansion of the wavefunctions has been applied. Following the standard procedure of the perturbation theory it is straightforward to conclude that the terms associated with the same power of the perturbing parameter on both sides of Eq. (9) have to be equal. In particular, it is possible to extract from all terms contributing to the matrix elements in Eq. (9) those for which $n + m = 1$. This means that for this particular case the wavefunctions in the matrix elements of Eq. (9) are the first order corrections, and in terms of the Rayleigh–Schrödinger perturbation theory they have the following form:

$$\Psi_k = \Psi_k^0 + \sum_{Xx} \frac{\langle Xx | V_\mathrm{CF} | \Psi_k \rangle}{E_k^0 - E_{Xx}} | Xx \rangle \tag{10}$$

where $|Xx\rangle$ denotes the states x of the intermediate, excited configurations X which are of the opposite parity to the parity of the states of the $4\mathrm{f}^N$ configuration. As a result, the left-hand side of Eq. (9) represents the transition amplitude defined within the standard Judd Ofelt theory. The remaining matrix elements of Eq. (9) are also evaluated with the wavefunctions of the Judd Ofelt approach. It should be mentioned that a similar analysis might be performed with the functions which describe the perturbing influence of some other physical mechanisms such as, for example, electron correlation or spin orbit interaction. In such a case, however, the analysis has to be based on the double perturbation approach. Furthermore, in order to include all possible third order terms contributing to the transition amplitude, the wavefunctions have to be limited up to second order in both perturbations simultaneously. For the sake of clarity, the present discussion of the analysis is limited to its simplest version which is based on the first order corrections to the wavefunctions.

The matrix elements of Eq. (9) contain the tensor operators

$$\boldsymbol{r} \Rightarrow r C^{(1)} \tag{11}$$

$$\nabla^{(1)} \Rightarrow \frac{\delta}{\delta r} C^{(1)} + \frac{1}{r} \nabla^{*(1)} \tag{12}$$

where ∇^* is defined by its off-diagonal reduced matrix elements between one electron states, the angular momenta of which differ from each other by one.

In terms of effective operators and within the approximations of the standard Judd Ofelt theory, the equality in Eq. (8) has the following form [7]:

$$\sum_{tp}^{\mathrm{odd}} \sum_{kq} \sum_{l'}^{\mathrm{even}} B_p^t (-1)^q \begin{pmatrix} t & 1 & k \\ p & \rho & -q \end{pmatrix} A_t^k(l')$$
$$\Bigg[2\epsilon_k [k]^{1/2} \left\langle 4\mathrm{f} \left| \frac{\delta}{\delta r} \right| \varrho^t(4\mathrm{f} \rightarrow l') \right\rangle$$
$$+ a(l') \left\langle 4\mathrm{f} \left| \frac{1}{r} \right| \varrho^t(4\mathrm{f} \rightarrow l') \right\rangle - (2\epsilon_k [k]^{1/2} (E_\mathrm{f} - E_i)$$
$$+ \epsilon_k^* a) \langle 4\mathrm{f} | r | \varrho^t(4\mathrm{f} \rightarrow l') \rangle \Bigg] \langle 4\mathrm{f}^N \Psi_\mathrm{f} | U^{(k)}(4\mathrm{f},4\mathrm{f}) | 4\mathrm{f}^N \Psi_i \rangle = 0 \tag{13}$$

where the factors ϵ_k and ϵ_k^* select even and odd values of k, respectively

$$\epsilon_k = \tfrac{1}{2}(1 + (-1)^k), \quad \epsilon_k^* = \tfrac{1}{2}(1 - (-1)^k)$$

The angular term in Eq. (13) is the same as in the standard Judd Ofelt theory

$$A_t^k(l') = [k]^{1/2} \begin{Bmatrix} t & k & 1 \\ \mathrm{f} & l' & \mathrm{f} \end{Bmatrix} \langle \mathrm{f} \| C^{(1)} \| l' \rangle \langle l' \| C^{(t)} \| \mathrm{f} \rangle \tag{14}$$

and

$$a(l') = \frac{\langle \mathrm{f} \| \nabla^{*(1)} \| l' \rangle}{\langle \mathrm{f} \| C^{(1)} \| l' \rangle} \tag{15}$$

$$a = \sum_{s=2,4,6} R^s(4\mathrm{f},4\mathrm{f},4\mathrm{f},4\mathrm{f}) \langle \mathrm{f} \| C^{(s)} \| \mathrm{f} \rangle^2 - R^0(4\mathrm{f},4\mathrm{f},4\mathrm{f},4\mathrm{f}) \tag{16}$$

The radial integrals of Eq. (13) are expressed in terms of the perturbed functions of the Judd Ofelt approach, and they are defined as follows:

$$\varrho^t(4\mathrm{f} \rightarrow l') = \sum_{n'}^{\mathrm{exc}} \frac{\langle 4\mathrm{f} | r^t | n'l' \rangle}{\Delta(4\mathrm{f}, n'l')} P_{n'l'}(r) \tag{17}$$

The perturbed functions contain the perturbing influence of single excitations from the 4f shell to all excited one electron states of l' symmetry, and they are the solutions of appropriate differential equations [8].

Eq. (13) has the form of a linear combination of terms associated with various crystal field parameters with odd ranks. It is interesting to note that this relation is satisfied for a distinct electric dipole transition, since the coefficients of B_p^t for k even depend directly on the energy of the particular transition. This dependence is reinforced by the matrix elements of unit tensor operators with the functions which describe the states involved in the radiative process. Thus, for the transition j described by $\Psi_\mathrm{f} \leftarrow \Psi_i$ Eq. (13) has the general form

$$b_{j1} B_{p_1}^{t_1} + b_{j2} B_{p_2}^{t_2} + \cdots + b_{jr} B_{p_r}^{t_r} = 0 \ \text{ for } j = 1,2,\ldots,l,$$
$$\text{and } r \leq l \tag{18}$$

where in fact

$$b_{jm} \equiv b_{jm}(\text{transition } j\text{: f}\leftarrow i)$$

The relation obtained for the odd-rank crystal field parameters is analogous to that which connects the even-rank crystal field parameters, and it should be understood in the same manner. This means that similarly as in the case of Eq. (3), here the crystal field parameters of odd rank are related to each other. In both cases the values of coefficients a_{im} in Eq. (3) and b_{jm} in Eq. (18) depend on the model applied for their evaluation. In both cases the equations are understood in an approximate way, since both are in fact satisfied exactly only if the eigen solutions are used. Similarly as in the case of energy investigations where the relations in Eq. (3) are used to determine the crystal field parameters of even rank, the relations in Eq. (18) might be useful to alleviate the task of establishing a similar scheme for the odd-rank crystal field parameters.

It should be mentioned that taking into account the second order corrections to the wave functions in Eq. (9), a relation between the values of the crystal field parameters based on the third order contributions to the transition amplitude is obtained. At the same time it should be kept in mind that the present analysis is performed beyond the point charge approximation of the electrostatic model, and the relations demonstrated here connect the crystal field parameters which are understood within the strict meaning of their name as numerical factors appropriate for certain symmetry. Although the analysis presented here might be taken at first sight as questionable, the potential use of its results at least deserves further discussion supported by numerical calculations.

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