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Angular distribution of 4f electrons in the presence of a crystal field

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Résumé. — La répartition angulaire des électrons 4f en présence de champ cristallin a été obtenue en appliquant le formalisme des opérateurs de Stevens. En symétrie axiale, la localisation progressive des électrons 4f de l’axe z vers le plan perpendiculaire peut être corrélée avec la variation de \( M_J \), selon le signe du facteur de Stevens \( \alpha_J \). En symétrie cubique, dû au mélange des états \( |JM_J> \) dans les fonctions d’onde, la distribution angulaire consiste en plusieurs lobes, suivant leur composition réelle.

Abstract. — The angular distribution of 4f electrons in the presence of a crystal field has been derived by applying the Stevens operators formalism. For axial symmetry the progressive localization of the 4f electrons from the z-axis to the plane perpendicular may be mainly correlated with the variation of \( M_J \) according to the sign of the Stevens factor \( \alpha_J \). For cubic symmetry, due to the mixing of the \( |JM_J> \) states in the 4f wavefunctions, the angular distribution consists in several lobes depending on their actual composition.

The properties of rare-earth 4f-electrons are generally well described in the Russell-Saunders scheme by considering the set of \( 2J+1 \) functions \( |LSJM_J> \) (or \( |JM_J> \)) representing the basis of the ground multiplet with angular momenta \( L \), \( S \) and \( J \), satisfying the Hund’s rule. In a crystal this \( 2J+1 \) degeneracy of the ground multiplet is removed by the Crystalline Electric Field (CEF) due to the neighbouring charges, and split into several CEF levels according to the symmetry of the crystal [1]. The Stevens’ « operator equivalent » method [2] constitutes a very convenient technique to calculate quantitatively this effect of the crystal field, and to obtain the relative energy position of the various CEF levels as well as their nature, in particular with regard to the CEF ground state.

Owing to the mixing of the one-electron wavefunctions in the \( |JM_J> \) functions, the angular distribution of the 4f-electrons is no more described by the spherical harmonics \( Y^L_M(\theta, \phi) \). A representation in terms of « cigars » or « pancakes » has been often used for the \( |JM_J^\text{prim}> \) and \( |JM_J^\text{max}> \) states, but it is too simplistic. The aim of this paper is to show that the Stevens formalism allows a true description of the spatial distribution of the 4f-shell, in addition to the use mentioned above. This method will be applied to axial and cubic symmetries.

1. Axial symmetry.

Let us first consider the simple case where there is no mixing in the CEF wavefunctions, which are thus pure \( |JM_J> \) states. This is roughly realized in a crystal when the second-order CEF term \( B^2 \) is preponderant [3]. The corresponding total n-electron wavefunction \( \Psi_{J,M_J}(\vec{r}_1, ..., \vec{r}_n; \sigma_1 ... \sigma_n) \) in real space includes the angular \( \vec{r} \) and spin \( \sigma \) coordinates of each of the \( n \) 4f-electrons. The radial part of the wavefunctions will not be considered here since this paper is concerned only with their angular distribution. For a given \( M_J \), the probability \( P_{J,M_J}(\theta, \phi) \) of finding a 4f-electron at the angular position \((\theta, \phi)\) (in spherical coordinates) may be expanded in spherical harmonics:

\[
P_{J,M_J}(\theta, \phi) = \sum_{LM} P^L_M(J, M_J) Y^L_M(\theta, \phi)
\]

with

\[
P^L_M(J, M_J) = \int P_{J,M_J}(\theta, \phi) Y^L_M(\theta, \phi) \, d\vec{r}
\]
These expansion coefficients $P^L_{M}(J, M_J)$ may be evaluated by using the Stevens operators formalism [3]:

$$P^L_{M}(J, M_J) = e^M_L \theta_L(J) \langle J M_J | \tilde{O}^M_L | J M_J \rangle \tag{3}$$

where the $e^M_L$'s are the numerical coefficients of corresponding spherical harmonics $Y^M_L$, $\theta_L(J)$ the Stevens coefficients of rank $L$ and $\tilde{O}^M_L$ are the generalized Stevens operators [4].

The only terms in equation (3) which are non-zero are those with even $L$ and $M = 0$. For the remaining coefficients we find the following expressions:

$$P^0_0(J, M_J) = \frac{1}{4 \sqrt{\pi}}$$

$$P^2_0(J, M_J) = \frac{5}{4 \sqrt{\pi}} \alpha_J < M_J | O^2_0 | M_J >$$

$$P^2_0(J, M_J) = \frac{3}{16 \sqrt{\pi}} \beta_J < M_J | O^2_0 | M_J > \tag{4}$$

$$P^6_0(J, M_J) = \frac{1}{32 \sqrt{\pi}} \gamma_J < M_J | O^6_0 | M_J >$$

where $\alpha_J$, $\beta_J$, $\gamma_J$ are usual notations of $\theta_L(J)$ and the $O^L_M$'s are the reduced Stevens operators [3]:

$$O^L_M = \frac{1}{2}(\tilde{O}^L_M + \tilde{O}^{-L}_M). \tag{5}$$

These expressions (4) show that the angular distribution of the states $| J, M_J >$ has axial symmetry with respect to the $z$-axis. The corresponding probabilities $P_{J, M_J}(\theta)$ are given in figure 1 for various rareearths and all positive values of $M_J$ (the values $- M_J$ give the same spatial distribution as $+ M_J$).

The main feature of the curves is their growing complexity as the quantum number $J$ increases. In particular, several lobes may exist in different directions for the same $| J, M_J >$ state, the exact form of which depends on the relative magnitudes of $\alpha_J$, $\beta_J$ and $\gamma_J$. The simplest figures are those for cerium and samarium ($J = \frac{5}{2}$) and also for terbium ($J = 6$):

they are reminiscent of the usual « cigar » and « pancake» representations for the $| J, M^{\text{min}}_J >$ and $| J, M^{\text{max}}_J >$ states. In addition the reorientation of the localization of the f-electrons from about the $z$-axis to the $(xy)$ plane as a function of $M_J$ may be easily followed.

Furthermore the angular distribution of the states $| J, M^{\text{min}}_J >$ and $| J, M^{\text{max}}_J >$ may be obviously correlated with the sign of the Stevens factor $\alpha_J$ : a negative (positive) $\alpha_J$ value gives a $| J, M^{\text{max}}_J >$ state localized near the $(xy)$ plane ($z$-axis). The opposite holds for the $| J, M^{\text{min}}_J >$ state. In fact the factors $\beta_J$ and $\gamma_J$ also play a role, but their influence is weak with regard to the effect of $\alpha_J$. More precisely, the centre of gravity $Z_g$ of the upper part of each configuration $z > 0$ may be readily derived from equation 1:

$$Z_g(J, M_J) = 2 \int_{z > 0} P_{J, M_J}(\theta, \phi) \cos \theta \, d\theta$$

$$= \sqrt{\pi} \left[ \frac{P^0_0}{4} + \frac{\sqrt{5}}{4} P^2_0 - \frac{1}{8} P^4_0 + \frac{\sqrt{13}}{64} P^6_0 \right]. \tag{6}$$

It follows that, for a given rare-earth, $Z_g$ is a monotonic function of $M_J$, in a way directly related to the sign of $\alpha_J$; $P^2_0$ makes the main contribution to this variation. This result is quite consistent with a quantum approach of the nature of the ground state. Indeed, positive point charges along the $z$-axis should favour $4f$ orbitals localized near the $z$-axis, that corresponds to $| J, M^{\text{min}}_J >$ ($| J, M^{\text{max}}_J >$) as the ground state, if $\alpha_J$ is negative (positive). Precisely this ground state is predicted in crystal field theory when the second-order CEF parameter $A^2_2 \langle r^2 \rangle$ is negative, as is the case for positive point charges along the $z$-axis [3].

2. Cubic symmetry.

Let us now consider the case of a cubic symmetry. The CEF wavefunctions are no longer pure but consist of a mixing of different $| J, M_J >$. In addition a certain degeneracy may exist for some CEF levels, according to the symmetry [5]. A CEF level associated with the representation $\Gamma$ of the cubic group and having the multiplicity $m_\Gamma$ contains $m_\Gamma$ wavefunctions $\Psi_{r,i}$:

$$\Psi_{r,i} = \sum_{M_J} < J M_J | \Psi_{r,i} > | J M_J >. \tag{7}$$

For each of them the spherical harmonics expansion coefficients may be calculated:

$$P^L_{M}(\Psi_{r,i}) = \int \Psi_{r,i} |^2 Y^L_M d\theta d\phi$$

$$= \sum_{M_J M^\prime_J} < J M_J | \Psi_{r,i} > * \times$$

$$\times < J M_J | \Psi_{r,i} > P^L_{M}(J M_J; J M^\prime_J) \tag{8}$$

where

$$P^L_{M}(J M_J; J M^\prime_J) = e^M_L \theta_L(J) < J M_J | \tilde{O}^M_L | J M_J > \tag{9}$$

is obtained again by using the Stevens operators formalism [3]. According to the symmetry, the sum of all contributions to the level $\Gamma$ should be considered to exactly represent the corresponding angular distribution of $4f$-electrons:

$$P^L_{M}(\Gamma) = \frac{1}{m_\Gamma} \sum_{r,i} P^L_{M}(\Psi_{r,i}). \tag{10}$$

For cubic symmetry, only a few coefficients are non-zero, and we find the following expression for the total
probability distribution associated with the CEF level of symmetry $\Gamma$:

$$P(\theta, \phi) = P_0^0(\Gamma) \ Y_0^0 +$$

$$+ P_2^0(\Gamma) \left[ Y_4^0 + \frac{\sqrt{5}}{14} (Y_4^+ + Y_4^-) \right]$$

$$+ P_6^0(\Gamma) \left[ Y_6^0 - \frac{7}{\sqrt{2}} (Y_6^+ + Y_6^-) \right].$$

These functions are drawn in figure 2 for the rare-earth series and for all possible cubic representations $\Gamma$. Several values of the parameter $x$, in the notation of reference [5], have been selected for these levels where the exact composition of the wavefunctions is not fixed but depends on the relative strength of fourth- and sixth-order CEF parameters (described by $x$).

It is worth noting that the representation in terms of «cigars» or «pancakes» is not applicable to cubic symmetry. The actual spatial distribution of 4f-electrons consists of several lobes pointing along particular directions, according to the composition of the wavefunctions of the level considered. For instance, for $J = 5/2$ (cerium and samarium), the $Y_6^0(\Gamma^{-})$ 4f-electrons are mainly localized near the fourfold (threefold) axes, and this may be readily
correlated with the nature of the ground state obtained by starting from a simple point charge model for the crystal field [3].

Besides the connection with the nature of the ground state in presence of crystal field, the knowledge of the spatial electron density may be helpful in the interpretation of the magnetic rare-earth form factor, which can be obtained by using polarized neutrons [6]. This magnetic form factor, i.e. the Fourier transform of the magnetization density, consists of a spin and an orbital contribution and differs from the electronic rare-earth form factor. However, as a first approximation, the spin density reflects the electron density for the light rare-earths, while it is rather representative of unpaired electrons when the 4f-shell is more than half-filled [7]. Thus the asphericity of the electron density, which is described in this paper, may account, at least in part, for the anisotropy of the magnetic form factor.

A direct experimental determination of the 4f-shell electronic density, by X-ray scattering for example, seems still premature at the present time with the
conventional X-ray sources. However, new possibilities, such as the synchrotron source, should possibly allow to observe in the future the 4f-shell charge density anisotropy.

In summary, we have shown how the Stevens operators formalism allows one to obtain the angular distribution of the rare-earth 4f-electrons in the Russel-Saunders scheme, according to the symmetry of their configuration within the $|J, M_J\rangle$ basis. This has been applied to axial and cubic symmetries. Such spatial distributions should be helpful in the representation of the 4f-shell configurations in presence of crystal field.

References

[4] These $\hat{O}_M^\pm$s are identical to the operators $\hat{O}_L^{\pm M}$ of the reference