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Note

Nonlinear-Multiple-Function Simultaneous Least Squares Fitting Procedure

INTRODUCTION

Sometimes physicists working in experimental Physics are faced with the analysis of data coming from different sources, whose interpretation may follow from quite different physical origins, but with the interesting (and desirable) situation that one or more of the physical parameters used in the analysis are common to various of the experiments. In the present work the analysis is restricted to data coming from two different and independent sources, although the procedure may easily be extended to more general cases.

The standard procedure to analyse two sets of data obtained from two different experiments on the same physical system is to analyse each of them *separately* and then to compare the similarities or the discrepancies between both sets of results. On physical grounds the common parameters must have the same value and in this work a procedure is outlined as to how this aim may be accomplished by combining both sets of data in a *simultaneous* treatment. Our motivation was to use all possible physical constraints to determine the common parameters.

In the next section the basic theory is outlined, and in the last section an example is given.

THEORY

The general treatment of nonlinear least-squares fit to a given functional form developed by Deming [1] will be used as the basis for the present procedure. Let us consider two sets of data described by

$$y = f(x, P_1, P_2) \tag{1a}$$

$$z = g(x, P_2, P_3), \tag{1b}$$

where x is the independent variable and P_1, P_2, P_3 are the parameters to be determined, and where P_2 is common to both descriptions. The data are provided in the form

$$X_i,\ Y_i,\ W_{yi}, \qquad 1 \leqslant i \leqslant N, \tag{2a}$$

$$X_j,\ Z_j,\ W_{zj}, \qquad 1 \leqslant j \leqslant M, \tag{2b}$$

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where Y_i and Z_j are measured values of the properties y and z when the independent variable takes values X_i and X_j; while W_{yi} and W_{zj} are weights assigned to the corresponding data points (X_i, Y_i) and (X_j, Z_j), respectively.

In general, it is expected that,

$$y_i = f(X_i, P_1, P_2) \neq Y_i, \qquad 1 \leqslant i \leqslant N, \tag{3a}$$

$$z_j = g(X_j, P_2, P_3) \neq Z_j, \qquad 1 \leqslant j \leqslant M, \tag{3b}$$

and therefore P_1, P_2, and P_3 are determined to minimize S, the weighted sum of the squares of the deviations,

$$S = \sum_{i=1}^{N} W_{yi}(Y_i - y_i)^2 + \sum_{j=1}^{M} W_{zj}(Z_j - z_j)^2. \tag{4}$$

In order to proceed it is necessary to linearize Eqs. (3a) and (3b) in their dependences on the parameters to be determined, and this is accomplished by means of a Taylor power series expansion of the function given by Eqs. (1a) and (1b), on the parameters about the initial values P_{01}, P_{02}, and P_{03}. If we define C_1, C_2, and C_3 by

$$C_1 = P_1 - P_{01} \tag{5a}$$

$$C_2 = P_2 - P_{02} \tag{5b}$$

$$C_3 = P_3 - P_{03} \tag{5c}$$

the Gauss normal system of the equations results,

$$(1, 1)\, C_1 + (1, 2)\, C_2 + (1, 3)\, C_3 = (1, 0) \tag{6a}$$

$$(1, 2)\, C_1 + (2, 2)\, C_2 + (2, 3)\, C_3 = (2, 0) \tag{6b}$$

$$(1, 3)\, C_1 + (2, 3)\, C_2 + (3, 3)\, C_3 = (3, 0), \tag{6c}$$

where

$$(i, j) = \sum_{k=1}^{N} W_{yk} f_{pi}^{k} f_{pj}^{k} + \sum_{n=1}^{M} W_{zn}\, g_{pi}^{n}\, g_{pj}^{n} \tag{7a}$$

$$(i, 0) = \sum_{k=1}^{N} W_{yk} f_{pi}^{k}(Y_k - y_k) + \sum_{n=1}^{M} W_{zn}\, g_{pi}^{n}(Z_n - z_n) \tag{7b}$$

with

$$f_{pi}^{k} = \left.\frac{\delta f}{\delta P_i}\right|_{P_1 = P_{10},\, P_2 = P_{20},\, x = X_k} \tag{8a}$$

$$g_{pi}^{n} = \left.\frac{\delta g}{\delta P_i}\right|_{P_2 = P_{20},\, P_3 = P_{30},\, x = X_n}. \tag{8b}$$

The solution of Eqs. (6a)–(6c) gives the corrections to the initial values of the parameters, and from Eqs. (5a)–(5c) we obtain

$$P_{11} = P_{01} + C_1 \tag{9a}$$

$$P_{12} = P_{02} + C_2 \tag{9b}$$

$$P_{13} = P_{03} + C_3. \tag{9c}$$

These values for the parameters are used in turn as initial values and a new iteration is performed to correct the values P_{11}, P_{12}, and P_{13} for the parameters given by Eqs. (9a)–(9c). The procedure is iterated until convergence is achieved to the desired degree of approximation, which may be expressed in the form that changes in the parameters and/or in S between two successive iterations that are below a certain arbitrary value.

Once the convergence has been obtained, the values for the parameters providing the best simultaneous fit to Eqs. (1a) and (1b) in the least-squares sense have been determined.

It has been shown by Deming [2] that an estimate of the standard deviation in the ith parameter being fitted is given by

$$P_i = \left[\frac{S}{N+M-n} A_{ii}^{-1}\right]^{1/2}, \tag{10}$$

where n is the number of parameters being fitted (3 in the present case), and A_{ii}^{-1} indicates the element (i, i) of the inverse matrix to that of the system of Eqs. (6a)–(6c).

The experimental uncertainties in both dependent variables and in the independent variable are taken into account through the effective weights [1, 3, 4],

$$W_{yi} = [(\Delta y_i)^2 + (f_x^i \Delta x_i)^2]^{-1}, \qquad 1 \leqslant i \leqslant N, \tag{11a}$$

$$W_{zj} = [(\Delta z_j)^2 + (g_x^j \Delta x_j)^2]^{-1}, \qquad 1 \leqslant j \leqslant M, \tag{11b}$$

where $(\Delta x_i, \Delta y_i)$ are the experimental uncertainties affecting the data point (X_i, Y_i) (similarly for $(\Delta x_j, \Delta z_j)$), and

$$f_x^i = \left.\frac{\delta f}{\delta x}\right|_{P_1 = P_{01},\, P_2 = P_{02},\, x = X_i}, \quad 1 \leqslant i \leqslant N, \tag{12a}$$

$$g_x^j = \left.\frac{\delta g}{\delta x}\right|_{P_2 = P_{02},\, P_3 = P_{03},\, x = X_j}, \quad 1 \leqslant j \leqslant M. \tag{12b}$$

EXAMPLE

An example, in which the parameters to be fitted are involved in a strong nonlinear form in Eqs. (1a)–(1b), is that provided by

$$\Delta\nu_Q(T) = \nu_Q(0) - \nu_Q(T) = \frac{3T^4}{T_D^3}\int_0^{T_D/T} \frac{x^3}{(e^x - 1)}\,dx + \frac{500}{\exp(h\nu_E/kT) - 1} \tag{13a}$$

$$C(T) = \frac{9RT^3}{T_D^3}\int_0^{T_D/T} \frac{x^4 e^x}{(e^x - 1)^2}\,dx + \frac{3R(h\nu_E/kT)^2 \exp(h\nu_E/kT)}{[\exp(h\nu_E/kT) - 1]^2}, \tag{13b}$$

where T is the temperature; h, k, and R are Planck's, Boltzmann's, and the gas constants, respectively. The parameters to be determined are T_D and ν_E, which are the Debye temperature and the Einstein frequency, respectively, characteristics of the crystalline solid under investigation. Equation (13a) describes a typical temperature dependence of the NQR (nuclear quadrupole resonance) transition frequency measured in kHz [5, 6]; while Eq. (13b) describes a typical specific heat expression for six normal modes: 3 acoustics and 3 optic [7].

The data to be fitted was generated by means of Eqs. (13a)–(13b), using $T_D = 100$ K and $\nu_E = 100\ \text{cm}^{-1}$, and the value were dispersed in a Gaussian-random way with standard deviations of 2 kHz and 2% for $\Delta\nu_Q(T)$ and $C(T)$, respectively. Table I shows one particular set of data and the values produced with the obtained parameters: $T_D = (98.233 \pm 0.0057)$ K and $\nu_E = (100.18 \pm 0.12)\ \text{cm}^{-1}$.

It is interesting to mention that in the case in which the dependence of Eqs. (1a)–(1b) on the parameters is a linear one, the first iteration produces the final values. On the other hand, if the parameters are involved in a nonlinear form, several iterations are needed before convergence is achieved. Table II shows the values for the parameters, obtained in the example, after each iteration, starting from different initial guessed values.

The program is written in Basic for the Commodore PET 2001 computer, and a listing is available upon request.

TABLE I

Data Used and Values Determined for the NQR Frequency and the Specific Heat

T (K)	$\Delta\nu_{Q\text{exp}}$ (kHz)	$\Delta\nu_{Q\text{calc}}$ (kHz)	C_{exp} $(J/\text{mol } K)$	C_{calc} $(J/\text{mol } K)$
5			0.2418	0.2562
10	0.60	0.20		
15			5.6877	5.6781
20	4.30	2.81		
25			15.1800	15.4268
30	13.70	11.65		
35			23.4448	24.4483
40	26.10	28.43		
45			31.3605	31.1789
50	53.50	52.04		
55			34.9928	35.8719
60	79.00	80.71		
65			37.7319	39.1282
70	111.30	113.00		
75			40.7179	41.4272
80	145.60	147.89		
85			43.9971	43.0894
90	186.90	184.68		
95			45.7958	44.3206
100	224.50	222.88		
105			44.7777	45.2534
110	263.90	262.17		
115			44.6634	45.9748
120	299.60	302.29		
125			47.5434	46.5428
130	347.30	343.07		
135			47.7316	46.9973
140	384.20	384.37		
145			46.3083	47.3662
150	428.60	426.11		
155			46.3255	47.6695
160	471.40	468.20		
165			47.7183	47.9217
170	513.20	510.59		
175			47.3500	48.1336
180	549.70	553.22		
185			48.7830	48.3132
190	594.40	596.07		
195			48.2661	48.4667
200	636.90	639.09		

TABLE II

Values for T_D, ν_E, and S Obtained at Each Iteration for Different Initial Values.

Iteration	T_D (K)	ν_E (cm^{-1})	S
0	+100.0000	+100.0000	170.980
1	+ 98.1990	+100.1820	39.492
2	+ 98.2326	+100.1802	39.442
0	+200.0000	+ 50.0000	700864.220
1	−265.4045	+ 77.5762	417452.502
2	+ 94.3701	+ 86.4021	21390.004
3	+ 97.3702	+ 98.2079	404.167
4	+ 98.2131	+100.1394	39.596
5	+ 98.2327	+100.1802	39.442
0	+ 50.0000	+150.0000	329326.789
1	+ 82.4187	+ 73.6757	135841.401
2	+ 92.9680	+ 93.0386	6715.532
3	+ 97.7857	+ 99.6598	73.119
4	+ 98.2293	+100.1775	39.443
5	+ 98.2327	+100.1802	39.442
0	+ 50.0000	+ 50.0000	1463485.580
1	+ 75.6493	+ 75.1321	149833.034
2	+ 91.5756	+ 93.8813	6686.251
3	+ 97.6540	+ 99.7895	70.473
4	+ 98.2279	+100.1789	39.443
5	+ 98.2327	+100.1802	39.442
0	+150.0000	+150.0000	135509.206
1	+ 47.4357	+ 77.9977	444805.004
2	+ 79.9207	+ 96.6547	25228.109
3	+ 95.1202	+100.2570	503.244
4	+ 98.1241	+100.1879	39.962
5	+ 98.2324	+100.1803	39.442
6	+ 98.2327	+100.1802	39.442

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