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2007 J. Phys. A: Math. Theor. 40 2063

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On a complementary scale of crystal-field strength

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Received 5 June 2006, in final form 14 January 2007

Published 14 February 2007

Online at stacks.iop.org/JPhysA/40/2063

Abstract

A new measure of the crystal-field strength, complementary to the conventional one, is defined. It is based on spherical averages $|B_{k0}|_{\text{av}}$ or $|\sum_k B_{k0}|_{\text{av}}$, $k = 2, 4, 6$, of the crystal-(ligand)-field Hamiltonian \mathcal{H}_{CF} parametrizations, i.e. on the axial crystal-field (CF) parameters averaged over all the reference frame orientations. It is proved that they are equal to $|\mathcal{H}_{\text{CF}}^{(k)}|_{\text{av}}$ and $|\mathcal{H}_{\text{CF}}|_{\text{av}}$, respectively. While the traditional CF strength measure has been established on the parametrization modules, it means on the second moment of the CF energy levels, the new introduced scale employs rather the first moment of the energy modules and reveals a better resolving power. This complementary measure enables us to differentiate the strength of various iso-modular parametrizations according to the classes of rotationally equivalent ones. Using both the compatible CF strength scales one may draw more accurate conclusions about the Stark levels arrays and, in particular, their total splitting.

PACS number: 71.70.Ch

1. Introduction

Among solid state experimentalists, especially spectroscopists, there is still a need for a reliable scale quantitatively characterizing the crystal-field interaction effect, i.e. the so-called crystal-field strength. Having such a parameter one could directly verify and compare various CF Hamiltonian \mathcal{H}_{CF} parametrizations, which may come from different experimental data fittings. The problem is that in the majority of cases the orientations of the reference frames associated with these parametrizations are unknown.

Although such a conventional scale of the CF strength has been introduced over 20 years ago [1, 2], in some cases it seems to be insufficiently precise. It employs the basic rotational invariants of the \mathcal{H}_{CF} , i.e. the modules of its 2^k -pole components $\mathcal{H}_{\text{CF}}^{(k)}$ defined as

$M_k = (\sum_q |B_{kq}|^2)^{1/2}$, as well as the global \mathcal{H}_{CF} modulus $M = (\sum_k \sum_q |B_{kq}|^2)^{1/2}$. In the first case the partial crystal-field strength $S_k = (\frac{1}{2k+1})^{1/2} \cdot M_k$ is defined, whereas in the second case the global crystal-field strength $S = (\sum_k S_k^2)^{1/2}$ is given. Throughout the paper the tensor (Wybourne) notation for the CF Hamiltonian and the crystal-field parameters (CFPs), $\mathcal{H}_{\text{CF}} = \sum_k \sum_q B_{kq} C_q^{(k)}$, is consistently used [3]. The above summations over k and q indices run, in each individual case, over strictly specified values according to the kind of the central ion and its point symmetry.

Both the parameters S_k and S as such are not a direct measure of the actual magnitude of the initial state splitting since the CF effect depends also on the properties of the paramagnetic ion subjected to the \mathcal{H}_{CF} . In fact, the system response to the \mathcal{H}_{CF} perturbation reflects the symmetry of the electron density distribution of the central ion open-shell. For instance, an S-type ion like Gd^{3+} feels no crystal field (in the first order of perturbation), no matter how it is strong.

The effect of splitting can be expressed most simply by the second moments σ_k^2 or σ^2 of the CF sublevels within the initial state upon switching on the $\mathcal{H}_{\text{CF}}^{(k)}$ (or \mathcal{H}_{CF}) perturbation. In fact, the second moment is easily represented by the scalar CF strength parameters, either S_k or S (section 2). However, although the effective $\mathcal{H}_{\text{CF}}^{(k)}$ multipoles (for $k = 2, 4, 6$) contribute to the energy of individual Stark levels independently (as an algebraic sum), between the σ_k^2 (or σ^2) and S_k^2 (or S^2) there are always fulfilled simple linear relations. As it is proved these relations essentially confine both the maximal ($\Delta\mathcal{E}_{\text{max}}$) and minimal ($\Delta\mathcal{E}_{\text{min}}$) nominally allowed splittings of the initial state (section 3). What is even more the actual CF splittings (ΔE) can be additionally restricted (section 5). Naturally, all the iso-modular \mathcal{H}_{CF} parametrizations correspond to the same CF strengths S_k and S . However, apart from the M_k and M modules, there exist also spherical averages of the $\mathcal{H}_{\text{CF}}^{(k)}$ or \mathcal{H}_{CF} . They distinguish, in turn, the classes of the rotationally equivalent \mathcal{H}_{CF} parameterizations that refer to the same actual CF potential, but are expressed in variously oriented reference frames. Interestingly, they turn out to be the averages of the axial parameter modulus $|B_{k0}|_{\text{av}}$, $k = 2, 4, 6$ (in the case of $\mathcal{H}_{\text{CF}}^{(k)}$) or $|\sum_k B_{k0}|_{\text{av}}$ for the global \mathcal{H}_{CF} . The average means the integration over all the reference frame orientations, i.e. over the solid angle 4π . Thus, the $|B_{k0}|_{\text{av}}$ and $|\sum_k B_{k0}|_{\text{av}}$ are directly equal to $|\mathcal{H}_{\text{CF}}^{(k)}|_{\text{av}}$ and $|\mathcal{H}_{\text{CF}}|_{\text{av}}$, respectively (section 4).

Although the new CF strength scale based on the above integral averages is in principle consistent with the conventional one, it reveals a better resolving power. Applying the new measure to the iso-modular parametrizations gives different new strength parameters. This is exemplified below for several cases (section 5). The introduced CF strength gradation, being more subtle comparing to the conventional one, gives also the additional valuable information about the Stark levels array for various iso-modular \mathcal{H}_{CF} s and the initial state total splitting. In this paper we confine ourselves to the pure model states of the zero-order approximation which have a well-defined angular momentum quantum number and the corresponding degeneracy. These could be for instance Russell–Saunders coupled states $|\alpha LSJ\rangle$ coming from the ^{2S+1}L terms, where α stands for the remaining quantum numbers needed for their complete determination. Such states have a well-defined quantum number J and the degeneracy $2J + 1$. The derivation of the analogical expressions including J -mixing effects [4] or a transformation to other functional bases of the zero-order approximation can be accomplished by using standard angular momentum re-coupling techniques [4–8]. The CF splitting of p^1 , d^1 and f^1 one-electron configurations as well as a typical complex state 3H_4 for various iso-modular $\mathcal{H}_{\text{CF}}^{(k)}$, $k = 2, 4, 6$, have been analysed as examples (section 5). In the first three cases we avoid the complex states re-coupling procedure, which is a side issue to

the problem under consideration. Since we study various iso-modular Hamiltonians $\mathcal{H}_{CF}^{(k)}$, all CFPs values and the Stark levels energies are given in M_k units.

2. Conventional definition of the CF strength parameter

The comparison and scaling of the CF impact can be based upon the two types of scalar quantities, M_k and/or M , since both of them are rotationally invariant. Such a scalar CF strength parameter was given firstly by Auzel and Malta [1, 2] as (in the original notation):

$$N_v = \left[\sum_{k,q} |B_q^k|^2 \left(\frac{2\pi}{2k+1} \right) \right]^{1/2},$$

which is in fact M in the space spanned by spherical harmonics Y_q^k . In other words, N_v is a norm representing a distance in this space. Currently there are two definitions widely used in the literature [9–12]:

$$S_k = \left(\frac{1}{2k+1} \sum_q |B_{kq}|^2 \right)^{1/2} = \left\{ \frac{1}{2k+1} \left[B_{k0}^2 + 2 \sum_{q>0} [(\text{Re } B_{kq})^2 + (\text{Im } B_{kq})^2] \right] \right\}^{1/2}, \quad (1)$$

for $k = 2, 4$ and 6 in the case of 2^k -pole \mathcal{H}_{CF} component, and

$$S = (S_2^2 + S_4^2 + S_6^2)^{1/2} \quad \text{or} \quad S = \left[\frac{1}{3} (S_2^2 + S_4^2 + S_6^2) \right]^{1/2}, \quad (2)$$

for the global $\mathcal{H}_{CF} = \sum_k \mathcal{H}_{CF}^{(k)}$ [4].

A word of caution is worthy at this point. The S_k or S can differ according to \mathcal{H}_{CF} parametrization (the type of operators) applied. They can be compared with each other only after a proper recalculation. Since both these quantities are independent of the assumed axis system if we know them we can verify whether the original CFP data sets and the transformed ones are compatible. Additionally, having the strengths S_k or S we can compare the CFP data sets even when the axis systems have not been explicitly defined. Undoubtedly these quantities play a central role in the CF theory, and what is also important and useful, they are linked to the second moment of the Stark levels within the particular initial state $|\alpha SLJ\rangle$ [4, 13].

The second moment of the sublevels $|n\rangle$ within $|\alpha SLJ\rangle$ state upon switching on the \mathcal{H}_{CF} perturbation is defined by

$$\sigma^2(|\alpha SLJ\rangle) = \frac{1}{2J+1} \sum_n [E_n - \bar{E}(|\alpha SLJ\rangle)]^2, \quad (3)$$

where the energy centre of gravity of the state $|\alpha SLJ\rangle$ Stark levels is given as

$$\bar{E}(|\alpha SLJ\rangle) = \frac{1}{2J+1} \sum_n E_n,$$

and E_n is the energy of the $|n\rangle$ sublevel. Since \mathcal{H}_{CF} is diagonal in the $|n\rangle$ basis and the second-order effect of the \mathcal{H}_{CF} interaction is neglected [4] we have

$$\sigma^2(|\alpha SLJ\rangle) = \frac{1}{2J+1} \text{Tr}\{\mathcal{H}_{CF}^2\}.$$

Hence, according to the 3- j symbols orthogonality [2, 5, 13]

$$\sigma^2(|\alpha SLJ\rangle) = \frac{1}{2J+1} \sum_k S_k^2 (|\langle \alpha SLJ || C^{(k)} || \alpha SLJ \rangle|)^2. \quad (4)$$

The terms $\langle \alpha SLJ || C^{(k)} || \alpha SLJ \rangle$ are the double-bar (or reduced) matrix elements of the spherical tensor operators. According to Wigner–Eckart theorem [14] they are independent of the reference frame orientation. The origin and physical meaning of these terms stem from the following relationships presented below [5–8, 15]:

$$\langle \alpha SLJM_J | C_q^{(k)} | \alpha SL'J'M'_J \rangle = (-1)^{J-M_J} \begin{pmatrix} J & k & J' \\ -M_J & q & M'_J \end{pmatrix} \langle \alpha SLJM_J || C^{(k)} || \alpha SL'J' \rangle,$$

where the reduced matrix element follows the 3- j factor. Further use of the tensor formalism yields

$$\langle \alpha SLJ || C^{(k)} || \alpha SL'J' \rangle = (-1)^{S+L'+J+k} [(2J+1)(2J'+1)]^{1/2} \\ \times \begin{Bmatrix} J & J' & k \\ L' & L & S \end{Bmatrix} \langle \alpha SL || C^{(k)} || \alpha SL' \rangle,$$

and the double-reduced matrix element follows now the 6- j symbol. Alternatively, we can also employ the matrix elements of the unit operators $U^{(k)}$ [5–8, 15], i.e. the normalized equivalents of $C^{(k)}$ s, since

$$\langle \alpha SL || C^{(k)} || \alpha SL' \rangle = \langle \alpha SL || U^{(k)} || \alpha SL' \rangle \langle l || C^{(k)} || l \rangle,$$

where l is the angular momentum quantum number of the open-shell electrons. The reduced matrix elements of the $U^{(k)}$ operators have been compiled by Nielson and Koster [16], whereas the 3- j and 6- j symbols are given in the tables by Rotenberg *et al* [7].

In fact, the simple relation (equation (4)) between the σ_k^2 and S_k^2 can also be proved employing the Vieta's formulae for the roots of the $\mathcal{H}_{CF}^{(k)}$ matrix characteristic polynomial

$$E^n + a_1 E^{n-1} + a_2 E^{n-2} + \dots + a_n = 0,$$

which is here of order of $n = 2J + 1$. All its coefficients and roots must be real what implies automatically from the \mathcal{H}_{CF} hermiticity. Interestingly, some characteristics of the sublevels spectrum can be described in terms of the elementary algebra. Firstly, as the energy centre of gravity of the initial state ought to be conserved, i.e. $\sum_{i=1}^n E_i = 0$, the a_1 coefficient standing at E^{n-1} must vanish. Secondly, since $0 = (\sum_i E_i = 0)^2 = \sum_{i=1}^n E_i^2 + 2 \sum_{i>j} E_i E_j$, the second moment, i.e. the sum of the root squares (divided by $2J + 1$) is equal to $\frac{-2a_2}{2J+1}$. It can be also shown that in the simplified notation for the reduced matrix element representing only the last quantum number we get

$$-2a_2 = \frac{1}{2k+1} M_k^2 \langle J || C^{(k)} || J \rangle^2.$$

Hence, the relationship between the σ_k^2 and S_k^2 is given by the simple formula (equation (4))

$$\sigma_k^2 = \frac{1}{2J+1} S_k^2 \langle J || C^{(k)} || J \rangle^2. \quad (5)$$

In other words σ_k is proportional to S_k . Finally, the free term of the characteristic polynomial is given as $a_n = (-1)^n E_1 E_2 \dots E_n$, which may be also helpful analysing the solutions. For instance, if one of the roots is zero then the free term vanishes.

The problem becomes more complex for the global CF strength S (equation (2)) since then the components S_k^2 contribute to the sum with their weights $\langle J || C^{(k)} || J \rangle^2$ (equation (4)). This is why, in this case, there is no straightforward proportionality between σ^2 and S^2 . Since σ is a positively defined quadratic form of S_k , the contributions of the \mathcal{H}_{CF} 2^k -poles into σ^2 cannot compensate themselves. However, the condition that σ^2 is constant for various iso-modular \mathcal{H}_{CF} s does not exclude a possible differentiation in the CF sublevels sequence and structure, as well as in the initial state total splitting. In fact, σ and S could be correlated similarly as σ_k

and S_k in the previous case, but only if the elements $\langle J||C^{(k)}||J \rangle$ were equal to each other for all k . Nevertheless, for the global CF strength the second moment of the Stark levels within a particular $|\alpha SLJ\rangle$ state is defined directly in terms of S_2 , S_4 and S_6 . Auzel and Malta [2] made an attempt to average the σ^2 quadratic form transforming the corresponding ellipsoid $\sum_k S_k^2 \langle J||C^{(k)}||J \rangle^2$ in the k -space to a sphere of the same volume $\sum_k S_k^2 [\Pi_k \langle J||C^{(k)}||J \rangle^2]^{1/3}$ with a radius equal to the geometric mean of the three ellipsoid axes. In practice, unfortunately, this elegant approach does not always lead to acceptable results.

In the literature the overall effect of the CF interaction is often characterized by a quantitative comparison of the CF strength [17–20]. Additionally, a systematic correlation between the free ion parameters and the CF strength is observed, namely an increase in the CF interaction results in the reduction of the free-ion parameters magnitude [17]. The CF strength rises in the RE series when the ionic radius of the RE^{3+} host cation decreases [19]. The physical meaning of the CF strength scalar parameter manifests also in its increase with pressure applied to the sample [21, 22]. The CF strength parameter has also been used to compare the root mean square error obtained for crystal fields of different strength, however, its usage in such a case is restricted only to a comparison of the identical site symmetries [10, 23]. Furthermore, within the second-order CF approximation, the shift in the energy centre of gravity of a particular $^{2S+1}L_J$ state due to the J -mixing effects is a simple linear function of the S_k^2 [4, 17].

The concept of the S_k^2 or S can be further extended to define the quantities C_k and C_G [13] as normalized ‘scalar products’ of any two compared parametrizations. Such quantities represent the ‘angles’ between the two considered parametrizations and may serve as a convenient measure of the closeness, i.e. the correlation between any two CFPs sets.

3. The correspondence between the nominally allowed splittings of $|J\rangle$ state and the second moment of its Stark levels

The second moment σ^2 of the CF levels essentially limits a formally allowed range of the initial state $|J\rangle$ total splittings $\Delta\mathcal{E}$ for different iso-modular \mathcal{H}_{CFs} . Such a confinement of the energy splitting differs for non-Kramers and Kramers ions what is specified in details below.

Let us study the first case of an integer J , i.e. the non-Kramers ions. Since the σ^2 must be constant the minimal hypothetical splitting $\Delta\mathcal{E}_{\min}$ of the $(2J+1)$ -fold degenerate state takes place when J levels achieve an identical energy of $\frac{J+1}{2J+1}\Delta\mathcal{E}_{\min}$, while the remaining $J+1$ levels correspondingly $\frac{-J}{2J+1}\Delta\mathcal{E}_{\min}$, or vice versa. This is referred further as type I splitting. Then

$$\sigma^2 = \frac{J(J+1)(\Delta\mathcal{E}_{\min})^2}{(2J+1)^2}, \quad \Delta\mathcal{E}_{\min} = \sigma \frac{2J+1}{\sqrt{J(J+1)}}. \quad (6)$$

In turn, the maximal hypothetical splitting $\Delta\mathcal{E}_{\max}$ occurs if one level achieves the $\Delta\mathcal{E}_{\max}/2$ energy, one $-\Delta\mathcal{E}_{\max}/2$, and the remaining $(2J-1)$ levels stay at zero energy. This case is referred below as type II splitting. Then

$$\sigma^2 = \frac{2(\Delta\mathcal{E}_{\max}/2)^2}{2J+1}, \quad \Delta\mathcal{E}_{\max} = \sigma \sqrt{2(2J+1)}. \quad (7)$$

Based on the above formulae we have

$$\frac{\Delta\mathcal{E}_{\max}}{\Delta\mathcal{E}_{\min}} = \sqrt{\frac{2J(J+1)}{2J+1}}. \quad (8)$$

Let us also consider, following Auzel and Malta [2], the case of the homogenous splitting $\Delta\mathcal{E}_{\text{hom}}$ (what corresponds to equal distances between levels), when

$$\sigma^2 = \frac{2(1+4+\dots+J^2)(\Delta\mathcal{E}_{\text{hom}}/2J)^2}{2J+1} \quad \text{and} \quad \Delta\mathcal{E}_{\text{hom}} = 2\sigma \sqrt{\frac{3J}{J+1}}. \quad (9)$$

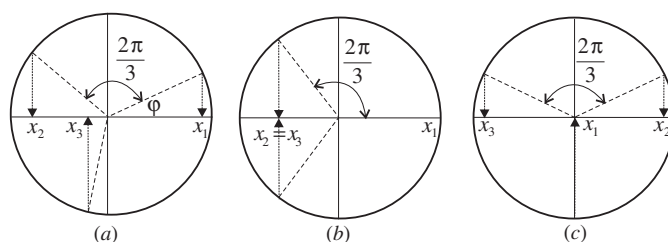


Figure 1. Crystal-field splitting of $|J = 1\rangle$ state—geometrical interpretation (x is the energy) (a) $\Delta\mathcal{E}^{(2)} = x_1 - x_2$ (general case); (b) $\Delta\mathcal{E}_{\min}^{(2)} = x_1 - x_2$, and (c) $\Delta\mathcal{E}_{\text{hom}}^{(2)} = \Delta\mathcal{E}_{\max}^{(2)} = x_2 - x_3$.

Below it will be referred as type III splitting. For example, for $J = 4$ we get $\Delta\mathcal{E}_{\min} = \sigma \frac{9}{2\sqrt{5}} = 2.01\sigma$, $\Delta\mathcal{E}_{\max} = \sigma 3\sqrt{2}\sigma = 4.24\sigma$, $\Delta\mathcal{E}_{\text{hom}} = 4\sigma\sqrt{3/5} = 3.10\sigma$, and finally the ratio $\frac{\Delta\mathcal{E}_{\max}}{\Delta\mathcal{E}_{\min}} = 2.11$.

For $J = 1$ we have $\Delta\mathcal{E}_{\min} = \sigma \frac{3}{\sqrt{2}}$, $\Delta\mathcal{E}_{\max} = \Delta\mathcal{E}_{\text{hom}} = \sigma\sqrt{6}$. The ratio $\frac{\Delta\mathcal{E}_{\max}}{\Delta\mathcal{E}_{\min}} = 2/\sqrt{3} = 1.16$ and so the $\Delta\mathcal{E}$ variation is strictly narrowed down. Interestingly, it has a simple graphical interpretation. Namely, as is known, the three real roots of a third-order equation must fulfil the Cardan's formulae graphically presented in figure 1(a), where the angle φ is a function of the equation coefficients. The minimal and maximal splittings $\Delta\mathcal{E}$ correspond to the solutions marked by the arrows in figures 1(b) and (c), respectively.

Let us now analyse the Kramers ions with a half integer J . Here, the two cases should be taken into account. Firstly, if an even number of doublets $(2J + 1)/2$ occurs the minimal $|J\rangle$ state splitting takes place when $(2J + 1)/4$ doublets achieve the energy of $\Delta\mathcal{E}_{\min}/2$, and the remaining $(2J + 1)/4$ doublets correspondingly $-\Delta\mathcal{E}_{\min}/2$. Then,

$$\sigma^2 = \frac{4[(2J + 1)/4](\Delta\mathcal{E}_{\min}/2)^2}{2J + 1}, \quad \Delta\mathcal{E}_{\min} = 2\sigma.$$

In turn, the maximal splitting $\Delta\mathcal{E}_{\max}$ will appear if one of the doublets reaches the energy of $\Delta\mathcal{E}_{\max}/2$, and the second the energy of $-\Delta\mathcal{E}_{\max}/2$, while all the rest of the levels remain at zero energy. Now,

$$\sigma^2 = \frac{4(\Delta\mathcal{E}_{\max}/2)^2}{2J + 1}, \quad \Delta\mathcal{E}_{\max} = \sigma\sqrt{2J + 1},$$

and hence

$$\frac{\Delta\mathcal{E}_{\max}}{\Delta\mathcal{E}_{\min}} = \frac{\sqrt{2J + 1}}{2}.$$

Secondly, for an odd number of the Kramers doublets we obtain $\Delta\mathcal{E}_{\min} = \frac{2\sigma(2J+1)}{\sqrt{(2J+3)(2J-1)}}$ and $\Delta\mathcal{E}_{\max} = \sigma\sqrt{2J + 1}$, with the ratio $\frac{\Delta\mathcal{E}_{\max}}{\Delta\mathcal{E}_{\min}} = \frac{1}{2}\sqrt{\frac{(2J+3)(2J-1)}{2J+1}}$.

The homogenous splitting $\Delta\mathcal{E}_{\text{hom}}$ for an even number of doublets ($J = (4k + 3)/2$) and for an odd number of doublets ($J = (4k + 1)/2$), where $k = 0, 1, \dots$, amounts correspondingly to $\sigma\sqrt{\frac{3(2J-1)}{J}}$ and $2\sigma\sqrt{\frac{3(2J-1)}{2J+3}}$. By way of example, if $J = 9/2$ (five doublets), then $\Delta\mathcal{E}_{\min} = \sigma\frac{5}{\sqrt{6}} = 2.04\sigma$, $\Delta\mathcal{E}_{\max} = \sigma\sqrt{10} = 3.16\sigma$, and $\Delta\mathcal{E}_{\text{hom}} = 2.83\sigma$. In the case of the Kramers ions the $\Delta\mathcal{E}$ variation range turns out to be more narrowed than that for the non-Kramers ions, what can be seen comparing the $\Delta\mathcal{E}_{\min}$ and $\Delta\mathcal{E}_{\max}$ for e.g. $J = 4$ and $J = 9/2$, respectively. Finally, taking the most extreme case of $J = 15/2$ for f-electron configurations with eight doublets (e.g. for Dy^{3+} , Er^{3+}), we would obtain $\Delta\mathcal{E}_{\min} = \sigma\frac{16}{3\sqrt{7}} = 2.02\sigma$, $\Delta\mathcal{E}_{\max} = 4\sigma$ and $\Delta\mathcal{E}_{\text{hom}} = 2.37\sigma$.

4. Comparison between the conventional $S_k = \frac{1}{2k+1}M_k$ and alternative $S'_k = |\mathcal{H}_{CF}^{(k)}|_{av}$ CF strengths

4.1. *The spherical averages of the axial parameter absolute values $|B'_{k0}|_{av}$ and $|\sum_k B'_{k0}|_{av}$, where $k = 2, 4, 6$*

Rotating the reference frame by the two Euler angles α and β we obtain, within an accuracy of the third Euler angle γ about the z axis, all the equivalent \mathcal{H}_{CF} parametrizations [5, 24]. Their relevant axial parameters for a 2^k -pole component are given as

$$\begin{aligned} B'_{k0} &= \sum_{q=-k}^k \mathcal{D}_{0q}^{(k)}(\alpha, \beta, 0) B_{kq} = \sum_{q=-k}^k C_q^{(k)}(\beta, \alpha) B_{kq} \\ &= C_0^{(k)}(\beta) B_{k0} + 2 \sum_{q=1}^k C_q^{(k)}(\beta) \cos q(\alpha + \varphi_q) |B_{kq}|, \end{aligned} \tag{10}$$

where $\mathcal{D}_{0q}^{(k)}(\alpha, \beta, \gamma)$ are the elements of the middle row rotation matrix, $C_q^{(k)}(\beta, \alpha) = \left(\frac{4\pi}{2k+1}\right)^{1/2} Y_q^k(\beta, \alpha)$ are the spherical tensors, and $C_q^{(k)}(\beta) = (-1)^q \left[\frac{(k-q)!}{(k+q)!}\right]^{1/2} P_k^q(\cos \beta)$, where $P_k^q(\cos \beta)$ are the associated Legendre functions, $B_{kq} = |B_{kq}| e^{iq\varphi_q}$, and $B_{k-q} = (-1)^q |B_{kq}| e^{-iq\varphi_q}$. The primed parameters correspond to the transformed parametrization while the unprimed to the initial one. It can be directly proved that $(B'_{k0})_{av} = 0$ and $(\sum_k B'_{k0})_{av} = 0$, whereas the average absolute values

$$\begin{aligned} |B'_{k0}|_{av} &= \frac{1}{4\pi} \int_0^{2\pi} \int_0^\pi |B'_{k0}(\alpha, \beta)| \sin \beta \, d\beta \, d\alpha, \\ \left| \sum_k B'_{k0} \right|_{av} &= \frac{1}{4\pi} \int_0^{2\pi} \int_0^\pi \left| \sum_k B'_{k0}(\alpha, \beta) \right| \sin \beta \, d\beta \, d\alpha, \end{aligned} \tag{11}$$

as the rotational averages are the discriminants of the equivalent parametrizations [24]. Interestingly, the above averages can be used to estimate the CF strength independently of the conventional scale based on the S_k or S .

The remaining B_{kq} CFPs ($q \neq 0$) transform themselves accordingly to the other rows of the rotation matrix $\mathcal{D}^{(k)}$, appropriately for each q individually. Their average absolute values, as a separate issue, are not considered in this paper.

4.2. *The spherical averages of the absolute values of the partial $|\mathcal{H}_{CF}^{(k)}|_{av}$ and global $|\mathcal{H}_{CF}|_{av}$ CF Hamiltonians*

Since the expression

$$\mathcal{H}_{CF}^{(k)} = \sum_{q=-k}^k B_{kq} C_q^{(k)}(\beta, \alpha),$$

where β and α are the spherical angle coordinates in the central-ion reference system, is identical with that for B'_{k0} (equation (10)), the following important identity holds

$$|\mathcal{H}_{CF}^{(k)}|_{av} = \frac{1}{4\pi} \int_0^{2\pi} \int_0^\pi |\mathcal{H}_{CF}^{(k)}(\alpha, \beta)| \sin \beta \, d\beta \, d\alpha = |B'_{k0}|_{av}. \tag{12}$$

It means that the average of the absolute value of a 2^k -pole $\mathcal{H}_{CF}^{(k)}$ component turns out to be equal to the average of the absolute value of the relevant axial parameter B_{k0} . The above

Table 1. The spherical averages of five representative iso-modular $\mathcal{H}_{\text{CF}}^{(2)}$ s, $S'_2 = |\mathcal{H}_{\text{CF}}^{(2)}|_{\text{av}}$, according to equations (11)–(13), expressed in M_2 units. Only B_{2q} CFPs are given, $B_{2-q} = (-1)^q B_{2q}^*$.

No	$\mathcal{H}_{\text{CF}}^{(2)}$ composition			$S'_2 = \mathcal{H}_{\text{CF}}^{(2)} _{\text{av}}$
	B_{20}	B_{21}	B_{22}	
1	1	0	0	0.385
2	$\frac{1}{\sqrt{5}}$	$\frac{1}{\sqrt{5}}$	$-\frac{1}{\sqrt{5}}$	0.381
3	$\frac{1}{\sqrt{5}}$	$\frac{1}{\sqrt{5}}$	$\frac{1}{\sqrt{5}}$	0.374
4	$\frac{1}{\sqrt{5}}$	$\frac{1}{\sqrt{5}} e^{i\pi/4}$	$\frac{1}{\sqrt{5}}$	0.369
5	0	0	$\frac{1}{\sqrt{2}}$	0.368

identity, obvious when we properly interpret the rotation angles in both cases of averaging, associates $|B'_{k0}|_{\text{av}}$ with the complementary measure of the CF strength S'_k ,

$$S'_k = |\mathcal{H}_{\text{CF}}^{(k)}|_{\text{av}} = |B'_{k0}|_{\text{av}}. \quad (13)$$

Although this identity for S'_k is limited to a given 2^k -pole $\mathcal{H}_{\text{CF}}^{(k)}$ component, it can be generalized for the global \mathcal{H}_{CF} ,

$$S' = \left| \sum_k \mathcal{H}_{\text{CF}}^{(k)} \right|_{\text{av}} = \left| \sum_k B'_{k0} \right|_{\text{av}}. \quad (14)$$

Contrary to the conventional CF strengths S_k and S (equations (1) and (2)) constant for all the iso-modular parametrizations, the new evaluated S'_k and S' strengths vary within certain ranges. It is discussed in the next section. To conveniently compare both the measures let us express S'_k in a form of the product $f_k \cdot M_k$ with a factor f_k . These two measures are compatible if f_k is close to $\sqrt{\frac{1}{2k+1}}$ (equation (1)), i.e. correspondingly to 0.447, 0.333 and 0.277 for $k = 2, 4$ and 6 . Their consistence is demonstrated and discussed in details below (section 5), where, by way of example, the CF splittings of p^1, d^1 and f^1 electron configurations with the spin–orbit coupling intentionally neglected, and the 3H_4 state for various iso-modular $\mathcal{H}_{\text{CF}}^{(k)}$ s are provided.

Since the complementary scale refers to various iso-modular $\mathcal{H}_{\text{CF}}^{(k)}$ parametrizations having fixed S (and σ^2) the barycenter shifts are the same for all of them [4].

5. Numerical results and discussion

5.1. Crystal-field splitting of p^1, d^1 and f^1 electron configurations for various iso-modular $\mathcal{H}_{\text{CF}}^{(k)}$ s, $k = 2, 4, 6$

We consider the model interaction when any iso-modular $\mathcal{H}_{\text{CF}}^{(k)}$ ($k = 2, 4, 6$) acts on the initial states with well-defined angular momentum quantum numbers. All the quantities under discussion, i.e. the new CF strength parameters S'_k , the total splittings $\Delta E^{(k)}$, the second moments σ_k^2 of the CF levels and the averages of the Stark energy modules $|E_n^{(k)}|_{\text{av}}$, are consistently given in M_k units.

Tables 1–3 compile only 5, 10 and 11 chosen representative iso-modular ($M_k = 1$) $\mathcal{H}_{\text{CF}}^{(k)}$ parametrizations for the three effective 2^2 -, 2^4 - and 2^6 -pole components, respectively. They have been selected from the numerous sets of the iso-modular parametrizations

Table 2. The spherical averages of ten representative iso-modular $\mathcal{H}_{\text{CF}}^{(4)}$ s, $S'_4 = |\mathcal{H}_{\text{CF}}^{(4)}|_{\text{av}}$, according to equations (11)–(13), expressed in M_4 units. Only B_{4q} CFPs are given, $B_{4-q} = (-1)^q B_{4q}^*$.

No	$\mathcal{H}_{\text{CF}}^{(4)}$ composition					$S'_4 = \mathcal{H}_{\text{CF}}^{(4)} _{\text{av}}$
	B_{40}	B_{41}	B_{42}	B_{43}	B_{44}	
1	1	0	0	0	0	0.287
2	$\frac{1}{2}\sqrt{\frac{7}{3}}$	0	0	0	$\frac{1}{2}\sqrt{\frac{5}{6}}$	0.280
3	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3} e^{i\pi/2}$	$\frac{1}{3}$	$\frac{1}{3}$	0.277
4	$\frac{1}{3}$	$-\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3}$	0.276
5	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3}$	$-\frac{1}{3} e^{i\pi/2}$	$\frac{1}{3}$	0.273
6	0	0	$\frac{1}{\sqrt{2}}$	0	0	0.269
7	0	0	0	$\frac{1}{\sqrt{2}}$	0	0.266
8	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3}$	0.265
9	$\frac{1}{3}$	$\frac{1}{3} e^{i\pi/4}$	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3}$	0.261
10	0	0	0	0	$\frac{1}{\sqrt{2}}$	0.251

Table 3. The spherical averages of eleven representative iso-modular $\mathcal{H}_{\text{CF}}^{(6)}$ s, $S'_6 = |\mathcal{H}_{\text{CF}}^{(6)}|_{\text{av}}$, according to equations (11)–(13), expressed in M_6 units. Only B_{6q} CFPs are given, $B_{6-q} = (-1)^q B_{6q}^*$.

No	$\mathcal{H}_{\text{CF}}^{(6)}$ composition							$S'_6 = \mathcal{H}_{\text{CF}}^{(6)} _{\text{av}}$
	B_{60}	B_{61}	B_{62}	B_{63}	B_{64}	B_{65}	B_{66}	
1	1	0	0	0	0	0	0	0.239
2	$\frac{1}{\sqrt{13}}$	$\frac{1}{\sqrt{13}}$	$\frac{1}{\sqrt{13}}$	$\frac{1}{\sqrt{13}}$	$-\frac{1}{\sqrt{13}}$	$\frac{1}{\sqrt{13}}$	$\frac{1}{\sqrt{13}}$	0.231
3	$\frac{1}{\sqrt{13}}$	$\frac{1}{\sqrt{13}}$	$-\frac{1}{\sqrt{13}}$	$\frac{1}{\sqrt{13}}$	$\frac{1}{\sqrt{13}}$	$\frac{1}{\sqrt{13}}$	$\frac{1}{\sqrt{13}}$	0.228
4	$\frac{1}{\sqrt{13}}$	$\frac{1}{\sqrt{13}}$	$-\frac{1}{\sqrt{13}}$	$\frac{1}{\sqrt{13}}$	$-\frac{1}{\sqrt{13}}$	$\frac{1}{\sqrt{13}}$	$\frac{1}{\sqrt{13}}$	0.227
5	$-\frac{1}{\sqrt{13}}$	$\frac{1}{\sqrt{13}}$	$\frac{1}{\sqrt{13}}$	$\frac{1}{\sqrt{13}}$	$\frac{1}{\sqrt{13}}$	$\frac{1}{\sqrt{13}}$	$\frac{1}{\sqrt{13}}$	0.225
6	$\frac{1}{\sqrt{13}}$	$-\frac{1}{\sqrt{13}}$	$\frac{1}{\sqrt{13}}$	$\frac{1}{\sqrt{13}}$	$\frac{1}{\sqrt{13}}$	$\frac{1}{\sqrt{13}}$	$\frac{1}{\sqrt{13}}$	0.223
7	$\frac{1}{2\sqrt{2}}$	0	0	0	$\pm\frac{\sqrt{7}}{4}$	0	0	0.223
8	$\frac{1}{\sqrt{13}}$	$\frac{1}{\sqrt{13}}$	$\frac{1}{\sqrt{13}}$	$\frac{1}{\sqrt{13}}$	$\frac{1}{\sqrt{13}}$	$\frac{1}{\sqrt{13}}$	$-\frac{1}{\sqrt{13}}$	0.222
9	0	$\frac{1}{\sqrt{2}}$	0	0	0	0	0	0.219
10	$\frac{1}{\sqrt{13}}$	$\frac{1}{\sqrt{13}}$	$\frac{1}{\sqrt{13}}$	$\frac{1}{\sqrt{13}}$	$\frac{1}{\sqrt{13}}$	$\frac{1}{\sqrt{13}}$	$\frac{1}{\sqrt{13}}$	0.213
11	0	0	0	0	0	0	$\frac{1}{\sqrt{2}}$	0.195

in order to uniformly cover the observed ranges of the $|\mathcal{H}_{\text{CF}}^{(k)}|_{\text{av}}$ variations (in M_k): (0.368, 0.385), (0.251, 0.287) and (0.195, 0, 239) for $k = 2, 4, 6$, respectively. The relevant S_k is constant and correspondingly equals to 0.447, 0.333 and 0.277.

The survey includes scores of formally possible both actual and virtual $\mathcal{H}_{\text{CF}}^{(k)}$ parametrizations for each k . The iso-modular parametrizations strikingly differing in the components contribution, as well as those of the equalized composition have been intentionally tested. To ensure the most general approach the signs and phases of the individual components of the parametrizations have been treated freely.

Table 4. The total crystal-field splitting $\Delta E^{(2)}$ of p^1 configuration (with ls coupling neglected) and the average absolute values of $E_n^{(2)}$ in the crystal-field potentials given in table 1. All the values are given in M_2 units.

No	$ \mathcal{H}_{CF}^{(2)} _{av}$	$\Delta E^{(2)}$	$ E_n^{(2)} _{av}$
1	0.385	0.600	0.267
2	0.381	0.656	0.262
3	0.374	0.683	0.250
4	0.369	0.692	0.239
5	0.368	0.693	0.231

$$\sigma_2 = \sqrt{2/25} = 0.283, \Delta\mathcal{E}_{\min}^{(2)} = 0.600, \Delta\mathcal{E}_{\text{hom}}^{(2)} = \Delta\mathcal{E}_{\max}^{(2)} = 0.693 \text{ (equations (6)–(9))}.$$

Table 5. The total crystal-field splittings $\Delta E^{(2)}$ and $\Delta E^{(4)}$ of d^1 configuration (with ls coupling neglected) and the average absolute values of $E_n^{(2)}$ and $E_n^{(4)}$ in the crystal-field potentials given in tables 1 and 2. All the values are given in M_2 and M_4 units, respectively.

No	$ \mathcal{H}_{CF}^{(2)} _{av}$	$\Delta E^{(2)}$	$ E_n^{(2)} _{av}$
1	0.385	0.572	0.229
2	0.381	0.572	0.227
3	0.374	0.572	0.221
4	0.369	0.572	0.217
5	0.368	0.572	0.213

$$\sigma_2 = \sqrt{2/35} = 0.239, \Delta\mathcal{E}_{\min}^{(2)} = 0.488, \Delta\mathcal{E}_{\text{hom}}^{(2)} = 0.676, \Delta\mathcal{E}_{\max}^{(2)} = 0.756 \text{ (equations (6)–(9))}$$

	$ \mathcal{H}_{CF}^{(4)} _{av}$	$\Delta E^{(4)}$	$ E_n^{(4)} _{av}$
6	0.287	0.476	0.152
7	0.280	0.363	0.174
8	0.277	0.449	0.169
9	0.276	0.437	0.169
10	0.273	0.463	0.164
11	0.269	0.426	0.159
12	0.266	0.398	0.159
13	0.265	0.549	0.137
14	0.261	0.555	0.132
15	0.251	0.564	0.113

$$\sigma_4 = \sqrt{2/63} = 0.178, \Delta\mathcal{E}_{\min}^{(4)} = 0.363, \Delta\mathcal{E}_{\text{hom}}^{(4)} = 0.503, \Delta\mathcal{E}_{\max}^{(4)} = 0.564 \text{ (equations (6)–(9))}$$

For all the three effective 2^k -poles the highest observed $|\mathcal{H}_{CF}^{(k)}|_{av}$ values refer to the purely axial crystal fields ($q = 0$), i.e. for $B_{k0} = 1$, whereas the lowest $|\mathcal{H}_{CF}^{(k)}|_{av}$ s to the fields characterized by the maximal contribution of the $q = \pm k$ components, i.e. for $B_{k\pm k} = 1/\sqrt{2}$. Naturally, the equivalent $\mathcal{H}_{CF}^{(k)}$ parametrizations (physically identical but expressed in various reference systems) yield an identical $|\mathcal{H}_{CF}^{(k)}|_{av}$. In the light of the above precondition on the correlation between q and k for the extremal $|\mathcal{H}_{CF}^{(k)}|_{av}$ values and the convincing results of the vast numerical experiment, these evaluated limits have been assumed to be binding.

As it implies from tables 4–6 there exists a mapping between the above S'_k strengths and the $\Delta E^{(k)}$ and $|E_n^{(k)}|_{av}$ magnitudes. As it has been shown in the paper this quantitative mapping is determined by the roots of the $\mathcal{H}_{CF}^{(k)}$ matrix characteristic polynomial, and the key

Table 6. The total crystal-field splittings $\Delta E^{(2)}$, $\Delta E^{(4)}$ and $\Delta E^{(6)}$ of f^1 configuration (with ls coupling neglected) and the average absolute values of $E_n^{(2)}$, $E_n^{(4)}$ and $E_n^{(6)}$ in the crystal-field potentials given in tables 1–3. All the values are given in M_2 , M_4 and M_6 units, respectively.

No	$ \mathcal{H}_{CF}^{(2)} _{\text{av}}$	$\Delta E^{(2)}$	$ E_n^{(2)} _{\text{av}}$
1	0.385	0.600	0.190
2	0.381	0.603	0.191
3	0.374	0.607	0.192
4	0.369	0.608	0.193
5	0.368	0.608	0.193
$\sigma_2 = \sqrt{4/75} = 0.231$, $\Delta\mathcal{E}_{\min}^{(2)} = 0.467$, $\Delta\mathcal{E}_{\text{hom}}^{(2)} = 0.693$, $\Delta\mathcal{E}_{\max}^{(2)} = 0.864$ (equations (6)–(9))			
	$ \mathcal{H}_{CF}^{(4)} _{\text{av}}$	$\Delta E^{(4)}$	$ E_n^{(4)} _{\text{av}}$
6	0.287	0.394	0.121
7	0.280	0.417	0.119
8	0.277	0.449	0.116
9	0.276	0.458	0.117
10	0.273	0.464	0.115
11	0.269	0.478	0.113
12	0.266	0.482	0.115
13	0.265	0.399	0.129
14	0.261	0.363	0.129
15	0.251	0.358	0.131
$\sigma_4 = \sqrt{2/99} = 0.142$, $\Delta\mathcal{E}_{\min}^{(4)} = 0.287$, $\Delta\mathcal{E}_{\text{hom}}^{(4)} = 0.426$, $\Delta\mathcal{E}_{\max}^{(4)} = 0.531$ (equations (6)–(9))			
	$ \mathcal{H}_{CF}^{(6)} _{\text{av}}$	$\Delta E^{(6)}$	$ E_n^{(6)} _{\text{av}}$
16	0.239	0.408	0.107
17	0.231	0.326	0.130
18	0.228	0.365	0.120
19	0.227	0.379	0.123
20	0.225	0.445	0.106
21	0.223	0.420	0.112
22	0.223	0.346	0.127
23	0.222	0.422	0.112
24	0.219	0.468	0.097
25	0.213	0.481	0.097
26	0.195	0.501	0.072
$\sigma_6 = \frac{10}{13\sqrt{33}} = 0.134$, $\Delta\mathcal{E}_{\min}^{(6)} = 0.271$, $\Delta\mathcal{E}_{\text{hom}}^{(6)} = 0.402$, $\Delta\mathcal{E}_{\max}^{(6)} = 0.501$ (equations (6)–(9))			

part of the matrix elements is the product $(-1)^{J-M_J} B_{kq} \begin{pmatrix} J & k & J' \\ -M_J & q & M_J' \end{pmatrix}$. The remaining factors coming into the matrix elements are common and play the role of a scaling factor. In the below examples of the CF splitting of one-electron states with $J = J' = l$, for $l = 1, 2$ and 3 , these are the double-bar (reduced) matrix elements $\langle l || C^{(k)} || l \rangle$.

It should be, however, pointed out that such mappings $S'_k \longleftrightarrow \Delta E^{(k)}$, $S'_k \longleftrightarrow |E_n^{(k)}|_{\text{av}}$, $\Delta E^{(k)} \longleftrightarrow |E_n^{(k)}|_{\text{av}}$ are neither straightforward nor explicit. On the increase of the initial state degeneracy $2J + 1$ they become more difficult to be interpreted due to a large variety of possible splitting schemes. Nevertheless, one may presume a marked tendency: the greater S'_k the greater $|E_n^{(k)}|_{\text{av}}$ and the smaller $\Delta E^{(k)}$ (type I splittings). Oppositely, for a small S'_k type II splittings are expected. However, such reasoning does not take into consideration neither the unique characteristics of the $|\mathcal{H}_{CF}^{(k)}|_{\text{av}}$ nor the space density distribution of unpaired electrons

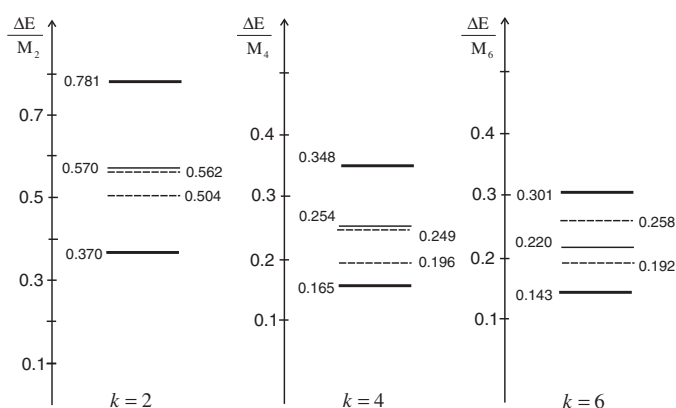


Figure 2. Nominally admissible $\Delta\mathcal{E}^{(k)}$ (bold solid borders) and the actual $\Delta E^{(k)}$ ranges (dashed borders) of the total splittings of the 3H_4 state subjected to the iso-modular $\mathcal{H}_{CF}^{(k)}$ s. The $\Delta\mathcal{E}_{\text{hom}}^{(k)}$ are also given (thin solid lines).

in the states of various J . The analysis of tables 4–6 seems to be instructive from this point of view, indeed.

On the other hand, the admissible spans $\Delta\mathcal{E}^{(k)}$ for a fix M_k , i.e. the relevant σ_k , are known. From the above mappings it implies that only certain $\Delta\mathcal{E}^{(k)}$ values, and the splitting schemes corresponding to them, can actually occur. Depending on the initial state quantum number J and the multipole's rank k some restrictions are imposed on the $\Delta E^{(k)}$ (tables 4–6). They are listed briefly below.

For $l = 1$ (p-electrons) and $k = 2$ the full nominal range of the $\Delta\mathcal{E}^{(2)}$ and all types of splittings (I, II and III) can occur. More particularly, $\Delta E^{(2)}$ can vary from $0.600M_2$ to $0.693M_2$ (table 4).

For $l = 2$ (d-electrons) and $k = 2$ the magnitude of $\Delta E^{(2)}$ is constant and amounts to $0.572M_2$ for each the iso-modular $\mathcal{H}_{CF}^{(2)}$. It corresponds to the splittings similar to type I. Other splittings, including e.g. $\Delta\mathcal{E}_{\text{hom}}^{(2)}$, are inadmissible in this case (table 5).

For $l = 2$ (d-electrons) and $k = 4$ again the full nominal range of the $\Delta\mathcal{E}^{(4)}$ is admitted beginning from the smallest $0.363M_4$ for the cubic $\mathcal{H}_{CF}^{(4)}$, up to the highest $0.564M_4$ for $\mathcal{H}_{CF}^{(4)} = \frac{1}{\sqrt{2}}C_4^{(4)} + \frac{1}{\sqrt{2}}C_{-4}^{(4)}$ (table 5).

Further, for $l = 3$ (f-electrons) and $k = 2$, $\Delta E^{(2)}$ only weakly depends on S'_2 , varying in the whole range merely from $0.600M_2$ to $0.608M_2$, i.e. somewhat below the $\Delta\mathcal{E}_{\text{hom}}^{(2)}$, i.e. it resembles roughly type III splittings (table 6).

Next, for $l = 3$ and $k = 4$ the possible $\Delta E^{(4)}$ varies from $0.358M_4$ to $0.482M_4$, i.e. in the vicinity of the $\Delta\mathcal{E}_{\text{hom}}^{(4)}$ (table 6).

Finally, for $l = 3$ and $k = 6$ the allowed $\Delta E^{(6)}$ varies from $0.326M_6$ to $0.501M_6$ and covers almost the entire nominal range including its upper limit, excluding however the smallest splittings (table 6).

The obtained results may be generalized for the states with J or L equal to 1, 2 or 3, multiplying $\Delta E^{(k)}$ and $|E_n^{(k)}|_{\text{av}}$ by the scaling factors $\langle J||C^{(k)}||J\rangle$ or $\langle L||C^{(k)}||L\rangle$, respectively.

5.2. Crystal-field splitting of 3H_4 state in various iso-modular $\mathcal{H}_{CF}^{(k)}$ s, $k = 2, 4, 6$

Finally let us turn to the analysis of splitting of the nine-fold degenerate 3H_4 state subjected to the iso-modular $\mathcal{H}_{CF}^{(k)}$ s given in tables 1–3. The correlated values of S'_k , $\Delta E^{(k)}$ and $|E_n^{(k)}|_{\text{av}}$

Table 7. The total crystal-field splitting $\Delta E^{(2)}$, $\Delta E^{(4)}$ and $\Delta E^{(6)}$ of the 3H_4 state and the average absolute values of $E_n^{(2)}$, $E_n^{(4)}$ and $E_n^{(6)}$ in the crystal-field potentials given in tables 1–3. All the values are given in M_2 , M_4 and M_6 units, respectively.

No	$ \mathcal{H}_{CF}^{(2)} _{\text{lav}}$	$\Delta E^{(2)}$	$ E_n^{(2)} _{\text{lav}}$
1	0.385	0.504	0.163
2	0.381	0.543	0.170
3	0.374	0.562	0.164
4	0.369	0.560	0.164
5	0.368	0.524	0.155
$\sigma_2 = 0.184$, $\Delta\mathcal{E}_{\min}^{(2)} = 0.370$, $\Delta\mathcal{E}_{\text{hom}}^{(2)} = 0.570$, $\Delta\mathcal{E}_{\max}^{(2)} = 0.781$ (equations (6)–(9))			
	$ \mathcal{H}_{CF}^{(4)} _{\text{lav}}$	$\Delta E^{(4)}$	$ E_n^{(4)} _{\text{lav}}$
6	0.287	0.215	0.079
7	0.280	0.227	0.073
8	0.277	0.249	0.070
9	0.276	0.241	0.071
10	0.273	0.232	0.073
11	0.269	0.230	0.064
12	0.266	0.232	0.067
13	0.265	0.231	0.077
14	0.261	0.229	0.076
15	0.251	0.196	0.077
$\sigma_4 = 0.082$, $\Delta\mathcal{E}_{\min}^{(4)} = 0.165$, $\Delta\mathcal{E}_{\text{hom}}^{(4)} = 0.254$, $\Delta\mathcal{E}_{\max}^{(4)} = 0.348$ (equations (6)–(9))			
	$ \mathcal{H}_{CF}^{(6)} _{\text{lav}}$	$\Delta E^{(6)}$	$ E_n^{(6)} _{\text{lav}}$
16	0.239	0.202	0.058
17	0.231	0.192	0.069
18	0.228	0.249	0.051
19	0.227	0.212	0.060
20	0.225	0.224	0.062
21	0.223	0.233	0.059
22	0.223	0.245	0.053
23	0.222	0.233	0.061
24	0.219	0.258	0.052
25	0.213	0.208	0.059
26	0.195	0.206	0.058
$\sigma_6 = 0.071$, $\Delta\mathcal{E}_{\min}^{(6)} = 0.143$, $\Delta\mathcal{E}_{\text{hom}}^{(6)} = 0.220$, $\Delta\mathcal{E}_{\max}^{(6)} = 0.301$ (equations (6)–(9))			

are compiled in table 7. The scaling factors $\langle J = 4 || C^{(k)} || J = 4 \rangle = \langle J = 4 || U^{(k)} || J = 4 \rangle \langle f || C^{(k)} || f \rangle$ required here for the coupled initial state ($L = 5$, $S = 1$, $J = 4$), are equal to -1.2365 , -0.7389 and 0.7706 for $k = 2, 4, 6$, respectively. Hence $\sigma_2 = 0.184M_2$, $\sigma_4 = 0.082M_4$ and $\sigma_6 = 0.071M_6$, whereas the global second moment of the Stark levels takes the form

$$\sigma^2 = \frac{1}{9} \left[\frac{1}{5} (-1.2365)^2 M_2^2 + \frac{1}{9} (-0.7389)^2 M_4^2 + \frac{1}{13} (0.7706)^2 M_6^2 \right].$$

The formally allowed $\Delta\mathcal{E}^{(k)}$ corresponding to the above second moments σ_2 , σ_4 , σ_6 are marked in figure 2 by the bold solid lines.

As we can see in figure 2 from the set of all potentially admissible total splittings $\Delta\mathcal{E}^{(k)}$ only certain $\Delta E^{(k)}$ may be realized (those between the dashed lines), and consequently, only certain splitting schemes (roughly those between types I and III) can occur. For instance, in the case of all the three effective multipoles neither $\Delta\mathcal{E}_{\max}^{(k)}$ nor $\Delta\mathcal{E}_{\min}^{(k)}$ are possible, whereas

$\Delta\mathcal{E}_{\text{hom}}^{(k)}$ can appear solely for the 2^6 -pole. Based on table 7 it is also seen that for all the three effective $\mathcal{H}_{\text{CF}}^{(k)}$ s the highest $\Delta E^{(k)}$ are achieved for intermediate S'_k values.

6. Conclusions

The conventional CF scales S_k or S with the associated second moments of the CF levels σ_k or σ cannot distinct the iso-modular $\mathcal{H}_{\text{CF}}^{(k)}$ or \mathcal{H}_{CF} parametrizations. They can be however differentiated by another scale—the spherically averaged $S'_k = |\mathcal{H}_{\text{CF}}^{(k)}|_{\text{av}}$ and $S' = |\mathcal{H}_{\text{CF}}|_{\text{av}}$. It is proved that the S'_k variation ranges for all the iso-modular parametrizations are limited and lie slightly below the relevant S_k magnitudes. The span of these ranges amounts to 5, 10 and 20% of their values for $k = 2, 4, 6$, respectively. There exists also a direct mapping between the complementary strength and both the total splittings $\Delta E^{(k)}$ and $|E_n^{(k)}|_{\text{av}}$, which may be interpreted more clearly for the initial states of low degeneracy. Such mapping allows us to estimate the expected total splittings $\Delta E^{(k)}$ or ΔE and characterize their spectrum. It is shown that not all the nominally admitted total splittings $\Delta\mathcal{E}^{(k)}$ or $\Delta\mathcal{E}$, determined by the modules M_k or M i.e. the second moments σ_k or σ , can actually occur. This essentially confines the set of the allowed splitting schemes and may be instructive for experimentalists.

References

- [1] Auzel F 1979 *Mater. Res. Bull.* **14** 223
- [2] Auzel F and Malta O L 1983 *J. Physique* **44** 201
- [3] Wybourne B G 1965 *Spectroscopic Properties of Rare Earths* (New York: Wiley)
- [4] Leavitt R P 1982 *J. Chem Phys.* **77** 1661
- [5] Edmonds A R 1960 *Angular Momentum in Quantum Mechanics* (Princeton, NJ: Princeton University Press)
- [6] Judd B R 1963 *Operator Techniques in Atomic Spectroscopy* (New York: Mc Graw-Hill)
- [7] Rotenberg M, Bivins R, Metropolis N and Wooten J K Jr 1963 *The 3-j and 6-j Symbols* (Cambridge, Ma: MIT Press)
- [8] Newman D J and Ng B K C (ed) 2000 *Crystal Field Handbook* (Cambridge, Ma: MIT Press) chapter 3
- [9] Burdick G W and Reid M F 2004 *Mol. Phys.* **102** 1141
- [10] Chang N C, Gruber J B, Leavitt R P and Morrison C A 1982 *J. Chem. Phys.* **76** 3877
- [11] Yeung Y Y and Newman D J 1985 *J. Chem. Phys.* **82** 3747
- [12] Rudowicz C and Qin J 2004 *J. Lumin.* **110** 39
- [13] Newman D J and Ng B K C (ed) 2000 *Crystal Field Handbook* (Cambridge, Ma: MIT Press) chapter 8
- [14] Kaplan I G 1975 *Symmetry of Many Electron Systems* (New York: Academic)
- [15] Mulak J and Gajek Z 2000 *The Effective Crystal-field Potential* (Amsterdam: Elsevier)
- [16] Nielson C W and Koster G F 1963 *Spectroscopic Coefficients for pⁿ, dⁿ and fⁿ Configurations* (Cambridge, Ma: MIT Press)
- [17] Liu G K 2005 *J. Solid State Chem.* **178** 489
- [18] Malta O L, Antic-Fidancev E, Lemaitre-Blaise M, Milicic-Tang A and Taibi M 1995 *J. Alloys Compd.* **228** 41
- [19] Antic-Fidancev E, Hölsa J and Lastusaari M 2002 *J. Alloys Compd.* **341** 82
- [20] Lavin V, Babu P, Jayasankar C K, Martin I R and Rodriguez V D 2001 *J. Chem. Phys.* **115** 10935
- [21] Jayasankar C K, Ramanjaneya Setty K, Babu P, Tröster T and Holzapfel W B 2004 *Phys. Rev. B* **69** 214108
- [22] Surenda Babu S, Babu P, Jayasankar C K, Tröster T, Sievers W and Wortman G 2006 *J. Phys. C.: Condens. Matter* **18** 1927
- [23] Leavitt R P, Gruber J B, Chang N C and Morrison C A 1982 *J. Chem. Phys.* **76** 4775
- [24] Mulak J and Mulak M 2005 *J. Phys. A: Math. Gen.* **38** 6081