On-line evaluation of mono-exponential decays

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This Note describes the algorithm used within AcqNmr for three-parameter mono-exponential fits noisy decay functions sampled at N values of the timing parameter τ.

Let $[m_k]$ and $[\tau_k]$ be, respectively, the arrays of average data-window magnitudes and of the arrayed parameter values (the index k ranges over all considered blocks, assumed to be n in number, n≥3). These data are to be fitted by the theoretical formula (the hypothesis)

(1) $$m_k(\tau_k) = a + be^{-r\tau_k}$$

where a,b, and r are some as yet unknown parameters. This requires a non-linear, three-parameter, least-squares fit in which one minimizes the quantity

(2) $$Q(a,b,r) = \sum_k \left[m_k(\tau_k) - \left(a + be^{-r\tau_k}\right)\right]^2$$

with respect to a, b and r.

It is convenient to split the task into two distinct parts.

1. Assuming the value of r to be fixed, the formula is linear with respect to a and b. The optimal values of these two parameters are therefore easily determined using standard linear-correlation formulae [1,2,3]. The resulting 'optimal' values of a and b, denoted as a_1, b_1, and the corresponding value of Q and Q_1 thus become non-linear functions of r, i.e., $a_1=a_1(r)$, $b_1=b_1(r)$ and $Q_1=Q_1(r)$, with $Q_1(r)$ being approximately quadratic around its absolute minimum.
2. Using the function which calculates $Q_1(r)$ for any value of r, its minimum value is then determined numerically using the standard Brendt's algorithm [4]. Clearly, if the minimum of $Q_1(r)$ occurs at $r = r_2$ then $Q_2=Q_1(r_2)=Q(a_1(r_2),b_1(r_2),r_2)$ coincides with the absolute minimum of Q(a,b,r).

What we have gained in addition to the optimal fit is the possibility to evaluate the function $Q_1(r)$ for any r in the vicinity of the optimum at r_2, where we expect it to be approximately quadratic with the quadratic coefficient related to the *confidence interval* of r. Notice that, along the curve $Q_1(r)=Q(a_1(r),b_1(r),r)$, the parameters a,b are dynamically varied, keeping them optimal for every single value of r. This is essential since otherwise the error estimates for r would be grossly over-optimistic.

Numeric values of the *confidence interval* are based on the least significant increment of Q. Assuming that the optimum value Q_2 of Q is due entirely to random experimental errors (this, of course, is false for non-exponential decays), the least significant increment $\Delta_\alpha Q$ can be determined for any given significance level α by means of the *Fisher statistics* [2,3] with both degrees of freedom set to n-1. The confidence interval $\Delta_\alpha r$ for r then comprises the r values for which $Q_1(r)-Q_2 \le \Delta_\alpha Q$ and the *probable error* $e=\Delta_\alpha r/2$ is obtained, as usual, by setting $\alpha=0.69...$ This may sound complicated but it actually turns out that, in the quadratic case, the result is excellently approximated by the simple formula:

(3) $$e = \sqrt{\frac{1}{(n-1)}\frac{Q_2}{Q_1''(r_2)}}$$

where $Q_1''(r)$ is the second derivative of $Q_1(r)$ which is easily estimated numerically by standard methods.

References:

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