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USE OF ORTHONORMAL POLYNOMIALS TO FIT ENERGY SPECTRUM DATA FOR WATER TRANSPORTED THROUGH MEMBRANE

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1 Introduction

The curve fitting to experimental data frequently uses information about uncertainties in both dependent and independent variables. In a previous paper by one of us and coauthor [1], the Extended Orthonormal Polynomial Expansion Method (EOPEM) was presented, accounting for errors in both variables, with references to other methods and a comparative test. A bibliography for the period 1878-1974 is given in [2]. Here application of EOPEM to water energy spectrum data of a new effect is presented, which could be useful in modeling a variety of important biological and environmental processes. We give here a further test of EOPEM by the classical Pearson's [3] data with York's [4] errors. A numerical experiment (cf. Tables anf Figure) demonstrates the main features of the EOPEM concerning the so called joint error corridor[1].

2 Remarks and notations concerning EOPEM

The test data consist of the experimental values $x, f, \sigma x, \sigma f$ of the independent variable x and of dependent variable f and their standard deviations σ_x, σ_f at the $i-$th point $x = x_i, f = f_i$, $i = 1, 2, \ldots M$. The input data interval $x \in [x_1, x_M]$ is transformed to the unit interval $q \in [-1, 1]$. The algorithm generates recursively orthonormal polynomials on the set $\{q_i, i = 1, 2, ...M\}$ $\{\Psi_k^{(0)}, k = 0, 1, \ldots\}$ and their derivatives $\{\Psi_k^{(m)}, m = 1, 2, \ldots\}$ using Householder-Forsythe three-term relation for orthogonal polynomials by Least Squares Method [5].

The generalized relation for one-dimensional generation of orthonormal polynomials and their derivatives ($m > 0$), and integrals ($m < 0$) in our OPEM is:

$$\Psi_{k+1}^{(m)}(q) = \gamma_{k+1}[(q - \alpha_{k+1})\Psi_k^{(m)}(q) - (1 - \delta_{k0})\beta_k \Psi_{k-1}^{(m)}(q) + m\Psi_k^{(m-1)}(q)] \quad (1)$$

One generates $\Psi_k^{(m)}(q)$ recursively, where γ_{k+1} is a normalizing coefficient and $\gamma_{k+1} = 1/\beta_{k+1}$. Coefficients α_{k+1}, β_k are scalar products of the polynomials in the test data: $\alpha_{k+1} = (\Psi_k, q\Psi_k)$ and $(1 - \delta_{k0})\beta_k = (\Psi_{k-1}, q\Psi_k)$.

The polynomials $\{\Psi_k^{(0)}\}$ satisfy the following orthogonality relations:

$$\sum_{i=1}^{M} w_i \Psi_k^{(0)}(q_i) \Psi_l^{(0)}(q_i) = \delta_{kl}$$

over the point set $\{q_i, i = 1, 2, \ldots M\}$ with weights $w = 1/\sigma_f^2$.

The approximation values f^a and $f^{(m)a}$ of function f and its derivatives of $f^{(m)}$ are expressed as :

$$f^{(m)a}(q) = \sum_{k=0}^{N} a_k \Psi_k^{(m)}(q) = \sum_{k=0}^{N} c_k q^k. \tag{2}$$

In a new, extended version (EOPEM) the optimal degree N of approximation polynomials in eq. (2) is selected by the algorithm using following criteria. First, the fitting curve f_n^a from the n-th approximation step, $n = 1, 2, ..,$ should belong to the joint error corridor $[f_n - S_n, f_n + S_n]$. The corridor is defined by the total variance [9] S_n^2 at point $q = q_i, f = f_i, i = 1, 2, ..., M$ as:

$$S_n^2 = {\sigma_f}^2 + (\partial f_{n-1}^a / \partial q)^2 \sigma_q^2. \tag{3}$$

Note, the joint corridor depends on the respective derivatives, calculated at the previous iteration. The function f^a should be linear over each neighborhood of given q_i, f_i. Second, for each step $n = 1, 2, ..$ the following χ_n^2-

$$\sum_{i=1}^{M} [f_n^a(q_i) - f_i]^2 w_n(q_i), w_n(q) = 1/S_n^2,$$

should be minimal. If the first criterion is satisfied, then the search for minimum of χ_n^2 is terminated. For details we refer to [1] ,[6]. Here we test EOPEM by the classical Pearson [3] straight line example, with errors proposed by York [4].(The errors in x are between 0.6% and 13.5% and for y are between 0.3% and 22.7%). Our results with two iterations are: $f = 5.3969 - 0.4638x$, compared with York exact procedure: $f = 5.463 - 0.4x$ and with Effective variance method (EVM) [2,7,8] (2 iterations) : $f = 5.396 - 0.463x$. It is evident that our results and EVM test are comparable. They give an error about 3% in the line slope compared to the exact York fit while the standard least square method gives about 30% error. The objective is to use of our LSM-EOPEM and to reduce the variables from $M + N$ to N (instead of powerful MINUIT algorithm).[10]

3 The experimental data fit

We apply EOPEM to fit data $\{x_{i,} f_i\}$ where x_i are the energy values of Hydrogen bonds in a water sample and f_i are values of a random function f called energy spectrum of the sample [11]. The spectrum is proportional to the energy probability distribution function [12] of the Hydrogen bond energy. It is calculated as a function [1] of contact angle probability distribution measured during evaporation of water sample's drops. Experiments [13,14] show that f is influenced by various physical interactions. Here we give a polynomial data approximation of a new effect connected with water transport influence on water spectrum.

One measures the energy spectrum of deionized water sample before and after its transport with velocity 3.10^{-3}m/sec through a nuclear filter. The nuclear filter is a 10μm thin folio with holes in it, produced by heavy ions bombarding the folio in an accelerator setup. Each hole has a diameter of 0.15μm. The energy spectrum of a water sample is shown on Fig.1. The ovals correspond to the energy spectrum data of a deionized water sample. The square marks correspond to data of the same sample (called treated sample) but measured immediately after its transport through the nuclear filter.

This transport can be considered in some sense as a model of a variety of biological processes involving biomembranes with presence of water. It also presents a model discussion for changes in water spectrum after water transport in natural filters available in the environment. One observes a statistically reliable effect of change of the spectrum data maximum to higher energies as a result of water transport through the holes of the membrane. It indicates the change in the distribution function of the water Hydrogen bond energy.

In Table 1 we give the corresponding numerical values in the following eight columns: the point number, the values of x, the errors σ_x, the values of f, the errors σ_f and the corresponding smoothed values after first approximation f_1^a, after second approximation f_2^a, the deviations $\Delta f_2 = f_2^a - f$ and the total errors S_2 defined by the eq.(3). The approximation f_1^a uses errors only in f (cf. [1]), while f_2^a takes into account the errors in both variables.

Table 1. Water data EOPEM fit by 11th degree polynomial

No.	x	σ_x	f	σ_f	f_1^a	f_2^a	δf_2	S_2
1	0.008	0.0006	0.0	0.01	0.0	-0.04	0.04	43.1212
2	0.0085	0.0006	5.6	1.72	5.60	5.60	-0.0026	3.2421
3	0.009	0.0007	17.16	1.75	17.16	17.15	0.0068	2.2546
4	0.0095	0.0008	11.45	2.44	11.48	11.48	-0.032	2.6841
5	0.100	0.0006	25.51	3.51	25.23	25.23	0.28	5.2135
6	0.105	0.0006	53.26	3.36	53.49	53.49	-0.23	3.7727
7	0.110	0.0011	44.22	2.68	43.26	43.26	0.96	7.0920
8	0.115	0.0011	14.01	1.44	14.4	14.40	-0.39	4.8377
9	0.120	0.0012	6.3	1.58	6.27	6.27	0.026	1.5804
10	0.125	0.0013	3.57	2.06	3.60	3.60	-0.030	2.5163
11	0.130	0.0013	6.50	1.26	6.47	6.48	-0.026	4.1807
12	0.135	0.0007	6.14	3.54	6.16	6.16	-0.015	7.0320
13	0.139	0.0007	8.58	4.99	8.53	8.53	0.05	36.0803

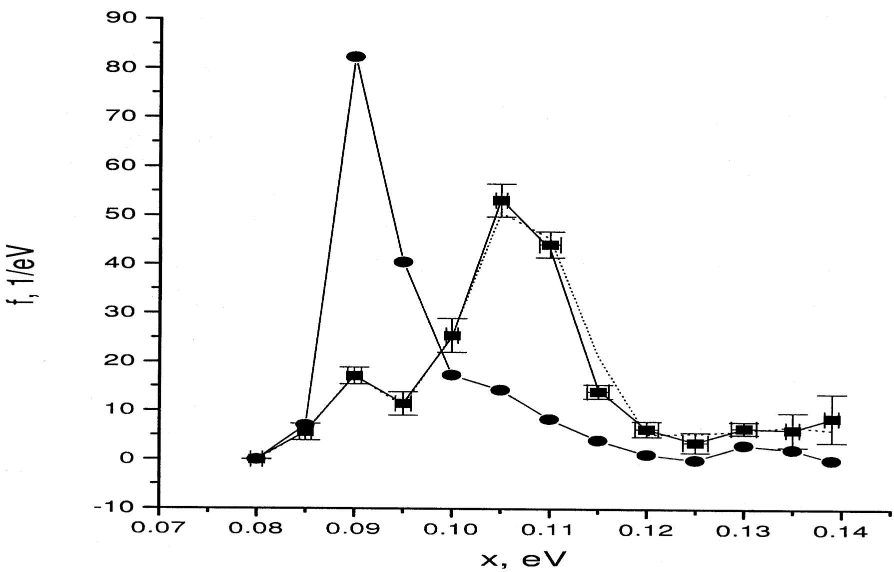

Figure 1: Water energy spectrum transport data (squares) of the treated sample with EOPEM fits: 11-th degree polynomial (continuous line), 9-th degree polynomial (dotted line). The ovals correspond to the untreated sample's spectrum data.

Already the second approximation f_2^a with a polynomial of 11-th degree satisfies the first criterion. The first approximation f_1^a gives for the normalized $\sqrt{\chi^2}$ the value 0. 2843 and the corresponding value f_2^a for second approximation is more than two times smaller, equal to 0.1259. It is evident that the deviations δf_2 are less than the total errors S, hence the first criterion is satisfied. The next approximation steps n show stability of f_n^a and χ_n^2 values of up to 3-rd order after the decimal point.

To demonstrate the requirement of the first criterion,we conducted the following calculation experiment. The approximation procedure was forced to proceed by polynomials of lower (9-th and 10-th) degrees N than the algorithm has chosen itself (11-th degree, cf. Table 1). When the degree N was restricted to $N \leq 10$ then the algorithm has chosen polynomial of 9-th degree. In this case only at point No. 8 the fitting curve lies out of the joint error corridor while for $N =$ 10-th degree this occurs at points No. 5,8. With the input data x, σ_x, f, σ_f from Table 1 the respective calculation outputs are arranged in Table 2: number of point, approximating values $f_1^a(9)$, $f_2^a(9)$ and $f_1^a(10)$, $f_2^a(10)$; deviations $\delta f_2^a(9)$, $\delta f_2^a(10)$ and total variances $S_2(9)$, $S_2(10)$. Here the numbers 9 and 10 in parentheses indicate the approximating polynomial degree.

Table 2. Water data EOPEM fits by 9th and 10th degree polynomials

No.	$f_1^a(9)$	$f_2^a(9)$	$f_1^a(10)$	$f_2^a(10)$	$\delta f_2^a(9)$	$\delta f_2^a(10)$	$S_2(9)$	$S_2(10)$
1	0.0001	-0.2409	0.0001	0.8141	0.2409	-0.8141	18.6549	23.3638
2	5.5605	5.6833	5.4915	5.0178	-0.0833	0.5822	5.4956	6.2573
3	17.3975	17.1967	17.6345	17.6271	-0.0367	-0.4671	2.3893	2.6789
4	10.0668	11.0139	9.3071	10.2734	0.4361	1.1766	2.6194	2.7015
5	30.1029	29.5335	31.1248	31.3175	-4.0235	-5.8075	4.8593	4.9518
6	50.9205	50.7383	51.4879	51.1738	2.5217	2.0862	3.4844	3.4378
7	42.0634	45.4471	41.3119	43.1623	-1.2271	1.0577	5.6740	5.7460
8	16.0924	21.1762	16.0517	19.9355	-7.1662	-5.9255	5.3019	5.0329
9	3.3969	5.1999	3.8322	5.5108	1.1001	0.7892	1.6329	1.6848
10	6.9941	5.3793	-6.1697	4.4974	-1.8093	-0.9274	2.3343	2.2408
11	5.9420	5.9638	6.1158	6.3386	0.5362	0.1614	1.8401	1.4594
12	7.3318	6.8504	6.8921	6.3996	-0.7104	-0.2596	3.9441	3.6720
13	8.2103	8.0986	8.3612	8.4860	0.4814	0.0940	8.0578	5.7339

4 Concluding Remarks

A new application of the algorithm with the orthonormal polynomials of Forsythe type involving errors in both variables is discussed. An accurate approximation of physical data for energy spectrum of water transported through membrane is presented. It permits to distinguish some important physical effects.

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Использование ортонормированных полиномов
для фитирования данных по энергетическим спектрам воды,
транспортированной через мембрану

Представлено новое применение подхода для аппроксимации кривых с помощью ортонормированных полиномов, когда заданы ошибки по обеим переменным. Описываются и аппроксимируются данные, свидетельствующие о новом эффекте изменения спектра воды после прохождения через пористую мембрану.

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Сообщение Объединенного института ядерных исследований. Дубна, 2001

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Use of Orthonormal Polynomials to Fit Energy Spectrum Data
for Water Transported through Membrane

A new application of our approach with orthonormal polynomials to curve fitting is given when both variables have errors. We approximate and describe data of a new effect due to change of water energy spectrum as a result of water transport in a porous membrane.

The investigation has been performed at the Laboratory of Information Technologies, JINR.

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