Multipole characteristics of the open-shell electron eigenstates

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Abstract

The second moment of the sublevels within the initial state $|\alpha_{SLJ}\rangle$ which constitutes a natural and adequate measure of the crystal-field (CF) effect can be redefined as

$$\sigma^2 = \frac{1}{2J+1} \sum_{k=2}^{4,6} S_k^2 A_k^2,$$

where $S_k = \left(\frac{1}{2k+1} \sum_q |B_{kq}|^2\right)^{1/2}$ is the so-called $2k$-pole CF strength, whereas $A_k = \langle \alpha_{SLJ} || C^{(k)} || \alpha_{SLJ} \rangle$ the reduced matrix element of the $k$-rank spherical tensor operator. Therefore, the CF effect depends on the sum of products of the two factors representing the identical multipole components of two different charge distributions. The term $A_k$ expresses the asphericity of the central ion open-shell, whereas the term $S_k$ the asphericity of its surroundings. When these two distributions do not fit each other the observed CF splitting can be unexpectedly weak even for considerable values of the total $S = \left(\sum_k S_k^2\right)^{1/2}$ and $A = \left(\sum_k A_k^2\right)^{1/2}$. The tabulated quantities of the $A_k (|\alpha_{SLJ}\rangle)$, as the $2k$-pole type asphericities, are the intrinsic characteristics of the electron states revealing their multipolar structure and hence their potential susceptibility to CF splitting separately for each effective multipole. For any chosen pair of a central-ion and CF potential the relevant $A_k$ and $S_k$ magnitudes, respectively, allow us to predict the scale of the related splitting. We can also compare the CF splitting of various states in the same CF potentials or the splitting of the same state in various CF potentials. Having the model $\sigma^2$ and their experimentally available counterparts we can evaluate the degree of admixing of the free-ion states. Since the independent quantities $S_k$ and $A_k$ occur as the scalar product in the formula for $\sigma^2$ the use of the total $S$ and $A$ notions should be critically considered.

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1. Introduction

The origin of the one-electron parametric CF Hamiltonian $\mathcal{H}_{CF} = \sum_{k,q} B_{kq} C_q^{(k)}$ [1-3], stemming from the spherical harmonic addition theorem [4-6], shows that it is a sum of products of two terms. They represent the identical multipole components of two different and independent charge distributions. The first term, expressed by the set of CF parameters (CFPs) $B_{kq}$, corresponds to the multipole distribution of the central ion surroundings potential. The second term $C_q^{(k)}$ refers exclusively to the multipole expansion of the angle parts of electron wave functions of the central ion open-shell. This inherent dichotomy is even more clear, independently of the reference frame, for the second moment of the sublevels within the initial state $|\alpha, SLJ\rangle$ [7-9]

$$\sigma^2 (|\alpha_{SLJ}\rangle) = \frac{1}{2J+1} \sum_{k=2,4,6} S_k^2 \left(\langle \alpha_{SLJ} || C^{(k)} || \alpha_{SLJ} \rangle\right)^2.$$ (1)
Here, the central-ion surroundings is represented by the $2^k$-pole CF strength parameters $S_k = \left( \frac{1}{2k+1} \sum_q |B_{kq}|^2 \right)^{1/2}$ [10-14]. In turn, the squares of the reduced matrix elements of the k-ring spherical tensor operator $(k = 2, 4, 6)$ [15-17] characterize the multipole structure of the central ion open-shell in the state $|\alpha SLJ\rangle$ and give a measure of its latent asphericity. The latter quantities determine the state susceptibility to CF splitting induced by the particular $2^k$-poles of the $\mathcal{H}_{CF}$. The symbol $\alpha$ in Eq.(1) stands for the remaining eigenvalues of the operators which are invariant with respect to the rotations and define the state $|\alpha SLJ\rangle$.

In the paper we present a thorough analysis of the reduced matrix elements of the spherical tensor operators $A_k = (\alpha SLJ||C^{(k)}||\alpha SLJ)$, $k = 2, 4, 6$. The $A_k$s for all the states coming from the ground terms of the basic electron configurations $p^n$, $d^n$ and $f^n$ are enclosed in Table 1. Additionally, the multipolar characteristics of many other interesting states chosen according to various criteria are comprised in Table 2. Among them there are the states of the extreme asphericity, those having the uniform or differentiated asphericity with respect to $k$, as well as the states of the repeated terms (with the same $L$ and $S$). The last column in the tables gives the total asphericity of the states $A = (\sum_k A_k^2)^{1/2}$, which is a counterpart of the total CF strength $S = (\sum_k S_k^2)^{1/2}$, used widely so far [10-14]. The complete database enclosing 283 ionic (atomic) terms and all the 923 $|\alpha SLJ\rangle$ states for $p^n(n = 1, 2)$, $d^n(n = 1, 2, 3, 4)$ and $f^n(n = 1, 2, 3, 4, 5, 6)$ configurations will be presented separately. The $(\alpha SLJ||C^{(k)}||\alpha SLJ)$ matrix elements for the remaining $l^{2(2l+1)-n}$ configurations are identical with those for the $l^n$ ones. The states derived from the half-filled electron configurations $l^{2l+1}$ do not yield any crystal-field splitting in the first order approximation [18], i.e. all the relevant diagonal reduced matrix elements are equal to zero. The asphericity $A_k$ changes from state to state and any correlation seems to be difficult to be found. Nevertheless, these seemingly random variations can be interpreted using the reduced matrix element factorization. Based on the tabulated characteristics of the initial states, even under limitations to the pure Russell-Saunders coupling, one can predict which CF potentials are effective for a given state or which states are sensitive to a given CF potential. The analyzed asphericities can also be helpful to verify any CF data.

2. General formulation

We start with the one-electron parametric form of the crystal-field Hamiltonian in the tensor notation by Wybourne [1]

$$\mathcal{H}_{CF} = \sum_i \sum_k \sum_q B_{kq} C^{(k)}_q (\vartheta_i, \varphi_i),$$

(2)

where $i$ runs over the central-ion open-shell electrons, precisely over their angle spherical coordinates, whereas $k$ and $q$ over all the effective multipole components of the CF potential.

In general, this one-electron approach describes correctly most of the problems involving the CF effect with satisfying accuracy. The best evidence of it is the long list of successful interpretations of various experimental results [19-22]. However, the origin of the $\mathcal{H}_{CF}$ formula Eq.(2) descending from the spherical harmonic addition theorem [4-6] allows us to interpret this expression in the spirit of the complete partition of the system into two separate multipolar subsystems – the central ion, and its surroundings (compare the expansion of $1/r_{ij}$). Keeping up the generality of the considerations from the viewpoint of the one-electron $\mathcal{H}_{CF}$ parametrization we may confine the problem to the electrostatic interaction of the individual ligand of charge $q$ and radius vector $\mathbf{R}(R, \Theta, \Phi)$ with an individual open-shell electron of the radius vector $\mathbf{r}(r, \vartheta, \varphi)$. Then, for $R > r$ [2,3]

$$\mathcal{H}_{CF} = \frac{q \cdot e}{|\mathbf{R} - \mathbf{r}|} = q \cdot e \sum_k \sum_q \frac{r^k}{R^{k+1}} C^{(k)*}_q (\Theta, \Phi) \cdot C^{(k)}_q (\vartheta, \varphi).$$

(3)

In fact, the $\mathcal{H}_{CF}$ is the sum of the binary products of the terms representing the identical multipole components $(k, q)$ of the independent charge distributions in the common central-ion reference
frame. The set of CFPs \( B_{kq} = q \cdot e \left( r^k / R^{k+1} \right) C_q^{(k)}(\Theta, \Phi) \) refers to the multipolar distribution of the surroundings potential. The averaged \( \langle r^k \rangle \) over the radial distribution of the central-ion open-shell electron wave function commonly included into the \( B_{kq} \) does not violate the dychotomic separation \([1,3,6]\). In turn, the second distribution represented by \( C_q^{(k)}(\vartheta, \varphi) \) concerns exclusively the angle distribution of the open-shell electron density of the unperturbed central ion and constitutes its intrinsic characteristics. The crucial point is that only the products of the identical complex-conjugate multipole components of both the distributions, in other words their scalar products, contribute to the \( \mathcal{H}_{\text{CF}} \). On the contrary, the orthogonal multipolar distributions of the central-ion electronic state and the surroundings potential do not contribute to the CF interaction.

### 2.1. Factorization of the \( \mathcal{H}_{\text{CF}} \) matrix elements

The crystal-field impact on the \((2J+1)\)-fold degenerate electron state \( |\alpha SLJ\rangle \) is determined by the \( \mathcal{H}_{\text{CF}} \) matrix elements \( \langle \alpha SLJM_J | \mathcal{H}_{\text{CF}} | \alpha SLJM'_J \rangle \) within the state. This statement holds true exclusively within the limits of the first order perturbational approach, it means taking into account only the diagonal matrix elements with respect to \( J \). Then, to describe the crystal field splitting of the \(|\alpha SLJ\rangle \) state it is sufficient to know its multipole characteristics and the relevant set of the CFPs. In the case of more complex initial eigenstates formed in various types of mixing mechanisms (higher order perturbations, simultaneous diagonalization) the multipolar characteristics are available including all the needed off-diagonal matrix elements of the operators \( C^{(k)} \) or \( U^{(k)} \) \([18]\).

The \( \mathcal{H}_{\text{CF}} \) matrix elements undergo a far-reaching factorization which provides understanding of their seemingly random variations from state to state arising simply from their origin. Using the Wigner-Eckart theorem in the first step of this factorization one gets \([4,15-17,23]\)

\[
\langle \alpha SLJM_J | B_{kq} C_q^{(k)} | \alpha SLJM'_J \rangle = (-1)^{J-M_J} B_{kq} \left( \begin{array}{cc} J & k & J \\ -M_J & q & M'_J \end{array} \right) \langle \alpha SLJ || C^{(k)} || \alpha SLJ \rangle. \tag{4}
\]

The first three factors on the right hand, i.e. the one defining the sign, the respective \( B_{kq} \) CFP, and the \( 3-j \) symbol, determine the splitting pattern of the \(|\alpha SLJ\rangle \) state in the assumed reference system. The last dimensionless term, the so-called double bar or reduced matrix element, independent of the reference frame, is the factor scaling the splitting. The factorization process can be continued further and for the particular case of the diagonal matrix elements it takes the form \([4,15-17,23]\)

\[
\langle \alpha SLJ || C^{(k)} || \alpha SLJ \rangle = (-1)^{S+L+J+k+1} \left\{ \begin{array}{ccc} J & J & k \\ L & L & S \end{array} \right\} \langle \alpha SL || C^{(k)} || \alpha SL \rangle, \tag{5}
\]

where the doubly reduced element (the last one independent on the \( J \) quantum number) is usually written down by means of the unit tensor operator \( U^{(k)} \) as \([18,23]\)

\[
\langle \alpha SL || C^{(k)} || \alpha SL \rangle = \langle \alpha SL || U^{(k)} || \alpha SL \rangle \langle l || C^{(k)} || l \rangle, \tag{6}
\]

where \( l = 1, 2 \) and \( 3 \) for \( p \), \( d \) and \( f \) electrons, respectively. The first factor in Eq.(5) defining the sign of the reduced element depends on the parity of the sum of four relatively autonomous numbers what undoubtedly leads to its random character. The \( 6-j \) symbol multiplied by the \((2J+1)\)-degeneracy degree of the state reveals, according to its physical meaning, what part of the final \(|\alpha SLJ\rangle \) function belongs to the orbital part \(|\alpha SL\rangle \). Since the \( \mathcal{H}_{\text{CF}} \) acts exclusively on the configurational coordinates of the electrons only this part is responsible for the CF interaction with the \( 2^k \)-pole component of the CF potential. The expressions \((2J+1) \left\{ \begin{array}{ccc} J & J & k \\ L & L & S \end{array} \right\} \) have their own extra sign, and their magnitudes span from 0 to 1. Only in certain cases for \( k = 2 \) they exceed 1 reaching the largest value of 1.1096 for the state \( ^7F_0(f^6) \) \([23,24]\). Finally, the doubly reduced matrix element depends on the way of coupling of the
n one-electron angular momentum \( l \) of the \( l^n \) configuration to the resultant \( L \), since each one-electron component state \(|lm\rangle\) reacts individually to the outer CF potential according to its orientation in the final reference frame. There are as many different doubly reduced matrix elements having the same \( L \) and \( S \) numbers as the different ways of the coupling. In the group-theory language – there are as many different terms of the same \( L \) and \( S \) as the irreducible representations \( D^{(L)} \) of the three-dimensional rotations group in the decomposition of the simple Kronecker product \( D^{(L)}(1) \times D^{(L)}(2) \ldots D^{(L)}(n) \) regarding however the Pauli exclusion principle. This differentiation of the states arising from their genealogy can be expressed equivalently by the Racah fractional parentage coefficients [1,17] or by the seniority numbers [1,5]. The doubly reduced matrix elements \( \langle \alpha SL||C^{(k)}||\alpha SL \rangle \) change from \(-1.8899 \) for the term \( ^1I(d^1) \) and \( k = 4 \) up to \( 2.5803 \) for the term \( ^1N(f^4) \) and \( k = 2 \). The absolute values of the one-electron reduced matrix elements \( \langle l||C^{(k)}||l \rangle \) differ only weakly from \( 1.0955 \) to \( 1.3663 \) for all the \( k = 1, 2 \) and \( 3 \) and \( l = 1, 2 \) and \( 3 \).

Additionally, there exists a one-to-one correspondence between the reduced matrix elements \( \langle \alpha SLJ||C^{(k)}||\alpha SLJ \rangle \) and the multiplicative Stevens coefficients \( \alpha, \beta, \gamma \) for \( k = 2, 4, 6 \), in his operator equivalent method [25,26]. In fact, the equivalent operator matrix elements \( \langle JM_J|\hat{O}^k_{2k}|JM'_J \rangle \) are equal to the \( 3 - j \) symbols \( \begin{pmatrix} J & k & J \\ -M_J & q & M'_J \end{pmatrix} \) with the accuracy to the constant coefficient.

2.2. The second moment of the sublevels within the initial state \(|\alpha SLJ\rangle\)

The second moment \( \sigma^2 (|\alpha SLJ\rangle) \) of the sublevels within the initial state \(|\alpha SLJ\rangle\) [7-9] (Eq.(1)) is a natural and adequate measure of the CF effect. It is an important invariant of the three-dimensional rotation group \( R_3 \). This property implies from the orthogonality of the \( 3 - j \) symbols [11,23]. In consequence, \( \sigma^2 \) is not literally dependent on the CFPs determining the splitting in any definite reference system but instead it depends on the invariant \( S_k \). As a result the contributions of the individual multipoles to the \( \sigma^2 \) are additive.

To simplify the notation let us introduce

\[
A_k(|\alpha SLJ\rangle) = \langle \alpha SLJ||C^{(k)}||\alpha SLJ \rangle. \tag{7}
\]

This dimensionless scalar depending only on the angle distribution of the electron density of the state \(|\alpha SLJ\rangle\) reflects its latent asphericity of the \( 2k \)-pole type. Now,

\[
\sigma^2 (|\alpha SLJ\rangle) = \frac{1}{2J+1} \sum_{k=2,4,6} S_k^2 A_k^2, \tag{8}
\]

which means that the CF effect is not only the function of the \( S_k \) and \( A_k \) magnitudes but primarily depends on the degree of overlapping of these two separate multipole distributions that characterize respectively the surroundings and the central ion. By analogy with the total CF strength notion \( S = (S_2^2 + S_4^2 + S_6^2)^{1/2} \) which refers to the asphericity of the surroundings we introduce the concept of the total asphericity of the central ion state \(|\alpha SLJ\rangle\)

\[
A = (A_2^2 + A_4^2 + A_6^2)^{1/2}. \tag{9}
\]

It bears the same advantages and faults as the total CF strength \( S \). Since the \( A_k \) are dimensionless energy dimension of the \( \sigma \) in Eq.(8) is ensured by the \( S \), i.e. by the CFPs unit.

The total asphericity \( A \) is 0 for all the terms coming from the half-filled configurations \( l^{2l+1} \) and terms \( S \) having \( L = 0 \). From among all the considered free-ion states the maximal value of \( A = 4.2225 \) (Table 2).
3. Review of the multipole characteristics of the initial eigenstates. Calculational results

The multipolar characteristics of the pure free-ion states \( |\alpha SLJ\rangle \) with respect to the \( 2^2 \)-, \( 2^4 \)- and \( 2^6 \)-multipoles active in the CF interaction are reviewed thoroughly below. From among all the 923 essentially various states of the simple \( p^n \), \( d^n \) and \( f^n \) electron configurations only 121 of them have been chosen for the presentation and analysis. Of necessity our discussion is here restricted only to this survey. The selected states are either the most important or the most distinguishable ones and properly illustrate their random-like variability. The reduced matrix elements of the spherical tensor operators \( A_k \), introduced in the paper as the \( 2^k \)-pole type asphericities which represent the multipolar character of the states as well as the total asphericity \( A = (\sum_k A_k^2)^{1/2} \) tentatively revealing the susceptibility of the states to CF splitting are compiled in Tables 1 and 2. The multipole components \( A_k \) have their own sign (Eq.(5)) which determines the sign of the energy eigenvalues, but is inessential in the second moment (Eqs (1,8)). Tables 1 and 2 contain also the \( A_k \) and \( A \) calculated for all the states \( ^{2S+1}L \) ignoring the spin-orbit coupling no matter how strong it is in relation to the CF interaction. The data for the ground terms of all the electron configurations are given in Table 1, whereas the data for the selected states are compiled in Table 2. In the latter one can find the multipolar characteristics of the states of the strongest or weakest susceptibility to CF splitting, the states selectively sensitive to the \( 2^2 \)-, \( 2^4 \)- and \( 2^6 \)-pole components of the \( \mathcal{H}_{CF} \), as well as sensitive to the three multipoles in a comparable measure, and finally the states coming from the repeated terms, i.e. of the same \( L \) and \( S \) numbers. The maximal global asphericity \( A = 4.2225 \) has been found for the state \( ^1N(f^4) \), whereas the highest asphericities for the respective multipoles amount to: \( |A_2| = 3.5254 \), \( |A_4| = 2.2589 \) and \( |A_6| = 2.7260 \) correspondingly for the states \( ^1N(f^4) \), \( ^1I(d^4) \) and \( ^1Q(f^6) \). The common feature of these top-level states is the largest possible \( L \) numbers (\( L = 10, 6, 12 \) respectively) and \( S = 0 \). The \( |A_k| \) and \( \bar{A} \) asphericities averaged over all the 923 states amount to: \( |\bar{A}_2| = 0.5244 \), \( |\bar{A}_4| = 0.3222 \), \( |\bar{A}_6| = 0.2904 \) and \( \bar{A} = 0.7967 \). The state \( ^4I_{11/2}(f^3) \) (Table 1) well represents the average susceptibility to CF splitting, and therefore can serve as the reference state.

The reduced matrix elements \( A_k = \langle J || C^{(k)} || J \rangle \) are composed of the five factors. This complexity is responsible for a seemingly stochastic distribution of \( A_k \) magnitudes and signs (subsection 2.1). The matrix elements for various \( k \) (the rows in Tables) are completely independent from each other as they belong to various multipoles, it means to the various irreducible representations of the \( R_3 \) group. For the fixed \( k \) (the columns in Tables) we can observe within the multiplets \( ^{2S+1}L \) certain systematic correlation between the \( A_k \) and \( J \) values of the relevant states. The largest absolute value of the \( \langle J || C^{(k)} || J \rangle \) element is reached for the state with \( J = L + S \) and it is close, as a rule, to the value calculated ignoring the spin. For the smaller \( J \), the corresponding \( A_k \)s decrease to rise for the smallest \( J \) number within the multiplet. This systematic correlation results from the ratio (Eq.(5)) and takes the form

\[
\frac{\langle J || C^{(k)} || J \rangle}{\langle J + n || C^{(k)} || J + n \rangle} = (-1)^n \frac{(2J + 1)}{(2J + 2n + 1)} \frac{\left( \begin{array}{ccc} J & J & k \\ L & L & S \end{array} \right)}{\left( \begin{array}{ccc} J + n & J + n & k \\ L & L & S \end{array} \right)}
\]

Figuratively, such a behaviour can be explained by the degree of the \( L \) and \( J \) vectors co-linearity. Based on the above relation we can find the ratios of the individual multipoles contributions to the second moment \( \sigma^2 \) of the sublevels within the initial states \( |\alpha SLJ\rangle \) of the same term \( |\alpha SL\rangle \).
4. Discussion

The distinction between the multipole characteristics of the states originating from the ground terms of the \( p^n \), \( d^n \) and \( f^n \) electron configurations is shown in Table 1. The observed dispersion of the \( A_k \) and \( A \) values confronted with the multipole characteristics of the involved CF potential provides understanding of the role of the individual multipoles of both the distributions in the formation of the actual splitting pattern.

As an example let us consider the \( f^2 \) configuration occurring in \( \text{Pr}^{3+} \) and \( \text{U}^{4+} \) ions. The states of the \( ^3H \) term, in particular the \( ^3H_6 \) one, are characterized by strong or averaged asphericity of all the three multipole types, whereas the states of the \( ^3F \) term by average or weak asphericity. The \( ^1I \) state is exceptionally likely to be affected by the quadrupolar \( (k=2) \) component of the \( \mathcal{H}_{\text{CF}} \), while the \( ^1G \) state by the higher order multipoles \( (k=4,6) \). Based on these data we can predict the states splittings in crystal fields of different point symmetries or to verify the proportions between the multipole terms in the involved \( \mathcal{H}_{\text{CF}} \). In turn, the states \( ^4I_{15/2}, ^4G_{11/2} \) and \( ^4F_{9/2} \) of the \( f^3 \) electron configuration are distinguished by the prevailing role of the \( 2^k- \), \( 2^1- \) and \( 2^2- \) pole component, respectively. This asphericity hierarchy of the states governs their splitting when the states are subjected to the particular \( \mathcal{H}_{\text{CF}} \).

Some selected \( |\alpha\text{SLJ}\rangle \) states which substantially differ in their multipolar characteristics are gathered in Table 2. However, due to the complex structure of the reduced matrix elements (subsection 2.1), only a cursory interpretation of the characteristics in terms of the intrinsic quantum numbers of the states is feasible. Specifically, the states of the highest total asphericity \( (A > 2.5) \) stand out by the large quantum numbers \( L \) and small \( S \) (mostly \( S = 0 \)). The states of the lowest asphericity \( (A < 0.2) \) are derived rather from the almost half-filled configurations and are characterized by average or small \( L \) and irregular \( S \) numbers (typically \( S = 1 \)). In turn, the states with the maximal \( A_2 \) asphericity show the same features as those of the high total \( A \). In case of the states with the highest \( A_4 \) asphericity no particular preferences for the \( L \) and \( S \) numbers are observed, although several of them descend from the \( d \)-electron configurations. Finally, the states with the highest \( A_6 \) asphericity arise rather from the almost half-filled configurations and they are characterized as a rule by large \( L \) numbers. The states of the selectively dominating component \( A_k \) (respective to the remaining two \( A_k \)s) are presented in rows 21–44 of Table 2. Among the states of the comparable contributions of the three multipoles intriguingly many of them come from the \( F \) terms. To have a detailed insight into the \( A_k \) and \( A \) distributions and their interpretation one has to carefully study the complete data set compiling the multipolar characteristics of all the states. The seemingly stochastic distribution of the \( A_k \) and \( A \) values (Tables 1 and 2) is well demonstrated by the chosen seven various \( ^3G_5 \) states of \( f^6 \) or \( f^8 \) configurations. In this case the ratios between the seven relevant \( A_k \)s are equal to the ratios between the seven corresponding reduced matrix elements \( \langle \alpha\text{SL}||U^{(k)}||\alpha\text{SL} \rangle \) with various \( \alpha \).

The formula for the \( \sigma^2 \) (Eq.(8)) gives the direct relationship (separately for the \( 2^k- \) pole contributions) between the total second moment representing the spectrum of the energy levels from the one hand, and both the \( S_k \) (dependent on the \( B_{kk} \) CFpS) and the \( A_k \) (the \( 2^k- \) pole characteristics of the \( |\alpha\text{SLJ}\rangle \) state) from the second hand. The relationship is sensitive to variations of the composing terms. It provides a convenient test for the correctness of the initial assumptions in the CFpS fitting procedure since the number of the involved variables is now considerably reduced. Applying the formula on the \( \sigma^2 \) we are able to narrow the set of possible splitting patterns and more easily localize the states being invisible in the spectroscopy. It allows us also to estimate the degree of admixture of the initial states comparing the actual \( A_k \)s with their free-ion counterparts.

Here, as an example, let us consider the well evidenced crystal-field splitting of the \( ^3H_4 \) and \( ^3H_6 \) states in the \( \text{Pr}^{3+}(f^2) \) ion in \( \text{LaF}_3 \) matrix of the \( C_2 \) point symmetry [27]. Unfortunately, the experimental energies of all the thirteen CF sublevels of the \( ^3H_6 \) states in this field remain unknown. From the spectroscopic data [27] result the following second moments: \( \sigma^2_{\text{exp}}(^3H_4) = 22103 \ (cm^{-1})^2 \) and \( \sigma^2_{\text{exp}}(^3H_6) = 12285 \ (cm^{-1})^2 \). Based on the CFpS derived from a fit to the experimental data using a \( C_{2v} \) approximation of the actual \( C_2 \) symmetry [27] we get: \( S_2^2 = 13105 \ (cm^{-1})^2 \), \( S_4^2 = 152758 \ (cm^{-1})^2 \) and
$S_0^2 = 272240 \ (cm^{-1})^2$. Substituting now the tabulated values (Table 1): $A_2 = -1.2367$, $A_4 = 0.7395$ and $A_6 = 0.7706$ for the $^3H_4$ state and $A_2 = -1.3100$, $A_4 = 0.6833$ and $A_6 = 0.4451$ for the $^3H_5$ state respectively, one obtains $\sigma^2_{\text{calc}}(^3H_4) = 29474 \ (cm^{-1})^2$ and $\sigma^2_{\text{calc}}(^3H_5) = 16416 \ (cm^{-1})^2$. The $\sigma^2_{\text{calc}}$ calculated for the model $A_k$s exceed the experimental $\sigma^2_{\text{exp}}$ by 30%, but interestingly their ratios remain exceptionally close to each other (Eq.(10))

\[
\frac{\sigma^2_{\text{exp}}(^3H_4)}{\sigma^2_{\text{exp}}(^3H_5)} = 1.799 \quad \text{and} \quad \frac{\sigma^2_{\text{calc}}(^3H_4)}{\sigma^2_{\text{calc}}(^3H_5)} = 1.795.
\]

It may be well to add that the ratios of the individual $2^k$-poles contributions to the total second moment are roughly 1 : 4 : 8 and 1 : 3 : 2 for the $^3H_4$ and $^3H_5$ states and $k = 2, 4, 6$, respectively. It means that the decrease of the $A_6$ asphericity is mainly responsible for the weaker splitting of the $^3H_5$ state.

Thus, despite of certain model inaccuracies which mainly concern the $A_k$s, the correct ratios of the $\sigma^2$ of various states are available by calculation (Eq.(10)). These ratios can help us to choose the proper parametrization of the $\mathcal{H}_{CF}$, as well as to verify any considered one.

Finally, with the expression for $\sigma^2$ (Eq.(8)) we can estimate the adequacy of the $S = (\sum k S_k^2)^{1/2}$ and $A = (\sum k A_k^2)^{1/2}$ concepts. Both these quantities are simultaneously rational only in the three following cases:

(i) if all the three values of $|A_k|$ $(k = 2, 4, 6)$ are close each other, i.e. $A_k^2 \simeq \frac{1}{3} A^2$ [9,11]; then $\sigma^2(|\alpha SLJ) \simeq \frac{1}{2J+1} (S_2^2 + S_4^2 + S_6^2) \frac{1}{3} A^2 = \frac{1}{2J+1} \frac{1}{3} S^2 A^2$;

(ii) if all the three values of $S_k$ $(k = 2, 4, 6)$ are close each other, i.e. $S_k^2 \simeq \frac{1}{3} S^2$; then $\sigma^2(|\alpha SLJ) \simeq \frac{1}{2J+1} \frac{1}{3} S^2 (A_2^2 + A_4^2 + A_6^2) = \frac{1}{2J+1} \frac{1}{3} S^2 A^2$;

(iii) if there is a fully random distribution of the $S_k$ and $A_k$ values leading to the approximation $S_2^2 A_2^2 + S_4^2 A_4^2 + S_6^2 A_6^2 \simeq \frac{1}{3} (S_2^2 + S_4^2 + S_6^2) (A_2^2 + A_4^2 + A_6^2) = \frac{1}{3} S^2 A^2$.

In all other cases the concepts of the total $S$ and $A$ lose the explicit link with the $\sigma^2$ and only their conventional qualitative interpretation remains in power.

Concluding, the above analysis reveals the equivalent role of both the multipole distributions and throw the light on the $S$ and $A$ physical meaning as well as on the limitations in their use.
Table 1: Multipole characteristics of the electron energy eigenstates \((2S+1L_J)\) coming from the ground terms of \(p^n\), \(d^n\) and \(f^n\) configurations (and similarly for \(p^{6-n}\), \(d^{10-n}\) and \(f^{14-n}\) configurations)

| No. | Electron configuration | Electron eigenstate | \(A_2 = \langle J||C^{(2)}||J\rangle\) | \(A_4 = \langle J||C^{(4)}||J\rangle\) | \(A_6 = \langle J||C^{(6)}||J\rangle\) | \(A = (A_2^2 + A_4^2 + A_6^2)^{1/2}\) |
|-----|------------------------|---------------------|--------------------------------------|--------------------------------------|--------------------------------------|--------------------------------------|
| 1   | \(p^1\)                | \(2P\)              | -1.0955                              | 0                                     | 0                                     | 1.0955                               |
| 2   | \(p^1\)                | \(2P_{3/2}\)        | -0.8944                              | 0                                     | 0                                     | 0.8944                               |
| 3   | \(p^1\)                | \(2P_{1/2}\)        | 0                                    | 0                                     | 0                                     | 0                                     |
| 4   | \(p^2\)                | \(3P\)              | 1.0955                               | 0                                     | 0                                     | 1.0955                               |
| 5   | \(p^2\)                | \(3P_2\)            | 0.8367                               | 0                                     | 0                                     | 0.8367                               |
| 6   | \(p^2\)                | \(3P_1\)            | -0.5477                              | 0                                     | 0                                     | 0.5477                               |
| 7   | \(p^2\)                | \(3P_0\)            | 0                                    | 0                                     | 0                                     | 0                                     |
| 8   | \(d^1\)                | \(2D\)              | -1.1952                              | 1.1952                               | 0                                     | 1.6903                               |
| 9   | \(d^1\)                | \(2D_{5/2}\)        | -1.1711                              | 0.7559                               | 0                                     | 1.3939                               |
| 10  | \(d^1\)                | \(2D_{3/2}\)        | -0.8944                              | 0                                     | 0                                     | 0.8944                               |
| 11  | \(d^2\)                | \(3F\)              | -0.5855                              | -1.7278                              | 0                                     | 1.8670                               |
| 12  | \(d^2\)                | \(3F_4\)            | -0.6007                              | -1.3698                              | 0                                     | 1.4957                               |
| 13  | \(d^2\)                | \(3F_3\)            | -0.4392                              | -0.2955                              | 0                                     | 0.5294                               |
| 14  | \(d^2\)                | \(3F_2\)            | -0.4098                              | -0.6261                              | 0                                     | 0.7483                               |
| 15  | \(d^3\)                | \(4F\)              | 0.5855                               | 1.7728                               | 0                                     | 1.8670                               |
| 16  | \(d^3\)                | \(4F_{9/2}\)        | 0.6117                               | 1.2732                               | 0                                     | 1.4125                               |
| 17  | \(d^3\)                | \(4F_{7/2}\)        | 0.3943                               | -0.1688                              | 0                                     | 0.4289                               |
| 18  | \(d^3\)                | \(4F_{5/2}\)        | 0.2760                               | 0.5940                               | 0                                     | 0.6550                               |
| 19  | \(d^3\)                | \(4F_{3/2}\)        | 0.3067                               | 0                                     | 0                                     | 0.3067                               |
| 20  | \(d^4\)                | \(5D\)              | 1.1952                               | -1.1952                              | 0                                     | 1.6903                               |
| 21  | \(d^4\)                | \(5D_4\)            | 1.2014                               | -0.4565                              | 0                                     | 1.2852                               |
| 22  | \(d^4\)                | \(5D_3\)            | 0.2928                               | 0.8864                               | 0                                     | 0.9335                               |
| 23  | \(d^4\)                | \(5D_2\)            | -0.2561                              | -0.3415                              | 0                                     | 0.4269                               |
| 24  | \(d^4\)                | \(5D_1\)            | -0.4583                              | 0                                     | 0                                     | 0.4583                               |
| 25  | \(d^4\)                | \(5D_0\)            | 0                                    | 0                                     | 0                                     | 0                                     |
| 26  | \(f^1\)                | \(2F\)              | -1.3663                              | 1.1282                               | -1.2774                              | 2.1843                               |
| 27  | \(f^1\)                | \(2F_{7/2}\)        | -1.3801                              | 0.9670                               | -0.3054                              | 1.7126                               |
| 28  | \(f^1\)                | \(2F_{5/2}\)        | -1.1711                              | 0.7560                               | 0                                     | 1.3939                               |
| No. | Electron configuration | Energy eigenstate | $A_2 = \langle J||C^{(2)}||J\rangle$ | $A_4 = \langle J||C^{(4)}||J\rangle$ | $A_6 = \langle J||C^{(6)}||J\rangle$ | $A = (A_2^2 + A_4^2 + A_6^2)^{1/2}$ |
|-----|------------------------|------------------|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|
| 29  | $f^2$                  | $^3H$            | -1.4555                           | 1.0249                           | 1.4837                           | 2.3174                           |
| 30  | $^3H_6$                |                  | -1.5158                           | 0.9583                           | 1.1386                           | 2.1242                           |
| 31  | $^3H_5$                |                  | -1.3100                           | 0.6833                           | 0.4451                           | 1.5431                           |
| 32  | $^3H_4$                |                  | -1.2367                           | 0.7395                           | 0.7706                           | 1.6340                           |
| 33  | $f^3$                  | $^4I$            | -0.6064                           | -0.7187                          | -2.2771                          | 2.4636                           |
| 34  | $^4I_{15/2}$           |                  | -0.6438                           | -0.6850                          | -1.7999                          | 2.0306                           |
| 35  | $^4I_{13/2}$           |                  | -0.5569                           | -0.4691                          | -0.6217                          | 0.9574                           |
| 36  | $^4I_{11/2}$           |                  | -0.5045                           | -0.3935                          | -0.3399                          | 0.7245                           |
| 37  | $^4I_{9/2}$            |                  | -0.4954                           | -0.4904                          | -1.1085                          | 1.3095                           |
| 38  | $f^4$                  | $^5I$            | 0.6064                            | 0.7187                           | 2.2771                           | 2.4636                           |
| 39  | $^5I_8$                |                  | 0.6562                            | 0.6797                           | 1.7060                           | 1.9501                           |
| 40  | $^5I_7$                |                  | 0.5524                            | 0.4042                           | 0.2398                           | 0.7253                           |
| 41  | $^5I_6$                |                  | 0.4796                            | 0.2613                           | -0.3105                          | 0.6283                           |
| 42  | $^5I_5$                |                  | 0.4428                            | 0.2437                           | -0.2958                          | 0.5566                           |
| 43  | $^5I_4$                |                  | 0.4540                            | 0.4103                           | 0.7679                           | 0.9819                           |
| 44  | $f^5$                  | $^6H$            | 1.4555                            | 1.0249                           | -1.4837                          | 2.3174                           |
| 45  | $^6H_{15/2}$           |                  | 1.6095                            | 0.9134                           | -0.9000                          | 2.0579                           |
| 46  | $^6H_{13/2}$           |                  | 1.2375                            | 0.3128                           | 0.4146                           | 1.3421                           |
| 47  | $^6H_{11/2}$           |                  | 0.9587                            | -0.0108                          | 0.7152                           | 1.1961                           |
| 48  | $^6H_{9/2}$            |                  | 0.7786                            | -0.1423                          | 0.6845                           | 1.0464                           |
| 49  | $^6H_{7/2}$            |                  | 0.7176                            | -0.1129                          | 0.7035                           | 1.0112                           |
| 50  | $^6H_{5/2}$            |                  | 0.8458                            | 0.2978                           | 0                                | 0.8967                           |
| 51  | $f^6$                  | $^7F$            | 1.3663                            | -1.1282                          | 1.2774                           | 2.1843                           |
| 52  | $^7F_0$                |                  | 1.5159                            | -0.7188                          | 0.2277                           | 1.6931                           |
| 53  | $^7F_1$                |                  | 0.7277                            | 0.5125                           | -0.7419                          | 1.1587                           |
| 54  | $^7F_4$                |                  | 0.1528                            | 0.6075                           | 0.7650                           | 0.9888                           |
| 55  | $^7F_3$                |                  | -0.2277                          | 0.1880                           | -0.2129                          | 0.3640                           |
| 56  | $^7F_2$                |                  | -0.4382                          | -0.3984                          | 0                                | 0.5922                           |
| 57  | $^7F_1$                |                  | 0                                | 0                                | 0                                | 0                                |
| 58  | $^7F_0$                |                  | 0                                | 0                                | 0                                | 0                                |
Table 2: Multipole characteristics of selected electron eigenstates \((2S+1L_J)\) distinguished by: the strongest A (rows 1–10), very weak A (rows 11–20), domination* of \(|A_2|\) (rows 21–33), domination** of \(|A_4|\) (rows 34–41), domination*** of \(|A_6|\) (rows 42–44), the comparable contribution of \(|A_2|, |A_4|,\) and \(|A_6|\) (rows 45–56). In the last rows (57–63) there are seven states \(^3G_5\) coming from the seven various terms \(^3G\) of \(f^6\) configurations.

| No. | Electron configuration | Electron eigenstate | \(A_2 = \langle J||C^{(2)}||J\rangle\) | \(A_4 = \langle J||C^{(4)}||J\rangle\) | \(A_6 = \langle J||C^{(6)}||J\rangle\) | \(A = (A_2^2 + A_4^2 + A_6^2)^{1/2}\) |
|-----|----------------------|--------------------|------------------|------------------|------------------|------------------|
| 1   | \(f^4\)              | \(^1N\)            | -3.5254          | -1.7951          | 1.4760           | 4.2225           |
| 2   | \(f^3\)              | \(^2L_{7/2}\)      | -3.3430          | -0.2254          | 0.6523           | 3.4136           |
| 3   | \(f^6\)              | \(^1Q\)            | -1.5036          | -1.3591          | -2.7260          | 3.3969           |
| 4   | \(f^2\)              | \(^1I\)            | -3.0318          | 1.4375           | -0.4554          | 3.3861           |
| 5   | \(f^5\)              | \(^2O_{23/2}\)     | -2.5911          | -1.5800          | -0.6924          | 3.1128           |
| 6   | \(f^4\)              | \(^3M_{10}\)       | -2.4678          | 0                | -1.6235          | 2.9539           |
| 7   | \(f^4\)              | \(^1H(2)\)        | -2.6199          | -0.6833          | 0.4451           | 2.7439           |
| 8   | \(f^5\)              | \(^2K(4)_{15/2}\) | -2.4906          | 0.4092           | 0.9639           | 2.7018           |
| 9   | \(d^4\)              | \(^1I\)            | -1.2994          | -2.2589          | 0                | 2.6060           |
| 10  | \(d^2\)              | \(^1G\)            | -2.4026          | 0.9131           | 0                | 2.5703           |
| 11  | \(f^6\)              | \(^3G_{1/2}\)      | -0.0227          | -0.0296          | 0.0099           | 0.0386           |
| 12  | \(f^6\)              | \(^3H_{1/2}\)      | 0.0437           | 0.0228           | -0.0148          | 0.0515           |
| 13  | \(f^6\)              | \(^3F_{1/3}\)      | 0.0683           | -0.0125          | -0.0639          | 0.0944           |
| 14  | \(f^4\)              | \(^3G_{1/2}\)      | -0.0681          | -0.0887          | 0.0298           | 0.1157           |
| 15  | \(f^5\)              | \(^4F_{3/2}\)      | -0.0793          | -0.0696          | -0.0691          | 0.1261           |
| 16  | \(f^5\)              | \(^4I(3)_{11/2}\) | 0.0721           | 0.1218           | 0.0340           | 0.1456           |
| 17  | \(f^6\)              | \(^5F_{1/3}\)      | -0.0721          | -0.0940          | -0.0887          | 0.1480           |
| 18  | \(f^4\)              | \(^3H_{1/2}\)      | 0.1310           | 0.0683           | -0.0445          | 0.1543           |
| 19  | \(f^6\)              | \(^3H_{5/2}\)      | -0.0621          | 0.1520           | -0.0163          | 0.1650           |
| 20  | \(f^6\)              | \(^3G_{2/4}\)      | 0.1709           | 0.0059           | -0.0070          | 0.1711           |
| 21  | \(f^3\)              | \(^2L_{17/2}\)     | -3.3430          | -0.2254          | 0.6523           | 3.4136           |
| 22  | \(f^3\)              | \(^2F_{2/7/2}\)    | -1.6102          | -0.1026          | 0.0828           | 1.6156           |
| 23  | \(f^4\)              | \(^3G_{2/4}\)      | 0.5128           | 0.0176           | -0.0211          | 0.5135           |
| 24  | \(f^5\)              | \(^4H_{2/11/2}\)   | -0.3828          | 0.0079           | -0.0100          | 0.3830           |
| 25  | \(f^5\)              | \(^4H(3)_{11/2}\) | 0.3904           | 0.0477           | -0.0302          | 0.3945           |
| 26  | \(f^5\)              | \(^2L_{1/17/2}\)   | -1.6715          | -0.1127          | 0.3262           | 1.7068           |
| 27  | \(f^5\)              | \(^2N_{21/2}\)     | -1.7598          | -0.0817          | -0.0786          | 1.7634           |
| 28  | \(f^6\)              | \(^5H_{2/6}\)      | 1.1272           | -0.0184          | -0.1741          | 1.1407           |
| 29  | \(f^6\)              | \(^5I_{2/7}\)      | -1.0521          | 0.0385           | -0.1279          | 1.0605           |
| 30  | \(f^6\)              | \(^3F_{6/3}\)      | -0.6725          | -0.0487          | 0.1099           | 0.6818           |
| 31  | \(f^6\)              | \(^3G_{2/4}\)      | 0.1709           | 0.0059           | -0.0070          | 0.1711           |
| 32  | \(f^6\)              | \(^3G_{7/4}\)      | -0.9812          | -0.0064          | 0.0184           | 0.9814           |
| 33  | \(f^6\)              | \(^3L_{2/8}\)      | -1.2705          | -0.1478          | 0.2320           | 1.2999           |
| No. | Electron configuration | Electron eigenstate | $A_2 = \langle J||C^{(2)}||J\rangle$ | $A_4 = \langle J||C^{(4)}||J\rangle$ | $A_6 = \langle J||C^{(6)}||J\rangle$ | $A = (A_2^2 + A_4^2 + A_6^2)^{1/2}$ |
|-----|------------------------|---------------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|
| 34  | $f^3$                  | $2H(2)_{11/2}$      | -0.0076                          | 0.5373                          | 0.0066                          | 0.5374                          |
| 35  | $f^3$                  | $2H(2)_{9/2}$       | -0.0069                          | 0.4816                          | 0.0057                          | 0.4817                          |
| 36  | $f^5$                  | $2H(2)_{11/2}$      | -0.0038                          | 0.2686                          | 0.0033                          | 0.2686                          |
| 37  | $f^5$                  | $2H(2)_{9/2}$       | -0.0035                          | 0.2408                          | 0.0029                          | 0.2408                          |
| 38  | $f^6$                  | $^3G(4)_1$          | 0.0103                           | 0.2824                          | 0.0326                          | 0.2845                          |
| 39  | $f^6$                  | $^3G(5)_5$          | -0.0597                          | 0.3596                          | 0.0065                          | 0.3646                          |
| 40  | $f^6$                  | $^3G(5)_3$          | -0.0458                          | 0.2451                          | 0.0029                          | 0.2494                          |
| 41  | $f^6$                  | $^1N(2)$            | -0.2044                          | 1.2618                          | 0.1626                          | 1.2885                          |
| 42  | $f^6$                  | $^5G(2)_{5}$        | -0.0491                          | 0.0322                          | 0.4586                          | 0.4623                          |
| 43  | $f^6$                  | $^5G(2)_{4}$        | -0.0362                          | -0.0327                         | 0.4948                          | 0.4972                          |
| 44  | $f^6$                  | $^5G(2)_{3}$        | -0.0302                          | -0.0438                         | 0.4935                          | 0.4964                          |
| 45  | $f^4$                  | $^3G(3)$            | -0.8086                          | -0.7396                         | 0.7706                          | 1.3397                          |
| 46  | $f^6$                  | $^3G(3)$            | -0.2696                          | -0.2465                         | 0.2569                          | 0.4466                          |
| 47  | $f^1$                  | $^2F$               | -1.3663                          | 1.1282                          | -1.2774                         | 2.1843                          |
| 48  | $f^2$                  | $^3F$               | 0.4554                           | -0.3761                         | 0.4258                          | 0.7281                          |
| 49  | $f^3$                  | $^4F$               | 0.6831                           | -0.5641                         | 0.6387                          | 1.0921                          |
| 50  | $f^4$                  | $^5F$               | -0.6831                          | 0.5641                          | -0.6387                         | 1.0921                          |
| 51  | $f^5$                  | $^6F$               | -0.4554                          | 0.3761                          | -0.4258                         | 0.7281                          |
| 52  | $f^6$                  | $^7F$               | 1.3663                           | -1.1282                         | 1.2774                          | 2.1843                          |
| 53  | $f^6$                  | $^7F_3$             | -0.2277                          | 0.1880                          | -0.2129                         | 0.3640                          |
| 54  | $f^5$                  | $^4F(3)_{9/2}$      | -0.0793                          | -0.0696                         | -0.0691                         | 0.1261                          |
| 55  | $f^4$                  | $^1L(1)$            | -1.0938                          | -1.1329                         | 0.9100                          | 1.8188                          |
| 56  | $f^5$                  | $^4K(2)_{11/2}$     | -0.5945                          | -0.6108                         | -0.7334                         | 1.1244                          |
| 57  | $f^6$                  | $^3G(1)_5$          | -0.0277                          | -0.0521                         | -0.1259                         | 0.1390                          |
| 58  | $f^6$                  | $^3G(2)_5$          | 0.2089                           | 0.0103                          | 0.0893                          | 0.2274                          |
| 59  | $f^6$                  | $^3G(3)_5$          | -0.2799                          | -0.2174                         | 0.1631                          | 0.3901                          |
| 60  | $f^6$                  | $^3G(4)_5$          | 0.0126                           | 0.4980                          | -0.4137                         | 0.6475                          |
| 61  | $f^6$                  | $^3G(5)_5$          | -0.0597                          | 0.3596                          | 0.0065                          | 0.3646                          |
| 62  | $f^6$                  | $^3G(6)_5$          | 0.3602                           | 0.2853                          | -0.2503                         | 0.5232                          |
| 63  | $f^6$                  | $^3G(7)_5$          | -1.1988                          | -0.0112                         | -0.2335                         | 1.2214                          |
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