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Fitting of parameters to represent the circular dichroism and transition intensities of $4f^N$–$4f^N$ transitions of lanthanide ions

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Abstract

The general problem of fitting transition intensities and circular dichroism for $4f^N$–$4f^N$ transitions in lanthanide compounds is examined. In particular, we focus on the problems of multiple minima and choice of minimization function. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

The first detailed theoretical treatments of lanthanide $4f^N$–$4f^N$ electric dipole transitions were given by Judd [1] and Ofelt [2]. Judd carried out fits to transition intensities between J multiplets. Axe [3] applied Judd's formalism to fits to intensity data for transitions between crystal-field levels. These parametrization schemes, and extensions of them, have now been applied to hundreds of data sets [4] and are a standard tool of lanthanide spectroscopy [5].

Judd's [1] J-multiplet parametrization is the most general one-electron, spin-independent, parametrization possible. However, the Judd–Axe crystal-field level parametrization contains implicit superposition-model assumptions and Newman and Balasubramanian [6] showed that this parametrization is not completely general. They introduced two different general parametrizations. One, similar to that used by Axe, but with more parameters, was adapted by Reid and Richardson [7,8] and has been widely applied [4,9–11]. The other separates the polarized intensities for different orientations of the electric vector of the radiation. This second parametrization was recently used by Burdick et al. [12] to show that there is an algebraic multiplicity which for most symmetries leads to several distinct sets of A_{tp}^{λ} intensity parameters that give identical intensities.

The equations governing the transition intensities are non-linear and to determine the parameters the spectrum must be fitted using an iterative non-linear least-squares technique [13]. The non-linearity gives rise to multiple local minima. The electric dipole intensity parameters can also be used to parametrize circular dichroism [14]. Although circular dichroism is linear in the parameters, we shall see that the introduction of a non-standard χ^2 function will produce multiple solutions.

In this paper, we focus on the fitting of intensities and circular dichroism. We discuss the problems that arise from the non-linearity of the equations and also consider the different possible choices of minimization function. We will show that the choice of minimization function has an impact on the number of local minima and the parameter values that we obtain from the fits.

2. Analysis of the equations

Our aim is to represent transition intensities between crystal-field levels of the $4f^N$ configuration by a parametric model which describes the physics of the interaction between light and matter. There are two problems that arise when fitting the parameters to the observed spectrum.

The first problem, discussed by Burdick et al. [12], is that there will be ambiguities in the parameterization of the electric dipole operator since we can measure, in the case of intensities, only the square of the transition amplitude. The second problem is that the equations are non-linear so there will not be a direct transformation between the data and the parameters. The fitting technique is necessarily iterative, and there is no guarantee that we will be able to

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find the true global minimum. We will now consider these problems in turn.

2.1. Multiplicities in the parametrization

The first problem in determining intensity parameters is the algebraic multiplicity that arises from the nature of the equations themselves. This was the main result of Ref. [12] and can be summarized as follows. The transition intensity observed is proportional to sums of squares of matrix elements of the form:

$$|\langle f|D_{\mathrm{eff},q}|i\rangle|^2, \tag{1}$$

so there is ambiguity in the signs of the matrix elements. Following the work of Newman and Balasubramanian [6], Burdick et al. [12] parametrized the effective operator using a Cartesian basis, $r\in\{x, y, z\}$, as

$$D_{\mathrm{eff},r}=\sum_{\lambda l} B^{\lambda}_{lr}U^{(\lambda)}_{l}, \tag{2}$$

where the unit tensor operators $U^{(\lambda)}_{l}$ act on states of the f^N configuration. The set of parameters for each independent polarization (for example $\pi\equiv z$ and $\sigma\equiv x=y$ polarizations for uniaxial crystals) will have a sign ambiguity associated with them. The electric dipole transition operator is more commonly parameterized using an extension of the Judd–Axe parametrization [7]

$$D_{\mathrm{eff},q}=\sum_{\lambda tp} A^{\lambda}_{tp}\langle\lambda(p+q), 1-q|tp\rangle U^{(\lambda)}_{p+q}(-1)^q, \tag{3}$$

where $\lambda=2, 4, 6$, $p=\lambda$, $\lambda\pm1$, $q=0$, ±1, and $\langle\lambda(p+q), 1-q|tp\rangle$ is a Clebsch–Gordan coefficient. There are the same number of independent B^{λ}_{lr} and A^{λ}_{tp} parameters, and a straightforward transformation between them. Consequently, the sign ambiguities of the B^{λ}_{lr} will lead to several distinct sets of A^{λ}_{tp} parameters that give identical calculated intensities [5,12].

It is clear from Eq. (2) that the intensities for a single polarization may by parametrized by a subset of the full parameter set. In general, the full set of A^{λ}_{tp} parameters cannot be determined from intensities of only one polarization (e.g. σ or π).

2.2. Multiple minima and minimization functions

The second problem is that we are seeking the global minimum of a highly non-linear function. The standard function that is minimized in a least-squares fit is the Gaussian χ^2 function:

$$\chi^2_{\mathrm{G}}=\frac{1}{N-M}\sum_{i}^{N}\left(\frac{e_i-c_i}{\sigma_i}\right)^2, \tag{4}$$

where N and M are the number of data points and the number of parameters respectively, and c_i, e_i, and σ_i are the calculated intensities, experimental intensities and standard deviations for data point i. If the parametrization is linear in the parameters, the χ^2_{G} allows the fit to be written as a linear transformation between the data and the parameters which model it [13].

An alternative minimization function has often been used in the studies of transition intensities [10,15]. We refer to this as differential weighting. In this case the function to be minimized is

$$\chi^2_{\mathrm{DW}}=\frac{1}{N-M}\sum_{i}^{N}\left(\frac{e_i-c_i}{e_i+c_i}\right)^2. \tag{5}$$

The justification given for using this function is that it gives equal weighting to each experimental intensity measurement, so that the most intense transitions do not dominate. However, χ^2_{DW} is not a standard statistical function and there are some difficulties associated with its use. The terms in χ^2_{DW} can never become larger than 1, tending towards 1 when c_i approaches either zero or infinity. The nature of the function also leads to a larger number of local minima relative to fits using the χ^2_{G} function. Finally, the use of the χ^2_{DW} function can turn a linear problem, such as the fitting of circular dichroism, into a non-linear problem.

It is not necessary to use the χ^2_{DW} function in order to equally weight the data points. This result may be obtained with the χ^2_{G} function by setting the standard deviation σ_i of each data point equal to some constant fraction of the observed data (e.g. $\sigma_i=e_i$).

A serious problem for the fitting of intensities is the large number of local minima. In order to locate the global minimum it is necessary to carry out a thorough search of the parameter space. The approach we have taken is to generate random sets of starting parameters and then use a standard non-linear least squares algorithm [13] to locate the nearest local minimum. Repeating this process for several hundred initial parameter sets will eventually map out all the local minima and allow us to identify the global minimum.

2.3. Circular dichroism

Circular dichroism involves the interference between the electric and magnetic dipole operators and its effect can be described by the electric dipole parameters of (Eq. 2 or 3). For oriented crystals, circular dichroism may be measured using only *axial* polarization, so only those A^{λ}_{tp} which transform as the irrep for x, y (σ) polarization will be required. In this case is it more appropriate to use the parameterization of Eq. (2), where the electric dipole parameters are partitioned into two sets, the $\{B^{\lambda}_{l\sigma}\}$ and $\{B^{\lambda}_{l\pi}\}$.

The leading contribution to *axial* circular dichroism can be written as:

$$R_{fi}(\mathrm{axial})=-\frac{3}{2}\,\mathrm{Im}\sum_{q=\pm1}\langle f|-eD_{\mathrm{eff},q}|i\rangle\langle f|M^{(1)}_{q}|i\rangle^{*}, \tag{6}$$

where $M_q^{(1)}$ is the magnetic dipole operator and Im indicates the imaginary part [5,14]. An additional contribution comes from interference between the electric dipole operator and the electric quadrapole operator but this is generally much smaller. The inclusion of this contribution does not affect our argument.

Since $D_{\text{eff},q}$ appears linearly in Eq. (6) the circular dichroism is linear in the electric-dipole intensity parameters of Eqs. (2) or (3). This is in contrast to the intensity expression, Eq. (1), which is non-linear in the electric-dipole parameters. However, if the χ^2_{DW} function is used in the minimization calculation, the advantages of linearity are lost and many local minima arise.

3. Examples

We examine two different examples, the circular dichroism of samarium oxydiacetate and the transition intensities of neodymium-doped YAG.

3.1. Samarium oxydiacetate

Lanthanide ions in the lanthanide oxydiacetates occupy a centre of D_3 symmetry. In this point symmetry circular dichroism is allowed. If we consider *only* the circular dichroism spectrum it is possible to minimize the χ^2_{G} function by a standard linear least squares fit [13] that is effectively a transformation between the data and the parameters, yielding a single solution.

However, if the differential weighting function χ^2_{DW} is used, multiple local minima arise even though the equations governing circular dichroism (6) are inherently linear. The global minimum for this non-linear χ^2_{DW} was located by a random search of the parameter space, as described in Section 2.

The results for fits to samarium oxydiacetate (SmODA) are shown in Table 1. We show fits to the circular dichroism using both weighted ($\sigma_i = e_i$) and unweighted (σ_i constant) Gaussian fits, and differentially weighted fits. We also give the parameters that May et al. [14] derived from the intensity data. Note that the circular dichroism data can only determine the $B^\lambda_{l\sigma}$ parameters, not the full parameter set. Although there is broad agreement between the different fits, a change in minimization function results in quite large differences between the parameters.

We have discussed an example of fitting *only* to the circular dichroism spectrum to emphasize that this gives the possibility of doing a purely linear fit. In practice it is be more common to use both circular dichroism and intensity data. This gives the possibility of determining the absolute signs of the intensity parameters (see Ref. [16]). However, it is important to remember that the axial circular dichroism data only gives information on a subset of the intensity parameters.

Table 1
Intensity parameters for SmODA determined from circular dichroism and intensity data[a]

$A^\lambda_{l\sigma}$	Circular dichroism			Intensity
	GW	GUW	DW	
$B^2_{1\sigma}$	− 299	− 221	− 391	− 1195
$B^2_{2\sigma}$	− 66	− 23	− 169	− 495
$B^4_{1\sigma}$	− 208	− 558	− 101	− 550
$B^4_{2\sigma}$	− 295	− 769	7	− 1621
$B^4_{4\sigma}$	208	542	− 83	551
$B^6_{1\sigma}$	− 941	− 667	− 189	− 730
$B^6_{2\sigma}$	313	− 38	108	466
$B^6_{4\sigma}$	− 736	− 1725	− 1270	− 3531
$B^6_{5\sigma}$	352	− 310	− 210	− 875

[a] Three different fits to the circular dichroism data of May et al. [14] are given. These are: GW (Gaussian weighted), linear fit using the χ^2_{G} function of Eq. (4) with the σ_i set equal to e_i; GUW (Gaussian unweighted), linear fit with the σ_i set equal to 1; DW (differentially weighted), fit using the χ^2_{DW} function of Eq. (5). The last column is the fit of May et al. [14] to the intensity data. Parameters are in units of $i \times 10^{-13}$ cm.

3.2. Nd^{3+}:YAG

In the Nd^{3+}:YAG system, the Nd^{3+} centres have D_2 symmetry and the dipole transition operator transforms as different irreps for each of the three possible polarizations *x*,*y*,*z*. Consequently, if the general parameter set is used there will be eight distinct parameter sets that will produce identical calculated spectra [12]. However, if we restrict ourselves to parameters allowed by the superposition model (A^λ_{tp} with $t = \lambda \pm 1$) there is only one solution (up to an overall sign).

In Table 2 we list fits, using the superposition-model allowed parameters, for the two different minimization functions, χ^2_{DW} and χ^2_{G}. The former fit is similar to the fit obtained by Burdick et al. [10], Table V. The only difference is that in that paper, parameters with uncertainties greater than their values (A^2_{32}, A^6_{74}, and A^6_{76}) were set to zero. The χ^2_{G} fit gives parameters that are broadly

Table 2
The lowest minima for the superposition-model allowed parameters fitted to Nd^{3+}:YAG intensity data [10] using the χ^2_{G} and χ^2_{DW} minimization functions[a]

A^λ_{tp}	Differential	Gaussian
A^2_{32}	− 164±634	− 1507±370
A^4_{32}	1951±627	980±416
A^4_{52}	− 4160±440	− 157±500
A^4_{54}	3937±480	2386±360
A^6_{52}	917±710	− 715±656
A^6_{54}	− 7193±552	− 3820±580
A^6_{72}	1720±700	1950±556
A^6_{74}	493±794	− 3220±650
A^6_{76}	− 836±920	− 1450±650
	$\sqrt{\chi^2_{\text{DW}}} = 0.39$	$\sqrt{\chi^2_{\text{G}}} = 0.68$

[a] For the χ^2_{G} fit the σ_i are set equal to the e_i (see Eq. 4). Parameters are in units of $i \times 10^{-13}$ cm.

similar, but there are quite large differences. This clearly poses a problem for the physical interpretation of the parameters from such fits. Note that the value of χ^2_{G}, approximately double χ^2_{DW}, is expected from the definition of the functions (Eqs 4 and 5). Standard statistical theory [13] suggests that χ^2_{G} should be approximately unity for a realistic fit. In our fit, we have set $\sigma_i = e_i$, i.e. 100% uncertainty. For χ^2_{G} to be unity, the σ_i would have to be approximately 70% of the e_i. This uncertainty is too large to be realistic, suggesting that the model is not giving a good representation of the data.

In obtaining our fits we started from hundreds of starting points. Fits using the χ^2_{DW} function gave almost three times as many local minima as fits using the χ^2_{G} function (after allowance was made for the algebraic equivalence of parameter sets, as discussed in Section 2). In the χ^2_{G} fits, the global minimum was obtained in 33% of the fits, whereas for the χ^2_{DW} the global minimum was obtained in only 12% of the fits. We take this as an indication of the superiority of the χ^2_{G} minimization function.

Fits using the full set of intensity parameters were also carried out. The results were similar to Ref. [12], with $\sqrt{\chi^2_{\mathrm{DW}}} = 0.37$ and $\sqrt{\chi^2_{\mathrm{G}}} = 0.64$. As would be expected, these are smaller than the χ^2 values for the fits that use only the superposition-model allowed parameters.

3.3. Uncertainties in the data

It is of interest to investigate the effect of uncertainties in the intensity measurements on the stability and resolveability of the minima. Random Gaussian uncertainties with a standard deviation of 10% were added to the observed intensities and the intensity parameters were fitted to these altered spectra. This produced a distribution of χ^2 values. The process was repeated using the full 18 A^{λ}_{tp} and the restricted 12-parameter superposition model set.

The two χ^2 distributions are distinguishable, and are not the accidental result of the values of measurements or artifacts of the fitting process. However, the fact that the 18-parameter model gives lower χ^2 does not necessarily invalidate the superposition model, since any additional parameters will tend to reduce the χ^2 value. Other extensions to the parametrization, such as the inclusion of electron-correlation or spin–orbit interaction effects may be more important.

4. Conclusions

The equations governing transition intensities are inherently non-linear in the electric-dipole parameters, resulting in many local minima. To insure that the global minimum is found, it is necessary to exhaustively search the parameter space.

The standard Gaussian minimization function χ^2_{G} has several advantages over the differential weighting function χ^2_{DW}. The χ^2_{DW} function has non-standard statistical properties, leads to a much larger number of local minima, and turns the linear circular dichroism fit into a non-linear fit.

Different data-reduction techniques can lead to very different parameter sets. This complicates the physical interpretation of transition-intensity parameters. In comparing parameters from different experiments these variations must be taken into account.

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