Stellingen behorende bij het proefschrift

**PRECISION AND RESOLUTION IN
SPECTROSCOPIC MODEL FITTING**

door J.H. Swarte.

1

De concepten kritieke fout en kritieke energie, zoals in dit proefschrift gedefinieerd, zijn ook bruikbaar voor modelaanpassing met fouten in zowel de afhankelijke - als de onafhankelijke variabele.

2

Een belangrijk nadeel van de theorie van Unknown But Bounded Errors (UBBE) en de daaruit voortkomende 'mogelijke oplossingsverzameling' is dat niet-lineaire verschijnselen niet gedetecteerd worden. Hierdoor wordt het moeilijk eventuele a priori statistische kennis over de meetfouten te gebruiken.

Milanese, M. and Vicino, A. (1991), 'Estimation theory for nonlinear models and set membership uncertainty', *Automatica*, 27, 403-408.

3

Het gebruiken van discretiseringsschema's voor het oplossen van differentiaalvergelijkingen is geen eenvoudige, voor zichzelf sprekende bezigheid.

Stewart, I. (1992), 'Warning, handle with care', *Nature*, 355, 16-17.

4

De koppeling van de definitie van de eenheid van massa aan de De Broglie-golflengte is een goed idee. Deze definitie bevordert, onder andere, de uniformiteit binnen het *Système International*.

Wignall, J.W.G., (1992), 'Proposal for an absolute, atomic definition of mass', *Physical Review Letters*, 68, 5-8.

Het gebruik van de Discrete Fourier Transformatie (DFT) als numerieke benadering voor de continue Fourier Transformatie is vaak niet gerechtvaardigd.

'De stukken die de ministeriële bureaus verlaten, munten uit door gebrek aan styl, door slechte redactie.'
Deze uitspraak heeft nog maar weinig van haar geldigheid verloren.

Multatuli, Ideeën, uit Idee 451.

Hoe meer men leest, hoe minder men zelf bedenkt.

Het promotiereglement stelt geen eisen aan de originaliteit van stellingen behorende bij een proefschrift. Dit is terecht, want de wetenschap moet het, behalve van originaliteit, voor een belangrijk deel hebben van herhaling en bevestiging.

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Een kerk heeft geen bliksemafleider nodig.

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**PRECISION AND RESOLUTION IN
SPECTROSCOPIC MODEL FITTING**

PRECISION AND RESOLUTION IN SPECTROSCOPIC MODEL FITTING

PROEFSCHRIFT

ter verkrijging van de graad van doctor
aan de Technische Universiteit Delft,
op gezag van de Rector Magnificus, prof. drs. P.A. Schenck,
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Aan mijn ouders

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ABSTRACT

The effects of errors of observation on the solutions of spectroscopic model fitting were studied. The spectroscopic model consists of a weighted sum of peak shapes of the same nonlinearly parametric family. Three effects were distinguished: displacement of the solutions leading to imprecision, interchange of the geometrical proportions of the peaks and coincidence of the solutions preventing resolution of close peak parameters.

A hypersurface that divides the space of errors of observation into two parts is defined for each effect. Errors of observation located in the part containing the origin do not cause the effect in question, errors located in the other part do. The distance from the origin to the hypersurface is called critical norm. Errors of observation having a smaller norm can not cause the effect in question.

For least squares model fitting, the hypersurface can be approximated accurately by a hyperplane. This facilitates the decision in which part particular errors of observation are located. If the errors of observation are statistical, the probability of occurrence of the effect can easily be computed.

Numerical experiments with spectroscopic models show that the theory can easily be used in practice.

EXTENDED ABSTRACT

In this thesis a theory is developed that expresses the precision and resolution capabilities of nonlinear model fitting methods as a function of the errors of observation. Neither statistical nor asymptotical assumptions are used. The theory is valid for any number of observations and for any kind of errors of observation. The errors of observation may be either statistical, such as measurement noise or systematic, such as modeling errors. They are only assumed not to be excessively large.

It is assumed that a parametric model of the observations is available. Then, if there are no errors of observation, computation of the model parameters will be possible with infinite precision. It is the errors of observation that limit the precision and resolution of model fitting methods.

The theory is applied to nonlinear least squares fitting of *weighted sum models*, spectroscopic models in particular. These are weighted sums of functions of the same nonlinearly parametric family. They may also include an additional general function. They are then called *generalized weighted sum models*. The number of differently parameterized components is called the *order* of the model. The spectroscopic model, which consists of a sum of peak shapes and a baseline, is an example. The number of peaks is the order of the model.

The theory can be described as follows. Intuitively, problems with resolution and precision of model fitting solutions from error corrupted observations occur when two or more peaks overlap, i.e., when two or more components of the weighted sum model have nearly equal parameters. For the case of two overlapping peaks, the possible effects of errors of observation on the model fitting criterion and the model fitting solution are studied. Three effects are distinguished. They may be caused by increasing errors of observation in the following order.

First, the errors of observation may displace the solution from the exact parameter values in parameter space. This is called *displacement*. It is what is usually associated with precision. The structure and geometrical proportions of the criterion do not change. So the original global minimum remains global and the local minima remain local. Subsequently, the peak parameters in the solution may be interchanged

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compared to the exact parameters. The original geometrical proportions of the peaks are not maintained. They have been interchanged. The errors of observation made an originally local minimum the global minimum and vice versa. Consequently, the solution makes a sudden jump in parameter space as a function of the errors of observation. This is called *interchange* or *jumping*. Finally, the solutions for the individual peak parameters of two peaks may become equal to each other. They coincide. Resolution of the solutions is not obtained. In this case the structure of the criterion has changed. Two minima and a saddle point in between have degenerated into one single minimum as a function of the errors of observation. This minimum turns out to be equal to the solution of fitting a lower order model. The solution is thus of a lower order than the exact model underlying the observations. This effect is called *coincidence*.

The three effects are described mathematically. For each effect, the space of errors of observation is divided into two parts. Errors of observation located in the part containing the origin do not cause the effect. Errors of observation located in the other part do. The hypersurface separating these parts is defined mathematically. It is called the *boundary*.

The structural change of the criterion leading to coincidence is described mathematically using catastrophe theory. A discriminant that detects whether or not coincidence occurs is derived. It is called the *resolution discriminant*. The boundary associated with coincidence is also called *bifurcation set*.

Then the errors on the boundary closest to the origin are computed. These errors are called the *critical errors*, their energy *critical energy*. The critical errors and energy are a function of the exact parameters only. Errors of observation having smaller energy than the critical energy can certainly not cause the effect in question. They will be in the part of error space where the origin is.

This is certainly the most important property of the concept critical energy. It can be used in practice in two ways. Before the experiment is carried out, to test whether or not the experiment can meet the purposes. Afterwards, as a means to appreciate the solutions obtained.

An important property of critical errors associated with displacement is the following. These critical errors are not only the errors of observation having minimum energy, but they are also the errors, having a

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particular energy, causing maximum displacement in a certain direction in parameter space. Therefore, when all displacements associated with equal critical energy are selected, they enclose a region in parameter space in which all possible model fitting solutions will be located, for errors of observation having equal or smaller energy. This region containing all possible solutions is called *feasible region*.

Next, simple, approximate but accurate expressions for the critical errors and critical energy are derived. These expressions require much less computational effort than exact computation. They especially facilitate the computation of the feasible region. Furthermore, the boundaries in error space can accurately be approximated by hyperplanes defined by the critical error vectors. The inner product of errors of observation and the critical errors predicts in which part of the error space these errors of observation will be located. This rule is valid for statistical and/or systematic errors of observation and for any number of observations. For statistical errors of observation a simple scalar expression is derived that yields the probability of the solution being located in one of the two parts in error space.

Numerical experiments with spectroscopic models show the accuracy of the approximations made. Also, the practical usefulness of the theory is demonstrated by means of simulation experiments. The feasible region is demonstrated not to be overly pessimistic for statistical errors of observation, contrary to what might have been expected.

In conclusion, the concepts critical errors and feasible region are of theoretical and practical importance. Especially the approximate expressions are easy to use in practice by anyone who uses model fitting methods.

The concepts offer several opportunities for extending the range of applications. The weighted sum model may consist of other functions than of spectroscopic peaks. Examples are decaying exponentials describing radioactive decay, Gabor pulses describing sonar bursts or squared sinc functions describing diffraction patterns in optics. Moreover, the resolution discriminant, in combination with the concept critical errors, may be used as a means to decide how many components of a weighted sum model can be distinguished in the observations. Also the theory may be extended to functions of weighted sum models or weighted sum models in which the components are a function of several independent variables. An application in which both latter mentioned

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extensions are necessary is the fitting of a model to two-dimensional coherent diffraction patterns. All of the above applications are being studied at the moment.

In addition, an upper limit is derived to the displacement of the solutions of ℓ_p model fitting methods, for the fitting of general model functions. For given ℓ_p norm of the errors of observation, this upper limit defines another feasible region in parameter space in which all possible solutions are located. Simulation experiments with statistical errors of observation show that this feasible region only slightly over-estimates the displacement of model fitting solutions in practice.

PREFACE

For the convenience of the reader, the thesis has been composed in such a way that the chapters dealing with mathematical details may be skipped during a first reading without losing the thread of the thesis. These chapters are Chapters 4 and 5. In Chapter 3 the main ideas are described and in Chapter 6 the results of the mathematics and computations of Chapters 4 and 5 are summarized.

Since the analysis of spectroscopic observations has an interdisciplinary character, there is a nomenclatural problem. In the various disciplines of spectroscopy different names are used for identical concepts. For instance, the component parts of a spectrum are called peaks, lines, bands and profiles as well as model functions. The location of a peak is generally called after the physical quantity it represents: position, retention time, wavelength or frequency. In signal processing, model fitting is also called curve fitting, parameter estimation, identification as well as model regression. For each phenomenon one name is used consistently throughout the thesis. An exception is 'errors of observation', shortly called 'errors' when possible without ambiguity. When used for the first time, the names are in *italic* letter type. The Glossary summarizes the definitions and names. Furthermore, there is a list of symbols, that may be helpful to the reader. The references were, of course, the choice of the author. They are thought to be representative for the literature concerned.

INTRODUCTION

Quantitative analysis of experimental data is the subject of study in many natural and technical sciences. Examples are branches of analytical chemistry (Kowalski, 1984) such as spectroscopy (Ingle and Crouch, 1988) and chromatography (Snyder and Kirkland, 1979), nuclear magnetic resonance (Abraham, 1971), and crystallography (Stanisz et al., 1989).

Quantitative analysis of observations implies the use of a mathematical physical model of the observations. The model contains the desired physical quantities as *parameters*. Preferably it should also contain possible sources of *errors of observation*. In this thesis the availability of such a *parametric physical model* is the basic assumption. The numerical values of the desired parameters are then computed by means of *model fitting methods*. The fitting consists of varying the parameters of the model function in such a way that the model function fits best to the observations in the sense of a chosen *mathematical model fitting criterion*. The parameter values that minimize the criterion are called the *solutions*.

In *spectroscopy*, the model of observations generally consists of a sum of peaks, a baseline function and errors of observation. The model is:

$$w_n = g(x_n; \gamma) + \sum_{k=1}^K \alpha_k h(x_n; \beta_k) + \epsilon_n, \quad (1)$$

in which w_n is the n -th *observation* and x_n is the *measurement point*. There are N observations. The *peak shape* is $h(x; \beta_k)$. The $B \times 1$ parameter vector β_k contains the *peak parameters* of the k -th peak. Its components β_{ki} are, for instance, the location and width parameters of the peak. The peak shape might be a Gaussian or a Lorentzian function. In other applications, sinc functions, Gabor pulses, decaying exponentials or wavelets might be used as 'peak shapes'. The parameter α_k is the *amplitude* of the peak. It is assumed to be positive. The total number of peaks K is called the *order* of the model. The *baseline* $g(x; \gamma)$ is parametric in the $C \times 1$ vector γ . The parameters γ , α_k and β_k are called the *exact parameters*. The *errors of observation* are ϵ_n . They may be

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statistical or systematic. The latter are, for instance, modeling errors. Observations for which all errors are zero are called exact.

The aim of spectroscopic analysis is to get numerical values from the observations for the physical quantities represented by the exact parameters γ , α_k and β_k . These numerical values are obtained by minimizing the model fitting criterion and they are called the solutions. A further important quantity is the *precision* of the solutions. Precision is associated with to what extent the solutions and the exact parameters are equal to each other. The precision of the solutions depends on the errors of observation. If there are no errors of observation, the solutions can be computed with an infinite precision. They are then equal to the exact parameters γ , α_k and β_k .

Closely connected with the precision of the solutions is the problem of *resolving* the solutions for peaks with nearly equal peak parameters β_k , for instance, the location parameters of overlapping peaks. If two peaks overlap severely, they will be very similar to one peak. Figure 1 shows an example of two overlapping peaks.

Figure 1 Severely overlapping peaks. The solid line represents the sum, the dashed ones the individual peaks.

When there are no errors of observation, there is also no limit to the resolution of the parameters. However, from error corrupted observations made on overlapping peaks it will be difficult to decide how many

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peaks are present. If it is decided that there are more than one, it will be difficult to compute the solutions for the peak parameters. Relatively small errors may prevent the resolution of overlapping peaks. *Resolution* is considered to be the ability to distinguish between two overlapping peaks that have the same peak shape, but different values for the peak parameters β_k .

Van den Bos (1980, 1981, 1983, 1984, 1987, 1988) discovered that errors of observations may structurally change the model fitting criterion for weighted sum models. This structural change causes the solutions for *scalar* peak parameters β_k to *coincide*. In this way resolution of the solutions for the peak parameters is prevented by the errors of observation. He also derived a discriminant that detects whether or not resolution is possible for a particular set of observations and the use of a particular model fitting method. This so-called *resolution discriminant* is a function of the errors of observation. He arrived at these results by studying the model fitting criterion and the model fitting solution as a function of the errors of observation. These results are the starting point for the work in this thesis.

The purpose of this thesis is to describe the influence of additive errors of observation on the precision and on the resolution of model fitting methods. In particular, the precision and resolution of least squares model fitting applied to spectroscopic observations are considered.

The possible structures and the geometric proportions of model fitting criteria for spectroscopic models are studied as a function of the errors of observation. Then conditions are defined for such errors of observation causing a solution that may be considered meaningless. Each condition defines a *boundary* that divides the space of errors, the *error space*, into two parts. In the one part, the errors cause the meaningless solution. In the other part the errors do not. Since the origin of error space corresponds to exact observations, the origin is in the latter part. Moreover, an expression is derived for those errors that both yield the meaningless solution and have minimum norm. These errors are called the *critical errors*. Their norm is called *critical norm*.

The concepts critical errors and critical norm can be used as a practical measure for the influence of the errors of observation on the

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precision and resolution of model fitting methods. It is certain that errors having a smaller norm than the critical norm can not cause the meaningless solutions. Therefore, a meaningful solution is guaranteed when the errors of observation have a smaller norm. An experimenter who has a priori knowledge about the norm of the errors of observation is thus able to judge whether or not the experiment will be good enough to meet the purposes.

The critical errors are computed for least squares model fitting. A rule is derived that predicts in which part of the error space particular errors are located. Applications of the theory are studied for least squares model fitting of spectroscopic peaks such as Gaussian, Lorentzian and Voigtian peaks.

It is emphasized that no assumptions on the number of observations nor on the nature of the errors are necessary. Neither asymptotic nor statistical arguments are used. However, if a priori knowledge about the errors of observation is available, this can be incorporated.

The build-up of the thesis is as follows. Chapter 1 provides a short review of the traditional methods used in spectroscopic analysis. It also discusses the use of model fitting in spectroscopy and briefly reviews the peak shapes used in various branches of spectroscopy. Chapter 2 deals with the definitions and principles of model fitting. Chapter 3 starts with a short overview of theories from the literature on model fitting and the influence of, mostly statistical, errors of observation on the precision of the solutions. Then the main ideas of this thesis are described qualitatively, without mathematical detail. Chapter 4 is concerned with the mathematical formulation of the conditions for the boundaries in error space and with the computation of the critical errors. Chapter 5 deals with the computation of the critical errors and critical norm for the least squares criterion. Furthermore, the rule is derived that predicts in which part of the error space particular errors are located. Chapter 6 starts with a summary of the results of Chapter 4 and 5. Then the application of the theory to spectroscopic models is described. This chapter may be considered the most important one for the user of spectroscopic model fitting methods. Chapter 7 discusses the possibilities and the problems of the theory. Moreover, possible theoretical extensions and their applications are described. Chapter 8 contains the conclusions. Appendix A describes

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some properties of spectroscopic peak shapes, while Appendix B contains the derivation of the resolution discriminant. Finally, Appendix C describes some curiosities from the literature.

This chapter gives an overview of techniques used in the analysis of spectroscopic observations. These techniques are divided into two groups. Traditional techniques on the one hand, model fitting methods on the other. The advantages and disadvantages of the traditional techniques are discussed in Section 1.2, while model fitting is discussed in Section 1.3. It will be seen that the latter technique is favored by the author. Therefore, Section 1.4 discusses the most commonly used models for the peak shapes.

1.1 Introduction

The aim of spectroscopy is generally to identify and/or quantify the component parts of a material sample. The interaction between the component parts of the sample and the experimental setup produces the observations. These observations are called the *spectrum*. The spectrum generally consists of the so-called spectroscopic peaks, a baseline and errors of observation. The spectrum is analyzed by the experimenter in order to determine quantities such as the locations and areas of peaks. These quantities may correspond to physical quantities such as frequencies of electromagnetic waves, retention times, the total number of measured events or the concentration. The composition of the sample is determined from these quantities. Problems with the analysis of the spectrum may occur when there are errors of observation and when peaks overlap severely. Throughout the thesis, a spectrum is considered an x-y plot of location and amplitude. In figure 1.1 a typical example of a spectrum has been sketched.

Figure 1.1 *An example of a spectrum.*

The analysis of a spectrum can be carried out in various ways. The way chosen depends on the required precision and resolution and on the availability of proper instruments and computing methods. In Section 1.2 various traditional techniques that are widely used for the determination of the physical quantities and for the resolution of overlapping spectroscopic peaks are reviewed briefly. These techniques do not make use of a parametric model of the observations and are more or less based on intuition. Therefore, they are not sufficient when high precision and resolution are required. In this case, the use of a parametric physical model of the observations and of a model fitting method is necessary. A discussion of present applications of model fitting methods in spectroscopy is presented in section 1.3. In section 1.4 various models for peak shapes are described.

1.2 Analysis of spectra by means of traditional techniques

Though a parametric physical model of the observations is not used in the traditional kinds of spectroscopic analysis, it is assumed that the observations reflect the relevant physical properties. For instance, the location of the maximum of the peak corresponds to the frequency of

the radiation, the area of the peak to the number of events. The techniques described below are: geometrical techniques, the Rayleigh criterion, computation of the 'resolution', shoulder detection, second-order derivative methods and the discrete Fourier transform. The most obvious techniques are direct measurements from the spectrum, so-called geometrical techniques.

Geometrical techniques

If the demands concerning the precision of the results are not high, if the model of the observations is not exactly known or if there are no computing facilities, geometrical techniques may yield satisfactory results. A simple measurement with a graduated ruler, for instance, yields the location of the maximum of a peak. For the determination of the area various approximate geometrical integration methods exist (Dyson, 1990). Figure 1.2 shows an example of approximate peak integration requiring only a ruler.

Figure 1.2 *Approximate integration of a peak by means of triangularization. The area of the peak is approximately equal to the product $OP \cdot OL$.*

CHAPTER 1

In older days when the observations were plotted on paper by an x-y plotter, the peaks were cut out and weighed to determine the area of the peaks. Nowadays microcomputers facilitate the use of numerical integration and differentiation techniques. With these techniques the area and maxima of the peaks are easily computed.

A disadvantage of these geometrical techniques is that they will easily fail if the spectrum contains overlapping peaks. Moreover, they do not resolve overlapping peaks. In order to resolve overlapping peaks several tricks are used. The most obvious one is inspecting the spectrum visually, deciding how many peaks are present and then determining the desired quantities in some way or another. Some techniques that are used to decide how many peaks are present and are described below. The best known is the use of the Rayleigh criterion.

The Rayleigh criterion

The the Rayleigh criterion (Rayleigh, 1899; Jansson, 1984) is often used as a criterion for the limit of resolution. According to the criterion, resolution of two overlapping peaks is not fairly possible whenever the amplitude drop in between the maxima of a spectrum of two overlapping peaks is less than 19% of the maximum value. Figure 1.3 shows two overlapping Gaussian peaks with an amplitude drop of 19%.

Although it is no fundamental limit to the resolution, as is also indicated by the term 'superresolution' in the literature (Jansson, 1984), the criterion was useful in the days of Lord Rayleigh. He tried to distinguish two overlapping squared sinc peak shapes of a diffraction pattern. He concluded that the human visual system could fairly distinguish the two peaks until the main lobe of the one peak coincided with the first minimum of the other. This corresponds to an intensity drop of 19% of the maximum intensity. So, the Rayleigh criterion reflects rather a limitation of the human visual system than a fundamental limit to the resolution. Modern intensity measurement can do much better than the human visual system and consequently the resolution is much better. In fact, as stated in the Introduction, there is no limit to the resolution when there are no errors of observation and when the parametric model of the observations is available. In figure 1.4 part of the original paper of Lord Rayleigh has been reproduced.

Figure 1.3 Overlapping peaks with a 19% amplitude drop, corresponding to the Rayleigh criterion.

Let us now consider the distribution of brightness in the image of a double line whose components are of equal strength and at such an angular interval that the central line in the image of one coincides with the first zero of brightness in the image of the other. In fig. 1 the curve of brightness for one component is $ABCD$, and for the other $OA'C'$; and the curve representing half the combined brightnesses is $EBEF$. The brightness (corresponding to B) midway between the two central points A, A' is $\cdot 8106$ of the brightness at the central points themselves. We may consider this to be about the limit of closeness at which there could be any decided appearance of resolution. The obliquity corresponding to $u = \pi$ is such that the phases of the secondary waves range over a complete period, i.e. such that the projection of the horizontal aperture upon this direction is one wave-length. We conclude that a double line cannot be fairly resolved unless its components subtend an angle exceeding that subtended by the wave-length of light at a distance equal to the horizontal aperture*.

Figure 1.4 Part of the paper by Lord Rayleigh.

CHAPTER 1

'Resolution'

'Resolution' is defined in different ways in spectroscopy (Jansson, 1984; Schoenmakers, 1986; Dyson, 1990; Snyder and Kirkland, 1979). One definition is:

$$R = \frac{2 \Delta}{w_1 + w_2}, \quad (1.1)$$

in which R is the 'resolution', Δ is the separation between the maxima of the peaks and w_1 and w_2 are the widths at half maximum of the peaks. The respective authors all wish the number R to be as high as possible, since then the peaks can easily be resolved. Snyder and Kirkland (1979) state that for fair resolution of overlapping peaks the 'resolution' should be larger than about 0.7. The main disadvantage of the use of 'resolution' as defined above is its arbitrariness and its superfluity. When the 'resolution' can be computed with a certain precision, the peaks have already been resolved with certain precision. After all, the definition of 'resolution' contains the desired physical quantities such as the width and location of the peaks.

Shoulder detection

A technique for resolving overlapping peaks is to look for shoulders in the spectrum. A *shoulder* is said to be present when there are two points of inflection at the same decreasing 'branch' of the spectrum. The idea is that there are at least two peaks present when a shoulder is detected. A shoulder can be detected visually or by computing the (approximations of) derivatives of the observations. If two peaks overlap so much that there is just no dip between the maxima anymore, only one point of inflection is visible. This defines the *shoulder limit*. It is defined as a horizontal point of inflection. The first- and second-order derivatives of the observations at this point with respect to the location are thus simultaneously zero (Maddams, 1980). Figure 1.5 shows a spectrum of two overlapping peaks at the shoulder limit.

Figure 1.5 The shoulder limit. The sum (solid), individual peaks (dash-dot) and the scaled first-order derivative of the sum (dashed).

Second-order derivative technique

The use of the second-order derivative of the observations for detecting a shoulder in the spectrum led to a different use of the second-order derivative. The finding that the second-order derivative with respect to the independent variable of a peak shape has a minimum at the location of the maximum of the peak has led to looking for minima of the second-order derivative of the exact spectrum (Painter et al., 1981; Maddams, 1980; Holler et al., 1989). The locations of these minima are supposed to coincide with the maxima of the component peaks. This is true for single, symmetric and non-overlapping peaks. However, if the peaks overlap, the minima of the second-order derivative and the maxima of the exact spectrum do not exactly coincide and neither of them coincides exactly with the maxima of the component peaks. Figure 1.6 shows a spectrum of two overlapping peaks and the second order derivative. The maximum of the spectrum is indicated by T, the minimum of the second-order derivative by M and the location of one of the peaks by μ . It is clear that they do not coincide. In fact, if the

peaks overlap severely there is only one minimum in the second-order derivative. For Gaussian peaks of the same height and width, this happens when the peaks are separated by about 0.65 times the halfwidth (Maddams, 1980). Therefore, the peaks can not be resolved by looking for a minimum in the second-order derivative of the exact spectrum. Furthermore, possible errors of observation will disturb the determination of the derivatives severely.

Figure 1.6 *Spectrum of two equal overlapping Gaussian peaks together with the second-order derivative.*

Although these serious disadvantages have been noticed, they are not considered decisive for not using the technique (Maddams, 1980). Figure 1.7 shows an example of how a spectrum consisting of overlapping peaks is resolved into separate peaks by means of the second-order derivative technique. Close inspection of figure 1.7 shows that not all minima of the second-order derivative are supposed to represent a peak. Furthermore, the difference between the location of the peak and of the minimum are not taken into account.

There is even a more fundamental objection to the use of the second-order derivative technique. Generally, only a finite number of observations at discrete points is available, making it simply impossible to determine a derivative of the observations. The derivative is not defined for discrete functions.

Bottom: infrared spectrum between 1800 and 1500 cm^{-1} of a vitrinite concentrate, PSMC 49 [88.3% carbon (dmmf)], with individual curve-resolved bands. Top: second derivative of spectrum.

Figure 1.7 An example of the use of the second-order derivative technique (Painter et al. 1983).

The feelings of some users of the second-order derivative technique have been summarized in an answer I received after sending a letter to the editor of *Analytical Chemistry*, a major journal in analytical chemistry. In this letter I expressed my doubts about the use of the second-order derivative technique as a means to resolve overlapping peaks, and I mentioned the above disadvantages. The answer contained the following arguments as a justification for the use:

'Data processing based on second derivatives is a well established technique. There are many excellent books and articles written on this topic. The quantitative relationship between the original data and the second derivative form is rigorous mathematically. It is true that errors are introduced due to noise in the data. However, the magnitudes of such errors can be independently estimated. So the approximations do not necessarily invalidate the utility of this data processing technique.'

It may be commented that the answer starts with two subjective remarks. Then the editor apparently refers to a definition of the second-order derivative of a discrete function. This definition is not known to me. Finally, he writes something really interesting, namely

that the influence of the errors can be *independently* estimated. If 'estimate' means more than 'guess', he would do well to tell us how and why.

Discrete Fourier Transform

The final technique discussed here is the discrete Fourier transform (DFT). The spectroscopic observations are transformed according to the DFT and the transformed observations are inspected and used for analysis (Ferraro and Basile, 1985; Marshall and Verdun, 1990). The reason for using the DFT is that the original observations seem more difficult to interpret visually than the transformed observations. For instance, decaying oscillating signals become peak-like signals under transformation.

Most users of the DFT tacitly assume that the DFT is a good approximation of the continuous Fourier transform. The continuous model function in the original domain has a continuous Fourier transform. This transform can be computed analytically, under the assumption that the measurement points in the model run from minus to plus infinity. The resulting function may be more easily interpreted visually than the original model.

Using the DFT of the observations as an approximation for the continuous Fourier transform of the exact observations, however, has several disadvantages. First, in practice, the measurement points do not run from minus to plus infinity. Secondly, the exact observations are generally not a continuous function, but discrete samples. The exact observations are the product of the continuous model and a number of delta functions. The Fourier transform of this product is equal to the DFT of this product. However, according to the convolution theorem (Papoulis, 1962), this DFT is the convolution of the Fourier transform of the model function and the Fourier transform of the delta functions. Therefore, the numbers computed by the DFT are not equal to samples of the continuous Fourier transform of the model function. The sampling of the measurement points has a large influence on what is obtained as a DFT. Undesirable effects like 'aliasing' and 'leakage' may occur. Finally, the errors of observation are also transformed and this may cause unexpected effects.

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So, opposite to what is usually the purpose of the use of the DFT, the transformed observations are difficult to interpret. What meaning can be given to the transformed observations, other than that they are a one to one function, namely the DFT, of the original observations? If there is a model of the original observations, it is obvious to use this model and the original observations and not their transforms for the analysis of the spectrum. It is no use transforming the observations if nothing is gained.

The DFT, which is in fact least squares estimation of the Fourier coefficients of the observations (Van den Bos, 1989), may be a useful tool for developing a model of the process underlying the observations. However, the use of the transformed observations for computing numerical values for the physical parameters is not advisable. The answer I received to a letter sent to Applied Spectroscopy, a major journal in spectroscopy, in which these disadvantages of using a DFT for quantitative spectroscopic analysis were discussed, was the following:

'Thank you for your comments. I am sure over 10.000 owners of Fourier Transform - Infra Red would be shocked to hear this observation. The fact is that FT-IR is an excellent quantitative technique. It is used today in industry laboratories, quality control and governmental laboratories. We personally use it to measure volatile organic components in the atmosphere to ppb.'

In conclusion, the traditional techniques will give satisfactory results if the required precision and resolution are not very high. However, they will not be sufficient for getting precise quantitative results and optimum resolution of overlapping peaks. The disadvantages, which are mainly due to insufficient modeling of the observations, obstruct any decisive conclusion. A common disadvantage of all traditional techniques is that they do not take into account the errors of observation. The advantages, which consist of conceptual and computational ease, become ever less relevant as a result of the development of reliable and fast computers and software. This development enables anyone to use methods that make better use of the a priori knowledge about the observations, but that require more computations. For example, model fitting methods. Commercial software for spectroscopic model fitting is available, for instance, PeakfitTM and SpectralcalcTM.

However, an important disadvantage of model fitting is the difficulty of developing a parametric physical model of the observations. The next section discusses the use of model fitting in spectroscopy and the problems connected with it.

1.3 Analysis of spectra by means of model fitting methods

With the availability of fast, reliable and cheap computers and software, the use of model fitting methods becomes more and more popular in spectroscopy. These methods require a parametric physical model of the observations. Such a model contains all available a priori knowledge about the observations. The *model function* $f(x; \theta_K)$ is:

$$f(x; \theta_K) = g(x; \gamma) + \sum_{k=1}^K \alpha_k h(x; \beta_k) , \quad (1.2)$$

in which x is the *independent variable*. The *peak shape* is $h(x; \beta_k)$. The $B \times 1$ vector β_k contains the *peak parameters* of the k -th peak. Its components β_{ki} are, for instance, the location and width of the peak. The parameter α_k is the *amplitude* of the k -th peak. It is assumed to be positive. The number of peaks K is called the *order* of the model. The *baseline* is $g(x; \gamma)$. The $T \times 1$ vector θ_K contains the parameters γ , α_k and β_k . They are called *exact parameters*. The above model function $f(x; \theta_K)$ is called a *generalized weighted sum model*. 'Weighted sum', since it consists of a sum of functions $h(x; \beta_k)$ of the same nonlinearly parametric family, weighted with the amplitude α_k . 'Generalized' since there may also be an extra function $g(x; \gamma)$ present. The peak shape may be Gaussian or Lorentzian. Or it may be a sinc, squared sinc function or an exponentially damped sinusoid. So, the generalized weighted sum model also widely applies outside spectroscopy. The model may describe observations made on bursts of sonar pulses, multi-exponential decay or diffraction patterns.

The n -th observation w_n made on (1.2) can now be described as:

$$w_n = g(x_n; \gamma) + \sum_{k=1}^K \alpha_k h(x_n; \beta_k) + \epsilon_n \quad (1.3)$$

The measurement point x_n is assumed to be known exactly. There are N observations. The errors of observation are ϵ_n . They may be statistical errors or systematic, such as modeling errors. When all errors are zero, the observations are called *exact*.

The model fitting consists of varying vector t_K , corresponding to θ_K , in such a way that the model function $f(x_n; t_K)$ fits best to the observations (1.3) in the sense of a chosen model fitting criterion. Best known is the least squares criterion. In Chapter 2 the most common model fitting methods are described.

Many books and articles were published on model fitting (Draper and Smith, 1981; Ratkowski, 1990; Seber and Wild, 1989; Gonin and Money, 1989). However, the different fields of application are virtually isolated from each other. In spectroscopy also many articles appeared about the application of model fitting. These are mostly about the application of least squares model fitting (Fraser and Suzuki, 1966, 1969; Vandeginste and De Galan, 1975; Maddams, 1980; Scheeren et al., 1985), although Volkov and Kondrashov (1988, 1989) used least moduli model fitting. Du Pont De Nemours (Jansson, 1984) introduced the 'Model 310 Curve Resolver'. This machine lets the user decide visually what is 'best' by displaying both observations and model function, while varying the parameters. If the user decides that the fit is good enough, the machine is stopped and the parameters are printed. Instead of this visual criterion, many mathematical criteria are used. These are preferable, since the solution for the parameters depends only on the chosen model fitting criterion and on the observations, but not on the mood and taste of the user. Many commercial numerical software packages include model fitting, usually least squares model fitting. Recently, some specialized software packages dealing with spectroscopic model fitting are also available. For instance, PeakfitTM and SpectracalcTM. For reasons of completeness, also the linear fitting of standard spectra from libraries is mentioned, although this will not be considered separately in this thesis.

The main advantage of fitting a parametric physical model to the observations is that there is no limit to the precision nor to the resolution, when there are no errors of observation. The solutions obtained are then equal to the exact parameters. It is the errors of observation that limit the precision. Again there is a vast amount of literature on the influence of errors of observation on model fitting

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solutions (Ratkowski, 1990; Bates and Watts, 1980; Williams, 1962). The theories developed are nearly all based on statistical and asymptotic assumptions. In Chapters 3 and 4 a different approach is described. This approach is valid for any number of observations and is not based on statistical assumptions.

In spectroscopic literature, it is realized that the errors of observation limit the resolution of overlapping peaks (Maddams, 1980; Vandeginste and De Galan, 1975). However, despite numerical studies of the influence of statistical errors in spectroscopic analysis (Statham, 1978; Maddams, 1980; Vandeginste and De Galan, 1975), there is no applicable and general theory yet. Users of model fitting methods (Jansson, 1984) discovered that a range of parameters can be considered feasible, if the peaks overlap severely and errors of observation are present. This happens because the amplitudes and peak parameters of the overlapping peaks become nearly linearly dependent. Furthermore, it may happen that an excessively small amplitude for a peak is allowed by the user. Then this peak is fitted to the errors of observation instead of to a meaningful physical phenomenon (Maddams, 1980; Gingras, 1989). These properties of spectroscopic models in model fitting play an important part in the theory that is developed in the remaining chapters.

The main disadvantage of model fitting is that the modeling of the observations may be difficult. Much effort has been and still is put in modeling the peak shapes, instrumental effects and baseline. Stacey (1989) states that in many branches of spectroscopy the measurement techniques are so well developed that statistical measurement errors will no longer be the most important, but that systematic and modeling errors will take their place.

However, model fitting is indispensable when precise quantitative results are needed. This is recognized by many spectroscopists (Holler et al., 1989), although the difficulties and pitfalls of model fitting give rise to a sceptical attitude. In my opinion, there is a persuasive argument in favor of model fitting: undisputed and objective numerical values for the physical quantities concerned can only be obtained if the relation between the observations and the physical quantities under study is known. Therefore, it is important to develop a parametric model of the observations. Only if such a model is available, precise and undisputed quantitative results can be obtained.

1.4 Peak shapes

As stated in the previous section, though it may be hard, adequate modeling of the peak shape is a necessity. Stacey (1989) writes:

'The point I want to emphasize is that to most workers in high resolution spectroscopy, particularly if they are aiming at the highest precision, the mechanisms which broaden and shift spectral lines are a NUISANCE. But since they exist, they turn any spectroscopic investigation into a line profile study.'

Ideally, the peak shape would be an impulse, but due to several effects the peak shape broadens. These effects are inherent to the experimental setup. A detailed description of the physics of these effects is outside the scope of this thesis. The common properties of peak shapes assumed in this thesis are that peak shapes have two points of inflection and vanish at plus and minus infinity. A discussion of the most frequently used peak shapes and the underlying mechanisms is presented below. These shapes do not exactly represent the underlying physics, but the effects that are taken into account are often dominant, thus yielding a numerically satisfactory description of the peak shape. The mathematical expressions for the peak shapes will now be discussed. They are summarized in Table I.

Gaussian peak shape

One of the most frequently used peaks is the *Gaussian* peak. Its peak shape $h(x; \alpha, \mu, \sigma)$ is:

$$h(x; \alpha, \mu, \sigma) = \alpha \exp \left[-\frac{1}{2} \left(\frac{x - \mu}{\sigma} \right)^2 \right], \quad (1.4)$$

in which α , μ and σ are the amplitude, location and width of the peak, respectively. The Gaussian peak shape arises in spectroscopy when electromagnetic waves are produced by many particles that move disorderly. The waves produced by a moving particle have a wavelength slightly different from the waves sent by the same particle in rest. If there was an infinite number of particles which move in all directions

uniformly with a Maxwellian velocity distribution (Hollas, 1982, 1989; Jansson, 1984; Di Bartolo, 1968), the observer would see Gaussian distributed wavelengths. This is called *Doppler broadening*. A Gaussian peak shape will also result if there are many broadening processes sequentially. A sequence of broadening processes is described by the convolution of the individual processes. The central limit theorem (Feller, 1970) states that the result of sequential convolutions approximates a Gaussian distribution, when the second-order moments of the broadening processes that are convolved exist.

In chromatography, the Gaussian peak shape is often a good first approximation of the peak shape (Schoenmakers, 1986). More detailed modeling may be necessary if the experimental circumstances require so. A modification to the Gaussian peak shape used in chromatography is the *Exponentially Modified Gaussian*. This is a convolution of a Gaussian peak shape and an exponentially decaying function. It is meant to model the dead volumes in the chromatographic system (Naish and Hartwell, 1989). Detailed modeling of the physical process in chromatographic instruments and the resulting peak shape has been carried out by Smit et al. (1980a, 1980b).

Lorentzian peak shape

The *Lorentzian* peak shape $h(x;\alpha,\mu,\sigma)$ is:

$$h(x;\alpha,\mu,\sigma) = \frac{\alpha}{1 + \left[\frac{x-\mu}{\sigma} \right]^2}, \quad (1.5)$$

in which α , μ and σ are the amplitude, location and width of the peak, respectively. It originates from the collective behavior of radiating particles and the uncertainty principle. The particles that radiate decay from a higher energy state to a lower one. Since the mean transition time is finite, the energy difference between the states and thus the wavelength of the radiation is not defined sharply. It is spread somewhat, because of the uncertainty principle. The spectroscopist observes a broadened peak which has a Lorentzian shape (Di Bartolo, 1968). This broadening is called *natural broadening*. The natural

broadening is generally small compared to the broadening caused by other effects, especially for the higher frequency radiation. Similar to natural line broadening is the effect that occurs when the particles collide with each other before they decayed. The collision causes an instantaneous transition to a lower energy level and thus decreases the mean transition time. Therefore the energy of the radiation gets less well defined and the peak broadens. The peak shape is Lorentzian again. This mechanism is called *pressure* or *collision broadening*.

Voigtian peak shape

Gaussian and Lorentzian peak shapes are the most commonly used, since in many cases the experimental setup can be arranged in such a way that one of the broadening processes concerned is dominant and others are virtually non-existent. When both Doppler broadening and collision broadening are present and important, a convolution of these peak shapes is a good approximation of the combined effects. The result of this convolution is called a *Voigtian peak shape*. (Voigt, 1912; Armstrong, 1966). The Voigtian peak shape $h(x; \alpha, \mu, \sigma_G, \sigma_L)$ is defined as:

$$h(x; \alpha, \mu, \sigma_G, \sigma_L) = \alpha \int_{-\infty}^{\infty} \frac{\exp\left[-\frac{1}{2} \left(\frac{t}{\sigma_G}\right)^2\right]}{1 + \left(\frac{x - \mu - t}{\sigma_L}\right)^2} dt, \quad (1.6)$$

in which μ is the location of the peak, α is the amplitude and σ_L and σ_G are the Lorentzian and Gaussian width parameter, respectively. The computation of this peak shape poses some difficulties, since for each point of the peak the integral has to be evaluated numerically. Many approximations of the Voigt peak have been proposed (Noll and Pires, 1980; Drayson, 1976; Klim, 1981). Hummer (1965) published a table of the Voigtian peak with eight significant figures for different values of σ_L and σ_G . An accurate and fast way of computing the Voigtian peak has been proposed by Zakaraya and Ulstrup (1988). A Voigtian peak is something in between a Gaussian and a Lorentzian peak. The latter peaks

result for the limits $\sigma_L \rightarrow 0$ and $\sigma_G \rightarrow 0$, respectively. In figure 1.8 the three peak shapes have been plotted.

Figure 1.8 Gaussian (solid), Lorentzian (dashed) and Voigtian, with $\sigma_G = \sigma_L$, (dash-dot) peaks. The peaks have the same width at half maximum.

More detailed modeling of the combined effects leads to a modified Voigtian peak shape, called the *generalized Voigt peak* (Cope and Lovett, 1987; Ward et al., 1974; Lewis, 1989)

Miscellaneous peak shapes

There are other peak shapes used that sometimes do not really have a physical background, but that describe the experimental peaks in a numerically satisfactory way. One of these peaks is the so-called *intermediate Voigt peak*. This is a linear combination of a Gaussian and a Lorentzian peak shape. Another peak that is also in between a Gaussian and a Lorentzian peak shape is the *Pearson-VII peak shape* (Pearson, 1895, Stanisiz et al., 1989). In spectroscopy a simplified form of this peak is used, defined by:

$$h(x; \alpha, \mu, \sigma) = \frac{\alpha}{\left(1 + \frac{1}{n} \left[\frac{x - \mu}{\sigma} \right]^2 \right)^n}, \quad (1.7)$$

in which n is any positive number. Notice that when $n = 1$, this is a Lorentzian peak shape. When $n = 2$, it is called *modified Lorentzian* (Stanisz et al., 1989). A third peak shape (Zypkin, 1987) that is something in between a Gaussian and a Lorentzian peak shape is defined by:

$$h(x; \alpha, \mu, \sigma) = \frac{\alpha}{\cosh^2 \left[\frac{x - \mu}{\sigma} \right]}. \quad (1.8)$$

The so-called Galatry peak (Galatry, 1961) is also used. This peak contains the Voigt peak as a special case. A method for computing this peak and thus also the Voigtian peak is described by Ouyang and Varghese (1989). Finally, the well known sinc and squared sinc functions are used in optical spectroscopy. In NMR, exponentially damped sinusoids are used. Overviews of peak shapes and the physical mechanisms involved can be found in (Allard and Kielkopf, 1982; Ingle and Crouch, 1988)

Table I shows an overview of common peak shapes. Appendix A describes some relations between the different peak shapes and mathematical properties of the individual peaks.

Table I Mathematical functions of peak shapes

Name	Mathematical function
Gaussian	$\alpha \exp\left\{-\frac{1}{2} \left(\frac{x-\mu}{\sigma}\right)^2\right\}$
Lorentzian	$\frac{\alpha}{1 + \left(\frac{x-\mu}{\sigma}\right)^2}$
Voigtian	$\alpha \int_{-\infty}^{\infty} \frac{\exp\left\{-\frac{1}{2} \left(\frac{t}{\sigma_G}\right)^2\right\}}{1 + \left(\frac{x-\mu-t}{\sigma_L}\right)^2} dt$
Intermediate Voigt	$\alpha_G \exp\left\{-\frac{1}{2} \left(\frac{x-\mu}{\sigma_G}\right)^2\right\} + \frac{\alpha_L}{1 + \left(\frac{x-\mu}{\sigma_L}\right)^2}$
Pearson VII	$\frac{\alpha}{\left(1 + \frac{1}{n} \left(\frac{x-\mu}{\sigma}\right)^2\right)^n}$
Cosh ⁻²	$\frac{\alpha}{\cosh^2\left(\frac{x-\mu}{\sigma}\right)}$

This chapter deals with the definitions and principles of model fitting. After a general introduction, least squares, least moduli and minimax model fitting are described.

2.1 Introduction

The fitting of parametric models to observations by adjusting the parameters in the model function is called *model fitting*. This adjustment is such that the model fits best to the observations in some pre-defined sense. In this thesis the model of the *observations* w_n is:

$$w_n = f(x_n; \theta) + \epsilon_n \quad (2.1)$$

in which w_n is the n -th observation, x_n is the *measurement point*, which is assumed to be known exactly. The number of *measurement points* and their values are defined as the *design* of the experiment. There are N measurement points. The function $f(x_n; \theta)$ is called the *model function*. The model function is assumed to be continuous and at least twice differentiable with respect to θ . The 1×1 vector θ is the vector of *exact parameters*. They are to be determined. They are computed by fitting model function $f(x_n; t)$ to the observations in the sense of a chosen criterion. The 1×1 *parameter vector* t is varied such that the criterion is minimized. The value $\hat{t}$ that minimizes the criterion is called the *solution*. The precise mathematical form of the criterion is defined in equation (2.6). The n -th *error of observation* is ϵ_n . The errors are additive. They may be statistical or systematic. The observations are called *exact* when all errors are zero.

When model function $f(x_n; t)$ is linear in parameter vector t , the model fitting is called *linear*. When $f(x_n; t)$ is nonlinear in one or more elements of t , the model fitting is called *nonlinear*. An example of a nonlinear model is the weighted sum model (1.2).

The *deviation* $d_n(t)$ is defined as:

$$d_n(t) = w_n - f(x_n; t) \quad (2.2)$$

The $N \times 1$ vectors of all $d_n(t)$, w_n , $f(x_n; t)$ and ϵ_n are called $d(t)$, w , $f(t)$ and ϵ , respectively. The N -dimensional linear normed space of the observations is called the *observation space*. In this space, $f(t)$ can be plotted as a function of t . It describes a T -dimensional subspace that is called the *solution locus* (Box and Lucas, 1959). For linear model functions, the solution locus is flat, for nonlinear functions it is not. The errors of observation can also be represented in this space, yet they may also be represented in a separate space, the *error space*. This is a translation of the observation space with the origin at $f(0)$. The T -dimensional space of the parameters is called *parameter space*.

As an illustration, figure 2.1 shows a two dimensional observation space and the solution locus of the model function described by (2.3). The model function $f(x_n; b)$ consists of two Gaussian peaks with only one location parameter b :

$$f(x_n; b) = 0.55 \exp(-\frac{1}{2}(x_n - b)^2) + 0.45 \exp(-\frac{1}{2}(x_n + b)^2), \quad n=1, 2. \quad (2.3)$$

Figure 2.1 Solution locus in a two-dimensional observation space. Figure a) shows the whole solution locus, while figure b) shows the part of the solution locus near the observation vector w .

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The measurement points x_n are: $x_1 = -0.8$, $x_2 = 0.6$. The observations w_n are given by:

$$w_n = 0.55 \exp(-\frac{1}{2}(x_n - \beta)^2) + 0.45 \exp(-\frac{1}{2}(x_n + \beta)^2) + \epsilon_n, \quad n=1,2, \quad (2.4)$$

in which $\epsilon_1 = 0.015$ and $\epsilon_2 = -0.03$. The value of the exact parameter β is 0.5. Therefore, the peaks overlap severely. In figure 2.1, the observations are represented by vector $\mathbf{w}$ and the errors by vector ϵ .

It is now up to the user to decide what is the best fit. Usually, the point on the solution locus, defined by $\hat{\mathbf{t}}$, that has the smallest deviation vector $\mathbf{d}(\hat{\mathbf{t}})$ from the observation vector $\mathbf{w}$ is chosen as best. The magnitude of $\mathbf{d}(\hat{\mathbf{t}})$ is measured in the sense of a suitable norm. The ℓ_p norm will be used in this thesis. The ℓ_p norm of a vector $\mathbf{d}(\hat{\mathbf{t}})$ is defined as:

$$\|\mathbf{d}(\hat{\mathbf{t}})\|_p = \left(\sum_{n=1}^N |d_n(\hat{\mathbf{t}})|^p \right)^{1/p}, \quad (2.5)$$

in which $\|\mathbf{d}(\hat{\mathbf{t}})\|_p$ denotes the ℓ_p norm of vector $\mathbf{d}(\hat{\mathbf{t}})$. The subscript p may be any real number on the interval $[1, \infty)$.

This norm is called the *model fitting criterion*. In short: *criterion*. The parameter vector $\hat{\mathbf{t}}$ that absolutely minimizes the criterion is called the *solution*. The model fitting is:

$$\underset{\mathbf{t}}{\text{minimize}} \|\mathbf{w} - \mathbf{f}(\mathbf{t})\|_p = \underset{\mathbf{t}}{\text{minimize}} \|\mathbf{d}(\mathbf{t})\|_p = \underset{\mathbf{t}}{\text{minimize}} J(\mathbf{t}). \quad (2.6)$$

Throughout, the criterion will be referred to by $J(\hat{\mathbf{t}})$. When $\epsilon = 0$, solution $\hat{\mathbf{t}}$ is equal to the exact parameter vector θ .

The usual norms are the ℓ_1 , ℓ_2 and ℓ_∞ norms. Books that deal with model fitting are Gonin and Money (1989), Draper and Smith (1981), Seber and Wild (1989) and Ratkowski (1983, 1990).

2.2 Least squares

Use of the *Euclidean* or ℓ_2 norm is called *least squares* model fitting. The criterion is :

$$J(\mathbf{t}) = \sum_{n=1}^N d_n^2(\mathbf{t}) = \sum_{n=1}^N \left(w_n - f(x_n; \mathbf{t}) \right)^2. \quad (2.7)$$

Notice that this criterion is the square of the ℓ_2 norm of $\mathbf{d}(\mathbf{t})$. The exponent $1/p = 1/2$ of the definition (2.5) is left out for convenience. The solution $\hat{\mathbf{t}}$ of $J(\mathbf{t})$ is the same as the solution of $\sqrt{J(\mathbf{t})}$. Least squares model fitting corresponds to an orthogonal projection on the solution locus. Figure 2.2. shows part of the two dimensional observation space of equation (2.4) and the solution locus of equation (2.3). It also shows $\mathbf{w}$, $f(\beta)$ and the least squares solution $f(\hat{\mathbf{b}})$.

Figure 2.2 Least squares as orthogonal projection on the solution locus.

Since the criterion is differentiable everywhere, a first-order necessary condition for the solution is that the gradient of the criterion with respect to $\mathbf{t}$ vanishes at the solution. So:

$$\left. \frac{\partial J(\mathbf{t})}{\partial t_i} \right|_{\hat{\mathbf{t}}} = 0, \quad i = 1, \dots, T. \quad (2.8)$$

These equations are called the *normal equations*. The values for $\mathbf{t}$ that satisfy the normal equations are called *stationary points* $\hat{\mathbf{t}}$. Solution $\hat{\mathbf{t}}$ is among them. A second-order necessary condition for a minimum is that the Hessian matrix H of the criterion is positive semidefinite there. The Hessian matrix H is defined as the matrix with elements

$$H_{ij} = \frac{\partial^2 J(\mathbf{t})}{\partial t_i \partial t_j}, \quad i, j = 1, \dots, T. \quad (2.9)$$

A cross-section of a typical least squares criterion has been plotted as a function of the parameter vector $\mathbf{t}$ in figure 2.3.

Figure 2.3 Cross-sectional view of the least squares criterion in the neighborhood of the solution.

The numerical minimization of the criterion is facilitated by the differentiability of the criterion and by the existence of the normal equations. Therefore, the gradient and Hessian matrix of the criterion can be made use of in minimizing the criterion. Nowadays many good methods and computer programs are available for the minimization of the least squares criterion, for instance, routines from the book Numerical

Recipes (Press et al., 1986) or the FORTRAN program Varpro (Bolstad, 1977). The latter is especially useful for fitting weighted sum models. The above explains why least squares model fitting is so popular.

If the model is linear in the parameters, the least squares solution can be expressed in closed form (Draper and Smith, 1981).

A disadvantage of least squares model fitting is its sensitivity to outliers in the observations. Since each deviation $d_n(t)$ appears quadratically in the criterion, an outlier has a large influence on the criterion. This may lead to a large error in the solution. Finally, when the errors of observation are normally distributed, the least squares method is the maximum likelihood method.

2.3 Least moduli and minimax

Least moduli

Use of the so-called *sum* or ℓ_1 norm is called the *least moduli* model fitting. The criterion is:

$$J(t) = \sum_{n=1}^N |d_n(t)| = \sum_{n=1}^N |w_n - f(x_n; t)|. \quad (2.10)$$

This criterion is not differentiable everywhere, particularly not at the minimum. Therefore, the numerical minimization of the criterion with standard methods that use derivatives of the criterion may be problematic. However, there are many other methods for solving the ℓ_1 model fitting problem. A book which covers most methods is (Gonin and Money, 1989). Busovaca (1985) deals with some of the numerical problems that may occur in minimizing the ℓ_1 criterion. A typical one-dimensional cross-section of the ℓ_1 criterion as a function of parameter vector t is shown in figure 2.4.

The use of gradient methods is possible after a reformulation of the problem as a differentiable minimization problem with inequality constraints (Overton, 1982; Van den Bos, 1988; Gonin and Money, 1989). First- and second-order necessary conditions for the latter problem have been formulated by Kuhn-Tucker (1951). The least moduli method is popular for its robustness to outliers. If the errors of observation

have a Laplacian (exponentially) distribution, least moduli model fitting is the maximum likelihood method.

Figure 2.4 Cross-sectional view of the least moduli criterion in the neighborhood of the solution.

Minimax

A third method is use of the *maximum* or ℓ_∞ norm, resulting in minimax model fitting. The criterion is:

$$J(t) = \sup_t |d_n(t)| = \sup_t |w_n - f(x_n; t)|. \quad (2.11)$$

The ℓ_∞ criterion is not differentiable everywhere, but it may also be reformulated as a differentiable minimization problem with inequality constraints (Overton, 1982; Van den Bos, 1988; Gonin and Money, 1989). The book of Gonin and Money describes many methods for solving the ℓ_∞ model fitting problem. Minimax model fitting is the maximum likelihood method when the errors of observation are distributed uniformly.

2.4 Other methods

In all the above methods a modification can be introduced, namely the assignment of a weighting factor to each observation. This results in the so-called *weighted* ℓ_p model fitting. The criterion is now:

$$J(t) = \sum_{n=1}^N \left[\left| \frac{d_n(t)}{\sigma_n} \right|^p \right]^{1/p} = \sum_{n=1}^N \left[\left| \frac{w_n - f(x_n; t)}{\sigma_n} \right|^p \right]^{1/p}, \quad (2.12)$$

where σ_n is the weight attributed to the n -th deviation. Other criteria have also been proposed, generally functions of $d_n(t)$. Special functions of $d_n(t)$, leading to *robust* model fitting, have been proposed by Huber (1981) and Zypkin (1987).

In the remainder of this thesis only ℓ_p model fitting is considered, with emphasis on least squares model fitting.

CHAPTER 3 PRECISION AND RESOLUTION; A QUALITATIVE DESCRIPTION

This chapter is concerned with a qualitative description of the influence of errors of observation on precision and resolution of solutions of model fitting methods. First, a brief survey of the existing theories about precision is presented. Most of these theories are based on statistical and/or asymptotical assumptions about the observations, which is the main disadvantage in their application. Secondly, the ideas of a new theory that does not contain the above disadvantage are explained qualitatively, i.e., without going into mathematical detail. The mathematical details are described in Chapters 4 and 5.

3.1 Introduction

The major part of the literature on precision of model fitting methods is based on statistical assumptions about the errors of observation. The model of the observations w_n is usually taken as:

$$w_n = f(x_n; \theta) + \epsilon_n, \quad (3.1)$$

in which $f(x_n; \theta)$ is the model function, parametric in θ and evaluated at x_n . The errors of observation are ϵ_n . They are assumed to be statistical. Often it is also assumed that the probability density function of the errors or some of its properties, such as the mean and the variance, are known. Two main disadvantages are connected with theories based on these assumptions. First, the theories for nonlinear model fitting will be found to be asymptotic or approximate. Secondly, the influence of systematic errors of observation, such as modeling errors, can not be investigated.

The purpose of most theories is to derive statistical properties of the model fitting solutions from the above assumptions. Often so-called *confidence regions* in parameter space are derived. A confidence region is a region in parameter space in which the solution will be located with a certain probability. Since the parameter space is often multidimensional, the construction of regions in parameter space is quite

difficult. Therefore, the projections on the axes are used as *confidence intervals*. There is a huge amount of literature on confidence regions and estimators of parameters of nonlinear models, to mention a few: (Ratkowski, 1990; Beale, 1960; Hartley, 1964; Bates and Watts, 1980, 1981; Williams, 1962)

For *linear* least squares model fitting, the statistical properties of the solution can easily be derived, since a closed form solution exists (Draper and Smith, 1981). Also the confidence region in parameter space can easily be computed. The $100(1-\alpha)\%$ confidence region for normally distributed errors (Donaldson and Schnabel, 1987) is defined by:

$$J(\mathbf{t}) - J(\hat{\mathbf{t}}) \leq p s^2 F(p, n-p, 1-\alpha) \quad (3.2)$$

in which $\hat{\mathbf{t}}$ is the least squares solution, $F(p, n-p, 1-\alpha)$ is the tabulated value of an F-distribution with numerator degrees of freedom p and denominator degrees of freedom $n-p$, $1-\alpha$ denotes the significance level and s^2 denotes the estimated variance of the errors.

However, for *nonlinear* least squares or for other model fitting methods, a confidence region is far more difficult to compute analytically. Several approximate and asymptotic statistical results are found in the literature. For nonlinear least squares model fitting the most common approximation is the linearization of the model function around the solution. Then the confidence regions are computed using the theory for linear least squares model fitting.

Since the approximations will not always be accurate, the amount of nonlinearity is measured. This is achieved by introducing the *intrinsic curvature measure* and the *parameter-effect curvature measure*. The *intrinsic curvature measure* is the curvature of the solution locus, the *parameter-effect curvature measure* is rate of change of the model function on the solution locus as a function of the parameters (Bates and Watts, 1980; Ratkowski, 1983, 1990; Draper and Smith, 1981). The smaller the curvature measures, the more accurate the linearization. Sometimes, the parameter-effect curvature measure may be decreased considerably by a transformation of the parameters, yielding better approximate confidence intervals (Bates and Watts, 1981). However, what numerical values the curvature measures should have to get acceptable results is not clear. Another important disadvantage of using

linearizations is that it hinders the detection of typical nonlinear effects.

Other methods for computing confidence intervals and statistical properties of the model fitting solution are the *lack of fit method*, the *likelihood method* (Donaldson and Schnabel, 1987), *jack-knifing* (Kendall and Stuart, 1961; Efron and Gong, 1983) and *bootstrapping* (Efron, 1982). An overview of the performance of the above methods is given in Donaldson and Schnabel (1987).

An asymptotic result for the probability density function of the nonlinear least squares solution has been derived by Jennrich (1969). For independent errors with zero mean and finite variance σ^2 , he derived that, asymptotically, the distribution of the solutions, converges in probability to a normal distribution with expectation θ and covariance matrix

$$\sigma^2 \left\{ \left(\frac{\partial f(\theta)}{\partial \theta} \right)^T \left(\frac{\partial f(\theta)}{\partial \theta} \right) \right\}^{-1}, \quad (3.3)$$

in which $f(\theta)$ is the N-dimensional vector of all $f_n(\theta)$.

In conclusion, the main disadvantages of the theories on nonlinear model fitting in the major part of literature is that their results are asymptotical and often approximate. They cover neither the case of a relatively small number of observations nor systematic errors. Also, if linearizations are used, they do not reveal typical nonlinear effects.

However, in a recent review article, Pázman (1990) presented an *approximate* probability density function for the nonlinear least squares solution computed from small samples, i.e., from a finite number of observations. In this article and in the accompanying discussions, it was emphasized that the small sample properties of estimators are worth studying more extensively.

Van den Bos (1980, 1981, 1983, 1984, 1987, 1988) did so and he discovered that the structure of the model fitting criterion for a small number of observations may change under the influence of the errors of observation, causing the solutions for different components of the weighted sum model to exactly coincide.

Furthermore, he explained why this happens by analytical computations and numerical experiments, by starting with hypothetical exact observations and then adding errors. He considered the model fitting criterion as a function of the parameters and parametric in the errors of observation.

This is the starting point in this thesis. First the possible effects of errors of observation on the model fitting criterion and solution are distinguished. Then the errors that may cause these effects are computed. It has been found that for each effect the space of errors is divided into two parts. Errors located in one part cause the effect, errors located in the other part do not.

The advantages of this approach are that the theory developed is neither asymptotic nor approximate. It is valid for any number of observations and for any kind of errors of observation. The errors may be statistical as well as systematic.

Others who also dropped the a priori statistical assumption on the errors of observation are (Fogel, 1982; Norton, 1985; Milanese and Belforte, 1980; Milanese and Vicino, 1991; Walter and Piet-Lahanier, 1990). They assumed bounded, but otherwise unknown, errors of observation. The bound on the errors may be their largest absolute value or their sum of squares. Then they derived a region in parameter space in which the parameters are compatible with the observations and the assumption about the upper bound, the so-called *feasible solution set*. So they did not use a particular model fitting method, but computed all the possible parameters, meeting the assumptions. However, Fogel (1982) derived that for linear models the feasible solution set associated with the sum of squares bound is an ellipsoid in parameter space with the *least squares* solution as center. In addition, in a recent paper Milanese and Vicino (1991) showed that the boundary of the feasible solution set for errors with bounded absolute values is the contour of the *minimax* model fitting criterion. They called their theory UBBE, which is the acronym for Unknown But Bounded Errors. The main disadvantage of UBBE is that it does not use a model fitting criterion. Therefore, if the probability density function of the errors of observation is known, it will not be possible to compute the distribution of the solutions within the feasible solution set. For instance, for

statistical errors of observation, the probability of coinciding solutions can not be computed in this case, as opposed to the theory developed in this thesis. In Chapter 7 similarities of the different theories are discussed.

In the remainder of this thesis, the criterion is considered a function of the parameters and parametric in the errors of observation. The influence of the errors on the model fitting criterion is studied mainly for the least squares model fitting applied to generalized weighted sum models, spectroscopic models in particular. However, the theory is not restricted to least squares model fitting only, nor to the class of weighted sum models. The influence of errors of observation on other model fitting criteria are treated superficially in Chapters 4 and 6. However, if the theory is applicable to more general models, it will be mentioned.

3.2 Weighted sum models

In this section, some properties of weighted sum models are discussed. But first the definition of the generalized weighted sum model is given.

Throughout it is assumed that the *model function* $f(x_n; \theta_K)$ is a *generalized weighted sum model*:

$$f(x; \theta_K) = g(x; \gamma) + \sum_{k=1}^K \alpha_k h(x; \beta_k) , \quad (3.4)$$

in which x is the *independent variable*. The *baseline* $g(x; \gamma)$ is linearly and/or nonlinearly parametric in the $C \times 1$ vector γ . The *amplitude* of the k -th peak is α_k , also called *linear parameter*. It is assumed to be positive. The *peak shape* is $h(x; \beta_k)$. The elements β_{ki} of the $B \times 1$ vector β_k are called *peak parameters* or *nonlinear parameters*. The peak shape has two points of inflection and vanishes at plus and minus infinity, as assumed in Section 1.4. The number of peaks K is the order of the model. Both $g(x; \gamma)$ and $h(x; \beta_k)$ are assumed to be continuous and at least twice differentiable with respect to the parameters.

The *observations* w_n are defined by:

CHAPTER 3

$$w_n = f(x_n; \theta_K) + \epsilon_n = g(x_n; \gamma) + \sum_{k=1}^K \alpha_k h(x_n; \beta_k) + \epsilon_n, \quad (3.5)$$

in which x_n is the *measurement point*. It is assumed to be known exactly. There are N observations. The number N and the values of x_n are defined as the *design* of the experiment. The additive *errors of observation* are ϵ_n . They may be statistical and/or systematic, for instance, instrumental effects or modeling errors. The observations are called *exact* when the errors of observation are all zero. The K -th order *exact parameter vector* θ_K is defined as:

$$\theta_K = (\gamma^T \mid \alpha_1 \dots \alpha_K \mid \beta_1^T \mid \dots \mid \beta_K^T)^T. \quad (3.6)$$

It is the combination of parameter vector γ , linear parameters α_k and peak parameter vectors β_k . It has dimension $T_K = C + (B+1)K$. The subscript K of θ_K denotes the order of the model. The subscript k of α and β identifies the peak. The superscript T denotes transposition.

The model fitting consists of fitting $f_n(t_K)$ to the observations. The parameter vector t_K is defined as:

$$t_K = (c^T \mid a_1 \dots a_K \mid b_1^T \mid \dots \mid b_K^T)^T. \quad (3.7)$$

The vectors c and b_k correspond to the exact parameter vectors γ and β_k , respectively. The parameters a_k correspond to the amplitudes α_k . The parameters a_k are also called amplitudes. Analogously the elements of b_k are called peak parameters.

A remarkable property of weighted sum models is that any model is contained by a model of higher order. This can be understood by noticing that the $(K-1)$ -th order parameter vector θ_{K-1} can be composed out of a K -th order parameter vector θ_K by choosing two peak parameter vectors β_k in θ_K equal to each other. The model function $f(x; \theta_{K-1})$, with $(K-1)$ -th order parameter vector θ_{K-1} :

$$\theta_{K-1} = (\gamma^T \mid \alpha_1 \dots \alpha_{K-1} \mid \beta_1^T \mid \dots \mid \beta_{K-1}^T)^T, \quad (3.8)$$

is equal to $f(x; \theta_K)$, with K -th order parameter vector θ_K :

$$\theta_K = (\gamma^T \mid \alpha_1 \dots (1-\eta)\alpha_{K-1} \eta\alpha_{K-1} \mid \beta_1^T \mid \dots \mid \beta_{K-1}^T \mid \beta_K^T)^T, \quad (3.9)$$

in which η is an arbitrary real scalar, if $\beta_K = \beta_{K-1}$. This can be explained geometrically by observing that any peak can be composed out of two or more peaks, each with exactly the same peak parameters as is shown in figure 3.1. Consequently, the parameter space defined by θ_{K-1} is a subspace of the space defined by θ_K . This inclusion of lower order by higher order models is called *hierarchy* and is important in the further development of the theory. Any parameter vector θ_K that contains equal peak parameter vectors β_k is called *degenerate*.

Figure 3.1 Composition of one peak out of several others.

Another property of the weighted sum model is its symmetry. Permutation of pairs of α_k, β_k has no influence on the value of $f(x; \theta_K)$. A model with parameter vector

$$\theta_K = (\gamma^T \mid \alpha_1 \dots \alpha_{K-1} \alpha_K \mid \beta_1^T \mid \dots \mid \beta_{K-1}^T \mid \beta_K^T)^T \quad (3.10)$$

is equal to a model with parameter vector

$$\theta'_K = (\gamma^T \mid \alpha_1 \dots \alpha_K \alpha_{K-1} \mid \beta_1^T \mid \dots \mid \beta_K^T \mid \beta_{K-1}^T)^T. \quad (3.11)$$

The same is true for any sequence of pairs of α_k, β_k . From now, this symmetry will generally be disregarded. The structure and geometrical proportions of a model fitting criterion are studied in the neighborhood of one particular sequence of pairs $\hat{a}_k, \hat{b}_k$ of the model fitting solution $\hat{t}_K$.

Remarks on notation

The following abbreviated notation will be used:

The evaluation of a function at the measurement point x_n will be noted by a subscript n , thus $f(x_n; \theta)$ becomes $f_n(\theta)$. An evaluation at a certain $\bar{t}$ will be in the argument of the function. So:

$$f(x_n; t) \Big|_{\bar{t}} \quad (3.12)$$

will be written as:

$$f_n(\bar{t}) . \quad (3.13)$$

Further, $f_n(\theta)$, whether or not with a subscript K with θ , will denote the generalized weighted sum model

$$g_n(\gamma) + \sum_{k=1}^K \alpha_k h_n(\beta_k) , \quad (3.14)$$

unless stated otherwise.

3.3 Parasitic solutions in spectroscopic model fitting

Before the study of the influence of the errors of observation on the model fitting solution is started, certain solutions are excluded because of their obvious physical meaninglessness. These solutions are called *parasitic*. Parasitic solutions may result if no bounds are set to the values of the solution. In the following paragraphs two kinds of parasitic solutions are described.

Suppose error corrupted observations on a K -th order weighted sum model with two overlapping peaks are available. Without loss of generality, let these peaks be β_{K-1} and β_K . Suppose also both amplitudes of the overlapping peaks are solved for and are free to assume any value. Then one peak may be fitted mainly to the sum of the two overlapping peaks, while another one, with a very small solution for the amplitude, is fitted to the remaining deviations. The latter consist of the systematic component resulting from fitting the incorrect order and of the errors of observation. The solution will consist of approximately the $(K-1)$ -th order solution and meaningless solutions for the K -th peak parameters. This kind of parasitic solution was noticed in spectroscopic model fitting by Jansson (1984) and Gingras (1989). It can be avoided by assuming that the amplitudes a_K and a_{K-1} have the following relationship:

$$a_{K-1} = (1-\eta) a'_{K-1} \text{ and } a_K = \eta a'_{K-1}, \quad (3.15)$$

in which a'_{K-1} is solved for and is approximately equal to the $(K-1)$ -th order solution a_{K-1} . The real scalar η is fixed on an interval that is assumed to be physically meaningful. This interval may, for instance, be chosen as $(0.1, 0.9)$. Thus the dimension of parameter vector t_K is reduced by one, from T_K to T_K-1 . If a priori knowledge about the ratio of the amplitudes a_{K-1} and a_K is available this can be used directly by computing the value of η . Otherwise, the model with reduced vector t_K is fitted for various meaningful values of η and the best fit is taken as a solution.

Another kind of parasitic solution is the following. Suppose again that error corrupted observations were made on a K -th order weighted sum model with two overlapping peaks. Although a priori knowledge about the amplitudes and thus η may have been incorporated, still a parasitic solution may occur. The solution for the location parameter of one peak may be far out of the range of the measurement points x_n . Also, if there is no restriction on the amplitude, the amplitude of this peak may have an excessive value. The values of this peak, assumed in the range of the measurement points x_n , are very small. In fact, only one of the tails of this peak is fitted. The solution consists of approximately the $(K-1)$ -th order solution and a set of meaningless peak

parameters. Again, the latter peak is fitted mainly to the deviations of the $(K-1)$ -th order solution. The result is a parasitic solution.

In conclusion, parasitic solutions may appear if no bounds are set to the values for the solution. They can be avoided by both restricting the amplitudes and the location parameters of the peaks to values that are thought to be physically meaningful. From now, the first kind of parasitic solutions are avoided by introducing the factor η , defining the amplitude ratio, the second kind by assumption.

3.4 Precision and resolution

In this section, the effects are described of the errors of observation on the model fitting criterion, and thus on the model fitting solution, for fitting a weighted sum model. First, it is described when errors will, intuitively, cause problems with respect to precision and resolution. Also, the order of magnitude of the errors of observation dealt with in this thesis is established. Then the structure of the criterion for exact observations made on a K -th order weighted sum model is described. This structure is important for the development of the theory and will be used throughout the thesis. Then, in Section 3.4.3, the intuitive notions are elaborated.

3.4.1 Errors of observation

Intuitively, *errors of observation* are quantities that are small compared with the amplitude of hypothetical exact observations. If this is not the case, no meaningful solutions are to be expected at all. Suppose that observations corrupted by such errors were made on a K -th order weighted sum model. If the peaks are clearly visually separated, the main problem caused by the errors of observation is how precisely the parameters can be solved for. If, however, two or more peaks overlap severely, difficulties with resolution may be expected.

Suppose now that exact observations were made on a K -th order weighted sum model. Also suppose that two of the nonlinear peak parameter vectors of the model are nearly equal to each other. Without loss of generality, let these be β_{K-1} and β_K . Then, a $(K-1)$ -th order

model will fit quite well to these observations in the sense of a norm of the deviations $d_n(t_{K-1})$ defined by (2.2). If errors of observation of the same order of magnitude as the deviations $d_n(\hat{t}_{K-1})$ were present, this might confuse the determination of the correct order and prevent resolution of the peak parameters. In fact, if the errors of observation were equal to the additive inverses of $d_n(\hat{t}_{K-1})$, the observations w_n would be equal to exact observations made on a $(K-1)$ -th order weighted sum model.

It is concluded that parameter vectors β_{K-1} and β_K are considered to be close when all $|d_n(\hat{t}_{K-1})|$ are small compared with amplitude $\hat{a}_{K-1}$. So, close parameters give rise to a good fit of a lower order model, as expected intuitively. The fact that peak parameters are close does not necessarily mean that difficulties with resolution occur. Only when errors of observation of the same order of magnitude as $|d_n(\hat{t}_{K-1})|$ or larger are present, difficulties are to be expected. The above establishes the order of magnitude of the errors of observation mainly dealt with in this thesis.

3.4.2 The structure of the criterion

Next the structure of a ℓ_p criterion for K -th order exact observations is described. So, suppose again that exact observations were made on a K -th order weighted sum model. Also suppose that two of the nonlinear peak parameter vectors of the model are close. Without loss of generality, let these be β_{K-1} and β_K . The model of the observations is:

$$w_n = f_n(\theta_K) = g_n(\gamma) + \sum_{k=1}^{K-2} \alpha_k h_n(\beta_k) + (1-\eta)\alpha_{K-1} h_n(\beta_{K-1}) + \eta\alpha_{K-1} h_n(\beta_K). \quad (3.16)$$

The factor η has been introduced to prevent parasitic solutions. Let η be known and have the value 0.5. The K -th order parameter vector t_K is:

$$t_K = (c^T \mid a_1 \dots (1-\eta)a_{K-1} \quad \eta a_{K-1} \mid b_1^T \mid \dots \mid b_{K-1}^T \mid b_K^T)^T \quad (3.17)$$

$$= (c^T \mid a_1 \dots a_{K-1} \mid b_1^T \mid \dots \mid b_{K-1}^T \mid b_K^T)^T.$$

It is unknown and solved for. The criterion for K-th order exact observations has certainly a minimum at

$$\hat{\mathbf{t}}_K = (\gamma^T \mid \alpha_1 \dots (1-\eta)\alpha_{K-1} \ \eta\alpha_{K-1} \mid \beta_1^T \mid \dots \mid \beta_{K-1}^T \mid \beta_K^T)^T \quad (3.18)$$

and, for reasons of symmetry, also one at

$$\bar{\mathbf{t}}_K = (\gamma^T \mid \alpha_1 \dots (1-\eta)\alpha_{K-1} \ \eta\alpha_{K-1} \mid \beta_1^T \mid \dots \mid \beta_K^T \mid \beta_{K-1}^T)^T. \quad (3.19)$$

Notice that in (3.19) the peak parameter vectors β_{K-1} and β_K have been interchanged. The values of the criterion at $\hat{\mathbf{t}}_K$ and $\bar{\mathbf{t}}_K$ are both zero.

So, the criterion has at least two minima. Traveling on the criterion in parameter space from $\hat{\mathbf{t}}_K$ to $\bar{\mathbf{t}}_K$ means first going uphill, since $\hat{\mathbf{t}}_K$ is a minimum, and then going downhill to the equivalent minimum $\bar{\mathbf{t}}_K$. This means that a *saddle point* is somewhere in between (Van den Bos, 1984, 1988). This saddle point is:

$$\bar{\mathbf{t}}_K = (\hat{\mathbf{c}}^T \mid \hat{\mathbf{a}}_1 \dots (1-\eta)\hat{\mathbf{a}}_{K-1} \ \eta\hat{\mathbf{a}}_{K-1} \mid \hat{\mathbf{b}}_1^T \mid \dots \mid \hat{\mathbf{b}}_{K-1}^T \mid \hat{\mathbf{b}}_{K-1}^T)^T, \quad (3.20)$$

This is the point in the parameter space spanned by $\mathbf{t}_K$, generated by the solution $\hat{\mathbf{t}}_{K-1}$ of fitting a (K-1)-th order weighted sum model to the exact K-th order observations. Solution $\hat{\mathbf{t}}_{K-1}$ is:

$$\hat{\mathbf{t}}_{K-1} = (\hat{\mathbf{c}}^T \mid \hat{\mathbf{a}}_1 \dots \hat{\mathbf{a}}_{K-1} \mid \hat{\mathbf{b}}_1^T \mid \dots \mid \hat{\mathbf{b}}_{K-1}^T)^T. \quad (3.21)$$

This solution is called a (K-1)-th or *lower order solution*.

As has been shown in Section 3.2, a K-th order model contains all (K-1)-th order models. So, the parameter space spanned by $\mathbf{t}_K$ contains the space spanned by the (K-1)-th order parameter vector $\mathbf{t}_{K-1}$ as a subspace. In the latter space, $\hat{\mathbf{t}}_{K-1}$ is a minimum of the model fitting criterion. Since $\hat{\mathbf{t}}_{K-1}$ is a minimum, $\bar{\mathbf{t}}_K$ is, in the parameter space of $\mathbf{t}_K$, also in at least T_{K-1} directions a minimum of the K-th order criterion. For exact observations, $\bar{\mathbf{t}}_K$ will yield a good but not the best fit. After all, the solution is at θ_K . The minimum at θ_K is close to saddle point $\bar{\mathbf{t}}_K$, since the parameter vectors β_{K-1} and β_K were assumed close. The other equivalent minimum $\bar{\mathbf{t}}_K$ is close to both $\bar{\mathbf{t}}_K$ and

θ_K . The criterion for exact observations has thus, in the parameter space spanned by t_K , a cluster of three stationary points.

Next suppose η is no longer equal 0.5, but somewhat different. It is still assumed to be known. For continuity reasons, the structure of the criterion will change only slightly. There will still be two minima, one global minimum at $\hat{t}_K = \theta_K$,

$$\hat{t}_K = (\gamma^T \mid \alpha_1 \dots (1-\eta)\alpha_{K-1} \quad \eta\alpha_{K-1} \mid \beta_1^T \mid \dots \mid \beta_{K-1}^T \mid \beta_K^T)^T \quad (3.22)$$

and one local minimum at

$$\begin{aligned} \bar{t}_K &= (c^T \mid a_1 \dots (1-\eta)a_{K-1} \quad \eta a_{K-1} \mid b_1^T \mid \dots \mid b_{K-1}^T \mid b_K^T)^T \\ &\approx (\gamma^T \mid \alpha_1 \dots (1-\eta)\alpha_{K-1} \quad \eta\alpha_{K-1} \mid \beta_1^T \mid \dots \mid \beta_K^T \mid \beta_{K-1}^T)^T. \end{aligned} \quad (3.23)$$

The value of the criterion at $\hat{t}_K$ is again zero, but the value at $\bar{t}_K$ is not zero anymore. There will also be a saddle point, in the subspace $b_{K-1} = b_K$, at $\bar{t}_K$ generated by (K-1)-th order solution $\hat{t}_{K-1}$.

Figure 3.2 Cross-section of a differentiable criterion for exact observations on a K-th order weighted sum model, the so-called OSTM structure.

Figure 3.2 shows a cross-section of the structure of the criterion. This structure is called *OSTM structure* throughout. The abbreviation OSTM comes from One Saddle, Two Minima.

So, the criterion for exact observations has, in the parameter space spanned by t_K , a cluster of stationary points. The cluster generally contains three stationary points: the global minimum, the saddle point and the local minimum, close to each other. These stationary points are called *relevant*. Other possible minima of the criterion are not considered, since generally they will represent a bad fit. The above should be taken for granted now and it is explained more thoroughly in Chapter 4. The structure of the criterion in the part of parameter space around the relevant saddle point $\bar{t}_K$ has been found to be as shown in cross-sectional view in figure 3.2.

Anticipating on the next subsections, one effect caused by the errors of observation is already described. Suppose that, in a simulation experiment, errors of observation are added to exact observations on a K -th order weighted sum model with two overlapping peaks. Then, generally the solution will be displaced somewhat. However, it may also happen that the solution is displaced more, even to saddle point $\bar{t}_K$. Thus the K -th order solution $\hat{t}_K = \bar{t}_K$ is in the subspace defined by $b_{K-1} = b_K$. Then solutions $\hat{b}_{K-1}$ and $\hat{b}_K$ coincide, they are not resolved. Resolution of the overlapping peaks is thus not possible, as a result of the errors of observation. Resolution has been defined as the ability to distinguish between two overlapping peaks with the same peak shape but with different values for the peak parameters. The result is a $(K-1)$ -th order solution. The observations do not allow resolution of the peak parameters. In fact, the OSTM structure of the criterion has changed. The saddle point has become a minimum and the two other minima have disappeared. This is explained in in Section 3.4.3.3 and in Chapter 4. So, it may happen that, although the underlying observations with exact parameter vector θ_K are of order K , a solution of order $(K-1)$ is obtained. Or, if more peaks overlap, even of smaller order.

However, throughout it will be assumed that the model underlying the observations contains only two overlapping peaks and that the errors of

observation are not excessively large. This means that always a non-degenerate $(K-1)$ -th order solution exists. This also means that the structure of the criterion for exact K -th order observations around a relevant $(K-1)$ -th order solution is like described above. The different permutations of pairs $\hat{a}_k, \hat{b}_k$ of the $(K-1)$ -th order solutions are equivalent, as explained in Section 3.2. So, from now on only one $(K-1)$ -th order solution, called the $(K-1)$ -th order solution, is considered. The overlapping peaks of a K -th order model are always chosen as the $(K-1)$ -th and the K -th peak. The cases of more than two overlapping peaks or of two or more pairs of overlapping peaks are not considered. However, extending the theory developed in this thesis to cover these cases is possible. In Chapter 7 this is discussed.

In the next sections, it is explained what else may happen to the solution of fitting a weighted sum model to error corrupted observations. Starting with hypothetical exact observations, the effects of slowly increasing errors of observation are studied. Furthermore, these effects are named.

3.4.3 The influence of errors of observation

The results of the previous subsection are repeated briefly here. Suppose N observations w_n on a K -th second order weighted sum model and additive errors are available:

$$w_n = f_n(\theta_K) + \epsilon_n, \quad (3.24)$$

in which $f_n(\theta_K)$ is described by (3.16). The factor η is 0.5 and assumed to be known. Parameter vector t_K is solved for. Assume that, for the moment, the errors of observation are all zero. Then the criterion has a global minimum at $\hat{t}_K = \theta_K$ and, because of symmetry, also one at $\tilde{t}_K$, described by (3.19). So, the criterion has two minima and a saddle point somewhere in between. This saddle point is the solution for fitting the $(K-1)$ -th order weighted sum model to observations (3.24). Next suppose that η is no longer 0.5, but somewhat different. It is still assumed to be known. For continuity reasons, the structure of the criterion will change only slightly. There will still be two minima,

one global minimum at $\hat{t}_K$ and one local minimum at $\tilde{t}_K$ described by (3.23). There will also be a saddle point in the subspace $b_{K-1} = b_K$, at the $(K-1)$ -th order solution $\hat{t}_{K-1}$. Figure 3.3 shows again a cross-section of the OSTM structure of the criterion.

Figure 3.3 Cross-section of of the criterion for exact observations generated by (3.24) (OSTM structure).

Suppose now that, in a simulation experiment, arbitrary errors ϵ_n , multiplied by a factor ξ , are added to the observations. The criterion may now change its geometrical proportions and structure, as a function of the factor ξ . The influence of these changes on the solutions, also as a function of the factor ξ , are described below.

3.4.3.1 Precision - displacement of the solution

First assume that ξ is zero, there are no errors of observation. In the neighborhood of the absolute minimum, the criterion is a convex function of $|t_K - \theta_K|$. Now let ξ be small. So, small errors are added. Generally the minimum will change its position in parameter space somewhat, say from θ_K to:

$$\hat{t}_K = \theta_K + \delta\theta_K. \quad (3.25)$$

So the solution is displaced in parameter space as a result of the errors of observation. This displacement $\delta\theta_K$ is associated with the term precision. The larger $\|\delta\theta_K\|$, the lower the precision and vice versa. The terms precision and displacement will be used interchangeably throughout to indicate the above effect. Figure 3.4 shows a cross-section of the criterion for exact observations and for error corrupted observations in the neighborhood of the global minimum. The solution is displaced as a function of the errors of observation. The above is valid not only for weighted sum models, but for any model function, satisfying the above assumptions.

Figure 3.4 Displacement of the solution. Cross-section of the criterion for exact (solid) and error corrupted (dashed) observations.

Errors that certainly cause a displacement $\delta\theta_K$ are given by:

$$\epsilon_n = - \left[f_n(\theta_K) - f_n(\hat{t}_K) \right] \quad (3.26)$$

This is simply the difference between exact observations (3.24) with θ_K as the exact parameter vector and exact observations (3.24) with $\theta_K + \delta\theta_K$ as the exact parameter vector. If errors given by (3.26) are substituted in (3.24), the observations are equal to exact observations with $\theta_K + \delta\theta_K$ as the exact parameter vector. The norm of these errors is equal to the value of the criterion for exact observations at $\hat{t}_K$.

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Besides these errors, there are many others that cause this same displacement $\delta\theta_K$. All these errors together form a subspace of dimension $N - T_K$ in error space.

When T_K is one, so for a model with a scalar parameter, this subspace is a hypersurface. Then it is called the *boundary*. The boundary divides the error space into two *parts*. In the one part, the errors cause a displacement of the scalar solution $\hat{t}$ that is smaller than $\delta\theta$ or that is in opposite direction. Since the origin of error space corresponds to exact observations, the origin is in this part. In the other part, the errors cause a displacement larger than $\delta\theta$. The boundary can easily be defined mathematically. In Chapter 5, a rule is derived for least squares model fitting that predicts in which part particular errors are located.

3.4.3.2 Interchange - jumping of the solution

If the the factor ξ is increased, the solution will be displaced more. A further increase of ξ may change the geometrical proportions of the criterion. The errors of observation may cause the originally global minimum at

$$\hat{t}_K \approx (\gamma^T \mid \alpha_1 \dots (1-\eta)\alpha_{K-1} \eta\alpha_{K-1} \mid \beta_1^T \mid \dots \mid \beta_{K-1}^T \mid \beta_K^T)^T \quad (3.27)$$

to become a local minimum and the originally local minimum at

$$\begin{aligned} \tilde{t}_K &= (c^T \mid a_1 \dots (1-\eta)a_{K-1} \eta a_{K-1} \mid b_1^T \mid \dots \mid b_{K-1}^T \mid b_K^T)^T \\ &\approx (\gamma^T \mid \alpha_1 \dots (1-\eta)\alpha_{K-1} \eta\alpha_{K-1} \mid \beta_1^T \mid \dots \mid \beta_K^T \mid \beta_{K-1}^T)^T \end{aligned} \quad (3.28)$$

to become global. This is called *interchange*. The result is a solution in which the geometrical proportions of the two overlapping peaks have interchanged as well. The peak that has the largest amplitude and was, for instance, located to the left of the smaller peak is now located to the right of the smaller peak. The moment the local minimum becomes global, the solution makes a sudden *jump* in parameter space. This effect is called throughout *interchange* or *jumping*. Figures 3.5 and 3.6

show a cross-section of the criterion and the resulting solutions as a function of the errors of observation, respectively.

Figure 3.5 Cross-sections of the criterion for increasing errors of observation, causing interchange of the minima and jumping of the solution. The solid line is the criterion for exact observations, the dashed for error corrupted observations.

Figure 3.6 Jumping of the solution, occurring for increasing errors of observation.

Again, errors that certainly cause interchange are given by the difference signal:

$$\epsilon_n = - \left[f_n(\theta_K) - f_n(\tilde{t}_K) \right] \quad (3.29)$$

in which $\tilde{t}_K$ is the value of t_K at the local minimum of the criterion for exact observations. If expression (3.29) is substituted in (3.24), the observations w_n are equal to exact observations with $\tilde{t}_K$ as exact parameter vector. The norm of these errors is equal to the value at the local minimum of the criterion for exact observations with θ_K as the exact parameter vector. There are many other errors that also cause interchange. They form a subspace of dimension $N-1$. In fact, this subspace, called the *boundary*, divides the error space into two *parts* again. In the part containing the origin, the errors do not cause jumping of the solution. In the other, the errors do. The boundary can again be easily defined mathematically. Furthermore, in Chapter 5, an accurate approximation to the boundary for least squares model fitting is proposed, making it easy to predict in which part a particular set of N errors of observations are located.

3.4.3.3

Resolution - coincidence of solutions

A further increase of ξ may even change the *structure* of the criterion. This means that the number of minima and saddle points changes. If ξ is increased, the minima of the criterion may become less pronounced and become located closer to each other. A further increase may then cause the minima and the saddle point to *degenerate* into one single minimum. This degenerate minimum is at the $(K-1)$ -th order solution, so that *coincidence* of the peak parameters in the solution occurs. Then *resolution* of the peak parameters is no longer possible. This structure of the criterion will be called *OM*, which is the acronym for *One Minimum*. Figure 3.7 shows cross-sections of the criterion for increasing errors of observation. The solid line shows the criterion with the OSTM structure, the dashed line the intermediate form and the dash-dotted line the OM structure of the degenerated criterion. Figure

3.8 shows the coincidence of the solutions resulting from the the increasing errors of observation. The above effect is called *coincidence* or *degeneracy*. The concept *resolution* is connected to this effect.

Figure 3.7 Cross-sections of criteria for increasing errors, causing degeneracy of stationary points and coincidence of the solutions. The solid line is the OSTM structure, the dash-dotted line is the OM structure of the degenerate criterion.

Figure 3.8 Coincidence of the solutions.

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The degeneracy of the saddle point and the two neighboring minima into one minimum has been described by Van den Bos (1980, 1981, 1983, 1984, 1988). By using the catastrophe theory, he derived how the errors of observation cause this degeneracy, making the $(K-1)$ -th order solution the only, and thus global, minimum of the criterion. This degeneracy can be detected by the so-called *resolution discriminant*. The resolution discriminant is evaluated at the $(K-1)$ -th order solution and decides whether or not resolution of the solutions for the K -th order model is possible. It is a function of the observations and, therefore, of the errors. The mathematical derivation of the resolution discriminant is given in Chapter 4 and Appendix B. The resolution discriminant is approximately the second order necessary condition for a minimum of the K -th order criterion at $(K-1)$ -th order stationary point. It checks whether the $(K-1)$ -th order stationary point is a saddle point or a minimum. It checks the *nature* of the $(K-1)$ -th order stationary point. One might wonder whether or not errors exist that cause the creation of extra minima instead of degeneracy. In Section 4.2.3, it is shown that generally this is not the case for scalar peak parameters.

Errors that certainly cause degeneracy have already been mentioned. They are the additive inverses of $d_n(\hat{t}_{K-1})$ of fitting a $(K-1)$ -th order model to exact observations (3.24). So:

$$\epsilon_n = - \left[f_n(\theta_K) - f_n(\hat{t}_{K-1}) \right] \quad (3.30)$$

Substitution of (3.30) in (3.24) yields observations that are equal to exact observations on a $(K-1)$ -th order model. The norm of these errors is equal to the value of the criterion for exact observations at the $(K-1)$ -th order solution. There are many errors that cause degeneracy. They form a subspace of dimension $N-1$, called the *boundary*, that divides the error space into two parts again. In the part containing the origin, the errors do not cause degeneracy, so resolution is guaranteed. In the other, the errors do and the solutions coincide. Resolution is not possible. The boundary in error space that is associated with degeneracy will also be called *bifurcation set*, a name adopted from catastrophe theory. Again, it can easily be defined mathematically. Furthermore, in Chapter 5, an accurate approximation to the boundary for least squares model fitting is derived, making it easy to predict in which part a particular set of N errors is located.

3.5 Critical errors

In the previous sections, it has been described how the solution for fitting a weighted sum model can be influenced by the errors of observation. Three effects were distinguished: displacement, jumping and coincidence of the solutions. For each effect, errors causing this effect and their norm were given in the previous sections. However, errors may exist that are smaller, i.e., have a smaller norm, and have the same effect. In fact, there must be errors causing one of the effects, displacement, jumping or coincidence, and having the smallest norm of all errors causing the same effect. These errors are called *critical errors* $\hat{e}_n$. So, the critical errors are the worst possible errors in connection to a certain undesired effect. The norm of the critical errors is called *critical norm*. The critical norm is the smallest distance from the origin of the error space to the boundary. Figure 3.9 shows a hypothetical two-dimensional error space and a boundary. The critical error vector is also drawn. The computation of critical errors is the subject of Chapter 4 and 5.

Figure 3.9 Critical norm as the distance from origin to the boundary.

A natural choice for the critical norm for ℓ_p model fitting seems to be the ℓ_p norm. Although this choice is subjective, it seems rational to choose the same norm for measuring both the deviations and the

critical errors. So, for ℓ_2 model fitting, the critical errors are those errors that cause a certain effect and have minimum ℓ_2 norm. Of course, the *idea* of critical errors and critical norm remains the same if another choice is made. For instance, computing those errors that have minimum ℓ_1 norm and that cause the ℓ_2 model fitting solution to be displaced over a certain distance could, in principle, be carried out. However, this will not be considered in this thesis.

As has been mentioned in Section 2.2, the least squares criterion is not a norm, but the square of a norm, the ℓ_2 norm. Therefore, the square of the norm of the critical errors is considered for least squares model fitting. This quantity is called the *critical energy*.

The concepts critical errors and critical norm provide a quantitative link between errors of observation and the possible model fitting solutions. Therefore, they are a powerful tool to judge the limits of the experimental setup beforehand or to appreciate the model fitting solutions. Errors having smaller norm than the critical norm are certainly not able to cause the effect associated with the critical errors. For instance, if resolution of overlapping peaks with a certain difference between the location parameters is required, the critical norm associated with coincidence can be computed. When the errors of observation in a particular experiment are known to have a smaller norm, resolution is guaranteed.

The ratio of the critical norm to the norm of the signal defines the *critical error to signal ratio*. This ratio as a function of the difference between the exact parameters forms the *norm-difference diagram*. For each effect, displacement, jumping or coincidence, such a diagram can be computed and plotted. In such a diagram, two regions are distinguished: one in which the effect of errors of observation on the solution is certainly less than that of the critical errors and another in which the effect on the solution *may* be the same or larger than the effect of the critical errors. This splitting up the norms of errors of observation into two regions by using the critical norm may seem overly pessimistic. After all, the diagram is based on worst-case errors. However, numerical experiments with statistical errors of observation in Section 6.3 show that it is not.

It was assumed above that the exact parameters were known. The boundary in error space and the critical errors will generally be a function of the exact parameters. In practice, however, the exact parameters are

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not known. Still the concepts can be useful to appreciate the model fitting solutions obtained in an experiment. After solutions for the parameters have been obtained, these may be appreciated by computing the critical norm associated with a certain effect, using the solutions as exact parameters. The critical norm is then compared with, perhaps a guess of, the norm of the errors of observation. If the critical norm is considerably larger than the norm of the errors, the solution is acceptable, otherwise the solution is suspect. The fact that in practice the exact parameters are not known is not unique for the theory developed in this thesis. It is a difficulty that appears in nearly all theories about precision in nonlinear model fitting.

In the previous chapter, it was explained how the precision and resolution of solutions of model fitting methods depend on the errors of observation. In Section 4.1, an upper limit to the displacement of the solution for ℓ_p model fitting is derived, given the norm of the errors of observation. Then in Section 4.2 the conditions for the boundaries associated with displacement, jumping and coincidence of the solutions are formulated for least squares model fitting. Furthermore, the computation of the critical errors is formulated mathematically. It is explained how the critical errors can be used to derive an upper limit to the displacement. Also, the condition for coincidence, the resolution discriminant mentioned earlier, is derived. Finally, the same conditions for general ℓ_p model fitting are treated briefly in Section 4.3.

4.1 Precision in ℓ_p model fitting

In this section, an upper limit to the displacement of ℓ_p model fitting solutions is derived for arbitrary model functions. The model functions are thus not restricted for the class of weighted sum models. Therefore, the distinction between displacement, jumping and coincidence is dropped in this section. All three are considered a sort of displacement. After all, both jumping and coincidence of the solutions might be considered as special cases of displacement. Jumping of the solution, for instance, may be considered only a sudden and quite large displacement. The assumption concerning displacement made in Section 3.4.3.1 that the errors are small and that the criterion is a convex function of the difference between the parameters is also dropped here. Later, in Section 4.2, the distinction is valid again.

Suppose observations are available described by:

$$w_n = f_n(\theta) + \epsilon_n, \quad (4.1)$$

in which model function $f_n(\theta)$ is an arbitrary function. The influence of the errors of observation on the solution of the model fitting criterion is now examined. An upper limit to the displacement of this solution is derived.

Suppose that an ℓ_p model fitting method is used and the solution is $\hat{t} = \theta + \delta\theta$. Also suppose that the ℓ_p norm of the errors, $\|\epsilon\|_p$, causing this solution is known. Since the ℓ_p criterion

$$J(t) = \|f(\theta) + \epsilon - f(t)\|_p \quad (4.2)$$

is minimized, the following inequality holds:

$$\|f(\theta) + \epsilon - f(\hat{t})\|_p \leq \|\epsilon\|_p. \quad (4.3)$$

Making use of

$$f(\theta) - f(\hat{t}) = f(\theta) + \epsilon - \epsilon - f(\hat{t}) \quad (4.4)$$

and of the triangle inequality yields:

$$\begin{aligned} \|f(\theta) - f(\hat{t})\|_p &= \|f(\theta) + \epsilon - \epsilon - f(\hat{t})\|_p \\ &\leq \|f(\theta) + \epsilon - f(\hat{t})\|_p + \|\epsilon\|_p. \end{aligned} \quad (4.5)$$

Then by (4.3):

$$\|f(\theta) - f(\hat{t})\|_p \leq 2 \|\epsilon\|_p. \quad (4.6)$$

This result yields an *upper limit* for the possible displacement of solution $\hat{t}$ from θ for a given norm of the errors $\|\epsilon\|_p$. So, the contour of the ℓ_p model fitting criterion for exact observations at a height equal to twice the norm of the errors encloses a region in parameter space in which all possible solutions are located. This region is called the *feasible region*. The feasible region may consist of several disconnected regions.

Suppose, for instance, exact observations were made on a second order sum model with overlapping peaks and scalar peak parameters. The amplitudes are assumed to be known and the two peak parameters are

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solved for. The criterion has the OSTM structure, described in Section 3.4.2. Also suppose the criterion is contoured at a height less than the value of the criterion at the saddle point. Then two separate regions are found in parameter space. Figure 4.1 shows a cross-section of the criterion and figure 4.2 shows the contour of the criterion in parameter space. The feasible region consists of two disconnected parts.

Figure 4.1 Cross-section of the criterion for observations described above.

Figure 4.2 Contour of the criterion. There are two distinct but closed regions that form the feasible region.

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Equation (4.6) yields really an upper limit to the displacements. Errors of observation for which the solution reaches this upper limit do not necessarily exist. For instance, for least squares model fitting the limit may be reached only for specific model functions and thus for special solution loci. An example of such a special solution locus is presented in figure 4.3. In this case, for increasing errors, the solution will make a jump the moment the observation vector is closer to the one portion of the solution locus than to the other. The smallest error vector that can force the solution to the portion not containing the exact observations has a norm that is half the norm of the distance between the two portions. So, in the case of least squares, the upper limit can only be reached by jumping, not by a continuous displacement of the solution.

Figure 4.3 Solution locus for which the ℓ_2 upper limit can be reached.

Although the contour is an upper limit and therefore may be overly pessimistic, it yields a quantitative relation between the errors of observation and the displacement of the solutions. So, it quantifies the precision that can be obtained in model fitting. Furthermore, the practical usefulness of the upper limit is demonstrated by means of simulations with statistical errors of observation for least moduli, least squares and minimax model fitting in Section 6.4.

4.2 Critical errors in least squares model fitting

In Section 3.4 it was described qualitatively what effects errors of observation may have on the solutions of fitting weighted sum models to observations. In Section 3.5 the concept of critical errors was introduced. In the next sections, the conditions for the boundaries associated with displacement, jumping and coincidence are formulated for least squares model fitting. Also the problem of computing the critical errors is formulated mathematically. The problem is a minimization problem under equality constraints. In Chapter 5, the problem will be solved. The three cases, displacement, jumping and coincidence, are treated in separate subsections.

In the subsequent sections it is assumed that observations w_n of a K -th order weighted sum model with two overlapping peaks are available:

$$w_n = f_n(\theta) + \epsilon_n = g_n(\gamma) + \sum_{k=1}^K \alpha_k h_n(\beta_k) + \epsilon_n. \quad (4.7)$$

The two overlapping peaks are, without loss of generality, the $(K-1)$ -th and K -th peaks. The model function $f_n(t)$ is fitted in the sense of the least squares criterion:

$$J(t) = \sum_{n=1}^N d_n^2(t) = \sum_{n=1}^N \left[w_n - f_n(t) \right]^2. \quad (4.8)$$

The critical errors have been defined as the errors that cause either displacement, jumping or coincidence of the solutions and that have minimum norm. In the subsequent subsections the problem of computing the critical errors is defined mathematically. The unknowns in this problem are the errors of observation ϵ_n and sometimes a parameter vector. They have to be solved for. The solution for the critical error vector is called $\hat{e}$. The square of the ℓ_2 norm of the critical error vector is called *critical energy*.

4.2.1 Displacement

Assume that the errors of observation ϵ_n are so small, that no jumping nor coincidence of the solutions may have occurred. So solution $\hat{\mathbf{t}}$ is found in the neighborhood of $\boldsymbol{\theta}$ and the criterion is a convex function of $|\mathbf{t} - \hat{\mathbf{t}}|$ in the neighborhood of $\hat{\mathbf{t}}$. These assumptions guarantee that the minimum in question remains the global minimum. However, the following theory is valid not only for displacement of the global minimum, but also for displacement of any other stationary point. An example of this latter is given in Section 6.3.

The displacement $\delta\boldsymbol{\theta}$ of solution $\hat{\mathbf{t}}$ from the exact parameter $\boldsymbol{\theta}$ is defined as:

$$\hat{\mathbf{t}} = \boldsymbol{\theta} + \delta\boldsymbol{\theta}. \quad (4.9)$$

The criterion has a minimum at $\hat{\mathbf{t}}$. Therefore the first-order necessary conditions for a minimum should be met. Second-order necessary conditions for a minimum are met by assumption. In practice, this should be verified. For least squares model fitting, the first-order necessary condition (2.8) for a minimum is:

$$\frac{\partial J(\hat{\mathbf{t}})}{\partial t_i} = 0, \quad i = 1, \dots, T. \quad (4.10)$$

Substituting the least squares criterion $J(\mathbf{t})$ in (4.10) yields:

$$\sum_{n=1}^N d_n(\hat{\mathbf{t}}) \frac{\partial f_n(\hat{\mathbf{t}})}{\partial t_i} = 0, \quad i = 1, \dots, T. \quad (4.11)$$

Substituting the definition of $d_n(\mathbf{t})$ yields:

$$\sum_{n=1}^N \left\{ f_n(\boldsymbol{\theta}) + \epsilon_n - f_n(\hat{\mathbf{t}}) \right\} \frac{\partial f_n(\hat{\mathbf{t}})}{\partial t_i} = 0, \quad i = 1, \dots, T. \quad (4.12)$$

Equation (4.12) defines a subspace in error space, generally of dimension $N-T$. Errors in this subspace cause a displacement $\delta\boldsymbol{\theta}$. For a scalar

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parameter, the subspace is of dimension $N-1$. It is then a hyperplane. The hyperplane divides the error space into two parts. It is called the *boundary*.

The problem of computing the critical errors associated with a displacement over $\delta\theta$ to $\hat{t}$ for least squares model fitting thus takes the form:

$$\begin{aligned} &\text{minimize} && \sum_{n=1}^N \epsilon_n^2, \\ &\epsilon_1, \dots, \epsilon_n \end{aligned} \quad (4.13)$$

subject to:

$$\sum_{n=1}^N d_n(\hat{t}) \frac{\partial f_n(\hat{t})}{\partial t_i} = 0, \quad i = 1, \dots, T,$$

with $\hat{t} = \theta + \delta\theta$.

This is a minimization problem under equality constraints (Pierre, 1986; Pars, 1962). The solution of (4.13) is the critical error vector $\hat{e}$. The critical norm is the distance from the origin of error space to the subspace defined by (4.12). By using the critical error vector, which is a normal vector of the subspace, this subspace can be defined as:

$$\hat{e} \cdot \epsilon = \hat{e} \cdot \hat{e}. \quad (4.14)$$

By assumption, the errors of observation were so small that they could neither cause jumping nor coincidence of the solutions. Furthermore, the criterion was a convex function of $|t - \hat{t}|$ around $\hat{t}$. Therefore, the formulation of the problem is not restricted to weighted sum models only. It is valid for any model function $f_n(\theta)$. In Chapter 5, the problem (4.13) is exactly solved. Also an approximate but very accurate solution is derived which is much easier to compute.

Feasible region

As stated in Section 4.1, there will generally be no errors of observation that cause a displacement as far as the upper limit. Thus, the critical errors will generally not cause such a displacement. However, the concept of critical errors and critical energy can be used to derive a new upper limit to the displacement of the solution and a new feasible region for the solutions. After all, the critical errors displace the solution over a certain $\delta\theta$ and they have minimum energy. Therefore, the errors of observation that cause the *maximum* displacement of the solution in the *direction* of $\delta\theta$ in parameter space are the critical errors associated with this displacement.

A way of computing the maximum displacements in parameter space, associated with a certain a priori known energy of the errors of observation, is the following. First the solution is displaced in small steps in one particular direction in parameter space. For each step, the critical errors and their energy are computed. This energy is compared to the energy of the errors of observation known a priori. If both energies are equal, the associated displacement and solution t are stored. This can be done for each direction in parameter space. The so acquired solutions enclose a region in parameter space that can be reached *maximally*, given the energy of the errors of observation. This region is called *feasible region* again. To distinguish between the this feasible region and the one defined in Section 4.1, the former will be accompanied by the term 'associated with critical errors', if necessary.

Like the feasible region defined in Section 4.1, the feasible region associated with critical errors contains all possible solutions, but the last region will generally be smaller. After all, the boundary of the new feasible region can be reached for any model function. A solution will be on the boundary if the critical errors are added to the observations. A practical disadvantage of this new feasible region is the amount of computation that is required. For each displacement the critical errors should be computed, which means solving (4.13) each time. However, the approximate solution of (4.13) that is derived in Section 5.1 will drastically reduce the computational effort. Since the feasible region is based on 'worst case' errors, errors causing *maximum*

displacement, it may also be suspected to be overly pessimistic for experimental situations with statistical errors. Fortunately, numerical experiments in Section 6.3 demonstrate that this is not the case.

4.2.2 Jumping

Suppose exact observations were made on a weighted sum with two close peak parameter vectors. Then the least squares criterion has the OSTM structure described in Section 3.4.2. The global minimum is $\hat{\mathbf{t}}' = \theta_K$ and the local minimum is $\tilde{\mathbf{t}}'$.

Suppose now that, in a simulation experiment, errors of observation are added and that they are slowly increased. Jumping will occur if the values of the criterion at the two minima at $\hat{\mathbf{t}}$ and $\tilde{\mathbf{t}}$ are just equal. The two minima at $\hat{\mathbf{t}}$ and $\tilde{\mathbf{t}}$ correspond to the formerly global and local minima, respectively. So, the condition for interchange of the minima at $\hat{\mathbf{t}}$ and at $\tilde{\mathbf{t}}$ is:

$$J(\hat{\mathbf{t}}) = J(\tilde{\mathbf{t}}). \quad (4.15)$$

Substituting the least squares criterion for $J(\mathbf{t})$ yields:

$$\sum_{n=1}^N d_n^2(\hat{\mathbf{t}}) = \sum_{n=1}^N d_n^2(\tilde{\mathbf{t}}). \quad (4.16)$$

At both $\hat{\mathbf{t}}$ and $\tilde{\mathbf{t}}$, the criterion has a minimum, so the first-order necessary conditions for a minimum must be met. Second-order necessary conditions at $\hat{\mathbf{t}}$ and $\tilde{\mathbf{t}}$ are assumed to be met and are checked afterwards. Finally, the trivial condition $\hat{\mathbf{t}} \neq \tilde{\mathbf{t}}$ must be met. Thus the problem of computing the critical errors for jumping becomes the following minimization problem under equality constraints:

$$\begin{aligned} &\text{minimize} && \sum_{n=1}^N \epsilon_n^2, \\ &\epsilon, \tilde{\mathbf{t}}, \hat{\mathbf{t}} && \end{aligned} \quad (4.17)$$

subject to:

$$\sum_{n=1}^N d_n^2(\hat{\mathbf{t}}) = \sum_{n=1}^N d_n^2(\tilde{\mathbf{t}}),$$

$$\sum_{n=1}^N d_n(\hat{\mathbf{t}}) \frac{\partial f_n(\hat{\mathbf{t}})}{\partial t_i} = 0, \quad i = 1, \dots, T$$

and

$$\sum_{n=1}^N d_n(\tilde{\mathbf{t}}) \frac{\partial f_n(\tilde{\mathbf{t}})}{\partial t_i} = 0, \quad i = 1, \dots, T.$$

So the solution of (4.16) consists of $\hat{\mathbf{t}}$ and $\tilde{\mathbf{t}}$ and of critical error vector $\hat{\mathbf{e}}$. The minimization problem (4.16) is solved in Section 5.2. Also an approximate but very accurate solution is presented there.

The constraints of (4.16) define a subspace in error space associated with jumping. There are $2T+1$ equality constraints and $N+2T$ unknowns. Therefore, the subspace is generally of dimension $N-1$ and is thus a hypersurface. The hypersurface divides the error space into two parts. It is called the *boundary associated with jumping*. Notice that the boundary is a hypersurface and not a hyperplane, since the unknowns $\hat{\mathbf{t}}$ and $\tilde{\mathbf{t}}$ are nonlinearly present in the constraints of (4.16).

4.2.3 Coincidence

Suppose exact observations were made on a weighted sum with two overlapping peaks. The least squares criterion has the OSTM structure, described in Section 3.4.2.

Suppose now that, in a simulation experiment, errors of observation are added. In Section 3.4.3.3, it was stated that the resolution discriminant detects whether or not the solutions for the peak parameters can be resolved. The resolution discriminant is approximately the second-order necessary condition for a minimum at the $(K-1)$ -th order solution. First it is explained that this $(K-1)$ -th order solution is a stationary point of the K -th order criterion. Then the second-order necessary conditions for a minimum at the $(K-1)$ -th order solution are simplified. This is done by a sequence of transformations of parameter vector $\mathbf{t}_K$.

For scalar peak parameters, it will be proved, using catastrophe theory (Poston and Stewart, 1978), that there is really a structural change of the criterion and that the $(K-1)$ -th order stationary point

becomes the *only* minimum of the criterion in the relevant part of parameter space. Finally, the problem of computing the critical errors associated with coincidence is formulated mathematically.

Stationary points of the criterion

The explanation that the lower order solution is a stationary point of a higher order least squares criterion is as follows. Suppose that the solution of fitting a model of order $K-1$ to the observations is

$$\hat{\mathbf{t}}_{K-1} = (\hat{\mathbf{c}}_{K-1}^T | a_1 \dots a_{K-1} | \hat{\mathbf{b}}_1^T | \dots | \hat{\mathbf{b}}_{K-1}^T) . \quad (4.18)$$

Then $\hat{\mathbf{t}}_{K-1}$ satisfies the normal equations:

$$\frac{\partial J_{K-1}(\hat{\mathbf{t}}_{K-1})}{\partial t_i} = 0 \quad , \quad i = 1, \dots, T_{K-1} . \quad (4.19)$$

In Section 3.2, it has been shown that any higher order weighted sum model contains all lower order models. A point $\bar{\mathbf{t}}_K$ of the K -th order criterion generated by the $(K-1)$ -th order solution $\hat{\mathbf{t}}_{K-1}$ is:

$$\bar{\mathbf{t}}_K = (\hat{\mathbf{c}}_{K-1}^T | \hat{a}_1 \dots (1-\eta)\hat{a}_{K-1} \quad \eta \hat{a}_{K-1} | \hat{\mathbf{b}}_1^T | \dots | \hat{\mathbf{b}}_{K-1}^T | \hat{\mathbf{b}}_{K-1}^T) , \quad (4.20)$$

in which η is a real scalar. If $\bar{\mathbf{t}}_K$ is a stationary point of the criterion $J_K(\mathbf{t}_K)$ the normal equations should be met at $\bar{\mathbf{t}}_K$:

$$\frac{\partial J_K(\bar{\mathbf{t}}_K)}{\partial t_i} = 0 \quad , \quad i = 1, \dots, T_K . \quad (4.21)$$

Writing out (4.19) and (4.21) reveals that both systems of normal equations are equivalent.

So the $(K-1)$ -th order solution generates a stationary point of the higher order criterion. This stationary point is called *the $(K-1)$ -th order or lower order stationary point* $\bar{\mathbf{t}}_K$ of the criterion $J_K(\mathbf{t})$. This relation between the stationary points of the least squares criteria

for lower and higher order weighted sum model is called *hierarchy* again.

The normal equations (4.19) are not only satisfied by $(K-1)$ -th order solution $\hat{t}_{K-1}$, but by any stationary point $\tilde{t}_{K-1}$ of the $(K-1)$ -th order criterion $J_{K-1}(t_{K-1})$. They also generate stationary points of the higher order criterion.

The maximum number of K -th order stationary points generated by a stationary point of the $(K-1)$ -th order criterion can be derived as follows. Each peak parameter vector at a stationary point of the $(K-1)$ -th order model can be composed of a combination of two peak parameter vectors of the K -th order model in $\binom{K}{2}$ different ways. The maximum number of different combinations is therefore $(K-1)\binom{K}{2}$. So:

Any stationary point of a $(K-1)$ -th order least squares criterion generates maximally $\frac{(K-1)K!}{2(K-2)!}$ stationary points of a K -th order criterion.

Resolution discriminant

In Section 3.4.3.3, it has been explained that the nature of the $(K-1)$ -th order stationary point decides whether or not the solutions for the peak parameters coincide. If the $(K-1)$ -th order stationary point is a minimum of the K -th order criterion, the solutions for the peak parameters will coincide. Resolution is not possible. If it is a saddle point, the solutions do not coincide and resolution is obtained.

The nature of the stationary point determines the local structure of the criterion. The local structure of the criterion around the $(K-1)$ -th order stationary point will be the subject of study. Therefore the criterion is Taylor expanded around the $(K-1)$ -th order stationary point. In order to simplify the expansion, a sequence of linear transformations of the parameter vector will be carried out. This will also make the Taylor expansion suitable for applying catastrophe theory. Catastrophe theory will be used later in this section to prove for scalar peak parameters that the OSTM structure of the criterion indeed changes to the OM structure in which the $(K-1)$ -th order stationary point is the global minimum of the K -th order criterion.

So first, the criterion is Taylor expanded around the $(K-1)$ -th order stationary point. The parameters are the Taylor coordinates. The quadratic term contains the Hessian matrix at the $(K-1)$ -th order stationary point of the criterion. The eigenvalues of the Hessian matrix determine the nature of the stationary point. When all eigenvalues are positive, the $(K-1)$ -th order stationary point is a minimum.

Subsequently, the parameters are linearly transformed in such a way that the Hessian matrix H_K at the $(K-1)$ -th order stationary point is block diagonalized. One of the submatrices is the Hessian matrix H_{K-1} of the $(K-1)$ -th order criterion at the $(K-1)$ -th order stationary point. This matrix was assumed to be positive definite. After all, the $(K-1)$ -th order stationary point was generated by the $(K-1)$ -th order solution. Another submatrix R remains, the eigenvalues of which decide whether or not the whole Hessian matrix is positive semidefinite.

In order to prevent parasitic solutions, the factor η is introduced again, so $a_{K-1} = (1-\eta)a'_{K-1}$ and $a_K = \eta a'_{K-1}$. The introduction of η means that the parameter vector t_K is:

$$t_K = (c^T | a_1 \dots a_{K-2} a'_{K-1} | b_1^T | \dots | b_{K-2}^T | b_{K-1}^T | b_K^T)^T. \quad (4.22)$$

It has dimension $T_K = C + (B+1)K - 1$. The purpose of the linear transformations of the parameters is to have coordinates perpendicular to the subspace $b_{K-1} = b_K$ and coordinates tangent to this subspace. The criterion $J(t_K)$ has a $(K-1)$ -th order stationary point $\tilde{t}_K$ with $\tilde{b}_{K-1} = \tilde{b}_K$, generated by $(K-1)$ -th order solution $\hat{t}_{K-1}$. The Taylor expansion of $J(t_K)$ around this $(K-1)$ -th order stationary point $\tilde{t}_K$ is:

$$J(t_K) = J(\tilde{t}_K) + \frac{1}{2} (t_K - \tilde{t}_K)^T H_K (t_K - \tilde{t}_K) + O(t^3), \quad (4.23)$$

in which H_K is the Hessian matrix of dimension T_K of $J(t_K)$ at $\tilde{t}_K$. The elements $(H_K)_{ij}$ of the Hessian matrix are defined as:

$$(H_K)_{ij} = \frac{\partial^2 J(\tilde{t}_K)}{\partial t_i \partial t_j}, \quad i, j = 1, \dots, T_K. \quad (4.24)$$

The symbol $O(t^n)$ is the order symbol of Landau. It represents all terms of degree n and higher.

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The first linear transformation of the parameters is:

$${}^1\mathbf{t} = \mathbf{t}_K - \tilde{\mathbf{t}}_K. \quad (4.25)$$

Expansion (4.23) becomes:

$$J({}^1\mathbf{t}) = J(\tilde{\mathbf{t}}_K) + \frac{1}{2} {}^1\mathbf{t}^T \mathbf{H}_K {}^1\mathbf{t} + O({}^1\mathbf{t}^3), \quad (4.26)$$

So this transformation is a translation of the origin of parameter space to stationary point $\tilde{\mathbf{t}}_K$.

The second linear transformation is:

$${}^2\mathbf{t} = \mathbf{P} {}^1\mathbf{t} = \text{diag}(\mathbf{I}_{T-2B} \mathbf{Q}) {}^1\mathbf{t}, \quad (4.27)$$

in which $\mathbf{I}_{T-2B}$ is an $(T-2B) \times (T-2B)$ unity matrix, $\mathbf{Q}$ is a $2B \times 2B$ transformation matrix defined as:

$$\mathbf{Q} = \begin{bmatrix} (1-\eta)\mathbf{I} & \cdot & \eta \mathbf{I} \\ - & - & - \\ -\mathbf{I} & : & \mathbf{I} \end{bmatrix}, \quad (4.28)$$

$\mathbf{I}$ is a $B \times B$ unity matrix.

These two transformations yield the new parameter vector:

$${}^2\mathbf{t} = ({}^1\mathbf{c}^T | {}^1\mathbf{a}_1 \dots {}^1\mathbf{a}'_{K-1} | {}^1\mathbf{b}_1^T | \dots | (1-\eta){}^1\mathbf{b}_{K-1}^T + \eta{}^1\mathbf{b}_K^T | {}^1\mathbf{b}_K^T - {}^1\mathbf{b}_{K-1}^T)^T. \quad (4.29)$$

In these coordinates the Taylor expansion becomes:

$$\begin{aligned} J({}^2\mathbf{t}) &= J(\tilde{\mathbf{t}}_K) + \frac{1}{2} (\mathbf{P} {}^1\mathbf{t}^T)^T \mathbf{P}^{-T} \mathbf{H}_K \mathbf{P}^{-1} (\mathbf{P} {}^1\mathbf{t}) + O({}^1\mathbf{t}^3) \\ &= J(\tilde{\mathbf{t}}_K) + \frac{1}{2} {}^2\mathbf{t}^T \text{diag}(\mathbf{H}_{K-1} \mathbf{R}) {}^2\mathbf{t} + O({}^1\mathbf{t}^3). \end{aligned} \quad (4.30)$$

In (4.30), matrix $\mathbf{H}_{K-1}$ is the Hessian matrix of the $(K-1)$ -th order criterion at $\hat{\mathbf{t}}_{K-1}$. The Hessian matrix $\mathbf{H}_{K-1}$ is positive definite by assumption, since it is the Hessian matrix of the $(K-1)$ -th order criterion at the $(K-1)$ -th order solution. The $B \times B$ matrix $\mathbf{R}$ is a matrix of which the elements R_{ij} are defined by:

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$$R_{ij} = -2 \hat{a}_{K-1}^{(1-\eta)\eta} \sum_{n=1}^N d_n(\hat{t}_{K-1}) \frac{\partial^2 h_n(\hat{b}_{K-1})}{\partial b_{K-1,i} \partial b_{K-1,j}}, \quad i=1, \dots, B, \quad j=1, \dots, B. \quad (4.31)$$

Summarizing, the two linear transformations that block diagonalize the Hessian matrix of the criterion are:

$${}^1t = t_K - \tilde{t}_K \quad (4.32)$$

and

$${}^2t = P {}^1t = \text{diag}(I_{T-2B} \quad Q) {}^1t. \quad (4.33)$$

The second-order necessary condition for a minimum is that H_K is positive definite. A symmetric matrix is positive definite if all its eigenvalues are positive. In (4.30), Hessian matrix H_K has been transformed into a block diagonalized form, with a submatrix H_{K-1} and a submatrix R , defined by (4.31). The eigenvalues of H_{K-1} are positive by assumption. Therefore, the eigenvalues of R determine the nature of H_K and of the $(K-1)$ -th order stationary point. If *all* eigenvalues of R are positive the whole Hessian matrix H_K will be positive definite and a $(K-1)$ -th order solution will result.

The elements of R are functions of the observations, thus of the errors, and of $(K-1)$ -th order solution $\hat{t}_{K-1}$ only. In a simulation experiment, the value and sign of the element R_{ij} can be changed by manipulating the errors of observation, as can easily be understood by inspecting (4.31). After all, element R_{ij} depends on the product of $d_n(\hat{t}_{K-1})$ and a second-order derivative of the model function. This latter is relatively independent of the errors, since the $(K-1)$ -th order solution is relatively independent of the errors of observation. The deviations $d_n(\hat{t}_{K-1})$, however, depend strongly on the particular realization of the errors. Therefore, the eigenvalues of R may be manipulated by the errors of observation. However, it will not be certain whether or not errors can be found which cause all the eigenvalues to become positive simultaneously. Anyhow, errors exist that cause all eigenvalues of R to become zero. Inspection of (4.31) reveals that all elements R_{ij} vanish when the errors of observation are equal to the additive inverse of deviations $d_n(\hat{t}_{K-1})$ for exact K -th order observations. Coincidence of the solutions will now certainly occur,

since the observations are equal to exact observations on a (K-1)-th order model. Hessian matrix H_K is not positive definite now, but singular.

In Section 6.2, analytical computations and numerical experiments with regard to the eigenvalues of R are described for spectroscopic peaks.

Scalar peak parameters

Suppose now that the peak parameters b_k are scalar. So, for instance, only the locations of the peaks are unknown. The other peak parameters, such as the widths, are assumed to be known beforehand. Substitution of b_k in (4.23-33) yields a scalar second-order necessary condition, the *resolution discriminant*.

The first transformation is again:

$${}^1t = t_K - \bar{t}_K. \quad (4.34)$$

The second transformation is:

$${}^2t = P {}^1t = \text{diag}(I_{T-2} \ Q) {}^1t. \quad (4.35)$$

in which

$$Q = \begin{bmatrix} 1-\eta & \cdot & \eta \\ \cdot & \ddots & \cdot \\ -1 & \cdot & 1 \end{bmatrix}. \quad (4.36)$$

The new parameter vector 2t_K is:

$${}^2t = ({}^1c^T \mid {}^1a_1 \ \dots \ {}^1a_{K-1} \mid {}^1b_1 \mid \dots \mid (1-\eta){}^1b_{K-1} + \eta \ {}^1b_K \mid {}^1b_K - {}^1b_{K-1})^T. \quad (4.37)$$

The Taylor expansion becomes:

$$\begin{aligned} J({}^2t) &= J(\bar{t}_K) + \frac{1}{2} (P {}^1t^T)^T P^{-T} H_K P^{-1} (P {}^1t) + O({}^1t^3) \\ &= J(\bar{t}_K) + \frac{1}{2} {}^2t^T \text{diag}(H_{K-1} \ \rho) {}^2t + O({}^1t^3). \end{aligned} \quad (4.38)$$

The scalar resolution discriminant ρ is defined by:

$$\rho = -2 \hat{a}_{K-1} (1-\eta) \eta \sum_{n=1}^N d_n(\hat{t}_{K-1}) \frac{\partial^2 h_n(\hat{b}_{K-1})}{\partial b_{K-1}^2} . \quad (4.39)$$

To determine whether $\hat{t}_K$ is a saddle point or a minimum, only the sign of ρ is relevant. If ρ is negative, $\hat{t}_K$ will be a one-saddle. This implies that the criterion $J(t_K)$ has smaller values than $J(\hat{t}_K)$. These values are certainly not on the line $b_{K-1} = b_K$, so that a solution $\hat{t}_K$ with distinct parameters b_{K-1} and b_K can be found. If ρ is positive, $\hat{t}_K$ will be a minimum and the solutions coincide. Resolution has not been obtained. If $\rho = 0$, no decisive answer is possible yet.

The resolution discriminant ρ is a function of the $(K-1)$ -th order solution and of the observations, including the errors, only. In a simulation experiment, the sign of ρ can be changed by manipulating the errors of observation, as can easily be understood by inspecting (4.39). The second-order derivative of the model function is relatively independent of the errors of observation, since the $(K-1)$ -th order solution is relatively independent of the errors of observation. The deviations $d_n(\hat{t}_{K-1})$, however, depend strongly on the particular realization of the errors. So, errors can change the sign of ρ and thus the structure of the criterion.

In fact, the error space is divided into two parts. In the part containing the origin, the errors of observation do not cause a structural change. Resolution is guaranteed. In the other part, the errors of observation do cause a structural change. The solutions coincide and resolution is not possible. The boundary associated with coincidence is defined by $\rho = 0$ and the normal equations of fitting a $(K-1)$ -th order model.

Possible structures

The second-order condition alone is not sufficient for the $(K-1)$ -th order stationary point to be the *global* minimum, it may also be a local minimum. This should be checked separately. However, catastrophe theory (Poston and Stewart, 1978) can be applied in order to facilitate the

study of the possible structures of the criterion and to prove that the $(K-1)$ -th order stationary point becomes the global minimum.

Catastrophe theory describes the structural change of parametric functions as a function of their parameters. The function studied here is the criterion as a function of the parameter vector. The criterion is considered parametric in the errors of observation.

By applying catastrophe theory, it has been proved for differentiable model fitting criteria (Van den Bos, 1983, 1988; Van den Bos and Swarte, 1991) that the $(K-1)$ -th order stationary point becomes the global minimum of the K -th order criterion under influence of the errors, if the peak parameters are scalar. This is achieved as follows. As a result of the *Splitting Lemma* (Poston and Stewart, 1978), the possible structures of the criterion can be described in a relatively small number of coordinates, namely the number of possible vanishing eigenvalues of the Hessian matrix of the criterion. Equation (4.38) shows that in this case only one eigenvalue may vanish. Therefore only one coordinate is necessary. The detailed operations involved in applying the Splitting Lemma to the criterion with scalar peak parameters are in Appendix B. Here, only a description is given.

The operations required are the following. First, the K -th order criterion is Taylor expanded around the $(K-1)$ -th order stationary point to a degree to be specified later. The parameters are the Taylor coordinates again. Next, the coordinates are linearly transformed according to (4.34) and (4.35). Then all coordinates except the last are linearly transformed as to diagonalize Hessian matrix H_{K-1} . Subsequently, these coordinates are nonlinearly transformed to remove all third and higher degree terms in these coordinates. The result is a polynomial consisting of positive quadratic degree terms in the nonlinearly transformed coordinates and a polynomial in the last element of 2t_K . The nonlinearly transformed coordinates do not influence the structure of the criterion. Therefore, they are called the *inessential variables* and may be left out. The remaining coordinate ${}^1b_K - {}^1b_{K-1}$ is called *essential variable*.

According to the Splitting Lemma, the global structure of a parametric function with only one essential variable is fully determined by its Taylor expansion up to the degree of which the coefficient remains positive for all feasible values of its parameters. In this case, the errors of observation are the parameters. In Appendix B a

quartic polynomial in the essential variable is derived that determines all possible structures of the criterion. The result is:

$$J(\mathbf{t}_K) = J(\tilde{\mathbf{t}}_K) + \underbrace{\mathbf{p}^T \mathbf{H}'_{K-1} \mathbf{p}}_{\text{inessential}} + \underbrace{\frac{1}{2!} \rho q^2 + \frac{1}{3!} \sigma q^3 + \frac{1}{4!} \tau q^4}_{\text{essential}} + O(t^5), \quad (4.40)$$

in which $\mathbf{H}'_{K-1}$ is a diagonal matrix containing the eigenvalues of $\mathbf{H}_{K-1}$, $\mathbf{p}$ is the vector of inessential variables and $q = {}^1b_K - {}^1b_{K-1}$ is the essential variable, while

$$\rho = -2 \hat{a}_{K-1}^2 (1-\eta) \eta \sum_{n=1}^N d_n(\hat{\mathbf{t}}_{K-1}) \frac{\partial^2 h_n(\hat{b}_{K-1})}{\partial b_{K-1}^2}, \quad (4.41)$$

$$\sigma = -2 \hat{a}_{K-1}^2 (1-2\eta)(1-\eta) \eta \sum_{n=1}^N d_n(\hat{\mathbf{t}}_{K-1}) \frac{\partial^3 h_n(\hat{b}_{K-1})}{\partial b_{K-1}^3}, \quad (4.42)$$

and

$$\tau = 6 \hat{a}_{K-1}^2 \eta^2 (1-\eta)^2 \chi - \hat{a}_{K-1} \eta (1-\eta)(\eta^3 + (1-\eta)^3) \psi, \quad (4.43)$$

in which

$$\begin{aligned} \chi = & \sum_{n=1}^N \left[\frac{\partial^2 h_n(\hat{b}_{K-1})}{\partial b_{K-1}^2} \right]^2 \\ & - \sum_{k=1}^{K-1} \lambda_k \sum_{n=1}^N \left[\hat{a}_k \frac{\partial h_n(\hat{b}_k)}{\partial b_k} \frac{\partial^2 h_n(\hat{b}_{K-1})}{\partial b_{K-1}^2} \right]^2 \\ & - \lambda_{T-2} \sum_{n=1}^N \left[d_n(\hat{\mathbf{t}}_{K-1}) \frac{\partial^3 h_n(\hat{b}_{K-1})}{\partial b_{K-1}^3} \right]^2, \end{aligned} \quad (4.44)$$

in which λ_k is the k -th eigenvalue of $\mathbf{H}_{K-1}$, and

$$\psi = 2 \sum_{n=1}^N d_n(\tilde{\mathbf{t}}_{K-1}) \frac{\partial^4 h_n(\tilde{b}_{K-1})}{\partial b_{K-1}^4}. \quad (4.45)$$

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In order to investigate whether or not the expansion up to the quartic term in the essential variable in (4.40) is sufficient, the possible signs of the coefficients are computed. The coefficient ρ can easily change sign as has been shown before. The same reasoning applies for coefficient σ .

The first and second terms of (4.44) do not depend on the deviations $d_n(\hat{t}_{K-1})$. They depend on $\hat{t}_{K-1}$ and will therefore be relatively independent of the particular realization of the errors. Also, it is not difficult to show that their sum is positive. The third term of (4.44) and ψ in (4.45) contain the deviations $d_n(\hat{t}_{K-1})$, so the same reasoning applies as for ρ and σ . So, r consists of a nearly constant positive term and terms of order $\|d(\hat{t}_{K-1})\|_2$. The latter become smaller when the peak parameter get closer and the errors of observation get smaller. Therefore, these terms is negligible compared to the nearly constant positive term when the peak are close enough.

Equation (4.43) also shows that, for decreasing η , the first term decreases proportional to η^2 . The second term decreases linearly with decreasing η . Therefore, coefficient r may become negative if η is of the order $\|d(\hat{t}_{K-1})\|_2 / Na_{K-1}$ or smaller whenever ψ is positive. For $\eta = 0$, r is positive again, while ρ and σ are zero. The same applies if η approaches one. Such small values of η or $(1-\eta)$ lead to parasitic solutions and were not allowed. Therefore, the coefficient r is always positive and the expansion (4.40) is sufficient to describe the possible structures of the criterion. This also shows that errors of observation will not cause extra minima of the criterion, as stated in Chapter 3.

The possible structures of a quartic polynomial

$$a \frac{x^4}{4!} + b \frac{x^3}{3!} + c \frac{x^2}{2!} \quad (4.46)$$

are shown in figure 4.4.

Figure 4.4 Possible structures of a quartic polynomial.

The quartic polynomial has two real minima when the following relation between the coefficients a , b and c exists:

$$D = 3b^2 - 8ac > 0. \quad (4.47)$$

It has only one real minimum when $D \leq 0$. So the discriminant for structural change is the sign of D . If $b \neq 0$ and $c = 0$, there is only one minimum and a point of inflection. In the expansion (4.40) of $J(\mathbf{t}_K)$ the coefficients r , σ and ρ correspond to a , b and c , respectively. So, $D = 3\sigma^2 - 8\rho r$ is really the resolution discriminant. Those errors in error space for which $D = 0$ are called *bifurcation set* or *boundary associated with coincidence*. This set divides the error space into two parts. The part in which $D > 0$ contains the origin. It corresponds to the OSTM structure of the criterion in which the stationary point $\hat{\mathbf{t}}_K$, generated by the solution $\hat{\mathbf{t}}_{K-1}$ of $J(\mathbf{t}_{K-1})$, is a one-saddle. So resolution is possible. The part in error space where $D < 0$ corresponds to a minimum of $J(\mathbf{t}_K)$ at $\tilde{\mathbf{t}}_K$, so the solutions coincide. Resolution is no longer possible.

Generally, σ^2 will be small compared to ρr , so that the the sign of ρ may be used as resolution discriminant instead of D . From now on, the sign of ρ will be used as resolution discriminant. If the sign of ρ is used, when σ^2 is not negligible to ρr , there is only one minimum as well, but it will not exactly be on the line $b_{K-1} = b_K$.

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So far, it has been proved that, for scalar peak parameters, the structure of the K-th order least squares criterion can be described sufficiently by a quartic polynomial in ${}^1b_{K-1} - {}^1b_K$. Proceeding analogously and deriving the possible structures of the K-th order least squares criterion for vector valued peak parameters seems an enormous task, if possible at all. Therefore the second-order necessary conditions for a minimum are taken as the resolution discriminant in this case. Numerical experiments justify this choice.

Critical errors

Summarizing, the resolution discriminant for scalar peak parameters is:

$$D = 3\sigma^2 - 8\rho\tau, \quad (4.48)$$

in which ρ , σ and τ are defined by (4.41-45). Coincidence occurs when $D \leq 0$. The equation $D = 0$ defines the boundary or bifurcation set. The equation $D = 0$ is approximately equal to $\rho = 0$, with:

$$\rho = -2 \hat{a}_{K-1} (1-\eta) \eta \sum_{n=1}^N d_n(\hat{t}_{K-1}) \frac{\partial^2 h_n(\hat{b}_{K-1})}{\partial b_{K-1}^2}. \quad (4.49)$$

Using the approximate resolution discriminant ρ , the problem of computing the critical errors associated with coincidence for scalar peak parameters becomes:

$$\begin{aligned} &\text{minimize} \quad \sum_{n=1}^N \epsilon_n^2, \\ &\epsilon, \hat{t}_{K-1} \end{aligned} \quad (4.50)$$

subject to:

$$\sum_{n=1}^N d_n(\hat{t}_{K-1}) \frac{\partial^2 f_n(\hat{t}_{K-1})}{\partial t_i^2} = 0, \quad i=1, \dots, T_{K-1}$$

and

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$$\rho = -2 \hat{a}_{K-1} (1-\eta) \eta \sum_{n=1}^N d_n(\hat{t}_{K-1}) \frac{\partial^2 h_n(\hat{b}_{K-1})}{\partial b_{K-1}^2} = 0.$$

The unknowns in this problem are critical error vector $\hat{e}$ and $(K-1)$ -th order solution $\hat{t}_{K-1}$. There are $T_{K-1} + N$ unknowns and $T_{K-1} + 1$ constraints in (4.50). Therefore the subspace defined by the constraints of (4.50) is generally of dimension $N-1$. So, it is a hypersurface, called the *boundary associated with coincidence or bifurcation set*, that divides the error space into two parts.

For vector valued parameters the resolution discriminant is not a scalar, but consists of the demand that submatrix R , defined by (4.31), of the block diagonalized Hessian matrix is positive semidefinite. The problem is:

$$\begin{aligned} &\text{minimize} \quad \sum_{n=1}^N \epsilon_n^2, \\ &\epsilon, \hat{t}_{K-1} \end{aligned} \quad (4.51)$$

subject to:

$$\sum_{n=1}^N d_n(\hat{t}_{K-1}) \frac{\partial^2 f_n(\hat{t}_{K-1})}{\partial t_i^2} = 0 \quad , \quad i=1, \dots, T_{K-1}$$

and

the smallest eigenvalue of R is zero.

The condition that the eigenvalues of R are positive or zero means that R is positive semidefinite. The eigenvalues are generally nonlinear functions of the elements R_{ij} and thus of the errors ϵ_n .

If all but one eigenvalues are positive, the resolution discriminant is the upward zero crossing of the remaining eigenvalue. The dimension of the subspace defined by the constraints of (4.51) is then $N-1$. The hypersurface divides the error space into two parts. However, in some cases, the eigenvalues of R vanish simultaneously and the subspace is of dimension $N-2$ or less.

4.3 Critical errors in ℓ_p model fitting

For ℓ_p model fitting, the conditions that define the boundaries associated with displacement, jumping and coincidence of the solutions are similar to those for least squares model fitting. The displacement is again:

$$\hat{t} = \theta + \delta\theta . \quad (4.52)$$

The problem of computing the critical errors associated with displacement is:

$$\begin{aligned} &\text{minimize } \|\epsilon\|_p , \\ &\epsilon_1 \dots \epsilon_n \end{aligned} \quad (4.53)$$

subject to

$$\hat{t} = \theta + \delta\theta \text{ is a solution of the } \ell_p \text{ model fitting problem.}$$

The first-order necessary condition for a minimum of the ℓ_p criterion can be found in (Gonin and Money, 1989). For the least moduli and minimax criterion also in (Van den Bos, 1988). The boundary in error space is defined by the constraints of (4.53). The concept of critical errors can again be used to compute a feasible region for the solutions.

The condition for jumping is also the same as for least squares model fitting:

$$J(\hat{t}) = J(\tilde{t}) . \quad (4.54)$$

The problem of computing the critical errors associated with jumping is:

$$\begin{aligned} &\text{minimize } \|\epsilon\|_p , \\ &\epsilon, \tilde{t}, \hat{t} \end{aligned} \quad (4.55)$$

subject to:

In Chapter 4, the computation of the critical errors has been posed as a minimization problem with equality constraints. In this chapter, the problem is solved for critical errors associated with displacement, jumping and coincidence of the solutions of least squares model fitting. Moreover, approximate but accurate solutions are derived. Finally, the properties of critical errors are described. A rule that predicts in which part of the error space particular errors of observation are located is derived.

5.1 Displacement

In Section 4.2.1 it has been assumed that the errors of observation ϵ_n are so small, that no jumping nor coincidence of the solutions may have occurred. So, solution $\hat{t}$ is found in the neighborhood of θ and the criterion is a convex function of $|t - \hat{t}|$ in the neighborhood of $\hat{t}$. These assumptions guarantee that the minimum considered remains the global minimum. However, the following theory is valid not only for displacement of the global minimum, but for displacement of any other stationary point as well.

The problem of computing the critical errors for a displacement of the solution from θ to $\hat{t} = \theta + \delta\theta$ has been formulated in Section 4.2.1 as follows:

$$\underset{\epsilon}{\text{minimize}} \quad \sum_{n=1}^N \epsilon_n^2 \quad (5.1)$$

subject to

$$\sum_{n=1}^N d_n(\hat{t}) \frac{\partial f_n(\hat{t})}{\partial t_i} = 0, \quad i = 1, \dots, T,$$

with $\hat{t} = \theta + \delta\theta$.

The solutions $\hat{e}_n$ for the errors ϵ_n are the components of the $N \times 1$ vector $\hat{e}$. The errors ϵ_n appear linearly in the constraints of (5.1), so that a closed form expression for the critical errors $\hat{e}_n$ can be derived. According to the calculus of variations (Pierre, 1986; Pars, 1962), solution $\hat{e}$ is among the stationary points of the *Lagrangian function* $L(\epsilon, \lambda)$ with respect to ϵ and λ . For the above problem, the Lagrangian function is defined as:

$$L(\epsilon, \lambda) = \sum_{n=1}^N \left[\epsilon_n^2 + \sum_{i=1}^T \lambda_i d_n(\hat{t}) \frac{\partial f_n(\hat{t})}{\partial t_i} \right], \quad (5.2)$$

in which λ_i are the elements of the vector λ . They are called the *Lagrange multipliers*. Differentiating $L(\epsilon, \lambda)$ with respect to ϵ_n , equating the obtained expression to zero and solving the resulting equation, yields the following expression for $\hat{e}_n$:

$$\hat{e}_n = - \frac{1}{2} \sum_{i=1}^T \lambda_i \frac{\partial f_n(\hat{t})}{\partial t_i}. \quad (5.3)$$

So, the critical errors consist of a linear combination of the derivatives of the model function with respect to its parameters.

Differentiating $L(\epsilon, \lambda)$ with respect to λ yields the constraints of (5.1), which are the normal equations. The solution for λ can be obtained by substituting the expression (5.3) for $\hat{e}_n$ in the normal equations and solving the resulting set of equations. The equations thus obtained are linear in the Lagrange multipliers λ_i :

$$\sum_{n=1}^N \left[f_n(\hat{t}) - \frac{1}{2} \sum_{i=1}^T \lambda_i \frac{\partial f_n(\hat{t})}{\partial t_i} - f_n(\hat{t}) \right] \frac{\partial f_n(\hat{t})}{\partial t_j} = 0, \quad j=1, \dots, T. \quad (5.4)$$

The critical error vector is obtained by substituting the solutions $\hat{\lambda}_i$ of the system (5.4) into equation (5.3). The solution for the critical errors thus obtained is exact. No approximations have been made.

Approximate solution.

Inspection of the equations (5.4) reveals these are the normal equations obtained when

$$-\frac{1}{2} \sum_{i=1}^T \lambda_i \frac{\partial f_n(\hat{\mathbf{t}})}{\partial t_i} \quad (5.5)$$

is fitted in linear least squares sense to the values $f_n(\theta) - f_n(\hat{\mathbf{t}})$, with respect to the Lagrange multipliers λ_i . So, the least squares solution of the Lagrange multipliers λ_i makes

$$d_n(\hat{\mathbf{t}}) = f_n(\theta) + \hat{e}_n - f_n(\hat{\mathbf{t}}) \quad (5.6)$$

$$= f_n(\theta) - \frac{1}{2} \sum_{i=1}^T \lambda_i \frac{\partial f_n(\hat{\mathbf{t}})}{\partial t_i} - f_n(\hat{\mathbf{t}}) \quad , \quad n = 1, \dots, N,$$

as small as possible in the least squares sense.

Next, an approximate solution is derived by using the Taylor expansion of equation (5.6). The Taylor expansion of d_n in the coordinate θ around $\hat{\mathbf{t}}$ is:

$$d_n(\hat{\mathbf{t}}) = \sum_{i=1}^T \frac{\partial f_n(\hat{\mathbf{t}})}{\partial t_i} (\theta_i - \hat{t}_i) + O((\theta - \hat{\mathbf{t}})^2) - \frac{1}{2} \sum_{i=1}^T \lambda_i \frac{\partial f_n(\hat{\mathbf{t}})}{\partial t_i}. \quad (5.7)$$

Equation (5.7) shows that the linear terms of the Taylor expansion can be compensated by a proper choice of the multipliers λ_i .

Recall that in Section 4.2.1, $f_n(\theta)$ was assumed not to be any particular function, but to meet the assumptions made. If $f_n(\theta)$ is linear in the parameters, the quadratic and higher degree terms in $(\theta - \hat{\mathbf{t}})$ all vanish in (5.7). Then the Lagrange multipliers,

$$\hat{\lambda}_i = 2 (\theta_i - \hat{t}_i) \quad , \quad i = 1, \dots, T, \quad (5.8)$$

form the required solution, as they achieve the minimization by making all the $d_n(\hat{\mathbf{t}})$ exactly equal to zero. For nonlinear model functions, the linear terms in (5.7) will vanish for the same values of the Lagrange

multipliers. The $\hat{d}_n(\hat{t})$ are quadratic in $\delta\theta$ and consequently small if $\delta\theta$ is small. The values (5.8) for the Lagrange multipliers are not the required solutions, but as the required solutions are those for which $\sum_n \hat{d}_n^2(\hat{t})$, $n = 1, \dots, N$, is a minimum, the latter will bring the $\hat{d}_n(\hat{t})$ even closer to zero in the least squares sense. It follows directly from equations (5.6) and (5.7) that:

$$\hat{e}_n \approx - \left[f_n(\theta) - f_n(\hat{t}) \right]. \quad (5.9)$$

The right hand side is equal to the additive inverse of the deviation for exact observations at $\hat{t}$. The critical errors can thus easily be computed. This leads to the following conclusion:

For a (non)linear model function, the critical energy, associated with a displacement to $\hat{t}$, is (approximately) equal to the value at $\hat{t}$ of the least squares criterion for exact observations.

So, using this approximation, the feasible region associated with critical errors can relatively easily be computed. After all, if the energy E of the errors of observation is known a priori, the contour of the criterion at the height E encloses the feasible region. In conclusion:

The contour at height E of the least squares criterion for exact observations is (approximately) equal to the feasible region corresponding to energy E of the errors of observation.

The approximate critical errors certainly displace the solution over $\delta\theta$, but they are not the errors having smallest norm causing this displacement. Therefore, this approximation is too optimistic, in the sense that the contour at height E of the criterion always yields a smaller feasible region than the exact feasible region. However, numerical experiments in Sections 6.2 and 6.3 and (Swarte, 1991) show that the approximation is very accurate.

Geometrical view

A geometrical view of the displacement of the solution and the critical errors may help clarify the concept of critical errors and the approximate solution. Observations were generated according to:

$$w_i = 0.55 \exp(-\frac{1}{2}(x_i - \beta)^2) + 0.45 \exp(-\frac{1}{2}(x_i + \beta)^2) + \epsilon_i, \quad i=1,2 \quad (5.10)$$

with $x_1 = -0.8$, $x_2 = 0.6$, $\beta = 0.5$, $\epsilon_1 = 0.015$, $\epsilon_2 = -0.03$. Figure 5.1 shows the solution locus of this model in a two-dimensional observation space. Notice that this is the same solution locus as in Chapter 2, figure 2.1.

Figure 5.1 Solution locus and critical error associated with displacement of the solution.

The critical error vector associated with a displacement over $\delta\theta$ is the smallest vector of errors, with starting point $f(\theta)$, yielding a solution $\hat{t} = \theta + \delta\theta$. Since least squares model fitting is an orthogonal projection on the solution locus, the smallest vector starting at $f(\theta)$ whose projection is at $f(\theta + \delta\theta)$ can easily be constructed in figure 5.1. Figure 5.1 shows that the approximate computation will be accurate, if the solution locus is relatively flat.

CHAPTER 5

Now that the critical errors for displacement have been computed, one may wonder whether or not there are errors of observation ϵ_n that do not displace the solution at all. Since least squares model fitting is the orthogonal projection on the solution locus, errors that are orthogonal to the solution locus do not displace the solution. They satisfy the following equation:

$$\sum_{n=1}^N \epsilon_n \frac{\partial f_n(\theta)}{\partial t_i} = 0, \quad i = 1, \dots, T. \quad (5.11)$$

5.2 Jumping

Assume that exact observations were made on a K-th order weighted sum model with two overlapping peaks. Therefore, the criterion has the OSTM structure. The global minimum of this criterion is $\hat{t}'$, the local minimum is $\tilde{t}'$. The minimization problem for computing the critical errors associated with jumping has been defined in Section 4.2.2 as:

$$\begin{aligned} &\text{minimize} \quad \sum_{n=1}^N \epsilon_n^2 \\ &\epsilon, \tilde{t}, \hat{t} \end{aligned} \quad (5.12)$$

subject to:

$$\sum_{n=1}^N d_n^2(\hat{t}) = \sum_{n=1}^N d_n^2(\tilde{t}),$$

$$\sum_{n=1}^N d_n(\hat{t}) \frac{\partial f_n(\hat{t})}{\partial t_i} = 0, \quad i = 1, \dots, T$$

and

$$\sum_{n=1}^N d_n(\tilde{t}) \frac{\partial f_n(\tilde{t})}{\partial t_i} = 0, \quad i = 1, \dots, T.$$

The critical error vector $\hat{\epsilon}$ and parameter vectors $\hat{t}$ and $\tilde{t}$ are among the stationary points of the Lagrangian function $L(\epsilon, \hat{t}, \tilde{t}, \lambda, \mu, \nu)$, with respect to ϵ , $\hat{t}$, $\tilde{t}$, λ , μ and ν . The Lagrangian function is:

$$L(\epsilon, \hat{t}, \tilde{t}, \lambda, \mu, \nu) = \sum_{n=1}^N \epsilon_n^2 + \lambda \left[\sum_{n=1}^N d_n^2(\hat{t}) - \sum_{n=1}^N d_n^2(\tilde{t}) \right] \quad (5.13)$$

$$+ \sum_{n=1}^N \sum_{i=1}^T \mu_i d_n(\hat{t}) \frac{\partial f_n(\hat{t})}{\partial t_i} + \sum_{n=1}^N \sum_{i=1}^T \nu_i d_n(\tilde{t}) \frac{\partial f_n(\tilde{t})}{\partial t_i},$$

in which λ and the elements of the $T \times 1$ vectors μ and ν are the Lagrange multipliers.

The first constraint of (5.12) can be rewritten by substitution of the definitions of $d_n(\hat{t})$ and $d_n(\tilde{t})$. The result is:

$$\sum_{n=1}^N \left[d_n(\tilde{t}) + d_n(\hat{t}) \right] \left[f_n(\hat{t}) - f_n(\tilde{t}) \right] = 0. \quad (5.14)$$

Using (5.14), the Lagrangian function becomes:

$$L(\epsilon, \hat{t}, \tilde{t}, \lambda, \mu, \nu) = \sum_{n=1}^N \left[\epsilon_n^2 + \lambda \left[d_n(\tilde{t}) + d_n(\hat{t}) \right] \left[f_n(\hat{t}) - f_n(\tilde{t}) \right] \right. \quad (5.15)$$

$$\left. + \sum_{i=1}^T \left[\mu_i d_n(\hat{t}) \frac{\partial f_n(\hat{t})}{\partial t_i} + \nu_i d_n(\tilde{t}) \frac{\partial f_n(\tilde{t})}{\partial t_i} \right] \right],$$

Differentiating the Lagrangian function with respect to ϵ , equating the result to zero and solving the resulting equation yields for $\hat{\epsilon}_n$:

$$\hat{\epsilon}_n = -\frac{1}{2} \lambda \left[f_n(\hat{t}) - f_n(\tilde{t}) \right] - \frac{1}{2} \sum_{i=1}^T \left[\mu_i \frac{\partial f_n(\hat{t})}{\partial t_i} + \nu_i \frac{\partial f_n(\tilde{t})}{\partial t_i} \right]. \quad (5.16)$$

The critical errors consist of a term compensating the difference between the values of the two minima and a linear combination of the derivatives of the model function with respect to the parameters, evaluated at both minima.

Differentiating the Lagrangian function with respect to the Lagrange multipliers and equating to zero yields the constraints of (5.12).

Substituting (5.16) into the constraints yields a system of equations that is linear in the Lagrange multipliers λ , μ and ν and the linear parameters $\hat{a}_k$ and $\tilde{a}_k$ and nonlinear in $\hat{c}$, $\tilde{c}$, $\hat{b}_k$ and $\tilde{b}_k$. This system has to be solved numerically. Substituting the solutions for $\hat{t}$, $\tilde{t}$, λ , μ and ν into (5.16) yields the critical errors. Notice that the condition $\hat{t} \neq \tilde{t}$, preventing a trivial solution of (5.12) is not explicitly used in solving the problem. This condition should be checked separately.

Approximate solution

In Section 3.4.3.2, it was shown that errors equal to the differences between the model function at θ_k and $\tilde{t}'$ will certainly cause jumping. The minima of the criterion were really interchanged, both their positions and values. So, these errors overdo. However, intuitively, a good guess for the critical errors may be half of these errors:

$$\hat{e}_n \approx -\frac{1}{2} \left[f_n(\theta_k) - f_n(\tilde{t}') \right], \quad (5.17)$$

in which the vector $\tilde{t}'$ is the position of the local minimum of the criterion for exact observations, like in Section 4.2. These errors will bring the local minimum down somewhat and the global minimum up. Compared with (5.16), in (5.17) the Lagrange multiplier λ equals one, while the terms with μ and ν are neglected. A geometrical motivation is given in the next paragraphs. In Section 6.2, Numerical experiment # 4, it is shown numerically to be an accurate approximation. Errors described by (5.17) nearly cause a jump of the solution as far as the upper limit derived in Section 4.1.

Geometrical view

Figure 5.2 *Solution locus and the critical error associated with jumping of the solution.*

The approximate expression (5.17) can be understood geometrically by inspecting the solution locus in figure 5.2. The observations (5.10) and the corresponding solution locus are used as an example again. In figure 5.2, two portions of the solution locus can be distinguished. The portions are separated by $f(0)$ on the solution locus. One portion corresponds to solutions with the original proportions of the peaks maintained and the other corresponds to interchange of the proportions of the peaks.

A motivation for the expression (5.17) is that $\tilde{t}'$ is a minimum of the criterion for exact observations. Therefore, $f(\tilde{t}')$ is the point on the other portion of the solution locus closest to $f(\theta_K)$. Observations w_n described by

$$w_n = \frac{1}{2} f(\theta_K) + \frac{1}{2} f(\tilde{t}') \quad (5.18)$$

will also yield a minimum of the criterion at $\tilde{t}'$. However, these observations will generally not yield a minimum at θ_K , but at $\theta_K + \delta\theta_K$. The value of this minimum is smaller than the value of the minimum at $\tilde{t}'$.

Hence, the exact critical errors should correct this. They will be slightly different from (5.17). Their norm will be larger. Generally, this correction is only small, so the approximation (5.17) is accurate.

5.3 Coincidence

The problem of computing the critical errors associated with coincidence is split up in scalar peak parameters and vector valued peak parameters. In the Section 5.3.1, the problem is solved for scalar parameters. In Section 5.3.2, the problem is considered for vector valued peak parameters.

5.3.1 Scalar parameters

Assume again that exact observations were made on a weighted sum model with two overlapping peaks. Therefore, the criterion has the OSTM structure. Using the resolution discriminant ρ , the problem of computing the critical errors associated with coincidence of b_{K-1} and b_K has been formulated in Section 4.2.3 as:

$$\begin{aligned} &\text{minimize} \quad \sum_{n=1}^N \epsilon_n^2 \\ &\quad \epsilon, \hat{t}_{K-1} \end{aligned} \quad (5.19)$$

subject to

$$\sum_{n=1}^N d_n(\hat{t}_{K-1}) \frac{\partial f_n(\hat{t}_{K-1})}{\partial t_i} = 0, \quad i = 1, \dots, T_{K-1}$$

and

$$\rho = \eta (1-\eta) \hat{a}_{K-1} \sum_{n=1}^N d_n(\hat{t}_{K-1}) \frac{\partial^2 h_n(\hat{t}_{K-1})}{\partial b_{K-1}^2} = 0,$$

in which:

$$\hat{f}_n(\hat{t}_{K-1}) = g_n(\hat{c}) + \sum_{k=1}^{K-1} \hat{a}_k h_n(\hat{b}_k). \quad (5.20)$$

The unknowns are the critical errors $\hat{e}_n$ and (K-1)-th order solution $\hat{t}_{K-1}$. The constraints of (5.19) are linear in the errors of observation ϵ_n and nonlinear in parameter vector $\hat{t}_{K-1}$.

The Lagrangian function $L(\epsilon, \hat{t}_{K-1}, \lambda, \mu)$ of this problem is:

$$L(\epsilon, \hat{t}_{K-1}, \lambda, \mu) = \sum_{n=1}^N \left[\epsilon_n^2 + \sum_{i=1}^{T_{K-1}} \lambda_i d_n(\hat{t}_{K-1}) \frac{\partial f_n(\hat{t}_{K-1})}{\partial t_i} + \mu d_n(\hat{t}_{K-1}) \frac{\partial^2 h_n(\hat{b}_{K-1})}{\partial b_{K-1}^2} \right]. \quad (5.21)$$

The elements of the $T_{K-1} \times 1$ vector λ and μ are the *Lagrange multipliers*. Differentiating the Lagrangian function with respect to ϵ , equating the result to zero and solving the resulting equation yields for $\hat{e}_n$:

$$\begin{aligned} \hat{e}_n = - \frac{1}{2} \sum_{i=1}^C \lambda_i \frac{\partial g_n(\hat{c}_{K-1})}{\partial c_i} \\ - \frac{1}{2} \sum_{k=1}^{K-1} \left[\lambda_{k+C} h_n(\hat{b}_k) + \lambda_{k+C+K-1} \frac{\partial h_n(\hat{b}_k)}{\partial b_k} \right] - \frac{1}{2} \mu \frac{\partial^2 h_n(\hat{b}_{K-1})}{\partial b_{K-1}^2}. \end{aligned} \quad (5.22)$$

The critical errors are a linear combination of the derivatives of the model function and the second-order derivative of the (K-1)-th peak shape, evaluated at lower order solution $\hat{t}_{K-1}$. Substitution of (5.22) into the constraints of (5.19) yields a system of equations, linear in the Lagrange multipliers and the linear parameters and nonlinear in the nonlinear parameters. The system can be solved numerically. Substitution of the solutions for λ , μ and $\hat{t}_{K-1}$ into (5.22) yields the critical errors.

Approximate computation.

Substitution of (5.22) into the constraints of (5.19) reveals that these are identical to the normal equations of linear least squares fitting the functions

$$\lambda_i \frac{\partial g_n(\hat{c}_{K-1})}{\partial c_i}, \quad (5.23)$$

$$\lambda_{k+C} h_n(b_k), \quad (5.24)$$

$$\lambda_{k+C+K-1} \frac{\partial h_n(b_k)}{\partial b_k} \quad (5.25)$$

and

$$\mu \frac{\partial^2 h_n(b_{K-1})}{\partial b_{K-1}^2} \quad (5.26)$$

to $f_n(\theta_K) - f_n(\hat{t}_{K-1})$ with respect to λ and μ . Thus the least squares solution for λ and μ makes:

$$d_n(\hat{t}_{K-1}) = f_n(\theta_K) + \hat{e}_n - f_n(\hat{t}_{K-1}) \quad (5.27)$$

$$= f_n(\theta_K) + \hat{e}_n - g_n(\hat{c}_{K-1}) - \sum_{k=1}^{K-1} \hat{a}_k h_n(\hat{b}_k), \quad n = 1, \dots, N,$$

as small as possible in least squares sense. In (5.27), $\hat{e}_n$ is described by (5.22). So, the Lagrange multipliers make $f_n(\theta_K) + \hat{e}_n$ as similar as possible to a $(K-1)$ -th order model in least squares sense. They have been found to do this very accurately (Van den Bos and Swarte, 1991).

Assume for the moment that the solution $\hat{t}_{K-1}$ of fitting the $(K-1)$ -th order model to observations corrupted by the critical errors, is available. Substitution of (5.22) and $\hat{t}_{K-1}$ into (5.27) and rearrangement of the elements yields a sum with six composing elements:

$$d_n(\hat{t}_{K-1}) = U + V + W + X + Y + Z, \quad (5.28)$$

$$U = g_n(\gamma) - g_n(\hat{c}_{K-1}), \quad (5.29)$$

$$V = -\frac{1}{2} \sum_{i=1}^C \lambda_i \frac{\partial g_n(\hat{c}_{K-1})}{\partial c_i}, \quad (5.30)$$

$$W = \sum_{k=1}^{K-2} \left[\alpha_k h_n(\beta_k) - \hat{a}_k h_n(\hat{b}_k) \right], \quad (5.31)$$

$$X = -\frac{1}{2} \sum_{k=1}^{K-2} \left[\lambda_{k+C} h_n(\hat{b}_k) + \lambda_{k+C+K-1} \frac{\partial h_n(\hat{b}_k)}{\partial b_k} \right], \quad (5.32)$$

$$Y = \left[\alpha_{K-1} h_n(\beta_{K-1}) + \alpha_K h_n(\beta_K) - \hat{a}_{K-1} h_n(\hat{b}_{K-1}) \right] \quad (5.33)$$

and

$$Z = -\frac{1}{2} \left[\lambda_{C+K-1} h_n(\hat{b}_{K-1}) + \lambda_{C+2K-2} \frac{\partial h_n(\hat{b}_{K-1})}{\partial b_{K-1}} + \mu \frac{\partial^2 h_n(\hat{b}_{K-1})}{\partial b_{K-1}^2} \right]. \quad (5.34)$$

Suppose that U is Taylor expanded around $\hat{t}_{K-1}$ in terms of $\gamma_i - \hat{c}_i$, W in $\alpha_k - \hat{a}_k$ and $\beta_k - \hat{b}_k$ and finally Y in $\alpha_{K-1} + \alpha_K - \hat{a}_{K-1}$, $\beta_{K-1} - \hat{b}_{K-1}$ and $\beta_K - \hat{b}_{K-1}$. Then the Lagrange multipliers in V , X and Z can be chosen in such a way that they make the linear terms of the Taylor expansion of U , W and Y vanish. These chosen values are:

$$\lambda_i = 2(\gamma_i - \hat{c}_i), \quad i=1, \dots, C, \quad (5.35)$$

$$\lambda_{k+C} = 2(\alpha_k - \hat{a}_k), \quad k=1, \dots, K-2, \quad (5.36)$$

$$\lambda_{k+C+K-1} = 2(\beta_k - \hat{b}_k), \quad k=1, \dots, K-2, \quad (5.37)$$

$$\lambda_{C+k-1} = 2(\alpha_{K-1} + \alpha_K - \hat{a}_{K-1}) \quad (5.38)$$

and

$$\lambda_{C+2K-2} = 2(\alpha_{K-1}\beta_{K-1} + \alpha_K\beta_K - (\alpha_{K-1} + \alpha_K)\hat{b}_{K-1}). \quad (5.39)$$

Furthermore, μ in (5.34) can be chosen so as to compensate a quadratic term of (5.33). This particular value of μ is:

$$\mu = \alpha_{K-1}(\beta_{K-1} - \hat{b}_{K-1})^2 + \alpha_K(\beta_K - \hat{b}_{K-1})^2. \quad (5.40)$$

Because of the assumption of close β_{K-1} and β_K and of the availability of $\hat{t}_{K-1}$, the linear terms will dominate the expansion near $\hat{t}_{K-1}$. The quadratic and higher degree terms of this Taylor expansion will be small. Therefore, the sum of all the squared $d_n(\hat{t}_{K-1})$ will also be small. This is true for chosen values of λ and μ described above. So it is certainly true for the actual least squares solution for λ . The critical errors $\hat{e}_n$ are therefore:

$$\begin{aligned}\hat{e}_n &\approx - \left[f_n(\theta_K) - f_n(\hat{t}_{K-1}) \right] \\ &= - \left[f_n(\theta_K) - g_n(\hat{c}) - \sum_{k=1}^{K-1} \hat{a}_k h_n(\hat{b}_k) \right].\end{aligned}\quad (5.41)$$

Now the precise value of $\hat{t}_{K-1}$ has to be computed. The solution of problem (5.19) is among the stationary points of the Lagrangian function (5.21). Differentiation of (5.21) with respect to t_{K-1} and using (5.22) yields:

$$\sum_{n=1}^N \hat{e}_n \frac{\partial g_n(c)}{\partial c_i} = - \frac{1}{2} \lambda_i \sum_{n=1}^N d_n(t_{K-1}) \sum_{j=1}^C \frac{\partial^2 g_n(c)}{\partial c_i \partial c_j}, \quad i=1, \dots, C, \quad (5.42)$$

$$\sum_{n=1}^N \hat{e}_n h_n(b_k) = 0, \quad k=1, \dots, K-1, \quad (5.43)$$

$$\sum_{n=1}^N \hat{e}_n \frac{\partial h_n(b_k)}{\partial b_k} = - \frac{\lambda_{k+C+K-1}}{2 a_k} \sum_{n=1}^N d_n(t_{K-1}) \frac{\partial^2 h_n(b_k)}{\partial b_k^2}, \quad k=1, \dots, K-2 \quad (5.44)$$

and

$$\sum_{n=1}^N \hat{e}_n \frac{\partial h_n(b_{K-1})}{\partial b_{K-1}} = - \frac{\mu}{2 a_{K-1}} \sum_{n=1}^N d_n(t_{K-1}) \frac{\partial^3 h_n(b_{K-1})}{\partial b_{K-1}^3}. \quad (5.45)$$

Substitution of $\hat{t}_{K-1}$ for t_{K-1} and of the solution of the multipliers into (5.42-45) makes the right-hand sides of these equations small. Deviations $d_n(\hat{t}_{K-1})$ in (5.42) and (5.44) are quadratic and in (5.45) cubic in the Taylor coordinates. The chosen Lagrange multipliers are

linear in the Taylor coordinates, so that the right-hand sides of (5.42,44) and (5.45) are cubic and quartic, respectively.

So equations (5.42-45) reveal that the critical errors $\hat{e}_n$ are approximately orthogonal to

$$\frac{\partial g_n(\hat{c}_{K-1})}{\partial c_i}, \text{ for } i=1, \dots, C, \quad (5.46)$$

and to

$$\frac{\partial h_n(\hat{b}_k)}{\partial b_k}, \text{ for } k = 1, \dots, K-1. \quad (5.47)$$

Thus the normal equations for fitting a (K-1)-th order model to observations corrupted by the critical errors reduce to:

$$\sum_{n=1}^N d_n^*(\hat{t}_{K-1}) \frac{\partial g_n(\hat{c}_{K-1})}{\partial c_i} \approx 0, \quad i=1, \dots, C \quad (5.48)$$

$$\sum_{n=1}^N d_n^*(\hat{t}_{K-1}) h_n(\hat{b}_k) = 0, \quad k=1, \dots, K-1 \quad (5.49)$$

$$\sum_{n=1}^N d_n^*(\hat{t}_{K-1}) \frac{\partial h_n(\hat{b}_k)}{\partial b_k} \approx 0, \quad k=1, \dots, K-1 \quad (5.50)$$

in which:

$$d_n^*(\hat{t}_{K-1}) = f_n(\theta_K) - g_n(\hat{c}) - \sum_{k=1}^{K-1} \hat{a}_k h_n(\hat{b}_k). \quad (5.51)$$

These equations are exactly the normal equations of fitting a (K-1)-th order model to exact K-th order observations. Therefore, $\hat{t}_{K-1}$ must be approximately equal to the solution of fitting a (K-1)-th order model to exact observations $f_n(\theta_K)$. Substitution of $\hat{t}_{K-1}$ into (5.41) or comparison of (5.27) and (5.51) yields:

The critical errors associated with coincidence are approximately equal to the additive inverse of the deviations of the best fitting

CHAPTER 5

(K-1)-th order model to exact K-th order observations.

Compared to the numerical solution of the system of nonlinear equations that arises from straightforward computation, this approximate solution is an enormous simplification. The fitting of a (K-1)-th order model to exact observations is sufficient to compute the critical errors. Furthermore, it will simplify the computation of the boundary associated with coincidence.

5.3.2 Vector valued peak parameters

The critical errors associated with coincidence of vector valued peak parameters $\mathbf{b}_{K-1}$ and $\mathbf{b}_K$ are more difficult to compute. The problem is:

$$\begin{array}{ll} \text{minimize} & \sum_{n=1}^N \epsilon_n^2 \\ \epsilon_1 \dots \epsilon_n & \end{array} \quad (5.52)$$

subject to

$$\sum_{n=1}^N d_n(\hat{\mathbf{t}}_{K-1}) \frac{\partial f_n(\hat{\mathbf{t}}_{K-1})}{\partial t_i} = 0, \quad i = 1, \dots, T_{K-1}$$

and

the smallest eigenvalue of $\mathbf{R}$ vanishes.

The elements R_{ij} of $\mathbf{R}$ have been defined as:

$$R_{ij} = -2 \hat{a}_{K-1}^{(1-\eta)\eta} \sum_{n=1}^N d_n(\hat{\mathbf{t}}_{K-1}) \frac{\partial^2 h_n(\hat{\mathbf{b}}_{K-1})}{\partial b_{K-1,i} \partial b_{K-1,j}}, \quad \begin{array}{l} i=1, \dots, B \\ j=1, \dots, B \end{array} \quad (5.53)$$

In Section 4.2.3, it has been shown that, generally, the errors ϵ_n do not appear linearly in the eigenvalues of $\mathbf{R}$. Therefore, differentiation of the Lagrangian function with respect to ϵ_n and equating to zero does not yield a closed form expression for $\hat{\epsilon}_n$. Also no approximate solution has been obtained. A clear definition of the boundary has also not been found. It will be shown in Section 6.2 that sometimes the dimension of

the subspace defined by the constraints of (5.53) is less than $N-1$. If two or more eigenvalues vanish simultaneously, the subspace will have a lower dimension than $N-1$ and will not divide the error space into two parts.

5.4 Properties of the boundary and critical errors

In this section, the properties are described of the respective boundaries and critical errors for least squares model fitting. In addition, it is described how the critical errors can be used to predict in which part of the error space particular errors are located.

The most important and obvious property of the critical errors has already been mentioned. If the energy of the errors of observation is smaller than the critical energy associated with a certain effect, this effect will certainly not occur. The critical energy thus defines a hypersphere in error space. Errors located inside this hypersphere can not cause the effect, whereas errors located outside this hypersphere *may* cause it. The use of the critical energy requires only a priori knowledge of the energy of the errors of observation, a scalar quantity. No a priori knowledge of the individual errors is required.

In Sections 3.4 and 5.1-5.3 it has been stated that for each effect, displacement, jumping and coincidence, a boundary divides the error space into two parts. In the part containing the origin the effect will not occur. In the other part it will. The boundary has dimension $N-1$. In the subsequent sections the three effects are treated separately again. A rule is derived that predicts in which part of error space particular errors of observation are located and thus whether or not the effect will occur.

5.4.1 Displacement

Assume again that the errors of observation are so small that they do not cause jumping nor coincidence. When the parameter θ is scalar, the subspace defined by (4.12) has dimension $N-1$. It is the boundary in error space associated with a displacement of the solution to $\hat{t} = \theta + \delta\theta$. It is defined by:

$$\sum_{n=1}^N \left\{ f_n(\theta) + \epsilon_n - f_n(\hat{t}) \right\} \frac{\partial f_n(\hat{t})}{\partial \hat{t}} = 0. \quad (5.54)$$

This is a hyperplane in error space defined by the critical error vector as follows:

$$\hat{\epsilon} \cdot \hat{e} = \hat{e} \cdot \hat{e}. \quad (5.55)$$

If the inner product of particular errors of observation ϵ and the critical error vector $\hat{e}$ is smaller than $\hat{e} \cdot \hat{e}$, the errors will be located in the part of error space containing the origin. If it is larger, they will be located in the other part. Figure 5.3 shows the two-dimensional observation space and part of the solution locus of (5.10). Observations in the part containing $f(\beta)$ cause a smaller displacement than $\delta\theta$.

Fig 5.3 Solution locus and boundary for two observations according to (5.10).

So, the following rule predicts when a displacement larger than $\delta\theta$ occurs:

$$\epsilon \cdot \hat{e} \geq \hat{e} \cdot \hat{e} , \quad (5.56)$$

or, equivalently,

$$\sum_{n=1}^N \epsilon_n \hat{e}_n \geq \sum_{n=1}^N \hat{e}_n^2 . \quad (5.57)$$

Notice that rule (5.56) requires information on the individual errors of observation.

In practice, the parameter is often not scalar. Hence, the subspace defined by (4.12) is of lower dimension than $N-1$. So it does not divide the error space into two parts. Therefore, (5.56) can not be used. However, in this case, the concept of the feasible region can be used, since this is valid for vector valued parameters too. In Section 5.1, it was shown that the contour of the least squares criterion approximately encloses the feasible region. Only knowledge about the energy of the errors of observation, a scalar quantity, is required for computing the feasible region. The usefulness of the feasible region and the accuracy of its approximation are demonstrated in Numerical experiments # 14-17 in Section 6.3.

5.4.2 Jumping

Using (5.14), the boundary associated with jumping is defined by:

$$\sum_{n=1}^N \left[d_n(\tilde{t}) + d_n(\hat{t}) \right] \left[f_n(\hat{t}) - f_n(\tilde{t}) \right] = 0 , \quad (5.58)$$

$$\sum_{n=1}^N d_n(\hat{t}) \frac{\partial f_n(\hat{t})}{\partial t_i} = 0 \quad , \quad i = 1, \dots, T \quad (5.59)$$

and

$$\sum_{n=1}^N d_n(\tilde{t}) \frac{\partial f_n(\tilde{t})}{\partial t_i} = 0 \quad , \quad i = 1, \dots, T. \quad (5.60)$$

Equations (5.58-60) are linear in the errors of observation and non-linear in $\hat{t}$ and $\hat{f}$. The boundary has dimension $N-1$.

It is now assumed that the boundary is approximately a hyperplane defined by:

$$\epsilon \cdot \hat{e} = \hat{e} \cdot \hat{e} . \quad (5.61)$$

If the approximation is accurate, rule (5.61) will again predict in which part of the error space particular errors are located. If $\epsilon \cdot \hat{e}$ is smaller than $\hat{e} \cdot \hat{e}$, the particular errors will be in the part of error space containing the origin and they will not cause jumping. If $\epsilon \cdot \hat{e}$ is larger than $\hat{e} \cdot \hat{e}$, the errors are in the other part of error space and they will cause jumping. So, the rule for jumping is:

$$\epsilon \cdot \hat{e} \geq \hat{e} \cdot \hat{e} . \quad (5.62)$$

Rule (5.62) is tested in Numerical experiment # 20 in Section 6.3.

Figure 5.4 shows the solution locus of the model (5.10). The boundary associated with jumping is also shown and is approximately straight. It has dimension $N-1 = 1$ in this case.

Figure 5.4 Solution locus of observations according to (5.10). The boundary associated with jumping is the dashed line.

5.4.3 Coincidence

The effect of coincidence is treated separately again for scalar and vector valued peak parameters.

Scalar peak parameters.

The boundary associated with coincidence of scalar peak parameters is defined by:

$$\sum_{n=1}^N d_n(\hat{t}_{K-1}) \frac{\partial f_n(\hat{t}_{K-1})}{\partial t_i} = 0, \quad i=1, \dots, T_{K-1} \quad (5.63)$$

and

$$\rho = -2 \hat{a}_{K-1} (1-\eta) \eta \sum_{n=1}^N d_n(\hat{t}_{K-1}) \frac{\partial^2 h_n(\hat{b}_{K-1})}{\partial b_{K-1}^2} = 0. \quad (5.64)$$

These conditions are linear in the errors of observation and nonlinear in $\hat{t}_{K-1}$. As shown in Section 5.3.1, equations (5.48-5.51) approximately define $\hat{t}_{K-1}$, which also satisfies the normal equations (5.63). Therefore, the boundary in the neighborhood of the critical error is approximately defined by $\rho = 0$. This condition is linear in the errors of observation, so the boundary is approximately a hyperplane in the neighborhood of the critical errors. The hyperplane is defined by:

$$\epsilon \cdot \hat{e} = \hat{e} \cdot \hat{e}. \quad (5.65)$$

The rule:

$$\epsilon \cdot \hat{e} \geq \hat{e} \cdot \hat{e}, \quad (5.66)$$

predicts in which part of the error space particular errors of observation are located. The rule is tested in Numerical experiments # 18-21 in Section 6.3.

Vector valued peak parameters

The boundary associated with coincidence is defined by the upward zero crossing of the smallest eigenvalue of $\mathbf{R}$. This boundary defines the part in which coincidence occurs. This is the part in which all eigenvalues are positive. Resolution is not possible in this part.

There are no good reasons to assume that this boundary will be flat in the relevant part of error space. After all, the definition of the boundary is highly nonlinear in the errors of observation.

If the eigenvalues are dependent and vanish simultaneously, the subspace defined by the vanishing eigenvalues has lower dimension than $N-1$ and, therefore, does not divide the error space into two parts.

5.4.4 Systematic and statistical errors of observation

In the previous section the errors of observation were assumed to be arbitrary. They could be systematic and/or statistical. Suppose now that systematic errors of observation are suspected to be present and that the contribution of these errors has not been included in the model of observations. The effect of systematic (modeling) errors can then easily be traced by using rules (5.56), (5.62) and (5.66).

Next, it is studied what will happen if the errors of observation are statistical and have known statistical properties, see also (Van den Bos, 1991a). It is assumed that the errors of observation ϵ_n are independent and have zero mean and finite variances σ_n^2 . Then, using the central limit theorem (Feller, 1970), the inner product $\epsilon \cdot e$ or

$$\sum_{n=1}^N \epsilon_n \hat{e}_n \quad (5.67)$$

is normally distributed with zero mean and variance :

$$\sum_{n=1}^N \sigma_n^2 \hat{e}_n^2. \quad (5.68)$$

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If the errors of observation have common variance σ^2 , this reduces to:

$$\sigma^2 = \frac{1}{N} \sum_{n=1}^N \hat{e}_n^2 \quad (5.69)$$

The probability of $\epsilon \cdot \hat{e} \geq \hat{e} \cdot \hat{e}$ becomes:

$$P(\epsilon \cdot \hat{e} \geq \hat{e} \cdot \hat{e}) = P(z \geq \frac{\|\hat{e}\|}{\sigma}) \quad (5.70)$$

Here, $\epsilon \cdot \hat{e}$ is normally distributed with variance described by (5.68) and z is standard normal. The use of (5.70) requires only a joint property of the errors of observation, namely the variance.

If the number of observations increases, the critical energy will increase as well. Therefore the probability of occurrence of the effect in question decreases when the number of observations increases, as is intuitively expected. Equation (5.70) is tested in Section 6.3

Feasible region

For displacement of vector valued parameters, the subspace defined by (5.54) is of dimension $N-T$ and does not divide the error space into two parts. Therefore rules (5.56) and (5.70) can not be used. However, the feasible region can be used. For the feasible region it has been assumed that the energy of the errors of observation is known exactly. The solutions are certainly located in the feasible region associated with this energy. In the case of independent normally distributed errors with zero mean and common variance σ^2 , the energy of the errors is chi-square distributed with mean $E = N\sigma^2$ and variance $2N\sigma^4$. The region in which the solutions will be located with a probability of at least $x\%$ can be determined by first computing the energy E_x from $P(E \leq E_x) = x\%$ and then computing the feasible region that goes with E_x . So, at least $x\%$ of the solutions will be located in the $x\%$ feasible region if the experiment is repeated. This is demonstrated in Numerical experiment # 15 and # 17 in Section 6.3.

5.5 Continuous design

In the previous chapters, the design of the experiment was assumed to be discrete. However, the theory developed can be extended for a continuous design. The continuous design has the advantage that it is relatively objective: there is only one continuous design, while there are infinite number of discrete designs. Moreover, the continuous design has another favorable property: the Fourier transform of the exact observations can often be computed. It is shown below that the whole problem of model fitting and of computing the critical errors can then be carried out in the Fourier domain. This may be advantageous if the model function in the original domain is difficult to compute numerically. In this Section, the expressions for critical errors for continuous observations are described.

Assume that instead of observations at discrete points continuous observations are available, described by:

$$w(x) = g(x; \gamma) + \sum_{k=1}^K \alpha_k h(x; \beta_k) + \epsilon(x). \quad (5.71)$$

The sampled functions and summations over n , appearing so far, should then be replaced by continuous functions and integrals over the whole real axis. The resulting integrals can, as opposed to the summations, often be computed in closed form, for instance, for Gaussian and Lorentzian peak shapes.

For example, the problem of computing the critical errors associated with displacement becomes:

$$\underset{\epsilon(x)}{\text{minimize}} \quad \int_{-\infty}^{\infty} \epsilon(x)^2 dx \quad (5.72)$$

subject to

$$\frac{\partial J(\mathbf{t})}{\partial t_i} = 0, \quad i = 1, \dots, T,$$

with $\mathbf{t} = \mathbf{t} + \delta \mathbf{t}$.

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The least squares criterion is:

$$J(\mathbf{t}) = \int_{-\infty}^{\infty} d(\mathbf{x}; \mathbf{t})^2 dx = \int_{-\infty}^{\infty} \left[f(\mathbf{x}; \boldsymbol{\theta}) + \epsilon(\mathbf{x}) - f(\mathbf{x}; \mathbf{t}) \right]^2 dx. \quad (5.73)$$

The Lagrangian function becomes:

$$L(\epsilon(\mathbf{x}), \hat{\mathbf{t}}, \boldsymbol{\lambda}, \mu) = \int_{-\infty}^{\infty} \epsilon(\mathbf{x})^2 dx + \sum_{i=1}^T \lambda_i \int_{-\infty}^{\infty} d(\mathbf{x}; \hat{\mathbf{t}}) \frac{\partial f(\mathbf{x}; \hat{\mathbf{t}})}{\partial t_i} dx. \quad (5.74)$$

Applying the Euler-Lagrange equation (Pierre, 1986) yields:

$$\hat{\epsilon}(\mathbf{x}) = -\frac{1}{2} \sum_{i=1}^T \lambda_i \frac{\partial f(\mathbf{x}; \hat{\mathbf{t}})}{\partial t_i}. \quad (5.75)$$

The system of normal equations (5.4) becomes:

$$\int_{-\infty}^{\infty} \left[f(\mathbf{x}; \boldsymbol{\theta}) - \frac{1}{2} \sum_{i=1}^T \lambda_i \frac{\partial f(\mathbf{x}; \hat{\mathbf{t}})}{\partial t_i} - f(\mathbf{x}; \hat{\mathbf{t}}) \right] \frac{\partial f(\mathbf{x}; \hat{\mathbf{t}})}{\partial t_j} dx = 0, \quad j=1, \dots, T. \quad (5.76)$$

The same can be done for jumping and coincidence.

The least squares criterion can easily be computed in the Fourier domain by making use of a generalization of Parseval's theorem (Papoulis, 1962). According to this theorem, the functions $f(\mathbf{x})$ and $g(\mathbf{x})$ satisfy:

$$\int_{-\infty}^{\infty} f(\mathbf{x}) g^*(\mathbf{x}) dx = \frac{1}{2\pi} \int_{-\infty}^{\infty} F(\omega) G^*(\omega) d\omega, \quad (5.77)$$

in which $F(\omega)$ and $G(\omega)$ are the Fourier transforms of $f(\mathbf{x})$ and $g(\mathbf{x})$, respectively. The superscript $*$ means complex conjugate. This theorem is used to compute the least squares criterion in the Fourier domain for the real model function $f(\mathbf{x}; \boldsymbol{\theta})$ and error function $\epsilon(\mathbf{x})$. Using (5.77) yields for the least squares criterion in the Fourier domain:

$$\begin{aligned}
J(\hat{t}) &= \frac{1}{2\pi} \int_{-\infty}^{\infty} \left[F(\omega; \theta) + E(\omega) - F(\omega; \hat{t}) \right] \left[F(\omega; \theta) + E(\omega) - F(\omega; \hat{t}) \right]^* d\omega \\
&= \frac{1}{2\pi} \int_{-\infty}^{\infty} \left| F(\omega; \theta) + E(\omega) - F(\omega; \hat{t}) \right|^2 d\omega.
\end{aligned} \tag{5.78}$$

Here, $F(\omega; \cdot)$ and $E(\omega)$ are the Fourier transforms of $f(x; \cdot)$ and $\epsilon(x)$, respectively.

By using the multiplication theorem again, the problem of computing the critical errors in the Fourier domain, for instance for displacement, becomes:

$$\begin{aligned}
&\underset{E(\omega)}{\text{minimize}} \quad \frac{1}{2\pi} \int_{-\infty}^{\infty} E(\omega)^2 d\omega \\
&\tag{5.79}
\end{aligned}$$

subject to

$$\frac{\partial J(\hat{t})}{\partial t_i} = 0, \quad i = 1, \dots, T,$$

with $\hat{t} = \theta + \delta\theta$.

This problem has exactly the same form as (5.72).

In this way the Fourier transform of the critical error $\hat{E}(\omega)$ can be computed if computation in the original domain poses too much difficulties. The approximate computation methods are equally well valid in the Fourier domain. The computation of the Voigtian peak shape, for instance, often poses numerical difficulties. The Voigtian peak shape is a convolution of a Gaussian and a Lorentzian peak shape. The Fourier transform of the Voigtian peak shape can be computed by using the convolution theorem. Then problem formulation (5.79) can be used to compute the critical errors $\hat{E}(\omega)$ in the Fourier domain. The inverse transform of $\hat{E}(\omega)$, however, will still contain an integral which is hard to compute. However, if only the critical energy is of interest, Parseval's theorem will help again. Since $\hat{E}(\omega)$ can easily be computed, just as its energy, the critical energy in the original domain follows directly from application of theorem (5.77).

Section 6.1 summarizes the results of Chapters 4 and 5 concerning the critical errors for least squares model fitting. It also reviews the properties of the critical errors. In Section 6.2, these results are applied to least squares fitting of Gaussian, Lorentzian and Voigtian peaks. The numerical experiments concern displacement, jumping and coincidence of the solutions. Furthermore, the accuracy of approximations made in Chapter 5 is numerically checked. Section 6.3 demonstrates the usefulness of the theory by means of simulation experiments with spectroscopic peaks and investigates the accuracy of the approximations of the boundaries by hyperplanes. In Section 6.4, various simulation experiments concerning the upper limit to the displacement derived in Section 4.1 are presented for least moduli, least squares and minimax model fitting.

6.1 Critical errors in least squares model fitting

In Chapter 3, the concept of critical errors has been introduced. The most important property of the critical errors has already been mentioned there: if the energy of the errors of observation is smaller than the critical energy associated with a certain effect, this effect will certainly not occur. The critical energy thus defines a hypersphere in error space. Errors located inside this hypersphere can not cause the effect in question. Errors located outside this hypersphere may cause the effect.

Furthermore, in Chapter 3 a *boundary* associated with displacement, jumping or coincidence that divides the error space into two parts has been defined. This boundary is thus of dimension $N-1$. Errors of observation in the part of the error space containing the origin do not cause the specified effect. Errors in the other part do cause the effect. A rule that predicts in which part particular errors of observation are located has been derived in Chapter 5. All these results are summarized below. Again the three effects, displacement, jumping and coincidence are distinguished and treated separately.

Displacement

It is assumed that the errors of observation ϵ_n are so small, that neither jumping nor coincidence of the solutions may have occurred. So, the solution $\hat{t}$ is displaced somewhat to $\theta + \delta\theta$, in the neighborhood of θ , and the criterion is a convex function of $|t - \hat{t}|$ in the neighborhood of $\hat{t}$. These assumptions guarantee that the considered minimum remains the global minimum. The critical errors $\hat{e}_n$ for displacing the solution from θ to $\hat{t} = \theta + \delta\theta$ are:

$$\hat{e}_n = -\frac{1}{2} \sum_{i=1}^T \lambda_i \frac{\partial f_n(\hat{t})}{\partial t_i} \quad (6.1)$$

Here, the multipliers λ_i are to be solved from the system of linear equations:

$$\sum_{n=1}^N \left[f_n(\theta) - \frac{1}{2} \sum_{i=1}^T \lambda_i \frac{\partial f_n(\hat{t})}{\partial t_i} - f_n(\hat{t}) \right] \frac{\partial f_n(\hat{t})}{\partial t_j} = 0, \quad j=1, \dots, T. \quad (6.2)$$

An approximate solution for the critical errors is given by:

$$\hat{e}_n \approx - \left[f_n(\theta) - f_n(\hat{t}) \right]. \quad (6.3)$$

So, the critical errors are approximately equal to the additive inverses of the deviations for exact observations at $\hat{t} = \theta + \delta\theta$. The critical energy is therefore approximately equal to the value of the least squares criterion for exact observations at $\theta + \delta\theta$. The critical errors and critical energy can easily be computed in this way.

For linear model functions the equality sign applies in (6.3). For nonlinear functions the approximation is very accurate, as is demonstrated in Numerical experiments # 2 and # 3 in the subsequent section.

The concept of critical errors and critical energy associated with displacement can be used to derive an *upper limit* to the displacement of the solution. After all, the critical errors displace the solution over a certain $\delta\theta$ and have minimum energy. Therefore, the errors of observation that cause the *maximum* displacement of the solution in the

direction of $\delta\theta$ in parameter space are the critical errors associated with this displacement. If the energy of the errors of observation $\|\epsilon\|_2^2$ is known a priori, all maximum displacements corresponding to this energy can be computed. Using the approximate critical errors, these maximum displacements form the contour of the least squares criterion for exact observations at the height $\|\epsilon\|_2^2$. Thus the contour encloses a feasible region in which all possible solutions are located. The practical usefulness of the feasible region is demonstrated in Numerical experiments # 14-17 in Section 6.3.

The boundary associated with a displacement of a scalar parameter θ to $\hat{t} = \theta + \delta\theta$ is a hyperplane. It is defined by:

$$\sum_{n=1}^N \left(f_n(\theta) + \epsilon_n - f_n(\hat{t}) \right) \frac{\partial f_n(\hat{t})}{\partial t} = 0. \quad (6.4)$$

The boundary has dimension $N-1$ and divides the error space into two parts. Errors located in the part containing the origin cause displacements smaller than $\delta\theta$ or in opposite direction. Errors located in the other part cause larger displacements. Hence, the inner product of an particular error vector ϵ and the critical error vector $\hat{e}$ predicts in which part of error space ϵ is found. Larger displacement occurs if:

$$\epsilon \cdot \hat{e} \geq \hat{e} \cdot \hat{e}, \quad (6.5)$$

or, equivalently,

$$\sum_{n=1}^N \epsilon_n \hat{e}_n \geq \sum_{n=1}^N \hat{e}_n^2. \quad (6.6)$$

The errors of observation may be systematic and/or statistical.

For statistical errors the following can be derived. Assume independent errors with zero mean and finite variance σ^2 . Then, by using the central limit theorem, the probability of $\hat{e} \cdot \epsilon \geq \hat{e} \cdot \hat{e}$ is approximately given by:

$$P(\hat{e} \cdot \epsilon \geq \hat{e} \cdot \hat{e}) = P(z \geq \frac{\|\hat{e}\|}{\sigma}). \quad (6.7)$$

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Here, $\hat{e} \cdot \epsilon$ is normally distributed with variance

$$\sigma^2 \sum_{n=1}^N \hat{e}_n^2 \quad (6.8)$$

and z is standard normal. If the number of observations increases, the critical energy will increase as well. Therefore, the probability of larger displacement decreases when the number of observations increases.

For displacement of vector valued parameters, the subspace defined by (6.4) is generally of dimension $N-T$. It does not divide the error space into two parts. Therefore the rules (6.5) and (6.7) can not be used. However, the concept *feasible region* can be used. When the energy of the errors of observation is known exactly, the solution is certainly found within the feasible region corresponding to this energy. In the case of statistical errors that are independent and normally distributed with zero mean and common variance σ^2 , the energy of the errors is chi-square distributed with mean $E = N\sigma^2$ and variance $2N\sigma^4$. The region in which the solutions will be found with at least $x\%$ probability can be determined by first computing the energy E_x from $P(E \leq E_x) = x\%$ and then the feasible region corresponding to E_x . At least $x\%$ of the solutions will be found in the $x\%$ feasible region if the experiment is repeated. This is demonstrated in Numerical experiments # 15 and # 17 in Section 6.3.

Jumping

Assume that exact observations were made on a weighted sum model with two overlapping peaks. Then, the criterion has the OSTM structure, defined in Section 3.4.2. The global minimum of this criterion is $\hat{t}' = \theta_K$, the local minimum is $\tilde{t}'$.

The critical errors $\hat{e}_n$ associated with interchange of the minima $\hat{t}$ and $\tilde{t}$ are approximately given by:

$$\hat{e}_n \approx -\frac{1}{2} \left\{ f_n(\theta_K) - f_n(\tilde{t}') \right\}. \quad (6.9)$$

The critical errors are approximately equal to half the additive inverses of the deviations at the local minimum for exact observations. So, the critical energy associated with jumping is approximately equal to a quarter of the value of the least squares criterion at the local minimum for exact observations. The accuracy of this approximation is shown in Numerical experiments # 4 and # 5.

The boundary of dimension N-1 in error space is defined by:

$$\sum_{n=1}^N d_n^2(\hat{t}) = \sum_{n=1}^N d_n^2(\tilde{t}) , \quad (6.10)$$

$$\sum_{n=1}^N d_n(\hat{t}) \frac{\partial f_n(\hat{t})}{\partial t_i} = 0 , \quad i = 1, \dots, T \quad (6.11)$$

and

$$\sum_{n=1}^N d_n(\tilde{t}) \frac{\partial f_n(\tilde{t})}{\partial t_i} = 0 , \quad i = 1, \dots, T. \quad (6.12)$$

In Section 5.4, it was assumed that the boundary is approximately a hyperplane defined by the critical error vector as:

$$\hat{e} \cdot \epsilon = \hat{e} \cdot \hat{e} . \quad (6.13)$$

So, the inner product of the critical error vector $\hat{e}$ and a particular error vector ϵ predicts in which part of the error space ϵ is found and thus whether or not they cause jumping. The rule for jumping is:

$$\hat{e} \cdot \epsilon \geq \hat{e} \cdot \hat{e} . \quad (6.14)$$

If $\hat{e} \cdot \epsilon \leq \hat{e} \cdot \hat{e}$, the errors do not cause jumping. Numerical experiments # 18 and # 19 show an application of rule (6.14).

For statistical errors the following can be derived. Assume again independent errors with zero mean and finite variance σ^2 . Then, by using the central limit theorem, the probability of $\hat{e} \cdot \epsilon \geq \hat{e} \cdot \hat{e}$ is approximately given by:

$$P(\hat{\mathbf{e}} \cdot \hat{\mathbf{e}} \geq \hat{\mathbf{e}} \cdot \hat{\mathbf{e}}) = P(z \geq \frac{\|\hat{\mathbf{e}}\|}{\sigma}). \quad (6.15)$$

Here, $\hat{\mathbf{e}} \cdot \hat{\mathbf{e}}$ is normally distributed with variance

$$\sigma^2 \sum_{n=1}^N \hat{e}_n^2 \quad (6.16)$$

and z is standard normal. Numerical experiment #20 shows an application of (6.16). Again, if the number of observations increases, the critical energy will increase as well. Therefore the probability of jumping decreases when the number of observations increases.

Coincidence

Two cases are distinguished, scalar and vector valued peak parameters.

Scalar peak parameters

Assume that exact observations were made on a weighted sum model with two overlapping peaks. Therefore, the criterion has the OSTM structure, as defined in Section 3.4.2.

The critical errors associated with coincidence of the solutions for the peak parameters b_{K-1} and b_K are approximately:

$$\begin{aligned} \hat{e}_n &\approx - \left\{ f_n(\theta_K) - f_n(\hat{t}_{K-1}) \right\} \\ &= - \left\{ f_n(\theta_K) - g_n(\hat{\mathbf{c}}) - \sum_{k=1}^{K-1} \hat{a}_k h_n(\hat{b}_k) \right\}, \end{aligned} \quad (6.17)$$

in which $\hat{t}_{K-1}$ is the solution resulting from fitting a (K-1)-th order model to exact K-th order observations. So, the critical errors associated with coincidence are approximately equal to the additive inverses of the deviations resulting from fitting this (K-1)-th order model to exact observations. The critical energy is thus approximately

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equal to the value of the least squares criterion for exact observations at the $(K-1)$ -th order stationary point. The accuracy of (6.17) is demonstrated in Numerical experiment # 8.

The boundary or *bifurcation set* associated with coincidence has dimension $N-1$ and is defined by:

$$\sum_{n=1}^N d_n(\hat{t}_{K-1}) \frac{\partial f_n(\hat{t}_{K-1})}{\partial t_i} = 0, \quad i=1, \dots, T_{K-1} \quad (6.18)$$

and

$$\rho = \eta (1-\eta) \hat{a}_{K-1} \sum_{n=1}^N d_n(\hat{t}_{K-1}) \frac{\partial^2 h_n(\hat{t}_{K-1})}{\partial b_{K-1}^2} = 0, \quad (6.19)$$

in which:

$$f_n(\hat{t}_{K-1}) = g_n(c) + \sum_{k=1}^{K-1} a_k h_n(b_k) \quad (6.20)$$

and ρ is the resolution discriminant. Coincidence of the solutions is detected by the sign of the resolution discriminant ρ . When $\rho \geq 0$, coincidence occurs.

The boundary is approximately a hyperplane defined by:

$$\hat{\mathbf{e}} \cdot \hat{\boldsymbol{\epsilon}} = \hat{\mathbf{e}} \cdot \hat{\mathbf{e}}. \quad (6.21)$$

If $\hat{\mathbf{e}} \cdot \hat{\boldsymbol{\epsilon}} \geq \hat{\mathbf{e}} \cdot \hat{\mathbf{e}}$, the errors of observation cause coincidence. If $\hat{\mathbf{e}} \cdot \hat{\boldsymbol{\epsilon}} \leq \hat{\mathbf{e}} \cdot \hat{\mathbf{e}}$, the errors do not cause coincidence. The errors of observation may be systematic and/or statistical again. An application of (6.21) is in Numerical experiment # 18.

For statistical errors the following can be derived. Assume again independent errors with zero mean and finite variance σ^2 . Then, by using the central limit theorem, the probability of $\hat{\mathbf{e}} \cdot \hat{\boldsymbol{\epsilon}} \geq \hat{\mathbf{e}} \cdot \hat{\mathbf{e}}$ is approximately given by:

$$P(\hat{\mathbf{e}} \cdot \hat{\boldsymbol{\epsilon}} \geq \hat{\mathbf{e}} \cdot \hat{\mathbf{e}}) = P(z \geq \frac{\|\hat{\mathbf{e}}\|}{\sigma}). \quad (6.22)$$

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Here, $\hat{e}_n$ is normally distributed with variance

$$\sigma^2 = \frac{1}{N} \sum_{n=1}^N \hat{e}_n^2 \quad (6.23)$$

and z is standard normal. Numerical experiment # 21 shows the application of (6.23). If the number of observations N increases, the critical energy will increase as well. Therefore the probability of coincidence decreases when the number of observations increases.

Vector valued peak parameters

Coincidence of the solutions for vector valued peak parameters is detected by the positive definiteness of the Hessian matrix of the criterion at the $(K-1)$ -th order stationary point. The relevant part of the Hessian matrix is a submatrix R defined by:

$$R_{ij} = -2 \hat{a}_{K-1}^{(1-\eta)\eta} \sum_{n=1}^N d_n(\hat{t}_{K-1}) \frac{\partial^2 h_n(\hat{b}_{K-1})}{\partial b_{K-1,i} \partial b_{K-1,j}}, \quad \begin{matrix} i=1, \dots, B \\ j=1, \dots, B \end{matrix} \quad (6.24)$$

When the eigenvalues of R are all positive, the Hessian matrix is positive definite and the solutions coincide. Since the errors of observation generally appear nonlinearly in the eigenvalues of R , no general solution has been obtained. Therefore, no boundary is derived and consequently also no rules like (6.21) and (6.22). Analytical examples and Numerical experiments # 11-13 in Section 6.2 will clarify things for Gaussian and Lorentzian peak shapes with vector valued peak parameters.

6.2 Verification for spectroscopic peaks

In this section, the effects displacement, jumping and coincidence are demonstrated for least squares fitting of spectroscopic peaks. Furthermore, the accuracy of the approximations made in the previous chapters are verified numerically, also for spectroscopic peaks.

The notation will be adapted to the notation commonly used in spectroscopy. The location parameters will be noted by μ and the width parameters by σ . So, contrary to what has been used so far, the elements of the peak parameter vector β_k are not called β_{ki} anymore, but μ_k and σ_k . The elements of peak parameter vector $\mathbf{b}$ are called m and s respectively.

6.2.1 Displacement

Numerical experiment # 1

The purpose of this experiment is to demonstrate the displacement of the solution as a function of the errors of observation. Observations on a single Gaussian peak were generated:

$$w_n = \alpha \exp \left[- \frac{1}{2} \left(\frac{x_n - \mu}{\sigma} \right)^2 \right] + \epsilon_n . \quad (6.25)$$

The exact parameters were: $\alpha = 1.0$, $\mu = 0.0$ and $\sigma = 1.0$. The design was defined by: $x_n = -1.75 + 0.25n$, $n = 1, \dots, 13$. The energy of the exact observations E_o was 6.94. The parameters α , μ and σ are called amplitude, location and width, respectively. Arbitrary errors ϵ_n were added, multiplied by an increasing factor ξ . For each ξ , the least squares solution $\hat{\mathbf{t}} = (a \ m \ s)^T$ of fitting the Gaussian peak,

$$f(t) = a \exp \left[- \frac{1}{2} \left(\frac{x_n - m}{s} \right)^2 \right] , \quad (6.26)$$

were computed. The amplitude a appears linearly in the normal equations and was solved for analytically. It was expressed as a function of m and s and substituted back into the criterion (Lawton and Sylvestre, 1971; Golub and Pereyra, 1973). Figure 6.1 shows the solutions as a function of the factor ξ . The solutions are obviously displaced as a function of increasing errors of observation. The magnitude of the displacement increases with increasing errors.

Figure 6.1 Solution of fitting one Gaussian peak to observations with increasing errors.

Numerical experiment # 2

The purpose of this experiment is to investigate the accuracy of the approximate computation of the critical errors associated with displacement. For the exact model (6.25), the critical errors were computed, both exactly by (6.2) and approximately by (6.3), for a displacement $\delta \theta = (\delta \mu \ \delta \sigma)^T = (0.1 \ 0.1)^T$ to $\hat{t} = (0.1 \ 1.1)^T$. The linear parameter was solved for analytically again and eliminated from t . The result in figure 6.2 shows the exact and approximate critical errors, represented by a solid and open circle, respectively. One sees that the approximation is very accurate.

Figure 6.2 Exact (solid) and approximate (open) critical errors for $\delta\theta = (0.1 \ 0.1)^T$

Numerical experiment # 3

In this experiment, the critical energy was computed exactly and approximately for different displacements, in order to investigate the accuracy of the approximate critical energy. The least squares solution for fitting the peak (6.26) to (6.25) was forced to move with L successive steps through parameter space, starting from $(\alpha \ \mu \ \sigma)^T$. The step $(\delta\mu \ \delta\sigma)^T$ was $(0.004 \ 0.004)^T$. In each step the exact critical energy E_d was computed. Subscript 'd' denotes displacement. Other subscripts that will be used throughout are: 'j' and 'c' denoting jumping and coincidence, respectively. Subscript 'o' means exact observations, as before.

The exact E_d was compared to the approximate E_d , which is the value of the least squares criterion for errorless observations at $(\mu + l\delta\mu \ \sigma + l\delta\sigma)^T$, in which l is the step number. Both E_d 's were divided by E_o in order to reduce the influence of the design of the experiment. The logarithms of these critical error to signal ratios were plotted as a function of the step number l . This is the energy-difference diagram as defined in Section 3.5. Figure 6.3 shows the result. The approximation is so accurate, even for rather large l that the curves overlap. In

practice, the energy of the errors will not be known equally accurately. Therefore, the use of the approximate critical energy is justified in practice. Seemingly small errors may displace the solution considerably. For example, a displacement of $(0.1 \ 0.1)^T$ can be attained for an error-to-signal energy ratio of about 0.0035. This corresponds to errors of about 6% of the amplitude.

Figure 6.3 Exact (solid) and approximate (dashed) critical energy for increasing displacement.

6.2.2 Jumping

The purpose of this section is to investigate jumping of the solution by means of numerical examples with Gaussian and Lorentzian peaks. Moreover, the accuracy of the approximate critical errors and critical energy associated with jumping is investigated.

Numerical experiment # 4

This experiment demonstrates interchange of the geometrical proportions of overlapping peaks and jumping of the solution. Observations on two overlapping Lorentzian peaks were generated, described by:

$$w_n = \frac{\alpha(1-\eta)}{1 + \left[\frac{x_n - \mu_1}{\sigma_1} \right]^2} + \frac{\alpha\eta}{1 + \left[\frac{x_n - \mu_2}{\sigma_2} \right]^2} + \epsilon_n. \quad (6.27)$$

The exact parameters were: $\alpha = 1.0$, $\mu_1 = -0.5$, $\sigma_1 = 1.0$, $\mu_2 = 0.5$, $\sigma_2 = 1.1$ and $\eta = 0.3$. The design was: $x_n = -1.75 + 0.25n$, $n = 1, \dots, 13$. The energy of the exact observations E_o was 5.37. Notice that the peaks are rather far apart, one whole halfwidth.

The fitted model was:

$$f_n(\mathbf{t}) = \frac{a(1-\eta)}{1 + \left[\frac{x_n - m_1}{s_1} \right]^2} + \frac{a\eta}{1 + \left[\frac{x_n - m_2}{s_2} \right]^2}, \quad (6.28)$$

with parameter vector $\mathbf{t} = (a \ m_1 \ s_1 \ m_2 \ s_2)^T$. The factor η was assumed to be known a priori. Then the approximate critical errors associated with jumping (6.9) were added, multiplied by an increasing factor ξ . For each ξ , the least squares solution was computed. The linear parameter a was solved for analytically, expressed as a function of b_1 and b_2 and substituted back into the criterion. Figure 6.4 shows the solutions for the elements of $\hat{\mathbf{t}}$ as a function of the factor ξ . Jumping of the solution occurs for $\xi = 1.08$. The originally tallest peak was originally located at the left-hand side. Its solution is located at the right-hand side. If the added errors were the exact critical errors, jumping would have occurred for $\xi = 1.0$. Therefore, the approximate critical errors appear to be quite accurate, even for this relatively widely separated peaks. The approximation will be accurate enough for most practical applications.

Figure 6.4 Solutions of fitting two overlapping Lorentzian peaks to observations with increasing errors.

Numerical experiment # 5

The purpose is to investigate the accuracy of the approximate critical energy associated with jumping (6.9). The critical energy was computed as a function of the distance between the two peaks for the exact model (6.27) with $\theta = (\alpha \mu_1 \sigma_1 \mu_2 \sigma_2)^T$. The exact amplitude and the exact widths were fixed to the following values: $\alpha = 1.0$, $\sigma_1 = 1.0$, $\sigma_2 = 1.1$ and $\eta = 0.3$. The design was again: $x_n = -1.75 + 0.25n$, $n = 1, \dots, 13$. The exact location parameters were varied: $\mu_1 = -\mu_2 = \xi$.

The critical energy associated with jumping E_j was computed, both exactly and approximately, as a function of ξ . The logarithms of the ratios of both the exact and approximate E_j to E_0 were computed as a function of ξ . Both E_j 's and E_0 are functions of $\theta = (\alpha \xi \sigma_1 - \xi \sigma_2)^T$. The resulting energy-difference diagram is shown in figure 5. Figure 5 shows that the approximation is again very accurate.

Figure 6.5 *Exact (solid) and approximate (dashed) critical energy associated with jumping for increasing difference between the location parameters.*

So far, only one possible interchange of the parameters has been considered. The originally tallest, left-hand and narrowest peak becomes the tallest, right-hand and widest peak. However, other interchanges of the peak parameters may also occur. The possible interchanges for Lorentzian and Gaussian peak shapes are discussed in numerical experiment #13.

6.2.3 Coincidence

The effect of coincidence is split up into two cases: scalar and vector valued peak parameters. For each case, it is investigated whether or not coincidence occurs. Also the exact and approximate critical errors are computed and compared.

*Scalar peak parameters**Numerical experiment # 6*

The purpose of this experiment is to show coincidence of the solutions. Observations were generated described by:

$$w_n = \alpha(1-\eta) \exp\left[-\frac{1}{2} \left(x_n - \mu_1\right)^2\right] + \alpha\eta \exp\left[-\frac{1}{2} \left(x_n - \mu_2\right)^2\right] + \epsilon_n \quad (6.29)$$

The exact parameters were: $\alpha = 1.0$, $\mu_1 = -0.5$, $\mu_2 = 0.5$ and $\eta = 0.3$. The design was: $x_n = -1.75 + 0.25n$, $n = 1, \dots, 13$. The energy E_0 of the exact observations was 6.15.

The approximate critical errors associated with coincidence, multiplied by a factor ξ , were added to the exact observations. Then the least squares solution $\hat{t} = (\hat{a} \ \hat{m}_1 \ \hat{m}_2)^T$ of fitting two Gaussian peaks was computed as a function of ξ . The factor η was assumed to be known a priori. Figure 6.6 shows the solutions as a function of ξ . The resolution discriminant ρ was also computed and indeed changed sign at $\xi = 1.0$.

Figure 6.6 Solutions of fitting two Gaussian peaks to observations with increasing error.

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Numerical experiment # 7

The purpose of this experiment is to show that the assumed value of η does not influence the effect of coincidence. The same observations were used as in the previous experiment, but a deliberately wrong value was assigned to η . The true value of η was 0.3. Here η was assumed to be 0.4. So, a modeling error was introduced. This modeling error should not influence the coincidence of the solutions, since the sign of ρ (6.19) is not dependent on the value of η . Figure 6.7 shows that coincidence indeed occurs for exactly the same value of ξ .

Figure 6.7 Solutions of fitting two Gaussian peaks to observations with increasing error. The *a priori* knowledge about η was wrong.

Numerical experiment # 8

This experiment shows the accuracy of the approximation for the critical energy associated with coincidence E_c for the model (6.29). The exact parameters $\alpha = 1.0$ and $\eta = 0.3$ were assumed known. The exact location parameters were varied: $\mu_1 = -\mu_2 = \xi$. The first order parameter vector $\mathbf{t}_1$ had two elements and was $(a \ m)^T$. Figure 6.8 shows the logarithms of the ratios of both the exact and approximate E_c to E_0 as a function of ξ .

Figure 6.8 Exact (solid) and approximate (dashed) critical energy as a function of ξ .

Numerical experiment # 9

The purpose of this experiment is to investigate the intuitive notion that the critical energy gets smaller when more parameters are computed. Therefore, the critical energy associated with coincidence of the two closest overlapping peaks of a second and a third order weighted sum model was computed as a function of the distance between the location parameters of the two closest peaks. The model was:

$$w_n = \alpha_1 \exp\left[-\frac{1}{2} \left[x_n - \mu_1\right]^2\right] + \alpha_2(1-\eta) \exp\left[-\frac{1}{2} \left[x_n - \mu_2\right]^2\right] + \alpha_2\eta \exp\left[-\frac{1}{2} \left[x_n - \mu_3\right]^2\right] + \epsilon_n. \quad (6.30)$$

First, the following exact parameters were fixed: $\alpha_1 = 1.0$, $\alpha_2 = 1.0$, $\eta = 0.3$ and $\mu_1 = -2.0$. The design was: $x_n = -3.75 + 0.25n$, $n = 1, \dots, 39$. The location parameters μ_2 and μ_3 were varied: $\mu_2 = -\mu_3 = \xi$. The second order parameter vector t_2 had four elements and was $(a_1 \ a_2 \ m_1 \ m_2)^T$. Figure 6.9 shows the logarithm of the ratio of the approximate critical energy E_c to E_0 as a function of ξ .

Secondly, the following exact parameters were fixed: $\alpha_1 = 0.0$, $\alpha_2 = 1.0$, $\eta = 0.3$ and $\mu_1 = 0.0$. The design was again: $x_n = -3.75 + 0.25n$, $n = 1, \dots, 39$. For these values of the exact parameters, model (6.30) reduces to a second order model. The location parameters μ_2 and μ_3 were varied: $\mu_2 = -\mu_3 = \xi$. The first order parameter vector t_1 had two elements and was $(a \ m)^T$. Figure 6.9 shows the logarithm of the ratio of E_c to E_0 as a function of ξ . The critical energy for a third order model is clearly less than that of a second order model, as was intuitively expected. The critical energy decreases when the number of unknown parameters increases. Therefore, this experiment affirms that always as much as possible a priori knowledge should be incorporated.

Figure 6.9 Critical energy as a function of ξ for a 2-nd (solid) and 3-rd (dashed) order model.

Numerical experiment # 10

A comparison between the exact critical energy associated with coincidence for the fitting of Gaussian, Lorentzian and Voigtian peaks was made. A continuous design was used. This had the advantage that the design was no longer present in the expressions for the critical errors and critical energy. Furthermore, the critical energy of the Voigtian

peaks could be computed by means of the method of Section 5.5. The exact observations were:

$$w(x) = \alpha h(x; \mu) + \alpha h(x; -\mu) , \quad (6.31)$$

in which the function $h(x; \mu)$ is a Gaussian, Lorentzian or Voigtian peak. The width parameters of the peaks were chosen such that the peaks all had the same width at half maximum. The ratio of the two width parameters of the Voigtian peak was chosen equal to one. The exact parameter $\alpha = 1.0$.

The critical energies were computed exactly, with $t_1 = (a m)^T$, as a function of the increasing exact location parameter μ . The critical energies were divided by the respective E_0 again. Figure 6.10 shows the logarithm of the ratios as a function of the distance between the two peaks. This distance was measured in halfwidths. As could have been expected, the critical energy of the Voigtian peak is something between the critical energies of Lorentzian and Gaussian peaks. It is clear that, in this case, the critical energies associated with coincidence do not differ very much.

Figure 6.10 Critical energy for Gaussian (solid), Lorentzian (dashed) and Voigtian (dash-dot) peaks as a function of the distance between the peaks.

*Vector valued peak parameters**Numerical experiment # 11*

This experiment demonstrates that coincidence occurs for vector valued parameters as well. The model of observations was:

$$w_n = \frac{\alpha(1-\eta)}{1 + \left[\frac{x_n - \mu_1}{\sigma_1} \right]^2} + \frac{\alpha\eta}{1 + \left[\frac{x_n - \mu_2}{\sigma_2} \right]^2} + \epsilon_n \quad (6.32)$$

The exact parameters were: $\alpha = 1.0$, $\eta = 0.3$, $\mu_1 = -0.5$, $\sigma_1 = 1.0$, $\mu_2 = 0.5$, $\sigma_2 = 1.1$. The design was: $x_n = -1.75 + 0.25n$, $n = 1, \dots, 13$. The amplitude α and the factor η were assumed to be known a priori and the amplitude of the first order solution was assumed to be known and equal to α . The first order parameter vector t_1 was thus b . The additive inverses of the deviations resulting from fitting a first order model to the exact observations were added, multiplied by a factor ξ . The least squares solution $\hat{t} = (\hat{m}_1 \hat{s}_1 \hat{m}_2 \hat{s}_2)^T$ for fitting two Lorentzian peaks was computed as a function of ξ . In addition, the eigenvalues of the Hessian matrix were computed. Figure 6.11 shows the results. Coincidence clearly occurred in this case with vector valued parameters and the eigenvalues predicted this.

Figure 6.11 Solutions of fitting two Lorentzian peaks to observations with increasing error. Also the eigenvalues of the Hessian matrix of the criterion are shown.

Numerical experiment # 12

The purpose is to show what will happen if, besides the vector valued peak parameters, the amplitude is also unknown. The model of observations was:

$$w_n = \alpha(1-\eta) \exp\left[-\frac{1}{2} \left(\frac{x_n - \mu_1}{\sigma_1}\right)^2\right] + \alpha\eta \exp\left[-\frac{1}{2} \left(\frac{x_n - \mu_2}{\sigma_2}\right)^2\right] + \epsilon_n. \quad (6.33)$$

The exact parameters were: $\alpha = 1.0$, $\eta = 0.3$, $\mu_1 = -0.5$, $\sigma_1 = 1.0$, $\mu_2 = 0.5$, $\sigma_2 = 1.1$. The design was: $x_n = -1.75 + 0.25n$, $n = 1, \dots, 13$.

The factor η was assumed to be known. The additive inverses of the deviations resulting from fitting a first order model to the exact observations were added, multiplied by a factor ξ . The least squares solution $\hat{\mathbf{t}} = (\hat{a} \ \hat{m}_1 \ \hat{s}_1 \ \hat{m}_2 \ \hat{s}_2)^T$ was computed as a function of ξ . Figure 6.12 shows that coincidence occurs only for $\xi = 1.0$. The coincidence does not persist for increasing ξ . On the other hand, interchange occurred for small ξ already and for $\xi > 1.3$ another interchange of peak parameters occurred. Therefore, only the solutions obtained for small ξ are meaningful.

Figure 6.12 Solutions of fitting two Gaussian peaks with vector valued peak parameters and unknown amplitude to observations with increasing errors. Also the eigenvalues of the Hessian matrix of the criterion are shown.

Figure 6.12 showed that there is no coincidence for increasing values of ξ , in the case of both unknown amplitude, location and width parameters. Why this happens is shown below.

The structure of the criterion will now be studied for a K-th order weighted sum model with two overlapping peaks. A common amplitude a'_{K-1} , both location parameters and both width parameters were assumed unknown. It is shown that, for both Gaussian and Lorentzian peak shapes, the Hessian matrix H_K of the least squares criterion is never positive definite in this case. Therefore, resolution is nearly always possible. Only if the Hessian matrix is singular, coincidence may occur. In Chapter 4, it has been explained that the relevant part of the Hessian matrix is the submatrix R , defined by (6.24). With unknown mutual amplitude a'_{K-1} , two location parameters m_{K-1} and m_K and two width parameters s_{K-1} and s_K , R becomes:

$$R = \begin{pmatrix} R_{11} & R_{12} \\ R_{12} & R_{22} \end{pmatrix} = \quad (6.34)$$

$$-2 \hat{a}_{K-1}(1-\eta)\eta \begin{pmatrix} \sum_{n=1}^N d_n(\hat{t}_{K-1}) \frac{\partial^2 h_n(\hat{b}_{K-1})}{\partial m_{K-1}^2} & \sum_{n=1}^N d_n(\hat{t}_{K-1}) \frac{\partial^2 h_n(\hat{b}_{K-1})}{\partial m_{K-1} \partial s_{K-1}} \\ \sum_{n=1}^N d_n(\hat{t}_{K-1}) \frac{\partial^2 h_n(\hat{b}_{K-1})}{\partial m_{K-1} \partial s_{K-1}} & \sum_{n=1}^N d_n(\hat{t}_{K-1}) \frac{\partial^2 h_n(\hat{b}_{K-1})}{\partial s_{K-1}^2} \end{pmatrix}$$

So, the peak parameter vector $\mathbf{b}_{K-1}$ is $(m_{K-1} \ s_{K-1})^T$. The dimension B of $\mathbf{b}_{K-1}$ is equal to 2.

The eigenvalues z_1 and z_2 of R are:

$$z_1 = (R_{11} + R_{22}) - \left[(R_{11} + R_{22})^2 - 4 (R_{11}R_{22} - R_{12}^2) \right]^{1/2}, \quad (6.35)$$

$$z_2 = (R_{11} + R_{22}) + \left[(R_{11} + R_{22})^2 - 4 (R_{11}R_{22} - R_{12}^2) \right]^{1/2}. \quad (6.36)$$

Equations (6.35-36) can be rewritten as:

$$z_1 = b - \left[b^2 - 4ac \right]^{1/2} \quad (6.37)$$

$$z_2 = b + \left[b^2 - 4ac \right]^{1/2}, \quad (6.38)$$

in which $b = R_{11} + R_{22}$ and $ac = 4 (R_{11}R_{22} - R_{12}^2)$.

The condition for coincidence is that both eigenvalues are positive. Therefore, the signs of both eigenvalues will be investigated for weighted sum models with both Gaussian and Lorentzian peak shapes. A Gaussian peak is given by:

$$h(x; \mathbf{b}) = \exp \left[-\frac{1}{2} \left(\frac{x-m}{s} \right)^2 \right]. \quad (6.39)$$

The derivatives of $h(x; \mathbf{b})$ with respect to the parameters are:

$$\frac{\partial h(x; \mathbf{b})}{\partial m} = \frac{(x-m)}{s^2} h(x; \mathbf{b}) \quad (6.40)$$

$$\frac{\partial h(x; \mathbf{b})}{\partial s} = \frac{(x-m)^2}{s^3} h(x; \mathbf{b}) \quad (6.41)$$

$$\frac{\partial^2 h(x; \mathbf{b})}{\partial m^2} = \frac{1}{s^2} \left[\frac{(x-m)^2}{s^2} - 1 \right] h(x; \mathbf{b}) \quad (6.42)$$

$$\frac{\partial^2 h(x; \mathbf{b})}{\partial s^2} = \frac{(x-m)^2}{s^4} \left[\frac{(x-m)^2}{s^2} - 3 \right] h(x; \mathbf{b}) \quad (6.43)$$

$$\frac{\partial^2 h(x; \mathbf{b})}{\partial m \partial s} = \frac{(x-m)}{s^3} \left[\frac{(x-m)^2}{s^2} - 2 \right] h(x; \mathbf{b}). \quad (6.44)$$

The second-order derivative with respect to the location parameter (6.42) is a linear combination of the peak shape $h(x; \mathbf{b})$, which is the derivative of $a'_{K-1} h(x; \mathbf{b})$ with respect to a'_{K-1} , and the first-order derivative with respect to the width parameter. Since the normal equations are satisfied at $\hat{t}_{K-1}$, the element R_{11} vanishes. Then ac is negative. This has direct implications for the possible values of the eigenvalues. The possibilities for the eigenvalues are:

$b > 0$ and $ac < 0$, which yields: $z_1 < 0$ and $z_2 > 0$
and

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$b < 0$ and $ac < 0$, which yields: $z_1 > 0$ and $z_2 < 0$.

Thus z_1 and z_2 have different signs or are both zero. Therefore $\mathbf{R}$ is never positive definite and resolution is always possible.

The same applies for the case of overlapping Lorentzian peaks. The Lorentzian peak is:

$$h(x; \mathbf{b}) = \frac{1}{1 + \left[\frac{x-m}{s} \right]^2} \quad (6.45)$$

The derivatives of the Lorentzian peak are:

$$\frac{\partial h(x; \mathbf{b})}{\partial m} = 2 \frac{(x-m)}{s^2} h^2(x; \mathbf{b}) \quad (6.46)$$

$$\frac{\partial h(x; \mathbf{b})}{\partial s} = 2 \frac{(x-m)^2}{s^3} h^2(x; \mathbf{b}) \quad (6.47)$$

$$\frac{\partial^2 h(x; \mathbf{b})}{\partial m^2} = - \frac{2}{s^2} h^2(x; \mathbf{b}) - 8 \frac{(x-m)^2}{s^4} h^3(x; \mathbf{b}) \quad (6.48)$$

$$\frac{\partial^2 h(x; \mathbf{b})}{\partial s^2} = -6 \frac{(x-m)^2}{s^4} h^2(x; \mathbf{b}) - 8 \frac{(x-m)^4}{s^6} h^3(x; \mathbf{b}) \quad (6.49)$$

$$= \frac{1}{s} \frac{\partial h(x; \mathbf{b})}{\partial s} - 8 \frac{(x-m)^2}{s^4} h^3(x; \mathbf{b}) = - \frac{\partial^2 h(x; \mathbf{b})}{\partial m^2}$$

$$\frac{\partial^2 h(x; \mathbf{b})}{\partial m \partial s} = -4 \frac{(x-m)}{s^3} h^2(x; \mathbf{b}) + 8 \frac{(x-m)^3}{s^5} h^3(x; \mathbf{b}) \quad (6.50)$$

As a result of equation (6.49), the elements R_{11} and R_{22} satisfy:

$$R_{11} = - R_{22} \quad (6.51)$$

This yields for the eigenvalues:

$$z_1 = 0 - \left[(0^2 - 4 (R_{11}R_{22} - R_{12}^2))^{1/2} \right] = - 2 \left[R_{22}^2 + R_{12}^2 \right]^{1/2} \quad (6.52)$$

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$$z_2 = 0 + \left[0^2 - 4 (R_{11}R_{22} - R_{12}^2) \right]^{1/2} = + 2 \left(R_{22}^2 + R_{12}^2 \right)^{1/2} \quad (6.53)$$

Hence the eigenvalues z_1 and z_2 are each other's additive inverses. Matrix R is never positive definite and resolution is nearly always possible.

In the above paragraphs, resolution was nearly always possible. The only exception is when both eigenvalues vanish. The subspace in error space, defined by the normal equations and the condition that both eigenvalues are zero, is of dimension $N-2$. It is atypical for errors of observation to be located in this subspace.

Since typically one eigenvalue of the Hessian matrix is negative for weighted sums of Gaussian or Lorentzian peaks with two overlapping peaks, the criterion will have two minima in the relevant part of the parameter space. So, the criterion will always have the OSTM structure.

In Table 6.1, the results for coincidence of the peak parameters of two overlapping peaks have been summarized. Column 1 contains the parameters that are solved for. Column 2 contains the parameters known a priori.

Table 6.1 Overview of possibilities for coincidence for Gaussian and Lorentzian peaks

fitted	known	coincidence
m_1, s_1	σ_1, σ_2, η	yes
a, m_1, m_2	σ_1, σ_2, η	yes
m_1, m_2 s_1, s_2	α, η	yes
a, m_1, m_2 s_1, s_2	$s_1 = s_2$ η	yes
a, m_1, m_2 s_1, s_2	η	no

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So for unknown amplitude, location and width parameters coincidence will not occur. This does not mean, however, that the solutions obtained, though resolved, are meaningful. Figure 6.12 showed that the solution may contain various combinations of the peak parameters that do not correspond to the exact peak parameters. The next experiment deals with the possible interchanges and the energies of the errors that make these interchanges possible.

Numerical experiment # 13

Observations on two overlapping Gaussian peaks were generated:

$$w_n = \alpha(1-\eta) \exp\left[-\frac{1}{2} \left(\frac{x_n - \mu_1}{\sigma_1}\right)^2\right] + \alpha\eta \exp\left[-\frac{1}{2} \left(\frac{x_n - \mu_2}{\sigma_2}\right)^2\right] + \epsilon_n. \quad (6.54)$$

The exact parameters were: $\alpha = 1.0$, $\eta = 0.3$, $\mu_1 = -0.5$, $\sigma_1 = 1.0$, $\mu_2 = 0.5$, $\sigma_2 = 1.1$. The design was: $x_n = -1.75 + 0.25n$, $n = 1, \dots, 13$.

The factor η was assumed to be known. So, the exact parameters of the two overlapping peaks 1 and 2 satisfied:

$$(1-\eta)\alpha > \eta\alpha, \quad \mu_1 < \mu_2 \quad \text{and} \quad \sigma_1 < \sigma_2. \quad (6.55)$$

The left peak was the tallest and the narrowest. The least squares solution for the peak parameters were identified by the amplitudes $(1-\eta)\alpha$ and $\eta\alpha$. The following solutions could have occurred that did not correspond to the proportions of the exact peaks. Therefore, they were considered meaningless solutions. The solution may have the following properties:

$$\hat{m}_1 < \hat{m}_2 \quad \text{and} \quad \hat{s}_1 > \hat{s}_2 \quad (6.56)$$

$$\hat{m}_1 > \hat{m}_2 \quad \text{and} \quad \hat{s}_1 > \hat{s}_2 \quad (6.57)$$

$$\hat{m}_1 > \hat{m}_2 \quad \text{and} \quad \hat{s}_1 < \hat{s}_2. \quad (6.58)$$

Property (6.57) corresponds to the situation in figure 6.4, while (6.56) corresponds to the situation in figure 6.12 for large ξ .

The order of magnitude of the energy of the errors needed to produce the above interchanges can be estimated as follows. Certainly, errors that are equal to the additive inverses of the deviations of exact observations at the interchanged parameter values will cause these interchanges. The values of the criterion at

$$((1-\eta)\alpha \ \eta\alpha \ \mu_1 \ \sigma_2 \ \mu_2 \ \sigma_1)^T, \quad (6.59)$$

$$((1-\eta)\alpha \ \eta\alpha \ \mu_2 \ \sigma_1 \ \mu_1 \ \sigma_2)^T \quad (6.60)$$

and

$$((1-\eta)\alpha \ \eta\alpha \ \mu_2 \ \sigma_2 \ \mu_1 \ \sigma_1)^T, \quad (6.61)$$

were 0.37 , 7.4×10^{-3} and 0.38 , respectively. These energies were much larger than the approximate critical energy associated with jumping $E_j = 4.2 \times 10^{-8}$. A better guess for the energies of errors causing interchange may be obtained by fitting a model with equal width parameters or equal location parameters to exact observations. The fitted models had parameter vectors $\mathbf{t}' = (a \ m_1 \ s_2 \ m_2 \ s_2)^T$ and $\mathbf{t}'' = (a \ m_1 \ s_1 \ m_1 \ s_2)^T$. The values of the criterion at solutions $\mathbf{t}'$ and $\mathbf{t}''$ were 8.7×10^{-4} and 2.6×10^{-3} , respectively. The value of the criterion at the first order stationary point was 8.7×10^{-4} . Notice that these energies are also much larger than the critical energy associated with jumping. Of course, the critical energies for (6.56) and (6.58) can be computed, but this is too laborious for the purpose pursued.

In a simulation experiment thousand sets of observations (6.54) were generated, with statistical errors. The errors of observation were independent and normally distributed with zero mean and variance σ^2 . The expected value of the energy of the errors was $N\sigma^2$, which was chosen equal to 2.6×10^{-3} . Each time the least squares solution $\hat{\mathbf{t}} = ((1-\eta)\hat{a} \ \hat{\eta}\alpha \ \hat{m}_1 \ \hat{s}_1 \ \hat{m}_2 \ \hat{s}_2)^T$ was computed. The number of times the various kinds of interchange occurred was counted. The results for (6.56), (6.57) and (6.58) were 62, 427 and 71 times, respectively.

6.2.4 Conclusions

The experiments in Section 6.2.3 have shown the displacement, jumping and coincidence of the solutions. Furthermore, they have shown that the

approximations to the critical errors and critical energy are very accurate, often more accurate than the energy of the errors will be known in practice. So, the concept of critical energy can be used in practice. If the errors of observation are known to have smaller energy, displacement, jumping or coincidence will not occur. As discussed in Section 3.5, this can be used in two manners. First, as a help to decide beforehand whether or not the experiment can meet the demands regarding precision and resolution. Secondly, as a way to appreciate the solutions obtained.

Finally, it has been shown that for Gaussian and Lorentzian peaks with unknown amplitude and unknown location and width parameters resolution is always obtained. The Hessian matrix of the criterion at the $(K-1)$ -th order stationary point is never positive definite. In this case however, although resolution is obtained, the solutions are not necessarily meaningful, since interchange of the geometrical peak proportions may have occurred.

6.3 Simulations concerning critical errors

The main purpose of this section is to investigate the approximation of the boundary by a hyperplane. If the approximation is accurate, rules (6.14) and (6.15) are valid. They predict what may happen to the least squares solutions. This is verified by simulations with statistical and systematic errors. A further purpose is to demonstrate the practical usefulness of the feasible region associated with critical errors. The statistical errors in the simulation experiments were generated by a pseudo-random generator from *Numerical Recipes* (Press et al., 1986).

Feasible region

Numerical experiment # 14

This experiment is meant to demonstrate the practical usefulness of the feasible region associated with critical errors. Therefore, thousand sets of observations were generated and the least squares model fitting solutions were computed. The solutions were plotted in

parameter space, together with the boundary that corresponds to the energy of the errors of observation. The observations were described by:

$$w_n = \alpha \exp\left(-\frac{1}{2} \left[\frac{x-\mu}{\sigma}\right]^2\right) + \epsilon_n. \quad (6.62)$$

The exact parameters were: $\alpha = 1.0$, $\mu = 0.0$, $\sigma = 1.0$. The design was: $x_n = -1.75 + 0.25n$, $n = 1, \dots, 13$. The errors ϵ_n were independent and normally distributed. The errors were normalized to energy E , i.e., the energy of the errors was equal to E in each experiment. The energy E was the critical energy associated with a displacement to $(0.0 \ 1.1)^T$. The least squares solution of fitting a Gaussian peak with parameter vector $\mathbf{t} = (a \ m \ s)^T$ was computed each time. Figure 6.13 shows the solutions, indicated by a dot, in the space spanned by m and s . The linear parameter a was expressed as a function of m and s again. The approximate feasible region corresponding to E was also plotted. The solutions are scattered all over the feasible region. So, in this experiment, although based on 'worst case errors', the feasible region is not overly pessimistic.

Figure 6.13 Feasible region for the solutions.

Numerical experiment # 15

Again thousand sets of observations were generated, described by (6.62). Also the least squares solution was computed for each set. The errors of observation were independent and normally distributed with zero mean and variance σ^2 . This time however, the variance was chosen such that the energy of the errors had a probability of 95% to be smaller than E_{95} . E_{95} was chosen as the critical energy for a displacement of the solution to $(0.1 \ 1.0)^T$. Figure 6.14 shows that the solutions were again scattered all over the feasible region. The expected value of the *maximum* number of solutions outside the 95% feasible region was 50. In this experiment only 2 solutions were outside the 95% feasible region. This means that the 95% feasible region can safely be used in practice. Perhaps a percentage less than 95 will suffice.

Figure 6.14 95% Feasible region for the solutions.

Numerical experiment # 16

In Section 3.5 it was said mentioned that it is problematic that the critical energy is a function of the exact parameters. The exact parameters are not known in practice. However, if the critical energy

mainly depends on the *difference* between the parameters but not on the particular values of the exact parameters, this does not matter.

In order to investigate whether or not the critical energy depends much on the particular values of the exact parameters, the size and shape of the feasible region were compared for different values of the exact parameters. For a nonlinear model function, the single Gaussian peak of (6.62), the feasible regions associated with an energy E were computed for two different sets of exact parameters. The exact parameters were: $\alpha = 1.0$, $\mu = 0.0$, $\sigma = 1.0$ and $\alpha = 1.0$, $\mu = 0.1$, $\sigma = 1.0$, respectively. The critical energy E was 3.02×10^{-2} both times. Figure 6.15 shows that the size and shape of feasible region does not depend much on the location in parameter space. Therefore, the concept of critical energy and feasible region appear to be useful in practice, either as a means to decide in advance whether or not the experiment can meet the demands regarding precision and resolution or as a help to appreciate the solution obtained.

For linear least squares the critical errors and, therefore, the size and shape of the feasible region are not a function of the exact parameters. They are only a function of the difference between the parameters.

Figure 6.15 Feasible regions for the solutions for different exact parameters.

Numerical experiment # 17

To show that the theory is also valid for linear least squares, the least squares fitting was considered of a quadratic polynomial with linear parameters a_1 and a_2 to observations described by:

$$w_n = \alpha_1 x_n + \alpha_2 x_n^2 + \epsilon_n. \quad (6.63)$$

Thousand sets of observations were generated and the least squares solution was computed each time. The values of the parameters were $\alpha_1 = 1.0$ and $\alpha_2 = 0.25$. The design was: $x_n = -1.75 + 0.25n$, $n = 1, \dots, 13$. The energy of the exact observations E_0 was 12.5.

The errors of observation were independent and normally distributed with zero mean and variance σ^2 . The variance was chosen such that the energy of the errors had a probability of 95% to be smaller than E_{95} . E_{95} was chosen as the critical energy for a displacement to $(0.9 \ 0.15)^T$. Its value was 0.29. The 95% feasible region was computed. Figure 6.16 shows that the solutions are scattered all over the feasible region again.

Figure 6.16 95% Feasible region and solutions for linear model fitting.

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Numerical experiments #18-21

Boundaries associated with jumping and coincidence.

The purpose of experiments # 18 - # 21 is to to test the rules (6.14) and (6.15) and to investigate whether or not the boundaries associated with jumping and coincidence may be approximated by a hyperplane defined by:

$$\hat{\mathbf{e}} \cdot \boldsymbol{\epsilon} = \hat{\mathbf{e}} \cdot \boldsymbol{\epsilon} , \quad (6.64)$$

in which $\hat{\mathbf{e}}$ is the critical error vector. This is investigated for two cases: scalar and vector valued peak parameters. In experiments #18 and #19, the accuracy of the approximation is investigated for modeling errors. In experiments #20 and #21, the approximation is investigated for statistical errors.

Therefore, observations on two overlapping Gaussian peaks with scalar peak parameters were generated, described by:

$$w_n = \alpha(1-\eta) \exp\left\{-\frac{1}{2} \left[x_n - \mu_1\right]^2\right\} + \alpha\eta \exp\left\{-\frac{1}{2} \left[x_n - \mu_2\right]^2\right\} + \epsilon_n. \quad (6.65)$$

The exact parameters were: $\alpha = 1.0$, $\eta = 0.3$, $\mu_1 = -0.5$, $\mu_2 = 0.5$. The design was: $x_n = -1.75 + 0.25n$, $n = 1, \dots, 13$. The energy of the exact observations E_o was 6.15.

Also, observations on two overlapping Gaussian peaks with vector valued peak parameters were generated, described by:

$$w_n = \alpha(1-\eta) \exp\left\{-\frac{1}{2} \left[\frac{x_n - \mu_1}{\sigma_1}\right]^2\right\} + \alpha\eta \exp\left\{-\frac{1}{2} \left[\frac{x_n - \mu_2}{\sigma_2}\right]^2\right\} + \epsilon_n. \quad (6.66)$$

The exact parameters were: $\alpha = 1.0$, $\eta = 0.3$, $\mu_1 = -0.5$, $\sigma_1 = 1.0$, $\mu_2 = 0.5$, $\sigma_2 = 1.1$. The design was again: $x_n = -1.75 + 0.25n$, $n = 1, \dots, 13$. The energy of the exact observations E_o was 6.34.

Notice that the peaks were relatively widely apart again. An experienced observer might see that the exact observations consist of two peaks.

All errors of observation were assumed to be equal to zero for the moment. The critical errors and energies associated with jumping and

coincidence were computed, both exactly and approximately. The critical energies E are identified again by the subscript 'j' or 'c' and a second subscript 'e' or 'a'. The subscripts mean jumping, coincidence, exact and approximate, respectively.

The results for (6.65) were:

$$\begin{aligned} E_{je} &= 2.94 \times 10^{-4}, & E_{ja} &= 2.81 \times 10^{-4}, \\ E_{ce} &= 1.76 \times 10^{-2} & \text{and} & E_{ca} = 1.79 \times 10^{-2}. \end{aligned}$$

So, the critical energy associated jumping was much smaller than the critical energy associated with coincidence.

The results for (6.66) were:

$$E_{je} = 2.1 \times 10^{-7} \quad \text{and} \quad E_{ja} = 1.7 \times 10^{-7}.$$

The critical energy associated with jumping was much smaller for model (6.66) than for (6.65). This demonstrates again the validity of the intuitive notion that the higher the number of unknown parameters, the lower the critical energy.

Numerical experiment # 18

This experiment shows the accuracy of rule (6.14) in case of modeling errors. In this experiment systematic errors of observation were added to (6.65). A baseline, which had not been modeled, was assumed to be present. The baseline $g(x; \gamma)$ was described as:

$$g_n(\gamma) = \gamma (x_n + 1.5). \quad (6.67)$$

By rule (6.14), jumping or coincidence occurs when:

$$\gamma \geq \frac{\hat{e.e}}{\hat{x.e}}, \quad (6.68)$$

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in which the $N \times 1$ vector $\mathbf{x}$ has elements $(x_n + 1.5)$. The values for γ were computed for exact and approximate critical errors associated with jumping and coincidence, substituted into (6.68). The results were:

$$\begin{aligned} \gamma_{je} &= -1.13 \times 10^{-2}, & \gamma_{ja} &= -1.09 \times 10^{-2}, \\ \gamma_{ce} &= -5.99 \times 10^{-2} & \text{and} & \gamma_{ca} = -6.30 \times 10^{-2}. \end{aligned}$$

The subscripts j, c, e and a mean jumping, coincidence, exact and approximate, as before.

In a simulation experiment, observations were generated described by (6.65) and errors described by (6.67) were added. For increasing values of γ , the least squares solutions $\hat{\mathbf{t}} = (\hat{a} \hat{m}_1 \hat{m}_2)^T$ were computed and plotted in figure 6.17.

In this figure, jumping occurred for $\gamma = -1.32 \times 10^{-2}$, which is close to the computed values. The values for γ are small, so that a baseline with a small slope can already seriously disturb the determination of the parameters. The absolute value of the maximum error occurring was only 3.96×10^{-2} . Coincidence occurred for $\gamma = -6.24 \times 10^{-2}$, which is also close to the predicted values. Rule (6.14) is quite accurate here, both for predicting jumping and coincidence. In practice, rule (6.14) will mostly be accurate enough.

Figure 6.17 Solutions of fitting two Gaussian peaks to observations with increasing modeling errors.

Numerical experiment # 19

A similar experiment was carried out for observations described by (6.66). The values of γ for which jumping should occur were computed with (6.68), the exact and approximate critical errors:

$$\gamma_{je} = -2.21 \times 10^{-3} \quad \text{and} \quad \gamma_{ja} = -1.94 \times 10^{-3} .$$

Observations described by (6.66) were generated and errors described by (6.67) were added again. For increasing values of γ , the least squares solutions $\hat{\mathbf{t}} = (\hat{a} \ \hat{m}_1 \ \hat{s}_1 \ \hat{m}_2 \ \hat{s}_2)^T$ were computed. Jumping occurred for $\gamma = -2.56 \times 10^{-3}$. Again the rule works quite well, although less accurately than in the case of scalar peak parameters.

Numerical experiment # 20

This experiment tests the rules (6.14) and (6.15) when used to predict jumping. Statistical errors of observation were added to the exact observations of both (6.65) and (6.66). The errors were independent and normally distributed with zero mean and standard deviation $i\sqrt{E_{ja}}$, $i = 1, \dots, 3$. For each i , 10000 sets of observations were generated and the least squares solutions were computed. The following numbers were computed:

- (1) the number of times jumping actually occurred,
- (2) the number of times the approximate critical errors predicted jumping,
- (3) the number of times this prediction failed,
- (4) the number of times the exact critical errors predicted jumping,
- (5) the number of times this prediction failed.

The probabilities of coincidence, computed by (6.15), for observations described by (6.65) in these experiments were 0.00002, 0.00005 and 0.0049 for $i=1, \dots, 3$, respectively. The actual number of coincidences were 0, 0 and 53, respectively. Therefore, only for $i=3$, the expected

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number of jumps was slightly smaller than in the case no coincidence could occur. The total number times the tests on jumping were carried out for $i=3$ was thus not 10000, but 9947. For observations described by (6.66), no coincidence will occur, so there are no difficulties in this case.

In Tables 6.2 and 6.3, the first column contains the value for i , the second contains the expected value μ_{ja} of the number of jumps, using (6.15) with the approximate critical energy. The third column contains the standard deviation σ_{ja} of this expected value. The other columns contain the scores described above.

Table 6.2 Actual number of jumps and expected values, for observations described by (6.65).

i	μ_{ja}	σ_{ja}	(1)	(2)	(3)	(4)	(5)
1	1587	37	1561	1643	402	1576	26
2	3085	46	3048	3088	575	3062	63
3	3687	48	3721	3627	651	3663	109

Table 6.3 Actual number of jumps and expected values, for observations described by (6.66).

i	μ_{ja}	σ_{ja}	(1)	(2)	(3)	(4)	(5)
1	1587	37	1555	1573	294	1568	30
2	3085	46	3048	3072	406	3082	57
3	3707	48	3717	3694	491	3701	84

Tables 6.2 and 6.3 clearly show that the number of failures is much smaller when using the exact critical errors than when using the approximate critical errors in rule (6.14). Thus the rule works better with the exact critical errors. The total number of actual jumps, is very accurately equal, within one standard deviation, to the expected value computed with (6.15).

In conclusion, the rules (6.14) and (6.15) are so accurate, that the

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boundary associated with jumping may in practice be considered approximately a hyperplane. Furthermore, the use of the approximate critical errors still yields reasonably accurate results.

Numerical experiment # 21

This experiment tests the rules (6.14) and (6.15) when used to predict coincidence. Therefore, statistical errors of observation were added to the exact observations of (6.65). The errors were independent and normally distributed with zero mean and standard deviation $i \cdot \sqrt{E_{ca}}$, $i = 1, \dots, 3$. For each i , 10000 sets of observations were generated and the least squares solution, $\hat{t} = (\hat{a} \ \hat{m}_1 \ \hat{m}_2)^T$ was computed each time. Five numbers were computed again:

- (1) the number of times coincidence actually occurred,
- (2) the number of times the approximate critical errors predicted coincidence,
- (3) the number of times this prediction failed,
- (4) the number of times the exact critical errors predicted coincidence,
- (5) the number of times this prediction failed.

In Table 6.4, the first column contains the value for i , the second contains the expected value μ_{ca} of the number of coincidences, using (6.15) with the approximate critical energy. The third column contains the standard deviation σ_{ca} of this expected value. The other columns contain the scores described above.

Table 6.4 Actual number of coincidences and expected values
for observations described by (6.65).

i	μ_{ca}	σ_{ca}	(1)	(2)	(3)	(4)	(5)
1	1587	37	1680	1550	278	1592	128
2	3085	46	3303	3035	570	3062	391
3	3707	48	4175	3685	794	3737	672

The most striking property of Table 6.4 is that the number of times coincidence occurred is significantly higher than the expected value computed by (6.15). Furthermore, the percentage of failures appears to increase when the variance of the errors of observation increases. This leads to the qualitative conclusion that the boundary associated with coincidence is not a hyperplane in error space, but a hypersurface that is 'bent' somewhat around the origin. Table 6.4 shows further that rule (6.14) works reasonably well for predicting coincidence of solutions for scalar peak parameters. Using the exact critical errors gives a better result than using the approximate critical errors. The difference is less obvious than for jumping.

Numerical experiment # 22

The purpose of this final simulation in this section is to demonstrate the three effects, displacement, jumping and coincidence. Also to show that the concept feasible region can be applied to displacement of other stationary points as well. Thousand sets of observations on two overlapping Gaussian peaks were generated, described by:

$$w_n = \alpha(1-\eta) \exp\left[-\frac{1}{2} \left(x_n - \mu_1\right)^2\right] + \alpha\eta \exp\left[-\frac{1}{2} \left(x_n - \mu_2\right)^2\right] + \epsilon_n, \quad (6.69)$$

where η defines the amplitude ratio. The exact parameters were: $\alpha = 1.0$, $\eta = 0.3$, $\mu_1 = -0.5$ and $\mu_2 = 0.5$. The design was: $x_n = -1.75 + 0.25n$, $n = 1, \dots, 13$. The approximate critical energies were: $E_j = 2.81 \times 10^{-4}$ and $E_c = 1.79 \times 10^{-2}$.

The errors were independent and normally distributed with zero mean and variance $\sigma^2 = E_c$. For each set of observations the least squares solution was computed. The 95% feasible region is shown in figure 6.18. The linear parameter was solved for again and substituted back into the criterion. The parameter space was plotted and transformed according $(1-\eta)m_1 + \eta m_2$ and $m_1 - m_2$. In this way the coinciding solutions are on the axis $m_1 - m_2 = 0$.

Since the critical energy associated with jumping is small compared to the energy of the errors, the approximation for the feasible region is not only valid for the minimum in the neighborhood of θ , but also

for minimum in the neighborhood of the originally local minimum. Furthermore, the energy of the errors may be considered small with respect to the criterion for fitting of a first order model. Therefore, the theory of the displacement of solutions and the feasible region associated with critical errors is also valid for the first order solution. All possible solutions, not only displaced solutions, but also interchanged and coincided solutions, are thus located within the contour.

The expected value for the number of coincidences was 159. The number of times coincidence occurred was 163. In figure 6.18, they are on the line $m_1 - m_2 = 0$. Interchange should have occurred in approximately half of the cases. Figure 6.18 shows this is the case. The solutions are clustered around the exact parameters and its interchanged equivalent and on the line $m_1 - m_2 = 0$.

Figure 6.18 95% Feasible region for solutions of fitting two Gaussian peaks.

6.3.1 Conclusions

The simulations in Section 6.3 showed that the concept of critical errors and critical energy can be used in practice. The feasible region associated with critical errors is not overly pessimistic for statistical errors. Rules (6.14) and (6.15) have been found to be accurate

enough to be useful in practice. Therefore, the assumption that the boundaries associated with interchange and coincidence may be approximated by a hyperplane defined by:

$$\hat{\mathbf{e}} \cdot \boldsymbol{\epsilon} = \hat{\mathbf{e}} \cdot \hat{\mathbf{e}}, \quad (6.70)$$

in which $\hat{\mathbf{e}}$ is the critical error vector, is justified. The widespread availability of reliable nonlinear least squares model fitting software (Bolstad, 1987, Press et al., 1986) enables anyone to use the concept of critical errors, rules (6.14) and (6.15) and feasible region in practice.

6.4 Simulations concerning the upper limit

In Section 4.1 an upper limit for the displacement of the solutions of ℓ_p model fitting has been derived. The upper limit is:

$$\|\mathbf{f}(\boldsymbol{\theta}) - \mathbf{f}(\hat{\mathbf{t}})\|_p \leq 2 \|\boldsymbol{\epsilon}\|_p. \quad (6.71)$$

Here, $\hat{\mathbf{t}} = \boldsymbol{\theta} + \delta\boldsymbol{\theta}$ and $\|\boldsymbol{\epsilon}\|_p$ is the ℓ_p norm of the errors. There were no restrictions on the model function $\mathbf{f}(\mathbf{x};\boldsymbol{\theta})$ nor on the size of the errors. The feasible region defined by (6.71) is the contour of the ℓ_p model fitting criterion at a height of twice the norm of the errors of observation. In this section, it is investigated for statistical errors whether or not feasible region associated with the upper limit is substantially too large.

For observations on one Gaussian peak and statistical errors, the least moduli, least squares and minimax model fitting solutions have been computed.

Numerical experiment # 23

The purpose of this experiment is to check whether or not the upper limit yields a too large feasible region. Observations were generated as:

$$w_n = \alpha \exp \left\{ -\frac{1}{2} \left[\frac{x_n - \mu}{\sigma} \right]^2 \right\} + \epsilon_n . \quad (6.72)$$

The exact parameters were: $\alpha = 1.0$, $\mu = 0.0$, $\sigma = 1.0$. The design was: $x_n = -1.75 + 0.25n$, $n = 1, \dots, 13$. The amplitude α was assumed to be known.

A Gaussian peak with parameter vector $\mathbf{t} = (m \ s)^T$ was fitted by means of least moduli, least squares and minimax model fitting, respectively. First, observations described by (6.72) were generated 500 times with normally distributed errors. The norm of the errors was normalized each time to half the value of the ℓ_p model fitting criterion at $(0.1 \ 1.0)^T$. The border of the feasible region will now contain $(0.1 \ 1.0)^T$. Each time the ℓ_p model fitting solution was computed and represented by a dot. The figures 6.19, 6.20 and 6.21 show the results for least moduli, least squares and minimax fitting, respectively. The feasible regions were plotted as a function of m and s . The feasible regions are indeed too large, but still yield a good estimate of the precision that can be expected.

Figure 6.19 Feasible region for solutions of least moduli fitting one Gaussian peak.

Figure 6.20 Feasible region for solutions of least squares fitting one Gaussian peak.

Figure 6.21 Feasible region for solutions of minimax fitting one Gaussian peak.

Numerical experiment # 24

The same experiment was carried out, but now the errors of observation had different distributions. For least moduli fitting, the errors of observation were Laplacian distributed. For minimax model fitting, the errors were uniformly distributed. Then, in both cases the fitting methods are maximum likelihood methods. The results in figures 6.22 and 6.23 show that the distribution of the solutions is not very different from that in figures 6.20 and 6.21. Again, the feasible region is too large.

Figure 6.22 Feasible region for solutions of least moduli fitting one Gaussian peak to observations with Laplacian distributed errors.

Figure 6.23 Feasible region for solutions of minimax fitting one Gaussian peak to observations with uniformly distributed errors.

This chapter starts with a discussion of the possible extensions of the theory developed in this thesis. Then the relations with other theories are discussed.

Extensions

The theory can be extended in several ways. Most obvious is using other model functions in the weighted sum model. Van den Bos (1981) has already studied the case of multi-exponential decay. Other examples are sums of sinc functions, of Gabor pulses or of acoustic wavelets. The theory can be applied without major changes. However, if these functions are strongly oscillating, the model fitting criterion will have several extra relevant minima (Van der Werff, 1989). So, extra attention is required in this case.

So far, the peak shapes were assumed a function of only one independent variable. However, the theory may be extended to peak shapes with several independent variables. The same effects are found to occur in this case (Van den Bos, 1991b). A possible application is the fitting of a model to a two-dimensional incoherent diffraction pattern.

Functions of weighted sum models may also be considered. A resolution discriminant can again be derived in this case. A possible application is the fitting model to a, whether or not two-dimensional, coherent diffraction pattern.

An extension of the theory that uses the special hierarchy of weighted sum models is a procedure called *hierarchical model fitting*. It was proposed by Van den Bos (1990). It is a procedure to decide relatively easily how many peaks can be distinguished and what their peak parameters are, without the requirement of detailed a priori knowledge. The procedure is as follows. Suppose error corrupted observations are available of a weighted sum model of unknown order with scalar peak parameters. First, a weighted sum model of the lowest order that roughly explains the observations is fitted. Then the resolution discriminant is used to decide whether or not a higher order model can

be fitted. If so, the model is fitted and the solution obtained is appreciated with the theory developed in this thesis. If the solution is meaningful, the procedure is repeated. It is repeated until the resolution discriminant is positive or until a solution results that is considered meaningless.

The theory can also be applied to weighted sum model with more than two close components. A resolution discriminant that detects coincidence of three scalar peak parameters has been derived (Van den Bos and Van der Werff, 1989). The theory is similar to the theory for two overlapping peaks, but more complex. The number of relevant minima of the criterion near the lower order stationary point is larger than two. Also the number of possible interchanges is higher.

The theory may be used to investigate which model fitting method may best be used under specified conditions. In addition, the best experimental design could be computed. This last has already been studied (Van den Bos, 1982), but the new theory on critical errors might elucidate and facilitate this study.

Finally, the theory may be used to study the sensitivity of model fitting solutions to the choice of the model function. The exact peak shape is often not known in practice. Therefore, it would be desirable to know to what extent model fitting solutions for quantities such as the peak area or peak location are sensitive to the choice of a model different from the true one. Will the fitting of a Gaussian peak to a non-Gaussian peak seriously influence the measured peak area? The answer may be found by using the theory.

In conclusion, many extensions are possible.

Relations with other theories

In Chapter 5, approximate expressions for the critical errors were derived. They were based on linearization of the model function with respect to the parameters. However, in Section 3.1, linearization was

said to be undesirable in general, since it can not reveal typical nonlinear effects. This seemingly contradiction is discussed below.

The linearization used in approximately computing the critical errors associated with displacement is a linearization of the model function like the one said to be undesirable. However, the assumptions made when computing the critical errors associated with displacement guarantee that no typical nonlinear effects occur. The other linearizations in approximately computing the critical errors associated with jumping and coincidence are carried out after the nonlinear effects were detected and described.

Anyway, contrary to theories that are based on linearization only, the approximate expressions deal with nonlinear effects and furthermore, if necessary, the exact expressions can be computed.

A striking property of all theories on confidence intervals, feasible solution sets and feasible regions is that the contour of the model fitting criterion is so important. The confidence region in equation (3.2) was defined as the contour of the criterion, the feasible regions in this thesis are defined by the contours, and also the feasible solution sets are in fact contours of a model fitting criterion. The theories differ in the computation of the heights of the contours and in whether the criterion for the real observations is used or the criterion for exact observations using nominal values for the parameters.

Another method to derive a confidence region for the solutions is described in *Numerical Recipes* (Press et al., 1986). It is proposed to use the solutions obtained from experiment as the exact parameters and synthesize many sets of alternative observations. These synthetic sets of observations are then used for model fitting. The solutions so obtained are stored and compared to each other and to the real solution. The distribution in parameter space of the synthetic solutions around the real solution is considered to reflect the real distribution around the exact parameters. Obviously, this technique will yield solutions distributed within the contour at the proper height of the criterion for exact observations using the real solution as hypothetical exact parameters. This has been shown in Section 6.3.

A really pragmatic person might ask the following question: Why all this theory, is the model fitting criterion itself not clear enough? In fact, the authors of Numerical Recipes (Press et al., 1986) also ask and answer this question when they state on page 531:

'Offered the choice between mastery of a five-foot shelf of analytical statistics books and middling ability at performing statistical Monte Carlo simulations, we would surely choose to have the latter skill.'

The author's opinion is that it has been worth studying model fitting methods and developing the new theory. Hopefully, model fitting users will take notice of it.

A general problem in applying model fitting theories is the fact that most theories use the exact parameters. The latter, of course, are not known. This problem is avoided for the theory developed in this thesis when using it to test beforehand whether or not the experimental setup is good enough to meet the demands. In this case the experimenter has to work with nominal values for the parameters anyway.

However, it can not be avoided when using the theory to appreciate the solutions obtained. The proper way to handle this situation is using the solutions as if they were the exact parameters. They are used to compute the critical energy in question. This energy is then compared to, perhaps a guess of, the energy of the errors of observation. Now it can be concluded whether or not the solutions could have been substantially different from what has been obtained. When the feasible region is computed using the solutions as if they were the exact parameters, the feasible region contains the real exact parameters. This can be proved by simply changing the roles of the exact parameters and the solution.

If the feasible region defined in Section 4.1 is used to appreciate an obtained solution, the region can be made smaller. In deriving the feasible region (4.6), the following inequality also resulted:

$$\|f(\theta) - \hat{f}(\hat{t})\|_p \leq \|f(\theta) + \epsilon - \hat{f}(\hat{t})\|_p + \|\epsilon\|_p. \quad (7.1)$$

Since a solution $\hat{t}$ has been obtained, the value of the ℓ_p criterion at the solution had been computed. So, the right-hand side of (7.1) contains two known quantities now, the value of the criterion and the a priori known norm of the errors. Therefore, equation (7.1) defines a

new and smaller region. This region around $\hat{t}$ certainly contains the exact parameter vector θ .

A second general problem in model fitting is the fast growing complexity with an increasing number of peak parameters. This problem is partly avoided when using the developed theory for computing the critical energy associated with jumping or coincidence. After all, in this case, only the two peak parameter vectors of the two overlapping peaks are important, irrespective of how many other parameters are to be solved for.

When using the feasible region, this growing complexity is a problem. So far, the best solution appears to be using the projections of the feasible region on the axes in parameter space. In this way independent but pessimistic feasible intervals for all parameters can be obtained. An alternative was given by Norton (1985). He computed feasible solution sets, as mentioned in Section 3.1, and approximated these sets by ellipsoids. In this way, the shape of the feasible solution set is not completely destroyed, as happens when projections are used. The same procedure might be applied to the feasible region.

Finally, a remark about resolution. Resolution has been defined here as the ability to distinguish between objects described by the same parametric function, but with different values for the parameters. In this way distinguishing between objects described by different parametric functions is not considered a matter of resolution, but rather of precision.

A theory has been developed which establishes a relation between model fitting solutions and the errors of observation. The approach in this thesis was to consider the model fitting criterion as a function of the parameters and parametric in the errors of observation. This approach is valid for any number of observations and for any kind of errors of observation, either statistical or systematic. A direct result is the upper limit to the displacement of model fitting solutions derived in Section 4.1.

The approach was applied to the fitting of weighted sum models, especially to the fitting of spectroscopic models. Three effects of errors of observation on the model fitting solutions were distinguished: displacement, jumping and coincidence of the solutions. A boundary that divides the error space into two parts is associated with each effect. Errors located in the one part do not cause the effect, errors located in the other do.

For least squares model fitting the boundary was defined mathematically. The errors on the boundary closest to the origin were computed. They were called critical errors. Their energy was called the critical energy. Errors having smaller energy can certainly not cause the effect in question. The critical errors associated with displacement can be used to compute a region in which all possible solutions are located.

Also approximate but accurate expressions for the critical errors and critical energy were derived. These expressions can easily be computed. The boundary can be approximated accurately by a hyperplane. This facilitates the decision in which part of error space arbitrary errors are located. This is especially suitable for investigating the influence of systematic errors of observation, such as modeling errors. It also makes it possible to compute the probability of the occurrence of jumping or coincidence for statistical errors with known variance. The concept of critical energy is especially useful in practice, since only a scalar quantity has to be known a priori, namely the energy of the errors. Furthermore, the feasible region for the solutions of the parameters is approximately but accurately defined by the contour of the least squares criterion at the height of the energy of the errors.

CHAPTER 8

The numerical experiments with spectroscopic models showed that the theory can easily and accurately be used in spectroscopic practice. It can be used in practice to investigate beforehand whether or not the experimental setup will be good enough to meet the demands. Also, the theory can be used to appreciate the obtained solutions afterwards.

The most important properties of the theory are its validity for non-linear model fitting, for any number of observations and for any kind of errors. In addition, it can easily be applied since it requires only the use of numerical minimization methods, which are available to every experimenter.

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LIST OF SYMBOLS

General

Vectors are denoted in small **bold** characters.

Matrices are denoted in capital **BOLD** characters.

Transposition of vectors and matrices is denoted by a superscript T

A function $f(x_n; \theta)$, evaluated at the point x_n and parametric in θ , is written as $f_n(\theta)$.

Greek characters

α_k	amplitude of the k-th peak
β_k	vector of exact peak parameters of the k-th peak
γ	vector of exact baseline parameters
$\delta\theta$	displacement in parameter space
ϵ_n	n-th error of observation
η	numerical factor, defines the ratio of the amplitudes a_{K-1} and a_k
θ	vector of exact parameters
λ_i	element of vector of Lagrange multiplier λ
λ	vector of Lagrange multipliers
μ	vector of Lagrange multipliers
μ	Lagrange multiplier, exact location parameter
ν	vector of Lagrange multipliers
ξ	numerical factor
ρ	approximate resolution discriminant, coefficient of quadratic term of Taylor series of the criterion
σ	coefficient of cubic term of Taylor series of the criterion, exact width parameter
τ	coefficient of quartic term of Taylor series of the criterion
ω	independent variable in Fourier domain of x

LIST OF SYMBOLS

Roman characters

a	subscript denoting 'approximate'
a_k	amplitude of the k-th peak
$\mathbf{b}_k$	vector of peak parameters of the k-th peak
c	subscript denoting 'coincidence'
$\mathbf{c}$	parameter vector of baseline
$d_n(t_K)$	deviation of K-th order model from the
$\hat{e}$	n-th observation at t_K
$\mathbf{e}$	vector of critical errors
e	subscript denoting 'exact'
$\hat{e}_n$	critical error at the measurement point x_n
$f_n(\theta)$	model function, parametric in θ , at x_n
$g_n(\gamma)$	baseline function, parametric in γ , at x_n
$h_n(\beta_k)$	peak shape function, parametric in β , at x_n
i	counter
j	counter, subscript denoting jumping
m	location parameter
n	counter
o	subscript denoting 'observations'
p	number that indicates the ℓ_p -norm
s	width parameter
$\mathbf{t}$	parameter vector of the model
w_n	n-th observation
x_n	n-th measurement point
z_i	i-th eigenvalue of a matrix

Capital characters

B	dimension of parameter vectors $\mathbf{b}$ and β
C	dimension of parameter vectors $\mathbf{c}$ and γ
D	resolution discriminant
E	energy

LIST OF SYMBOLS

$E(\omega)$	Fourier transform of errors of observation
$\hat{E}(\omega)$	Fourier transform of critical errors $\hat{e}(x)$
$F(\omega; \theta)$	Fourier transform of model function $f(x; \theta)$
H_K	Hessian matrix of the criterion $J(t_K)$
I_i	unity matrix of dimension i
$J(t_K)$	least squares estimation criterion of a weighted sum model of order K
K	order of model, number of peaks
L	Lagrangian function
N	number of observations
P	transformation matrix
Q	transformation matrix
R	submatrix of the Hessian matrix, used as resolution discriminant
T	dimension of parameter vectors t and θ

Mathematical characters

$\ \cdot \ _p$	ℓ_p -norm
$O(t^n)$	order symbol of Landau
$\text{diag}(A \ B)$	partitioned matrix with submatrices only at the diagonal:

$$\begin{bmatrix} A & . & 0 \\ . & . & . \\ 0 & . & B \end{bmatrix}$$

Acronyms

AIO	Assistant In Opleiding
OM	One Minimum
OSTM	One Saddle Two Minima
UBBE	Unknown But Bounded Errors

GLOSSARY

Term	Description
amplitude	linear parameter corresponding to the height of a peak.
baseline	function describing phenomena of a spectrum other than the spectroscopic peaks.
bifurcation set	boundary associated with coincidence.
boundary	hypersurface defined by a particular displacement, jumping or coincidence, dividing the error space into two parts.
close peak parameters	peak parameters of a K-th order model are close when a (K-1)-th order model fits well it, when $\max d_n(\hat{t}_{K-1}) \ll \hat{a}_{K-1}$.
confidence interval	projection of the confidence region on the axes of parameter space.
confidence region	region in parameter space in which all possible solutions are located with a certain probability.
coincidence	coincidence of the solutions for the peak parameters caused by a structural change of the criterion, preventing resolution of the peak parameters.
contour	hypersurface in parameter space consisting of all points yielding equal criterion values.

GLOSSARY

criterion	function of the parameters, describing the goodness of fit.
critical energy	energy of the critical errors.
critical errors	errors on the boundary closest to the origin.
critical norm	norm of the critical errors.
degeneracy	merging of stationary points of the criterion
degenerate parameter vector	parameter vector with equal peak parameter vectors.
design	definition of the experiment, i.e., the number and locations of the measurement points.
displacement	displacement of the solution in parameter space, leading to imprecision.
energy	sum of squares of observations or errors.
energy-difference diagram	diagram containing the critical energy as a function of the difference between the peak parameters.
errors of observation	quantities small compared to the amplitude of the observations, either statistical or systematic.
error space	space spanned by the errors of observation.
feasible region	region in parameter space containing all possible solutions, given the norm of the errors.

GLOSSARY

Hessian matrix	matrix of second-order partial derivatives.
interchange	interchange of the peak parameters in the solution, leading to interchange of the original geometrical proportions of two overlapping peaks.
jumping	jump of the solution in parameter space, leading to interchange.
Lagrangian function	function whose stationary points contain the solution of a minimization problem under equality constraints.
least moduli fitting	model fitting using the ℓ_1 norm.
least squares fitting	model fitting using the ℓ_2 norm.
minimax fitting	model fitting using the ℓ_∞ norm.
model	abstraction of reality.
model function	mathematical function describing the model.
model fitting	process of varying the parameters of the model function in such a way that the model fits best to the observations.
norm	scalar function $\ \cdot\ $ of $\mathbf{x}$ to measure distance, satisfying $\ \mathbf{x}\ \geq 0$, $\ \mathbf{x}\ = 0 \Leftrightarrow \mathbf{x}=\mathbf{0}$, $\ a\mathbf{x}\ = a \ \mathbf{x}\ $ and $\ \mathbf{x}_1+\mathbf{x}_2\ \leq \ \mathbf{x}_1\ + \ \mathbf{x}_2\ $.
norm-difference diagram	diagram containing the critical norm as a function of the difference between the peak parameters.
observation space	space spanned by the observations.

GLOSSARY

order	number of peaks of a weighted sum model.
parameter space	space spanned by the parameters.
parasitic solution	solutions with meaningless values for the peak parameters or amplitudes.
peak	observations described by a peak shape.
peak shape	parametric function describing a spectroscopic peak, having two points of inflection and vanishing at plus and minus infinity.
peak parameters	parameters of the peak shape.
precision	extent to which the model fitting solution is similar to the exact parameters.
resolution	ability of model fitting methods to distinguish between two overlapping peaks.
resolution discriminant	discriminant evaluated at the $(K-1)$ -th order solution predicting whether a K -th order model will have separate peak parameters.
solution	global minimum of the criterion.
solution locus	subspace in observation space defined by the model function.
spectrum	observations of spectroscopic process consisting of peaks, a baseline and errors of observation.
structural change	change of the number or nature of stationary points of a function.

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structure	the structure of a function is described by the number and nature of its stationary points.
upper limit	upper limit to the displacement of the solution.
weighted sum model	weighted sum of functions of the same nonlinearly parametric family.
ℓ_p -norm of x	$\left(\sum_{n=1}^N x_n ^p \right)^{1/p}.$

APPENDIX A PROPERTIES OF SPECTROSCOPIC PEAKS

In this Appendix some properties of and relations between spectroscopic peaks are described. First properties concerning the multiplication and convolution of peak shapes are given:

Gaussian peak shapes

The multiplication of two Gaussian peak shapes is:

$$\begin{aligned} \alpha_1 \exp\left\{-\frac{1}{2}\left(\frac{x-\mu_1}{\sigma_1}\right)^2\right\} \alpha_2 \exp\left\{-\frac{1}{2}\left(\frac{x-\mu_2}{\sigma_2}\right)^2\right\} \\ = \alpha_3 \exp\left\{-\frac{1}{2}\left(\frac{x-\mu_3}{\sigma_3}\right)^2\right\}, \end{aligned} \quad (\text{A.1})$$

in which

$$\alpha_3 = \alpha_1 \alpha_2 \exp\left\{-\frac{1}{2} \frac{(\mu_1 - \mu_2)^2}{(\sigma_1^2 + \sigma_2^2)}\right\}, \quad (\text{A.2})$$

$$\mu_3 = \frac{\mu_1 \sigma_2^2 + \mu_2 \sigma_1^2}{\sigma_1^2 + \sigma_2^2}, \quad (\text{A.3})$$

and

$$\sigma_3^2 = \frac{\sigma_1^2 \sigma_2^2}{\sigma_1^2 + \sigma_2^2}. \quad (\text{A.4})$$

So, the product of two Gaussian peak shapes is Gaussian.

Next the convolution of two Gaussian peak shapes is computed. This can be done directly or by using the Fourier transform and the convolution theorem. Direct computation requires a multiplication and an evaluation of a definite integral and means a lot of algebra. Here the

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second way is chosen. The Fourier transform of a Gaussian peak shape is:

$$F\left[\exp\left(-\frac{1}{2} \left(\frac{x-\mu}{\sigma} \right)^2 \right) \right] = \sigma \sqrt{2\pi} \exp\left(-\frac{1}{2} \sigma^2 \omega^2 \right) \exp(-i\mu\omega) , \quad (\text{A.5})$$

in which $F\{.\}$ is the Fourier transform operator and $i = \sqrt{-1}$. Notice that for $\mu = 0$, the Fourier transform of a Gaussian peak shape is Gaussian again. The convolution property is:

$$F\left[g(x)*h(x) \right] = G(\omega) H(\omega) , \quad (\text{A.6})$$

and

$$g(x)*h(x) = F^{-1}\left[G(\omega) H(\omega) \right] . \quad (\text{A.7})$$

So:

$$\begin{aligned} & \alpha_1 \exp\left(-\frac{1}{2} \left(\frac{x-\mu_1}{\sigma_1} \right)^2 \right) * \alpha_2 \exp\left(-\frac{1}{2} \left(\frac{x-\mu_2}{\sigma_2} \right)^2 \right) \\ &= F^{-1}\left[\alpha_1 \alpha_2 \sigma_1 \sigma_2 2\pi \exp\left(-\frac{1}{2} (\sigma_1^2 + \sigma_2^2) \omega^2 \right) \exp\left\{ -i(\mu_1 + \mu_2)\omega \right\} \right] \\ &= \alpha_3 \exp\left(-\frac{1}{2} \left(\frac{x-\mu_3}{\sigma_3} \right)^2 \right) , \end{aligned} \quad (\text{A.8})$$

in which:

$$\alpha_3 = \alpha_1 \alpha_2 \sigma_1 \sigma_2 \left[\frac{\pi}{2(\sigma_1^2 + \sigma_2^2)} \right]^{1/2} ,$$

$$\mu_3 = \mu_1 + \mu_2 ,$$

and

$$\sigma_3^2 = \sigma_1^2 + \sigma_2^2 .$$

So, the convolution of two Gaussian peak shapes is Gaussian again.

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Lorentzian peak shapes

The convolution of two Lorentzian peak shapes is computed in the same manner. The Fourier transform of the Lorentzian peak shape is:

$$F \left[\frac{1}{1 + \left[\frac{t-\mu}{\sigma} \right]^2} \right] = \pi \sigma \exp(-\sigma |\omega|) \exp(-i\mu\omega) , \quad \sigma > 0. \quad (A.9)$$

Using the convolution property (A.7) yields:

$$\begin{aligned} & \frac{\alpha_1}{1 + \left[\frac{x-\mu_1}{\sigma_1} \right]^2} * \frac{\alpha_2}{1 + \left[\frac{x-\mu_2}{\sigma_2} \right]^2} \\ &= F^{-1} \left[\alpha_1 \alpha_2 \pi^2 \sigma_1 \sigma_2 \exp \left[-(\sigma_1 + \sigma_2) |\omega| \right] \exp \left[-i(\mu_1 + \mu_2) \omega \right] \right] \\ &= \frac{\alpha_3}{1 + \left[\frac{x-\mu_3}{\sigma_3} \right]^2} , \end{aligned} \quad (A.10)$$

in which:

$$\alpha_3 = \frac{\alpha_1 \alpha_2 \pi \sigma_1 \sigma_2}{\sigma_1 + \sigma_2} ,$$

$$\mu_3 = \mu_1 + \mu_2 ,$$

and

$$\sigma_3 = \sigma_1 + \sigma_2 .$$

So, the convolution of two Lorentzian peak shapes is Lorentzian again.

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Asymptotic relations between peak shapes

The following asymptotic relations between peak shapes exist. First the relation between the Pearson VII for large n and the Gaussian peak shape is derived. The following equality holds:

$$\lim_{n \rightarrow \infty} \left[\frac{1}{1 + \frac{1}{n} \left(\frac{x-\mu}{\sigma} \right)^2} \right]^n = \exp \left(- \frac{1}{2} \left[\frac{x-\mu}{\sigma} \right]^2 \right) \quad (\text{A.11})$$

Proof from (Frazer and Suzuki, 1969):

The Taylor expansion of the natural logarithm of a Pearson VII peak shape is:

$$\begin{aligned} \ln \left[\frac{1}{1 + \frac{1}{n} \left(\frac{x-\mu}{\sigma} \right)^2} \right]^n &= - \left[\frac{x-\mu}{\sigma} \right]^2 + \frac{1}{2n} \left[\frac{x-\mu}{\sigma} \right]^4 \\ &\quad - \frac{1}{3n^2} \left[\frac{x-\mu}{\sigma} \right]^6 + o((x-\mu)^8) . \end{aligned} \quad (\text{A.12})$$

So the limit for $n \rightarrow \infty$ is:

$$\lim_{n \rightarrow \infty} \ln \left[\frac{1}{1 + \frac{1}{n} \left(\frac{x-\mu}{\sigma} \right)^2} \right]^n = - \left[\frac{x-\mu}{\sigma} \right]^2 . \quad (\text{A.13})$$

This establishes (A.11).

A similar result can be derived for $\cosh^{-n}$ peak shapes:

$$\lim_{n \rightarrow \infty} \cosh^{-n} \left[\frac{x-\mu}{\sqrt{n} \sigma} \right] = \exp \left(- \frac{1}{2} \left[\frac{x-\mu}{\sigma} \right]^2 \right) . \quad (\text{A.14})$$

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Proof:

The Taylor expansion of the natural logarithm of n multiplications of a $\cosh^{-1}$ peak shape is:

$$\begin{aligned} \ln \left[\cosh^{-n} \left(\frac{x-\mu}{\sqrt{n} \sigma} \right) \right] = & - \frac{1}{2} \left(\frac{x-\mu}{\sigma} \right)^2 + \frac{1}{12n} \left(\frac{x-\mu}{\sigma} \right)^4 \\ & - \frac{1}{45n^2} \left(\frac{x-\mu}{\sigma} \right)^6 + O((x-\mu)^8) . \end{aligned} \quad (\text{A.15})$$

So the result for $n \rightarrow \infty$ is:

$$\lim_{n \rightarrow \infty} \ln \left[\cosh^{-n} \left(\frac{x-\mu}{\sqrt{n} \sigma} \right) \right] = - \frac{1}{2} \left(\frac{x-\mu}{\sigma} \right)^2 , \quad (\text{A.16})$$

which establishes (A.14).

Reference

Fraser, R.D.B. and Suzuki, E. (1969). Resolution of overlapping bands: functions for simulating band shapes. *Analytical Chemistry*, **41**, 37-39.

APPENDIX B DERIVATION OF RESOLUTION DISCRIMINANT.

This Appendix contains the derivation of the resolution discriminant associated with coincidence of two scalar peak parameters for the least squares criterion. First, the K-th order weighted sum model is Taylor expanded. The Taylor coordinates are transformed as in Chapter 4, anticipating on the use of the *Splitting Lemma* (Poston and Stewart, 1978). Then the expansions of the deviations and of the least squares criterion are computed. Subsequently, the (K-1)-th order Hessian matrix is diagonalized and the cubic cross terms are removed. Finally, the expansion is split up into the essential and inessential part. The resolution discriminant then follows directly.

First, a short notation is introduced. The coefficients of the terms of the Taylor expansion are denoted as follows:

$$\frac{1}{p!} \left. \frac{\partial^p h_n(b_k)}{\partial b_k^p} \right|_{\tilde{b}_k} = h_n^{(p)} \quad (B.1)$$

The weighted sum model

$$f_n(t_k) = g_n(c) + \sum_{k=1}^{K-2} a_k h_n(b_k) + (1-\eta)a h_n(b_{K-1}) + \eta a h_n(b_K) \quad (B.2)$$

will now be expanded around the lower order stationary point

$$\tilde{t}_K = (\tilde{c} \mid \tilde{a}_1 \dots \tilde{a}_{K-2} \mid \tilde{a} \mid \tilde{b}_1 \dots \tilde{b}_{K-2} \tilde{b}_{K-1} \tilde{b}_K)^T, \quad (B.3)$$

with $\tilde{b}_{K-1} = \tilde{b}_K = \tilde{b}$.

First the coordinates are transformed as follows:

$${}^1c = c - \tilde{c}, \quad (B.4)$$

$${}^1a_k = a_k, \quad k = 1, \dots, K-1, \quad (B.5)$$

$${}^1a = a, \quad (B.6)$$

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$${}^1b_k = b_k - \tilde{b}_k \quad k = 1, \dots, K. \quad (B.7)$$

The Taylor expansion of $g_n(\mathbf{c})$ is:

$$g_n(\mathbf{c}) = \sum_{p=0}^{\infty} ({}^1\mathbf{c} \cdot \nabla_{\mathbf{c}})^p g_n(\tilde{\mathbf{c}}), \quad (B.8)$$

in which $\nabla_{\mathbf{c}}$ is $(\frac{\partial}{\partial c_1} \dots \frac{\partial}{\partial c_C})^T$, the nabla operator. The Taylor expansion of each of the first $(K-2)$ terms of (B.2) is:

$$a_k h_n(b_k) = \sum_{p=0}^{\infty} {}^1a_k h_n^{(p)} {}^1b_k^p, \quad k = 1, \dots, K-2. \quad (B.9)$$

The expansion of

$$(1-\eta)h_n(b_{K-1}) + \eta h_n(b_K) \quad (B.10)$$

in coordinates b_{K-1} and b_K around $\tilde{b}$ yields:

$$h_n^{(0)} + \sum_{p=1}^{\infty} h_n^{(p)} ((1-\eta){}^1b_{K-1}^p + \eta {}^1b_K^p). \quad (B.11)$$

Then the coordinates are transformed as follows:

$${}^2b_{K-1} = (1-\eta){}^1b_{K-1} + \eta {}^1b_K \quad (B.12)$$

$${}^2b_K = {}^1b_{K-1} - {}^1b_K. \quad (B.13)$$

All other coordinates remain unaltered, but, for convenience, they will also get the superscript 2.

By (B.12) and (B.13):

$${}^1b_{K-1} = {}^2b_{K-1} + \eta {}^2b_K \quad (B.14)$$

and

$${}^1b_K = {}^2b_{K-1} - (1-\eta){}^2b_K. \quad (B.15)$$

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Now the linear, quadratic, cubic and quartic terms of (B.11) are computed. The linear term of (B.11) becomes:

$$h_n^{(1)}((1-\eta)^1 b_{K-1} + \eta^1 b_K) = h_n^{(1)} {}^2b_{K-1}. \quad (B.16)$$

Further is:

$${}^1b_{K-1}^2 = ({}^2b_{K-1} + \eta^2 b_K)^2 = {}^2b_{K-1}^2 + 2\eta^2 b_{K-1} {}^2b_K + \eta^2 {}^2b_K^2 \quad (B.17)$$

$$\begin{aligned} {}^1b_K^2 &= ({}^2b_{K-1} - (1-\eta){}^2b_K)^2 \\ &= {}^2b_{K-1}^2 - 2(1-\eta){}^2b_{K-1} {}^2b_K + (1-\eta)^2 {}^2b_K^2 \end{aligned} \quad (B.18)$$

So:

$$\begin{aligned} &(1-\eta){}^1b_{K-1}^2 + \eta^1 b_K^2 \\ &= (1-\eta+\eta){}^2b_{K-1}^2 + 2\left[(1-\eta)\eta - \eta(1-\eta)\right]{}^2b_K {}^2b_{K-1} + \left[(1-\eta)\eta^2 + \eta(1-\eta)^2\right]{}^2b_K \\ &= {}^2b_{K-1}^2 + (1-\eta)\eta^2 b_K^2. \end{aligned} \quad (B.19)$$

So, the quadratic term of (B.11) becomes:

$$h_n^{(2)}({}^2b_{K-1} + \eta(1-\eta){}^2b_K). \quad (B.20)$$

Also:

$$\begin{aligned} {}^1b_{K-1}^3 &= ({}^2b_{K-1} + \eta^2 b_K)^3 \\ &= {}^2b_{K-1}^3 + 3\eta^2 b_{K-1}^2 {}^2b_K + 3\eta^2 {}^2b_{K-1} {}^2b_K^2 + \eta^3 {}^2b_K^3, \end{aligned} \quad (B.21)$$

$$\begin{aligned} {}^1b_K^3 &= ({}^2b_{K-1} - (1-\eta){}^2b_K)^3 \\ &= {}^2b_{K-1}^3 - 3(1-\eta){}^2b_{K-1}^2 {}^2b_K + 3(1-\eta)^2 {}^2b_{K-1} {}^2b_K^2 - (1-\eta)^3 {}^2b_K^3. \end{aligned} \quad (B.22)$$

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So:

(B.23)

$$(1-\eta)^1 b_{K-1}^3 + \eta^1 b_K^3 = {}^2b_{K-1}^3 + 3\eta(1-\eta)^2 b_{K-1}^2 b_K^2 - \eta(1-\eta)(1-2\eta)^2 b_K^3.$$

The cubic term of (B.11) is:

$$h_n^{(3)} ({}^2b_{K-1}^3 + 3\eta(1-\eta)^2 b_{K-1}^2 b_K^2 - \eta(1-\eta)(1-2\eta)^2 b_K^3). \quad (B.24)$$

Also:

$${}^1b_{K-1}^4 = ({}^2b_{K-1} + \eta^2 b_K)^4 \quad (B.25)$$

$$= {}^2b_{K-1}^4 + 4\eta^2 b_{K-1}^3 {}^2b_K + 6\eta^2 {}^2b_{K-1}^2 {}^2b_K^2 + 4\eta^3 {}^2b_{K-1} {}^2b_K^3 + \eta^4 {}^2b_K^4,$$

$${}^1b_K^4 = ({}^2b_{K-1} - (1-\eta)^2 b_K)^4 \quad (B.26)$$

$$= {}^2b_{K-1}^4 - 4(1-\eta)^2 b_{K-1}^3 {}^2b_K + 6(1-\eta)^2 {}^2b_{K-1}^2 {}^2b_K^2 - 4(1-\eta)^3 {}^2b_{K-1} {}^2b_K^3 + (1-\eta)^4 {}^2b_K^4.$$

So:

$$(1-\eta)^1 b_{K-1}^4 + \eta^1 b_K^4 = {}^2b_{K-1}^4 + 6\eta(1-\eta)^2 b_{K-1}^2 {}^2b_K^2 \quad (B.27)$$

$$- 4\eta(1-\eta)(1-2\eta)^2 b_{K-1} {}^2b_K^3 + \eta(1-\eta)((1-3\eta+3\eta^2)^2 b_K^4).$$

The quartic term of (B.8) is:

$$h_n^{(4)} ({}^2b_{K-1}^4 + 6\eta(1-\eta)^2 b_{K-1}^2 {}^2b_K^2 \quad (B.28)$$

$$- 4\eta(1-\eta)(1-2\eta)^2 b_{K-1} {}^2b_K^3 + \eta(1-\eta)((1-3\eta+3\eta^2)^2 b_K^4).$$

Substitution into (B.8) and multiplication with $a = {}^2a$ yields:

$$a \left[(1-\eta) h_n(b_{K-1}) + \eta h_n(b_K) \right] \quad (B.29)$$

$$= {}^2a \left[h_n^{(0)} + h_n^{(1)} {}^2b_{K-1} \right]$$

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$$\begin{aligned}
& + h_n^{(2)} ({}^2b_{K-1} + \eta(1-\eta){}^2b_K) \\
& + h_n^{(3)} ({}^2b_{K-1}^3 + 3\eta(1-\eta){}^2b_{K-1}{}^2b_K^2 - \eta(1-\eta)(1-2\eta){}^2b_K^3) \\
& + h_n^{(4)} ({}^2b_{K-1}^4 + 6\eta(1-\eta){}^2b_{K-1}^2{}^2b_K^2 \\
& - 4\eta(1-\eta)(1-2\eta){}^2b_{K-1}{}^2b_K^3 + \eta(1-\eta)((1-3\eta+3\eta^2){}^2b_K^4) + O(5) \Big].
\end{aligned}$$

Therefore, the deviation $d_n(\tilde{t}_K + {}^2t_K)$ becomes:

$$\begin{aligned}
d_n(\tilde{t}_K + {}^2t_K) &= w_n - \sum_{p=0}^{\infty} ({}^1c \cdot \nabla_c)^p g_n(\tilde{c}) \\
&- \sum_{k=1}^{K-2} \sum_{p=0}^{\infty} {}^2a_k h_n^{(p)} {}^2b_k^p - {}^2a \sum_{p=0}^4 h_n^{(p)} {}^2b_{K-1}^p - {}^2a \eta(1-\eta) h_n^{(2)} {}^2b_K^2 \\
&- {}^2a h_n^{(3)} \left[3\eta(1-\eta) {}^2b_{K-1}^2 {}^2b_K^2 - \eta(1-\eta)(1-2\eta) {}^2b_K^3 \right] \\
&- {}^2a h_n^{(4)} \left[6\eta(1-\eta) {}^2b_{K-1}^2 {}^2b_K^2 - 4\eta(1-\eta)(1-2\eta) {}^2b_{K-1} {}^2b_K^3 \right. \\
&\quad \left. + \eta(1-\eta)(1-3\eta+3\eta^2){}^2b_K^4 \right] + O(5),
\end{aligned} \tag{B.30}$$

in which w_n are the observations. So, the deviation $d_n(\tilde{t}_K + {}^2t_K)$ is equal to:

$$d_n(\hat{t}_{K-1} + {}^2t_{K-1}) + f_n({}^2a \mid \tilde{b} + {}^2b_{K-1} \mid \tilde{b} + {}^2b_K), \tag{B.31}$$

in which

$${}^2t_{K-1} = ({}^2c \mid {}^2a_1 \dots {}^2a_{K-2} \mid {}^2b_1 \dots {}^2b_{K-2} \mid {}^2b_{K-1})^T, \tag{B.32}$$

and

$$\begin{aligned}
& f_n({}^2a \mid \tilde{b} + {}^2b_{K-1} \mid \tilde{b} + {}^2b_K) \\
&= - \eta(1-\eta) {}^2a h_n^{(2)} {}^2b_K^2 \\
&- {}^2a h_n^{(3)} \left[3\eta(1-\eta) {}^2b_{K-1}^2 {}^2b_K^2 - \eta(1-\eta)(1-2\eta) {}^2b_K^3 \right]
\end{aligned} \tag{B.33}$$

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$$- 2a h_n^{(4)} \left[6\eta(1-\eta) {}^2b_{K-1}^2 {}^2b_K^2 - 4\eta(1-\eta)(1-2\eta) {}^2b_{K-1} {}^2b_K^3 + \eta(1-\eta)(1-3\eta+3\eta^2) {}^2b_K^4 \right] + O(5).$$

Squaring and summing the $d_n(\hat{t}_K + {}^2t_K)$ yields:

$$\begin{aligned} & \sum_{n=1}^N d_n^2(\hat{t}_{K-1} + {}^2t_{K-1}) + \sum_{n=1}^N f_n^2({}^2a \mid \bar{b} + {}^2b_{K-1} \mid \bar{b} + {}^2b_K) \\ & + 2 \sum_{n=1}^N d_n(\hat{t}_{K-1} + {}^2t_{K-1}) f_n({}^2a \mid \bar{b} + {}^2b_{K-1} \mid \bar{b} + {}^2b_K). \end{aligned} \quad (B.34)$$

The Hessian matrix H_{K-1} , which is positive definite, is now diagonalized by a not specified linear coordinate transform ${}^3t_{K-1}$. This transformation does not affect the coordinate 2b_K . The eigenvalues of matrix H_{K-1} are λ_i , $i = 1, \dots, T_{K-1}$. However, for convenience, the superscript 3 is also used for ${}^3b_K = {}^2b_K$. According to the Splitting Lemma, only one coordinate is essential in this case, since only one eigenvalue of K -th order Hessian matrix H_K can vanish.

The first sum does not contain any term in 3b_K , so only the second and third sums are considered. The cubic and higher degree cross terms containing ${}^3t_{K-1}$ can be removed by applying the algorithm described on pages 160-162 of *Catastrophe theory and its applications* (Poston and Stewart, 1978). The coordinate 3b_K is again not affected by these transformations. Then, the terms up to and including the fourth degree in the essential coordinate 3b_K are gathered from (B.34):

$$\begin{aligned} & - 2\eta(1-\eta) {}^3a \sum_{n=1}^N d_n(\hat{t}_{K-1}) h_n^{(2)} {}^3b_K^2 \\ & - 2\eta(1-\eta)(1-2\eta) {}^3a \sum_{n=1}^N d_n(\hat{t}_{K-1}) h_n^{(3)} {}^2b_K^3 \\ & - {}^3a \left[{}^3a \eta^2(1-\eta)^2 \sum_{n=1}^N (h_n^{(2)})^2 - 2\eta(1-\eta)(1-3\eta+3\eta^2) \sum_{n=1}^N d_n(\hat{t}_{K-1}) h_n^{(4)} \right] {}^3b_K^4 \end{aligned} \quad (B.35)$$

+ terms from the cubic cross terms.

These terms are:

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$$- 9 \lambda_{T-2} \eta^2 (1-\eta)^2 {}^3a^2 \sum_{n=1}^N \left[d_n(\hat{t}_{K-1}) h_n^{(3)} \right]^2 {}^3b_K^4, \quad (B.36)$$

in which λ is the eigenvalue associated with the coordinate ${}^3b_{K-1}$ and:

$$- \eta^2 (1-\eta)^2 {}^3a^2 \sum_{k=1}^{K-1} \lambda_k \sum_{n_1=1}^N \sum_{n_2=1}^N \left[{}^3a_k h_n^{(1)}(\hat{b}_k) h_n^{(2)} \right]^2 {}^3b_K^4, \quad (B.37)$$

in which λ_i is the i -th eigenvalue of H_{K-1} . The sum of expressions (B.35), (B.36) and (B.37) form the essential part of the criterion.

Resuming, the least squares criterion can be written as:

$$J(t_K) = J(\tilde{t}_K) + \underbrace{{}^4t_{K-1}^T H'_{K-1} {}^4t_{K-1}}_{\text{inessential}} \quad (B.38)$$

$$+ \underbrace{\frac{1}{2!} \rho {}^3b_K^2 + \frac{1}{3!} \sigma {}^3b_K^3 + \frac{1}{4!} \tau {}^3b_K^4 + O(t^5)}_{\text{essential}},$$

in which H'_{K-1} is a diagonal matrix containing the eigenvalues of H_{K-1} , ${}^4t_{K-1}$ is the vector of inessential variables and 3b_K is the essential variable, while

$$\rho = - 2 \hat{a}_{K-1} (1-\eta) \eta \sum_{n=1}^N d_n(\hat{t}_{K-1}) \frac{\partial^2 h_n(\hat{b}_{K-1})}{\partial b_{K-1}^2}, \quad (B.39)$$

$$\sigma = - 2 \hat{a}_{K-1} (1-2\eta)(1-\eta) \eta \sum_{n=1}^N d_n(\hat{t}_{K-1}) \frac{\partial^3 h_n(\hat{b}_{K-1})}{\partial b_{K-1}^3}, \quad (B.40)$$

and

$$\tau = 6 \hat{a}_{K-1}^2 \eta^2 (1-\eta)^2 \chi - \hat{a}_{K-1} \eta (1-\eta) (\eta^3 + (1-\eta)^3) \psi, \quad (B.41)$$

in which

$$\chi = \sum_{n=1}^N \left[\frac{\partial^2 h_n(\hat{b}_{K-1})}{\partial b_{K-1}^2} \right]^2 {}^3a^2 \quad (B.42)$$

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$$- \sum_{k=1}^{K-1} \lambda_k \sum_{n=1}^N \left[\hat{a}_k \frac{\partial h_n(\hat{b}_k)}{\partial b_k} \frac{\partial^2 h_n(\hat{b}_{K-1})}{\partial b_{K-1}^2} \right]^2,$$

$$- \lambda_{T-2} \sum_{n=1}^N \left[d_n(\hat{t}_{K-1}) \frac{\partial^3 h_n(\hat{b}_{K-1})}{\partial b_{K-1}^3} \right]^2$$

and

$$\psi = 2 \sum_{n=1}^N d_n(\tilde{t}_{K-1}) \frac{\partial^4 h_n(\tilde{b}_{K-1})}{\partial b_{K-1}^4}. \quad (B.43)$$

Therefore, a quartic polynomial describes the structure of the criterion sufficiently. The resolution discriminant is thus:

$$D = 3\sigma^2 - 8\rho\tau, \quad (B.44)$$

as in (4.48) on page 88 of this thesis.

Reference

Poston, T. and Stewart, I. (1978). *Catastrophe theory and its applications*. Pitman Publishing Ltd., London.

APPENDIX C CURIOSITIES

In this appendix, some curiosities from the literature are described. First an experiment is shown that is certainly beyond the limits of model fitting. Then a procedure used in computer enhanced spectroscopy is described. Finally, a rather bold statement is cited.

In Chapter 6, numerical examples demonstrated how sensitive the solutions for spectroscopic model fitting are if the fitted model contains overlapping peaks. In a paper published in Physical Review Letters, a spectrum with twenty-two overlapping peaks was claimed to be resolved by least squares model fitting. The spectrum and the resolved peaks are reproduced in figure C.1

FIG. 2. Experimental (error bars) and calculated (heavy line) Si 2p photoelectron spectrum of SiF₄. The calculated spectrum was constructed using parameters obtained from a nonlinear least-squares fit of the experimental data constrained as described in the text. Contributions from the individual bands and the base line are represented by the lighter lines.

Figure C.1 Reproduced from (Bozek et al., 1990).

The results are investigated for their validity by means of the theory developed in this thesis. Therefore, the critical energy associated with coincidence is computed for two overlapping Gaussian peaks of which the location parameters and a common amplitude are solved for. The design of the experiment was chosen such that it is

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representative for the design in figure C.1. The peaks were chosen to be at 112.40 eV and 112.42 eV. The amplitudes of the peaks were chosen 1800 and 750 counts, respectively. The widths of the peaks were considered known to be 0.1 eV. This approximately corresponds to the eleventh and the twelfth peaks counted from the left in figure C.1.

Then the critical energy was computed for 11 observations, spaced equally from 112.3 to 112.5 eV, similar to the design in figure C.1. The critical energy is 81 counts². If these peaks were 0.1 eV apart, the critical energy would be 27.8×10^3 counts².

In figure C.1, the error bars correspond to about 50 counts. So, the energy of the errors of observation is about 27.5×10^3 counts². This is much larger than the computed critical energy associated with coincidence. The probability of coincidence, computed by (6.15), is approximately 0.5. Even if the peaks were 0.1 eV apart, the probability of coincidence would have been 0.15. This is the case if only two overlapping peaks are considered. However, in this experiment there are twenty-two overlapping peaks plus a baseline. Probably a computer program in double precision will not be sufficient to compute the solutions correctly for exact observations in this case. Let alone for error corrupted observations. Therefore, to the author's opinion, the solutions for the peak parameters in figure C.1 are not meaningful at all. The authors of the cited paper seemed to realize the doubtfulness of their results and wrote: *'Since numerous partially resolved peaks combine to give the spectrum, it is difficult to unequivocally determine the spectral parameters using a least squares procedure.'*

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This example of inappropriate use of model fitting methods is not the only one in its kind. Griffiths et al. (1987) resolved a spectrum of seventeen overlapping peaks. They resolved this spectrum as follows:

In summary, therefore, the optimum procedure appears to be as follows:

1. The region of the spectrum to be studied is collected; this region should not be too wide, so that most bands are due to similar molecular vibrations and therefore have approximately the same width. The beginning and ending wavenumbers should be in spectral regions where there is minimal absorption by the sample.
2. The spectrum is converted to a linear absorbance format (or linear in the Kubelka-Munk function for diffuse reflectance spectra) so that bands have the correct profile.
3. The spectrum is base-line corrected; we usually calculate the base line from a straight line drawn between the first and last data points.
4. The inverse FT of the baseline-corrected spectrum is computed and stored.
5. This Fourier domain array is multiplied by a Bessel apodization function and by a series of exponential functions, $\exp(\pi'x)$, with γ' increased by 1 cm^{-1} each time and stored in separate files.
6. The forward FT of each of these files is calculated.
7. From a highly deconvolved spectrum ($\gamma' \sim \gamma_i$), the value of N is selected and the values of $\tilde{\nu}^0$ calculated using a center-of-gravity algorithm for each of these N bands.
8. The spectra in each of the files (corresponding to deconvolution with different values of γ') are curve-fitted, using the values of N and $\tilde{\nu}_i^0$ determined in step 7 as input; the input values of A_i^0 and γ_i are not critical and we generally use $A_i^0 = 1.0$ and $\gamma_i = 10\text{ cm}^{-1}$ for all N bands.
9. The values of standard deviation for each of these spectra are plotted against γ' and the optimum γ' selected from the point at which the standard deviation starts to increase.
10. The areas and center wavenumbers calculated in the curve-fitting program at this optimum value of γ' are believed to be the closest estimates to the true values.

Figure C.2 Reproduced from (Griffiths et al., 1987).

The author's comment to this procedure is that it is completely unclear what model should be fitted in step 8. The original spectrum has been transformed several times. Therefore, the introduced modeling errors will probably be so large that the resolution of the spectrum of overlapping peaks will not be possible in a meaningful way.

Finally, a bold statement is cited. It is cited from the conclusions of an article by Stephenson and Binsch (1980):

'So far as we are concerned, the problem of the analysis of high-resolution NMR spectra is solved.'

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SAMENVATTING

Precisie en resolutie in spectroscopische modelaanpassing

In dit proefschrift wordt beschreven welke effecten waarnemingsfouten hebben op de oplossingen verkregen door modelaanpassing van een gewogen som van spectroscopische pieken van dezelfde niet-lineair parametrische familie. Drie effecten worden onderscheiden: verplaatsing van de oplossing wat leidt tot imprecisie, verwisseling van de onderlinge geometrische verhoudingen van de pieken en samenvallen van de oplossingen voor de piekparameters, wat de resolutie van overlappende pieken verhindert.

Voor elk effect wordt een hyperoppervlak in de ruimte van waarnemingsfouten gedefinieerd dat die ruimte in tweeën deelt. Waarnemingsfouten gelegen in het deel dat de oorsprong bevat veroorzaken het bewuste effect niet, fouten in het andere deel wel. De afstand van de oorsprong tot het hyperoppervlak wordt kritieke norm genoemd. Waarnemingsfouten met een kleinere norm kunnen het bewuste effect zeker niet veroorzaken.

Voor kleinste-kwadratenmodelaanpassing kunnen de oppervlakken nauwkeurig benaderd worden door een hypervlak. Hierdoor kan gemakkelijk bepaald worden in welk deel van de foutenruimte willekeurige fouten gelegen zullen zijn en dus ook of het bewuste effect optreedt. Voor statistische fouten kan de kans dat het effect optreedt berekend worden.

Door middel van numerieke simulaties met spectroscopische modellen wordt duidelijk gemaakt dat de theorie bruikbaar is in de praktijk.

CURRICULUM VITAE

Joost Herman Swarte was born in Amstelveen, 14 March 1965. He grew up in Heerenveen where he finished secondary school, 'gymnasium β ', in 1983. In Februari 1988, he recieved his M.Sc. degree in applied physics from Delft University of Technology. From 1988 till Februari 1992 he worked towards his Ph.D.

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