The total energy splitting of ionic eigenstates
in the axial crystal fields

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Abstract

The relationship between the energy total splitting $\Delta E$ of the free-ion electron states in the axial crystal-fields and the second moment of that splitting $\sigma^2$ is thoroughly investigated. The non-Kramers and Kramers states with the quantum number $1 \leq J \leq 8$ in the axial crystal-fields of any multipolar composition but fixed $\sigma^2$ are considered. Since the crystal-field Hamiltonian $\mathcal{H}_{\text{CF}}$ is a superposition of the three effective multipoles various $\Delta E$ can correspond to a fixed $\sigma^2$ according to the resultant combination of the independent contributions. This $\Delta E$ variation range is the subject of the study. For the states under examination $\Delta E$ can take the values from $2.00\sigma$ to $3.75\sigma$, whereas the difference $\Delta E_{\text{max}} - \Delta E_{\text{min}}$, except the states with $J \leq 5/2$, amounts roughly to $\sigma$. For comparison, the one-multipolar $\mathcal{H}_{\text{CF}}$s yield accurately defined $\Delta E$ ranging from $2.50\sigma$ to $3.00\sigma$. The limitations of the allowed $\Delta E$ values exclude rigorously a number of virtually possible splitting diagrams. The documentary evidence for this restriction has been supplied in the paper collating the nominally admissible total energy splittings $\Delta \mathcal{E}$ (i.e. those preserving the $\sigma^2$) with the $(\Delta E_{\text{min}}, \Delta E_{\text{max}})$ ranges occurring in the actual axial crystal-fields. Although the $\Delta E$ unlike the $\sigma^2$ is not an essential characteristic and depends on the reference frame orientation, it is useful to know its dispersion range, particularly attempting to assign or verify complex electron spectra.

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1. Introduction

For crystal-field (CF) sublevels within any degenerate electronic state their energy center of gravity has to be preserved, i.e their first moment always equals zero. In turn, their second moment $\sigma^2$, as a rotational invariant, can serve as an appropriate measure of the real CF strength [1-5]. Comparing to $\sigma^2$ the total energy splitting of the state $\Delta E$ depending on the reference frame orientation is not in fact a marked characteristic. Nevertheless, it turns out to be really helpful to know the possible $\Delta E$ range. Such knowledge can be valuable especially for spectroscopists trying to assign the atomic spectra, as well as to verify the CF sublevels sequence. The above conditions for the first and second moments of the CF sublevels confine the range of the nominally allowed total splittings $\Delta \mathcal{E}$ and exclude some virtual splitting diagrams corresponding to the forbidden $\Delta \mathcal{E}$.

However, there appear certain additional restrictions on the total splitting $\Delta \mathcal{E}$. They result from the splitting capability of the CF Hamiltonian $\mathcal{H}_{\text{CF}}$ itself. In consequence, the range of the experimentally observed $\Delta E$ is a narrowed subrange of the nominally admissible $\Delta \mathcal{E}$. 

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The axial three-parameter $\mathcal{H}_{\text{CF}}$ in the tensor notation by Wybourne [6] will be considered

$$\mathcal{H}_{\text{CF}} = B_{20} C_{0}^{(2)} + B_{40} C_{0}^{(4)} + B_{60} C_{0}^{(6)},$$

where $B_{k0}$ are the axial crystal-field parameters (CFPs), and $C_{0}^{(k)}$ the axial components of the spherical tensor operator of the rank $k$.

On the one hand the energy of any CF sublevel is an algebraic sum of the three independent multipole contributions (i.e. the $2^{(k)}$-poles for $k = 2, 4$ and $6$). On the other hand, due to their independence resulting from the orthogonality of the relevant 3-j symbols [7,8] both the global second moment $\sigma^2$ and the partial second moments $\sigma^2_k$ are invariant with respect to the reference frame orientation. Furthermore the multipole contributions remain additive, $\sigma^2 = \sum_k \sigma^2_k$ (section 2). This is the framework determining the $\Delta E$ variation. Therefore, the problem resolves itself into the question – what is the admissible variation of the total splitting $\Delta E$ of a free ion state in the axial CFs yielding the same $\sigma^2$ but having different multipolar composition? To that end the maximal $\Delta E_{\text{max}}$ and minimal $\Delta E_{\text{min}}$ values of $\Delta E$ in combined three-multipolar axial CFs will be compared with the total splittings $\Delta E$ of the states in the individual $2^{(k)}$-pole axial fields. All the calculated $\Delta E$ are expressed in $\sigma$ units (section 5), so they are directly related to the well-defined experimental quantity $\sigma^2$. Thus, one avoids their explicite dependence on the detailed physical parameters characterizing the charge density distribution of the surroundings and the central-ion open shell. In consequence, the obtained results, particularly the ratio $\Delta E_{\text{max}}/\Delta E_{\text{min}}$, are free from the typical errors. It is easy to notice that the measure of the CF strength used in this paper is based on the produced splitting, precisely on $\sigma^2$. The conventional measure based on the CF strength $S$ or $S_k$ [1-5, 9] in view of the scalar product character of $\mathcal{H}_{\text{CF}}$ [4,5] is generally not adequate (section 3). The presented results refer to the pure Russel-Saunders coupled electronic states $|\alpha SLJ\rangle$ coming from the $2S+1L$ terms. Such states have a well-defined quantum number $J$, the degeneration $2J + 1$, and $\alpha$ stands for the remaining quantum numbers needed to determine the states completely. The calculations have been carried out for the states with $1 \leq J \leq 8$. Further extension of the analysis for the mixed states or those resulting from other couplings in the atom are feasible. To perform this it is enough to take into account the additivity of the CF effect with respect to the constituent $2^{(k)}$-poles in the $\mathcal{H}_{\text{CF}}$ and to utilize the tensor transformational properties of the states along with the standard angular momentum re-coupling techniques [7,8,10].

At the end of Discussion (section 6) a direct and instructive geometrical interpretation of the three parameter CF interaction with the effective three component multipolar electron charge distribution of the central paramagnetic ion in the three-dimensional coordinate system is revealed.
2. The axial crystal-field

The axial CF is characterized by the $C_{\infty v}$ point symmetry group. In consequence only three terms in the $\mathcal{H}_{\text{CF}}$ (Eq.(1)) from among 27 potentially possible are effective. A distinguished feature of the axial CF is the lack of mixing of the initial substates $|\alpha SLJM_J\rangle$ differing in $M_J$. It holds both for the individual $2^J(k)$-poles as well as their superpositions.

The $\mathcal{H}_{\text{CF}}$ non-zero matrix elements within the $(2J+1)$-fold $|\alpha SLJ\rangle$ state occur exclusively on the main diagonal as the algebraic sums

$$\sum_{k=2,4,6} (-1)^{J-M_J} B_{k0} \begin{pmatrix} J & k & J \\ M_J & 0 & -M_J \end{pmatrix} \left( \langle \alpha SLJ|C^{(k)}||\alpha SLJ \rangle \right),$$

where $\begin{pmatrix} J & k & J \\ M_J & 0 & -M_J \end{pmatrix}$ are the 3-j symbols [7,8,11], whereas $\langle \alpha SLJ|C^{(k)}||\alpha SLJ \rangle$ the multipolar characteristics of the state [4,6]. The total splitting $\Delta E$ of the initial state, the $B_{k0}$ CFPs, as well as sequence of the CF energy sublevels vary with the choice of the CF axis. However, the second moment of the sublevels always remains unchanged.

Since any sublevel energy is an algebraic sum of the contributions coming from the three effective multipoles one could rashly conclude that they can compensate either partially or even totally. The last extreme case would lead to the resultant spherical symmetry. This reasoning is however absolutely false since it ignores the fundamental independence of the individual additions resulting directly from the orthogonality of the corresponding 3-j symbols. These contributions transform themselves according to various irreducible representations of the $R_3$ group. For the axial CFs the relevant orthogonality property has the form [7,8]

$$\sum_{M_J} \begin{pmatrix} J & k & J \\ M_J & 0 & -M_J \end{pmatrix} \begin{pmatrix} J & k' & J \\ M_J & 0 & -M_J \end{pmatrix} = \frac{\delta(k, k')}{{2k+1}},$$

(2)

where $\delta(k, k')$ is the Kronecker delta. The orthogonality manifests itself in the additivity of the second moment:

$$\sigma^2 = \frac{1}{2J+1} \sum_k B_{k0}^2 \left( \langle \alpha SLJ|C^{(k)}||\alpha SLJ \rangle \right)^2.$$  

(3)

Such compensation can occur for an individual sublevel, but for the entire state the second moment must be conserved. In the axial CFs there exists only one difference in the splitting diagrams of the electron states $|\alpha SLJ\rangle$ between the non-Kramers and Kramers ions. For the non-Kramers case only one singlet $|M_J = 0\rangle$ appears, whereas in both cases all the remaining sublevels are always the doublets $| \pm M_J\rangle$. This is why the non-Kramers state $|J\rangle$ splits into $J$ doublets and one singlet, whereas the Kramers state $|J\rangle$ into even number $2(n+1)$ of doublets for $J = (4n+3)/2$, or into odd number of $(2n+1)$ doublets for $J = (4n+1)/2$ ($n = 0,1,2,\ldots$). The axial CFs, more precisely the
Effective axial CFs, can occur for more complex central ion coordinations due to the compensation of the off-diagonal terms in the relevant $\mathcal{H}_{\text{CFs}}$. As an example can serve here the CF of the Archimedean antiprism symmetry ($D_{4d} \equiv 82m$) [11, 12]. Such approximate antiprism symmetry is met among the uranium (4+) compounds, in particular with $O^{2-}$ or $F^{-}$ ligands [12-14]. It is worth noticing, that the hexagonal as well as trigonal (6) CFs are effectively axial for $d$-electrons.

3. The crystal-field strength

In order to compare CF splittings produced by various multipoles either individually or collectively, a universal accurate measure of the CF strength independent of the rank $k$ is deserved. Such a right measure provides the second moment of the CF sublevels within the initial state $|\alpha SLJ\rangle$. It can be defined by two equivalent ways [1-5]:

$$
\sigma^2 (|\alpha SLJ\rangle) = \frac{1}{2J+1} \sum_n [E_n - \bar{E} (|\alpha SLJ\rangle)]^2 = \frac{1}{2J+1} \sum_k S_k^2 (\langle \alpha SLJ||C^{(k)}||\alpha SLJ \rangle)^2 ,
$$

(4)

where the center of gravity of the Stark levels within the state $|\alpha SLJ\rangle$ is given by $\bar{E} (|\alpha SLJ\rangle) = \frac{1}{2J+1} \sum_n E_n$, $E_n$ is the energy of the $|n\rangle$ sublevel, and $S_k$ is the conventional CF strength of the $2^k$-pole [1-5,9] which here equals $\frac{1}{\sqrt{2k+1}} B_{k0}$. Finally, the dimensionless scalar $\langle \alpha SLJ||C^{(k)}||\alpha SLJ \rangle = A_k (|\alpha SLJ\rangle)$ [4-6] dependent only on the angle distribution of the electron density of the state $|\alpha SLJ\rangle$ and reflects its $2^k$-pole type aspherity.

Unfortunately, due to the crucial relationship $\sigma^2 = \frac{1}{2J+1} \sum_k S_k^2 A_k^2$, the second moment is the CF splitting measure that depends not only on the charge distribution surrounding the central ion (represented by the $S_k$ or CFPs), but simultaneously on the intrinsic characteristic of the state being affected by this CF impact (represented by $A_k$). The conventional measure of the CF strength [1-3,9] $S^2 = \sum_k \frac{1}{2k+1} S_k^2$, which for the axial CFPs resolves itself into the relation $S^2 = \frac{1}{5} B_{20}^2 + \frac{1}{7} B_{40}^2 + \frac{1}{13} B_{60}^2$, is generally not useful [4,5] because it ignores the scalar-product nature of Eqs (3) or (4). In the presented approach, having in mind the above limitation, the CFs have the same strength if they produce the splittings with the same second moment.

Fortunately, the CF effect of any three parameter axial $\mathcal{H}_{\text{CF}} (k = 2, 4, 6)$ can be analyzed conveniently in a three-dimensional coordinate system ($R, \theta, \phi$), which leads to an instructive geometrical interpretation (section 6). Taking the radius of the sphere $R = \sigma$, where $\sigma^2 = \frac{1}{2J+1} \sum_{k=2,4,6} \frac{1}{2k+1} B_{k0}^2 A_k^2$,
the energy of the sublevels \(|JM\rangle\) can be expressed in the form (in \(\sigma\) units):

\[
E_{JM} = (-1)^{J-M_J} \sqrt{5(2J+1)} \left( \begin{array}{ccc}
J & 2 & J \\
M_J & 0 & -M_J
\end{array} \right) \sin \theta \cos \phi \\
+ (-1)^{J-M_J} 3\sqrt{2J+1} \left( \begin{array}{ccc}
J & 4 & J \\
M_J & 0 & -M_J
\end{array} \right) \sin \theta \sin \phi \\
+ (-1)^{J-M_J} \sqrt{13(2J+1)} \left( \begin{array}{ccc}
J & 6 & J \\
M_J & 0 & -M_J
\end{array} \right) \cos \theta ,
\]

where the coordinates \(0 \leq \theta < \pi\) and \(0 \leq \phi < 2\pi\) define the multipolar superposition in the \(\mathcal{H}_{\text{CF}}\).

The first term stands for the \(2^2\)-pole (i.e. the quadrupole), the second for the \(2^4\)-pole, and the third one for the \(2^6\)-pole, respectively. Mapping the whole variation range of the \(\theta\) and \(\phi\) coordinates the upper and lower limits of the dominating absolute differences among the sublevels energies at each \((\theta, \phi)\) point can be numerically calculated. In this way we find the physically admissible maximum (\(\Delta E_{\text{max}}\)) and minimum (\(\Delta E_{\text{min}}\)) of the total splitting of the \(|\alpha SLJ\rangle\) state in the axial CFs yielding the same \(\sigma^2\).

It is also worth noticing that the presented approach avoids the direct dependencies upon \(B_{k0}\) and \(A_k\) values. In consequence, the results referring to the energy span of the electron states in the axial CFs are not burdened with typical errors introduced by \(B_{k0}\) and \(A_k\).

4. The second moment of the sublevels within the initial \(|\alpha SLJ\rangle\) state and its total nominally admissible CF splitting \(\Delta \mathcal{E}\)

The constant second moment of the CF sublevels, \(\sigma^2\), excessively narrows the range of the nominally allowed total splitting \(\Delta \mathcal{E}\) of the initial state \(|\alpha SLJ\rangle\). That limitation is different for the non-Kramers and Kramers ions. Let us also remind that not all the nominally admissible splitting diagrams can actually occur for ions in the real CFs due to a limited splitting capability of the relevant \(\mathcal{H}_{\text{CF}}\) (section 5).

Several hypothetical model energy diagrams in the axial CFs are compiled in Tables 1 and 2 to compare them with the actual splittings. The data refer to fifteen \(J\) values from 1 to 8. Table 1 encloses eight diagrams for the non-Kramers ions, whereas Table 2 seven diagrams for the Kramers systems. The schemes present the sublevels degeneration (in the parentheses), their energies expressed by the \(\Delta \mathcal{E}\) fraction, and the relevant expressions for the \(\Delta \mathcal{E}\) as a function of \(J\) with their corresponding values. Changing consistently the sign in all the three \(B_{k0}\) leads to the upside-down splitting diagrams. Comparing Tables 1 and 2 one can notice, as expected, that the total nominal splittings \(\Delta \mathcal{E}\) for the
non-Kramers ions somewhat exceed those for the Kramers ones with \( J \) numbers close to each other. By way of example, \( \Delta E_{\text{max}} \) of the \(|J = 8\rangle\) state amounts to 5.0497\( \sigma \) but only 4.0000\( \sigma \) for the Kramers \(|J = 15/2\rangle\) state. From Tables 1 and 2 results clearly the obvious inequality \( \Delta E \geq 2\sigma \). The critical equality \( \Delta E = 2\sigma \) is achieved only for the symmetric dichotomous splitting when half of the sublevels have energy \( \Delta E/2 \) and the second half \( (-\Delta E/2) \) (see e.g. diagram 2 in Table 2). Quite instructively behave also the limits of the \( \Delta E(J) \) for \( J \to \infty \). And so, on diagrams 2, 3 and 4 in Table 1, as well as on diagrams 2, 3, 4 and 5 in Table 2 the \( \Delta E \) tends to 2\( \sigma \). In contrary, it tends to infinity on diagrams 1, 6, 7 and 8 in Table 1, as well as on diagrams 1 and 7 in Table 2. The relationships \( \Delta E(J) \) for the two homogenous diagrams (5 in Table 1 and 6 in Table 2) differ but in both cases they tend to the same limit 3.4641\( \sigma \). Therefore, a question arises – can this value lie beyond the allowed range in the actual axial CFs? Anticipating the further analysis let us notice that such possibility could happen for sufficiently large \( J \) if the \( \Delta E_{\text{min}} \), i.e. the lower limit of the admissible splittings in the actual axial CFs, exceeded 3.4641\( \sigma \). For \( J = 8 \) \( \Delta E_{\text{min}} \) merely amounts to 2.4532\( \sigma \). Then, the homogenous sublevels pattern would be forbidden as not respecting the condition for \( \sigma^2 \).

In the next section we compare the nominally possible \( \Delta E \) with the actual \( \Delta E \) admissible in the axial CFs. It will allow us to estimate the scale of the restrictions imposed on the \( \Delta E \), as well as to exclude some types of the splitting diagrams.

5. Results

Table 3 comprises the physically admissible total splitting intervals \( (\Delta E_{\text{min}}, \Delta E_{\text{max}}) \) of the free-ion electron states with \( 1 \leq J \leq 8 \) for all possible superpositions of the three axial \( 2^k \)-poles in the \( \mathcal{H}_{\text{CF}} \) yielding the splitting of the constant second moment \( \sigma^2 \). The upper and lower limits of \( \Delta E \) have been calculated using Eq.(5) for the CF sublevels energy \( E_{JM}(\theta, \phi) \) in the axial fields within the three-dimensional frame based on the three \( 2^k \)-pole contributions \( (k = 2, 4, 6) \). In this method the whole digitized range of the angles \( 0 \leq \theta < \pi \) and \( 0 \leq \phi < 2\pi \) defining such multipolar composition of the superpositions is numerically swept up with the accuracy of \( \pi \cdot 10^{-4} \). The evaluation of the upper and lower limits has been facilitated by a short Fortran programme. The \( \Delta E_{\text{min}} \) calculations are somewhat more time-consuming comparing to \( \Delta E_{\text{max}} \) because of their more complex character (we are looking for the global minimum of the local maxima). In fact, the \( \Delta E_{\text{max}} \) has exclusively global character and can be easily found also analytically.

For comparison, the left side of Table 3 presents the \( \Delta E \) obtained for the pure individual CF multipoles producing the splittings of the same \( \sigma^2 \). Let us here remind that the \( \Delta E = 2\sigma \) determines the absolute minimum of the total splitting. Roughly, the values of \( \Delta E \) for the three individual
multipoles acting separately are close to each other for the fixed $J$ and vary from $2\sigma$ to $3\sigma$ when $J$ increases. These are rather moderate values somewhat lower than those characteristic for the homogenous diagrams (5 in Table 1 and 6 in Table 2). In consequence, the relevant schemes are slightly compressed with respect to the homogenous ones.

A good example of the real splitting resembling the nominal homogenous diagram is that for the system $J = 7/2$ and $k = 2$, where $\Delta E = 2.6183\sigma$ vs. $\Delta E = 2.6833\sigma$ on diagram 6 in Table 2. This analogy is confirmed by the sequence of the corresponding CF sublevels: $(2)(-0.583), (2)(-0.084), (2)(+0.251), (2)(+0.417)$, where the first bracket specifies the degeneration of the sublevel, whereas the second its energy expressed as a $\Delta E$ fraction. The splitting of clearly asymmetrical structure occurs in the system $J = 7/2, k = 6$ with $\Delta E = 2.4373\sigma$ vs. $\Delta E = 2.3094\sigma$ on diagram 7 in Table 2 with the following sublevels: $(2)(-0.644), (2)(+0.071), (2+2)(+0.356)$. In turn, the splitting of distinctly dichotomous character is met for $J = 5, k = 4$ with $\Delta E = 2.3531\sigma$ vs. $\Delta E = 2.1409\sigma$ on diagram 4 in Table 1, with characteristic sequence of the sublevels: $(2+2)(-0.500), (2)(+0.085), (2)(+0.335), (2+1)(+0.500)$. At last, the highest $\Delta E = 3.0461\sigma$ found for $J = 3, k = 6$ (Table 3) refers to the sequence of the sublevels: $(1)(-0.571), (2)(-0.172), (2)(+0.028), (2)(+0.429)$, which resembles the homogenous distribution (diagram 5 in Table 1).

Nevertheless, the problem of the main interest is the resultant effect of the three component $2^k$-poles on the states with different $J$. It manifests itself by the allowed minimal and maximal $\Delta E$ values (Table 3). The span of the range $(\Delta E_{\text{min}}, \Delta E_{\text{max}})$, apart from the trivial cases for $J \leq 5/2$, is roughly equal to $\sigma$ and slowly rises with increase in $J$. For the non-Kramers ions it attains slightly higher magnitudes. For $J = 8$ and $15/2$, the difference $\Delta E_{\text{max}} - \Delta E_{\text{min}}$ amounts to $1.2918\sigma$ and $1.1859\sigma$, respectively. When $J$ rises $\Delta E_{\text{max}}$ increases somewhat faster then $\Delta E_{\text{min}}$, and consequently the dependencies of $(\Delta E_{\text{max}} - \Delta E_{\text{min}})$ on $J$ for the non-Kramers and Kramers ions become similar.

Worthy noticing is a distinguished position of the states with $J = 4$. Apart from the $A_k$ factors related to their intrinsic genealogy these states distinguish themselves by the largest $(\Delta E_{\text{max}} - \Delta E_{\text{min}})$ difference (for $J \leq 8$), amounting to $1.4223\sigma$. Apparently, the most favorable conditions for collective interaction of the component multipoles must there occur. In the next section we collate the results gathered in Tables 1 and 2 with those from Table 3. It enables us to narrow the class of the nominally allowed CF splittings (preserving the $\sigma^2$) to the class of the actual splittings in the axial CFs.

6. Discussion

The maximal and minimal values of the nominally allowed $\Delta E$ are achieved in the axial CFs only for $J \leq 7/2$. It can be directly verified comparing the diagrams 1 and 2 in Tables 1 and 2 with the
magnitudes of $\Delta E_{\text{min}}$ and $\Delta E_{\text{max}}$ in Table 3. Beginning from $J = 4$ neither the upper limit nor the lower limit of the $\Delta E$ are attainable. A decisive criterion whether a hypothetical total energy splitting $\Delta E$ (nominally allowed) can really occur is the natural restriction $\Delta E_{\text{min}} \leq \Delta E \leq \Delta E_{\text{max}}$, for the specified $J$. From among fifteen diagrams considered in Tables 1 and 2 only four are admissible without restraint. Obviously, for the pure individual CF multipoles the relevant $\Delta E$ always lies within the range $(\Delta E_{\text{min}}, \Delta E_{\text{max}})$. The values of $J$ that disqualify the model splittings presented in Tables 1 and 2 (breaking the above inequalities) are compiled in Table 4. Therefore, some diagrams can be a priori rejected as physically unrealistic in the axial CFs. As is also seen, rather homogenous or close to them splitting diagrams are preferred.

There is an instructive geometrical interpretation of the CF sublevels energy as well as the conditions of their degeneration in the axial CFs. Let us start considering Eq.(5). This energy can be written in the following form

$$E_{JM} = a_{JM} x + b_{JM} y + c_{JM} z ,$$

where $a_{JM} = (-1)^{J-M_J} \sqrt{5(2J+1)} \begin{pmatrix} J & 2 & J \\ M_J & 0 & -M_J \end{pmatrix}$, $b_{JM} = (-1)^{J-M_J} 3 \sqrt{2J+1} \begin{pmatrix} J & 4 & J \\ M_J & 0 & -M_J \end{pmatrix}$, and $c_{JM} = (-1)^{J-M_J} \sqrt{13(2J+1)} \begin{pmatrix} J & 6 & J \\ M_J & 0 & -M_J \end{pmatrix}$ are the components of a vector associated with the coordinate frame orientation, whereas $x$, $y$, and $z$ stand for the $\vec{\sigma} = (\sigma_2, \sigma_4, \sigma_6)$ vector components in its partition with respect to the three $2^k$-poles. This is a general equation for a plane being normal to the vector $(a_{JM}, b_{JM}, c_{JM})$ and distant by $E_{JM}(a_{JM}^2 + b_{JM}^2 + c_{JM}^2)^{-1/2}$ from the reference frame origin. In this geometrical representation for a constant $\sigma^2$ refers to the fact that the whole space is reduced to the sphere $R = \sigma$. Thus, only those of the $B_{k0} \cdot A_k$ parameters (see Eq.(3)) which correspond to the intersection circles of the plane (Eq.(6)) with the sphere $R = \sigma$ fulfil the required conditions. Degeneration of the states occurs when such circles have a common point. The state of zero energy is represented by the plane passing through the $(0,0,0)$ point, therefore only the parameters corresponding to the great circles of the sphere $R = \sigma$ are then involved. Solely two linearly independent states with $E = 0$ are possible. All the remaining states with $E = 0$ should be represented by the planes belonging to the pencil whose axis is determined by the two intersection points of the two circles. However, among the reviewed states for $2 \leq J \leq 8$ no linear dependence of the vectors $(a_{JM}, b_{JM}, c_{JM})$ occurs and, in consequence, at most two-fold degeneration for $E = 0$ in the axial CFs can appear. The energy of each sublevel $E_{JM}$ is equal to the product of the distance of the relevant plane from the $(0,0,0)$ point and $(a_{JM}^2 + b_{JM}^2 + c_{JM}^2)^{1/2}$. This normalizing factor (in the plane equation) is bigger than 1 for almost all the states $|J, M_J\rangle$ in the axial CFs. The exception is
the $|1, \pm 1\rangle$ state for which it amounts to $1/\sqrt{2}$, as well as the states $|3/2, \pm 3/2\rangle$, and $|3/2, \pm 1/2\rangle$ when it equals 1. It means that all the states can reach $|E| > \sigma$. From the basic reasons it is impossible in the case of the doublet within the singlet-doublet system of the state $|J = 1\rangle$. Within the whole examined range of the $J$ number the maximal value of the normalizing factor was found to be 2.6975 for the state $|8, \pm 8\rangle$. The values $|E| < \sigma$ can be achieved freely since the angle between the vectors $(a_J, b_J, c_J)$ and $(\sigma_2, \sigma_4, \sigma_6)$ forming the scalar product can vary from 0 to $\pi$ through $\pi/2$ what excludes any limitation for the $|E|$ from the bottom.

The presented paper is devoted to the splitting capability of the axial CFs. Their $\mathcal{H}_{CF}$ interaction matrices have the non-zero elements only along the main diagonal. An intriguing question arises – how the total splitting problem looks in the case of general $\mathcal{H}_{CF}$? What are then the admissible ranges of the total splitting of the electron states in various CFs producing splittings of the same second moment $\sigma^2$? As staring point of such further analysis may serve the expression for the second moment $\sigma^2 = \frac{1}{2J+1} \sum_k S_k^2 A_k^2$. It turns out that neither the rank of the $B_{kq}$ CFPs (index $k$) nor their type (index $q$) have any significance from the $\sigma^2$ viewpoint. Therefore the $\sigma^2$ is fully determined exclusively by the sum $\sum_k S_k^2 A_k^2$.

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Table 1: The nominal total energy span $\Delta \mathcal{E}$ in hypothetical splitting diagrams of $|\alpha SLJ\rangle$ states of non-Kramers ions in axial crystal-fields (degeneration of the CF sublevels is given in the round parentheses, their energy as a fraction of $\Delta \mathcal{E}$, $\Delta \mathcal{E}(J)$ values are given in $\sigma$)

| No. | Splitting diagram | Quantum number $J$ | Energy span $\Delta \mathcal{E}[\sigma]$ |
|-----|-------------------|--------------------|----------------------------------------|
| 1   | maximum $\Delta \mathcal{E}$ | 1                  | 2.1213                                 |
|     |                   | 2                  | 2.7386                                 |
|     |                   | 3                  | 3.2404                                 |
|     |                   | 4                  | 3.6741                                 |
|     |                   | 5                  | 4.0620                                 |
|     |                   | 6                  | 4.4159                                 |
|     |                   | 7                  | 4.7434                                 |
|     |                   | 8                  | 5.0497                                 |
| 2   | minimum $\Delta \mathcal{E}$ | 1                  | 2.1213                                 |
|     |                   | 2                  | 2.0412                                 |
|     |                   | 3                  | 2.0209                                 |
|     |                   | 4                  | 2.0124                                 |
|     |                   | 5                  | 2.0082                                 |
|     |                   | 6                  | 2.0058                                 |
|     |                   | 7                  | 2.0043                                 |
|     |                   | 8                  | 2.0034                                 |
| 3   | $J$ even          | 2                  | 2.2361                                 |
|     |                   | 4                  | 2.1213                                 |
|     |                   | 6                  | 2.0819                                 |
|     |                   | 8                  | 2.0616                                 |
| 4   | $J$ odd          | 1                  | $-$                                    |
|     |                   | 3                  | 2.2913                                 |
|     |                   | 5                  | 2.1409                                 |
|     |                   | 7                  | 2.0918                                 |
Table 1 - cont.

| No. | Splitting diagram | Quantum number \( J \) | Energy span \( \Delta \mathcal{E}[\sigma] \) |
|-----|-------------------|-------------------------|-------------------------------------|
| 5   | homogenous splitting † | 1 | 2.1213 |
|     | \[ (2) , \quad \frac{J}{2J+1} \] | 2 | 2.6726 |
|     | \[ (2) , \quad \frac{J}{2J+1} + \frac{1}{2} \] | 3 | 2.9122 |
|     | \[ (2) , \quad \frac{J}{2J+1} + \frac{1}{2} \] | 4 | 3.0426 |
|     | \[ (1) , \quad -\frac{J}{2J+1} \] | 5 | 3.1239 |
|     | \[ (2) , \quad \frac{J}{2J+1} - \frac{1}{2} \] | 6 | 3.1791 |
|     | \[ (1) , \quad -\frac{J}{2J+1} \] | 7 | 3.2189 |
|     | \[ (2) , \quad \frac{J}{2J+1} - \frac{1}{2} \] | 8 | 3.2490 |

\[ \Delta \mathcal{E} = \sigma(2J + 1)\sqrt{\frac{3J}{(J+1)(2J+J+1)}} \]

| 6   | supreme asymmetric splitting | 1 | 2.1213 |
|     | \[ (2J) , \quad \frac{1}{2J+1} \] | 2 | 2.5000 |
|     | \[ (1) , \quad -\frac{1}{2J+1} \] | 3 | 2.8577 |
|     | \[ (2J-1) , \quad \frac{1}{2J+1} \] | 4 | 3.1821 |
|     | \[ (2) , \quad -\frac{1}{2J+1} \] | 5 | 3.4785 |
|     | \[ (1) , \quad -\frac{1}{2J+1} \] | 6 | 3.7527 |
|     | \[ (2J-1) , \quad \frac{1}{2J+1} \] | 7 | 4.0089 |
|     | \[ (2) , \quad -\frac{1}{2J+1} \] | 8 | 4.2501 |

\[ \Delta \mathcal{E} = \sigma\frac{2J+1}{\sqrt{2J}} \]

| 7   | | 1 | 2.1213 |
|     | \[ (2J - 1) , \quad \frac{2}{2J+1} \] | 2 | 2.0412 |
|     | \[ (2) , \quad -\frac{2}{2J+1} \] | 3 | 2.2137 |
|     | \[ (2J - 3) , \quad \frac{2}{2J+1} \] | 4 | 2.4054 |
|     | \[ (2) , \quad -\frac{2}{2J+1} \] | 5 | 2.5927 |
|     | \[ (2J - 3) , \quad \frac{2}{2J+1} \] | 6 | 2.7716 |
|     | \[ (2) , \quad -\frac{2}{2J+1} \] | 7 | 2.9417 |
|     | \[ (2J - 3) , \quad \frac{2}{2J+1} \] | 8 | 3.1038 |

\[ \Delta \mathcal{E} = \sigma\frac{2J+1}{\sqrt{2(2J-1)}} \]

| 8   | | 1 | — |
|     | \[ (2) , \quad 1/2 \] | 2 | 2.2361 |
|     | \[ (2J - 3) , \quad 0 \] | 3 | 2.6458 |
|     | \[ (2) , \quad -1/2 \] | 4 | 3.0000 |
|     | \[ (2J - 3) , \quad 0 \] | 5 | 3.1666 |
|     | \[ (2) , \quad -1/2 \] | 6 | 3.6056 |
|     | \[ (2J - 3) , \quad 0 \] | 7 | 3.8730 |
|     | \[ (2) , \quad -1/2 \] | 8 | 4.1231 |

\[ \Delta \mathcal{E} = \sigma\sqrt{2J+1} \]

† Other diagrams with the singlet not at the bottom but in different location lead to similar \( \Delta \mathcal{E}(J) \)
Table 2: The nominal total energy span $\Delta \mathcal{E}$ in hypothetical splitting diagrams of $|\alpha S L J \rangle$ states of Kramers ions in axial crystal-fields (degination of the CF sublevels is given in the round parentheses, their energy as a fraction of $\Delta \mathcal{E}$, $\Delta \mathcal{E}(J)$ values are given in $\sigma$)

| No. | Splitting diagram | Quantum number $J$ | Energy span $\Delta \mathcal{E}[\sigma]$ |
|-----|-------------------|--------------------|----------------------------------------|
| 1   | maximum $\Delta \mathcal{E}$ | 3/2 | 2.0000 |
|     |                    | 5/2 | 2.4495 |
|     |                    | 7/2 | 2.8284 |
|     |                    | 9/2 | 3.1623 |
|     |                    | 11/2 | 3.4641 |
|     |                    | 13/2 | 3.7417 |
|     |                    | 15/2 | 4.0000 |
|     | $\Delta \mathcal{E} = \sigma \sqrt{2J+1}$ | | |
| 2   | minimum $\Delta \mathcal{E}$ | 3/2 | 2.0000 |
|     | even number of doublets | 7/2 | 2.0000 |
|     |                    | 11/2 | 2.0000 |
|     |                    | 15/2 | 2.0000 |
|     | $\Delta \mathcal{E} = 2\sigma$ | | |
| 3   | minimum $\Delta \mathcal{E}$ | 3/2 | 2.0000 |
|     | odd number of doublets | 7/2 | 2.0000 |
|     |                    | 11/2 | 2.0000 |
|     |                    | 15/2 | 2.0000 |
|     | $\Delta \mathcal{E} = \sigma \sqrt{2(2J+1)(2J+3)}$ | | |
| 4   | $\left[ \begin{array}{c} 2J+1 \\ \ \ 2J-1 \end{array} \right]$, 1/2 | 5/2 | 2.4495 |
|     | (2) | 9/2 | 2.2361 |
|     | $\left[ \begin{array}{c} 2J-1 \\ \ \ 2J+1 \end{array} \right]$, -1/2 | 13/2 | 2.1605 |
|     | $\Delta \mathcal{E} = 2\sigma \sqrt{2J+1 \over 2J-1}$ | | |
| 5   | $\left[ \begin{array}{c} 2J+1 \\ \ \ 2J-3 \end{array} \right]$, 1/2 | 3/2 | 2.4495 |
|     | (2) | 7/2 | 2.2361 |
|     | $\left[ \begin{array}{c} 2J-3 \\ \ \ 2J+1 \end{array} \right]$, -1/2 | 11/2 | 2.1605 |
|     | $\Delta \mathcal{E} = 2\sigma \sqrt{2J-1 \over 2J-3}$ | | |
| No. | Splitting diagram | Quantum number $J$ | Energy span $\Delta \mathcal{E}[\sigma]$ |
|-----|------------------|------------------|------------------|
| 6   | homogenous splitting |                 |                  |
|     | $6$ |                  |                  |
|     | $[\begin{array}{c} 2 \end{array}, \frac{1}{2}]$ | $3/2$ | $2.0000$ |
|     | $\vdots$ | $5/2$ | $2.4495$ |
|     | $(2), \frac{-1}{2} + \frac{1}{2J-1}$ | $7/2$ | $2.6833$ |
|     | $(2), \frac{-1}{2} + \frac{2}{2J-1}$ | $9/2$ | $2.8284$ |
|     | $\vdots$ | $11/2$ | $2.9279$ |
|     | $[\begin{array}{c} 2 \end{array}, \frac{-1}{2}]$ | $13/2$ | $3.0000$ |
|     | $\Delta \mathcal{E} = 2\sigma \sqrt{\frac{3(2J-1)}{(2J+3)}}$ | $15/2$ | $3.0551$ |
| 7   | supreme asymmetric splitting |                 |                  |
|     | $7$ |                  |                  |
|     | $[\begin{array}{c} 2J-1 \end{array}, \frac{2}{2J+1}]$ | $3/2$ | $2.0000$ |
|     | $(2), \frac{-2}{2J-1}$ | $5/2$ | $2.1213$ |
|     | $\vdots$ | $7/2$ | $2.3094$ |
|     | $[\begin{array}{c} 2 \end{array}, \frac{-2}{2J+1}]$ | $9/2$ | $2.5000$ |
|     | $\vdots$ | $11/2$ | $2.6833$ |
|     | $[\begin{array}{c} 2 \end{array}, \frac{-2}{2J+1}]$ | $13/2$ | $2.8577$ |
|     | $\vdots$ | $15/2$ | $3.0237$ |
Table 3: The total splittings $\Delta E$ of $|\alpha SLJ\rangle$ states in axial $\mathcal{H}_{\text{CF}}$s yielding constant $\sigma^2$. Comparison of the $(\Delta E_{\text{min}}, \Delta E_{\text{max}})$ ranges for the $2^k$-pole superpositions with the $\Delta E$ values for the pure component multipoles (all values are given in $\sigma$)

| Quantum number | $k = 2$ | $k = 4$ | $k = 6$ | $\Delta E_{\text{min}}$ | $\Delta E_{\text{max}}$ |
|----------------|---------|---------|---------|--------------------------|--------------------------|
| $J$ $\frac{3}{2}$ | 2.1213  | —       | —       | 2.1213                   | 2.1213                   |
| 1              | 2.0000  | —       | —       | 2.0000                   | 2.0000                   |
| 2              | 2.3906  | 2.6725  | —       | 2.0413                   | 2.7385                   |
| 3/2            | 2.4056  | 2.3148  | —       | 2.1213                   | 2.4495                   |
| 2              | 2.5984  | 2.7717  | 3.0461  | 2.0208                   | 3.2403                   |
| 3              | 2.6183  | 2.5074  | 2.4373  | 2.0000                   | 2.8284                   |
| 4              | 2.7351  | 2.6154  | 2.8317  | 2.0802                   | 3.5025                   |
| 4              | 2.7528  | 2.3651  | 2.5848  | 2.1820                   | 3.1424                   |
| 5              | 2.8307  | 2.3531  | 2.6302  | 2.2186                   | 3.3534                   |
| 5              | 2.8444  | 2.5544  | 2.8953  | 2.3075                   | 3.3182                   |
| 6              | 2.9007  | 2.6944  | 2.9641  | 2.3350                   | 3.4603                   |
| 7              | 2.9125  | 2.7883  | 2.8964  | 2.3710                   | 3.4518                   |
| 8              | 2.9551  | 2.8478  | 2.8656  | 2.4081                   | 3.6067                   |
| 9              | 2.9640  | 2.8812  | 2.9306  | 2.4293                   | 3.6152                   |
| 10             | 2.9975  | 2.8957  | 2.9004  | 2.4532                   | 3.7450                   |
Table 4: The $J$ values disqualifying the model splitting diagrams in axial crystal-fields, $\Delta \mathcal{E} < \Delta E_{\text{min}}$ or $\Delta \mathcal{E} > \Delta E_{\text{max}}$

| Splitting diagram | Table 1 (non-Kramers ions) | Table 2 (Kramers ions) |
|-------------------|-----------------------------|-------------------------|
| 1                 | $J \geq 4$                  | $J \geq 9/2$            |
| 2                 | $J \geq 5$                  | $J = 7/2, 11/2, 15/2$   |
| 3                 | $J \geq 6$                  | $J = 9/2, 13/2$         |
| 4                 | $J \geq 5$                  | $J = 13/2$              |
| 5                 | without restraint           | $J = 11/2, 15/2$        |
| 6                 | $J \geq 5$                  | without restraint       |
| 7                 | without restraint           | without restraint       |
| 8                 | $J \geq 6$                  | —                       |
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