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A MONTE-CARLO APPROACH TO ERROR PROPAGATION

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Abstract—A Monte-Carlo approach to error propagation from input parameters of known variance (and covariance if available) properties through an arbitrarily complicated analytic or numerical transformation to output parameters is discussed. A simple random-number generator for a rectangular distribution function is shown to provide an economical and fairly efficient means of simulating the effects of using a normal distribution function.

1. INTRODUCTION

It is a truism that a numerical value of some physical quantity is meaningless without an estimate of its accuracy. Yet chemists have commonly been negligent in this aspect of their presentation of results (Quickenden & Harrison, 1982).

There are three main kinds of procedures that lead to numerical results. In the first kind, data directly from experiment, there are simple and direct means of assessing the inaccuracy, by repetition of measurements and by means of either graphical treatment or fitting by least-squares routines; for the latter, polynomial and multiple linear regression analyses (Ogilvie & Abu-Elgheit, 1982) can be easily carried out on minicomputers or even microcomputers. By these methods one can readily generate some estimate of the accuracy of the parameters related to sources or random error, but not systematic error and blunders. A second kind of procedure is a purely theoretical prediction of the magnitude of some quantity, such as an *ab initio* molecular-orbital computation of a molecular structure. Such calculations may be in principle exact, within the numerical precision of the computer, but any discrepancies with respect to precise and reliable experimental values may be attributed to inadequacies of the mathematical model of the physical system being simulated. In such cases, to make a precise estimate of the accuracy, in the sense of a standard deviation for a particular parameter, becomes very difficult, but orders of magnitude may be estimated, possibly on the basis of comparisons of previous theoretical results with existing experimental data.

The third kind of procedure involves the application of a theoretical model to interpret some experimental results in terms of a general theoretical function. An instance of this is the derivation of the parameters of a general potential-energy function of a diatomic molecule from wavenumber data for vibration-rotational transitions in infrared spectra; in this case the relationships between the potential-energy coefficients (c_j in the flexible function of Ogilvie (1981)) and the energy term-value coefficients Y_{kl} are of a simple form, although the actual expressions can be quite long (Ogilvie, 1983); the well established methods of error propagation (Clifford, 1973) can be used to relate the standard deviations of the Y_{kl}, directly assigned from experimental data, to those of the coefficients c_j (Ogilvie & Koo, 1976). In other cases, the relationship between the primary experimental quantities and the meaningful theoretical functions may be much more complicated, perhaps involving matrix inversions. Thus the equations required in the procedure for error propagation (Clifford, 1973) may become practically intractable, although in principle it may be possible to generate and to apply them. Moreover, the set of equations connecting the two levels of quantities is specific to the particular problem. Therefore a practicable method of error propagation without these disadvantages is desirable, and is proposed in the following sections.

2. A FORMAL PROCEDURE

Suppose that one has a set of input parameters $I_1, I_2, \ldots, I_i, \ldots, I_m$, collectively represented as **I**, and the corresponding set **O** of output parameters $O_1, O_2, \ldots, O_j, \ldots, O_n$. There is no particular restriction on the relative numbers of these parameters m and n; all that is required is a computationally well defined set of functional relationships, the transformations taking **I** into **O**, viz. $\mathbf{O} = O(\mathbf{I})$. If one makes a series of small deviations or variations δI_i in the individual I_i one at a time, then the corresponding variation δO_j of any output parameter O_j is

$$\delta O_j = \sum_{i=1}^{m} \delta I_i \frac{\partial O_j(I_1, I_2, \ldots, I_m)}{\partial I_i} + \text{higher order terms.}$$

If the variations δI_i are small (weak perturbations), the higher order terms may be neglected, so the relation becomes linear. In order to compute the derivatives $\partial O_j/\partial I_i$, the $(m + 1)$ calculations

$$O(I_1, I_2, \ldots, I_m)$$
$$O(I_1 + \epsilon_1, I, \ldots, I_m)$$
$$O(I_1, I_2 + \epsilon_2, \ldots, I_m)$$
$$\ldots\ldots\ldots\ldots$$
$$O(I_1, I_2, \ldots, I_m + \epsilon_m)$$

are necessary, in which ϵ_i is a small variation:

$$\epsilon_i/I_i \sim 10^{-3}, \quad \text{and} \quad \delta I_i = \epsilon_i I_i.$$

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Hence all the first-order effects for any input distribution of errors, correlated or not, may be found.

In order to check that the first-order calculations are sufficient, one can repeat the procedure with the m^2 sets, such as

$$O(I_1 + 2\epsilon_1, I_2, \ldots, I_m)$$
$$O(I_1, I_2 + 2\epsilon_2, \ldots, I_m)$$
$$\ldots\ldots\ldots$$

and

$$O(I_1 + \epsilon_1, I_2 + \epsilon_2, I_3, \ldots, I_m)$$
$$O(I_1 + \epsilon_1, I_2, I_3 + \epsilon_3, \ldots, I_m), \text{ etc.}$$

Then the results from these calculations are compared with those predicted from the previous set of first-order calculations. If the second-order terms prove not negligible, then the variances are dependent on the initial distribution. In the latter case, the procedure outlined in the next section should be preferable; otherwise the desired variances have been effectively determined according to the first-order calculations above.

3. A MONTE-CARLO PROCEDURE

This general numerical approach is essentially of the Monte-Carlo type whereby the input parameters are subjected to variation, according to a specific statistical distribution, with known variances and covariances taken into account, and then the effect on the resulting output parameters is observed.

We subject each input parameter I_i to variation according to some distribution function scaled according to the known standard deviation σ_i of I_i. If the quantities I_i are independent (correlation coefficients between different I_i pairs are sufficiently small to be negligible—in practice, magnitudes less than 0.8 may be small enough), then the distribution for each I_i is also independent, or approximately so; otherwise the correlation coefficients are used to relate the variations of I_i to other I_k within the set **I**. With all the I_i thus varied each time, the calculation of **O** from **I** is carried out N times, N being sufficiently large to ensure reproducible results, and the sums

$$\sum_{l=1}^{N} O_{jl} \quad \text{and} \quad \sum_{l=1}^{N} O_{jl}^2$$

are formed for each O_j. Hence an estimate s_i of the standard deviation of each O_i is simply given by:

$$s_j = \left[\left\{ \sum_{l=1}^{N} O_{jl}^2 - \left(\sum_{l=1}^{N} O_{jl} \right)^2 \Big/ N \right\} \Big/ (N-1) \right]^{1/2}.$$

There remains the problem of selection of the distribution function. One commonly supposes, in the absence of other knowledge, that the input parameters are subject to error according to a normal distribution function (with mean value $\bar{I}_i$ of I_i):

$$d(I_i) = \frac{e^{-(I_i - \bar{I}_i)^2/2\sigma_i^2}}{\sigma_i (2\pi)^{1/2}}.$$

In that case one should multiply the standard deviation σ_i of I_i by a normally distributed random number, and then add the result to I_i before the computation $O(\mathbf{I})$ to render **O**. It is of course necessary that this random number take both positive and negative values; if the distribution of such furnished values has a variance other than unity, then each random number would have to be scaled accordingly. Although some computer systems have available such a normally distributed random-number generator, practically all computers have a generator for random (actually pseudo-random) numbers uniformly distributed in the range zero to unity. Supposing that such a number is provided in response to the call RND, then one can easily generate a normal distribution through two independent calls of RND in the function

$$d_n = [-2 \log_e (\text{RND})]^{1/2} \cos [2\pi\ (\text{RND})]$$

in which $\log_e$ signifies a natural (not Briggsian) logarithm and the cosine function takes its argument in radians.

The standard deviation of this distribution d_n is unity. If all the input parameters $I_i + d_n\sigma_i$ are thus simultaneously varied (Rao, 1973) in the calculation, with the correlations taken into account as appropriate (Hurst & Knop, 1972; Page, 1974), then the output parameters O_j each lead to a value of s_j that also has the significance of a standard deviation, thus fulfilling the objective.

One should however also test the robustness of this procedure. For this purpose, another distribution function d_p, that occasionally provides values quite distant from the mean, is useful. The Pareto function (Johnson & Kotz, 1970), a family characterised by a parameter w,

$$d_p = [w_1 + (1 - 2w)/(w - 1) + (\text{RND})^{(-1/w)}]/w_2$$

is basically an exponential distribution. Two important values of w are 2.2, in which case the other quantities should take the values $w_1 = 2$ and $w_2 = 2$, and $w = 1.2$ for which $w_1 = 6$ and $w_2 = 20$. The subsidiary parameters $w_{1,2}$ are set to values such that the distribution has a mean of zero and a variance of unity; actually the function with $w = 1.2$ has an undefined standard deviation, but the scaling factor $w_2 = 20$ seems to provide a reasonable range of effective values of d_p (this value of w_2 should be checked on a particular computer before use). This family of Pareto distributions generates only positive numbers; given a sign function SGN(x) that takes the values SGN(x) $= -1$ if $x < 0$ and SGN(x) $= +1$ if $x > 0$, one can premultiply the Pareto distribution by a factor SGN(RND $- 0.5$) to make it double-sided. The final resulting distribution is

$$d_p = \text{SGN}(\text{RND} - 0.5)[w_1 + (1 - 2w)/(w - 1) + (\text{RND})^{(-1/w)}]/w_2.$$

If use of the Pareto function with either of the given values of w generates values of s_j that are comparable to the set of s_j determined by means of the normal distribution function, in both cases employing the correlation matrix appropriately, then one can have confidence that the estimates s_j of the standard deviations of the output parameters O_j are meaningful.

The normal distribution function d_n given above, although simple in form, is relatively uneconomical of computation time, because each call to the gener-

ator demands formation of two random numbers followed by computation of a logarithm, a square root, and a cosine. Other generators of random numbers according to a normal distribution are more complicated in form but more economical of computation time (Brent, 1974 and references therein). Alternatively one can simply use the uniform (or rectangular) distribution directly. The standard deviation of the distribution

$$d_r = 2(3)^{1/2}(\mathrm{RND} - 0.5)$$

is unity, and this function can obviously be made extremely economical to compute. Tests of this distribution on a transformation function $O(\mathbf{I})$, that has been demonstrated by means of the Pareto function to be robust to large perturbations, have shown that the estimates s_j of the uncertainty of the output parameters $\mathbf{O}$ are practically identical to the set of true standard deviations s_j generated by means of the normal distribution d_n.

4. CONCLUSIONS

Two procedures for the estimation of standard deviations of output parameters, related by means of arbitrarily complicated numerical or analytic functions, have been outlined in the previous sections. The purpose of each procedure is the same, but the amount of programming, additional to the basic procedure (that determines the values of the output parameters) in order to determine their standard deviations, may differ greatly between the two procedures.

In the formal procedure, extensive coding may have to be added in order to make the required variations of input parameters, one at a time serially (or two at a time to check the linearity). On the other hand, the Monte-Carlo procedure, that may in any case be necessary in pathological cases of non-linearity, requires minimal changes; a loop mechanism must be incorporated in order to run the required number N of cycles, and two subroutines suffice, one to produce the variations in all the input parameters each cycle, and the other to compute the sums and to determine from them the variation of the output parameters. The formal procedure requires fewer cycles through the transformation functions $O(\mathbf{I})$, $(m+1)$ or m^2 in number, compared to the Monte-Carlo procedure for which the number N of cycles required to yield reproducible results may vary, from typically a few hundred for the normal or rectangular distributions, or a few thousand for the Pareto distributions. (Of course one should use all such Monte-Carlo methods in at least duplicate runs, starting from a randomised generator seed, in order to confirm the reproducibility of the results.) Because programmer time may be more expensive than computing time, for a given problem, the latter disadvantage of the Monte-Carlo method may prove insignificant. Furthermore the Monte-Carlo procedure may be easily added to existing programs. However, if kept in mind at the design stage, the formal procedure can be fairly easily incorporated into new programs.

In summation, the Monte-Carlo procedure containing the rectangular distribution function provides a practical and fairly efficient means of estimating error propagated from input parameters of known standard deviations through any complicated transformation process to some collection of output parameters. One successful application of this procedure has been the determination of the Herman–Wallis coefficients in vibration-rotational spectroscopy, calculated from wavenumber and intensity data through potential-energy and dipole-moment functions and analytic matrix elements; not only are many of the expressions involved in this calculation quite long (up to a hundred terms), but also there are matrix inversions (Tipping & Ogilvie, 1982). In this case the direct analytic method of error propagation (Clifford, 1973) would have been at least quite cumbersome.

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