A.I Non-iterative method

This method is applied for fitting a double exponential function \[ N(t) \] when the available experimental decay data is at regular intervals of time \( t \).

The function \( N(t) \) satisfies the following difference equation

\[
N(t+2) - u N(t+1) + v N(t) = 0
\]

where \( u = \exp(-\lambda_1) + \exp(-\lambda_2) \)

\( v = \exp(-\lambda_1) \exp(-\lambda_2) \)

Let \( Y_j \) be the measured value at \( t = t_j \).

The least-squares fitting is made by minimizing the value of the sum squared residuals:

\[
Q = \sum_{i=1}^{N-2} (Y_{i+2} - u Y_{i+1} - v Y_i)^2
\]

where \( N \) is the number of data points. Since eqn. (3) is linear with respect to \( u \) and \( v \), the conventional least squares method can be used. Setting the partial derivative of \( Q \) with respect to each parameter to zero, the best estimates of \( u \) and \( v \) are

\[
u = (a_1 b_3 - a_3 b_1) / D
\]

\[
v = (a_1 b_2 - a_2 b_1) / D
\]
where \( D = a_2 b_3 - a_3 b_2 \)

\[
a_1 = \sum_i Y_{i+1} Y_{i+2}, \quad a_2 = \sum_i Y_i^2,
\]

\[
a_3 = \sum_i Y_i Y_{i+1}, \quad b_1 = \sum_i Y_i Y_{i+2},
\]

\[
b_2 = a_3, \quad b_3 = \sum_i Y_i^2
\]

Using the values of \( u \) and \( v \) thus obtained, the quadratic equation

\[
x^2 - ux + v = 0 \quad (6)
\]

is solved and the best values for \( \lambda_1 \) and \( \lambda_2 \) are determined from the two roots, \( x_1 \) and \( x_2 \) of eqn. (6)

\[
\lambda_1 = \ln x_1 \quad (7)
\]

\[
\lambda_2 = \ln x_2 \quad (8)
\]

Once the two decay constants \( \lambda_1 \) and \( \lambda_2 \) are obtained, \( N_1 \) and \( N_2 \) can be estimated by minimizing the sum of the squared residuals:

\[
Q' = \sum_{i=1}^{N} \left[ Y_i - N_1 \exp(\lambda_1 t_i) - N_2 \exp(-\lambda_2 t_i) \right]^2 \quad (9)
\]

This expression is also linear with respect to \( N_1 \) and \( N_2 \) and the best estimates of these parameters are determined from formulae similar to eqns (4) and (5).

\[
N_1 = (C_1 d_3 - C_3 d_1)/D' \quad (10)
\]

\[
N_2 = -(C_1 d_2 - C_2 d_1)/D' \quad (11)
\]
where

\[ D' = C_2d_3 - C_3d_2 \]

\[ C_1 = \sum_i Y_1 \exp(\lambda_1 t_1), \quad C_2 = \sum_i \exp(-2\lambda_1 t_1), \]

\[ C_3 = \sum_i \exp(-\lambda_1 + \lambda_2) t_1, \quad d_1 = \sum_i Y_1 \exp(-\lambda_2 t_1), \]

\[ d_2 = C_3, \quad d_3 = \sum_i \exp(-2\lambda_2 t_1). \]

The initial estimates of \( N_1, N_2, \lambda_1 \) and \( \lambda_2 \) obtained from eqns. (10), (11), (7) and (8) respectively are used for iterative calculation as described below.

A-II Iterative method

This method is applicable even when the available data are at irregular intervals of time \( t \). Let the decay data, \([N(t_i)]\) measured at different time interval \( t_i \), is dependent on four functional parameters \((N_1, N_2, \lambda_1 \text{ and } \lambda_2)\). In such a case the equation may be written as

\[ N(t) = f(t, N_1, N_2, \lambda_1, \lambda_2) \]  

(12)

Let \( N_1', N_2', \lambda_1' \), and \( \lambda_2' \) be the approximate values of \( N_1, N_2, \lambda_1 \) and \( \lambda_2 \) obtained from the method discussed in the earlier section. Let \( \alpha, \beta, \gamma \) and \( \delta \) denote corrections which are to be applied to \( N_1', N_2', \lambda_1' \) and \( \lambda_2' \)

\[ N_1 = N_1' + \alpha \]

\[ N_2 = N_2' + \beta \]

\[ \lambda_1 = \lambda_1' + \gamma \]

\[ \lambda_2 = \lambda_2' + \delta \]

(13)
then $N'(t) = f(t, N'_1, N'_2, \lambda'^1, \lambda'^2)$ \hfill (14)

is a function which approximates the function $N(t)$ more or less closely. The value of this approximating function corresponding to time $t_1$, $t_2$, ..., $t_n$ will be

$$N'_1(t_1) = f(t_1, N'_1, N'_2, \lambda'^1, \lambda'^2)$$
$$N'_2(t_2) = f(t_2, N'_1, N'_2, \lambda'^1, \lambda'^2)$$

................

$$N'(t_n) = f(t_n, N'_1, N'_2, \lambda'^1, \lambda'^2)$$ \hfill (15)

If we take eqn. (12) to be the best or most probable function and its graph to be the best representative curve, then the residual will be

$$v_1 = N(t_1, N'_1, N'_2, \lambda'_1, \lambda'_2) - N(t_1)$$
$$v_2 = N(t_2, N'_1, N'_2, \lambda'_1, \lambda'_2) - N(t_2)$$

................

$$v_n = N(t_n, N'_1, N'_2, \lambda'_1, \lambda'_2) - N(t_n)$$ \hfill (16)

where $N(t_1)$, $N(t_2)$, ..., $N(t_n)$ are observed decay data points corresponding to time $t_1$, $t_2$, ..., $t_n$ respectively.

Substituting the values of $N'_1$, $N'_2$, $\lambda'_1$ and $\lambda'_2$, as given by eqn. (13), in eqn. (15). Then for the first residual, the equation becomes

$$v_1 = f(t, N'_1 + \infty, N'_2 + \beta, \lambda'^1 + \gamma, \lambda'^2 + \delta) - N(t_1)$$ \hfill (17)
or \[ v_1 + N(t_1) = f(t_1, N_1, \alpha, N_2, \beta, \lambda_1, \gamma, \lambda_2) \] (18)

Expanding the right hand side of eqn. (18) by Taylor's theorem

\[ v_1 + N(t_1) = N(t_1, N_1, N_2, \lambda_1, \lambda_2) + \alpha \left( \frac{\partial N(t)}{\partial N_1} \right)_0 + \beta \left( \frac{\partial N(t)}{\partial N_2} \right)_0 + \gamma \left( \frac{\partial N(t)}{\partial \lambda_1} \right)_0 + \delta \left( \frac{\partial N(t)}{\partial \lambda_2} \right)_0 \]

+ terms involving high powers and products of \( \alpha, \beta, \gamma \) and \( \delta \) (19)

where

\[
\left( \frac{\partial N(t)}{\partial N_1} \right)_0 \text{ means } \left( \frac{\partial N(t)}{\partial N_1} \right)_t = t_1
\]

Since \( N'(t_1) = N(t_1, N_1', N_2', \lambda_1', \lambda_2') \) therefore by putting the value of \( N'(t) \) in eqn. (19), it becomes

\[ v_1 + N(t_1) = N'(t_1) + \alpha \left[ \frac{\partial N(t)}{\partial N_1} \right]_0 + \beta \left[ \frac{\partial N(t)}{\partial N_2} \right]_0 + \gamma \left[ \frac{\partial N(t)}{\partial \lambda_1} \right]_0 + \delta \left[ \frac{\partial N(t)}{\partial \lambda_2} \right]_0 \] (20)

Since \( \alpha, \beta, \gamma \) and \( \delta \) are small, therefore the high powers and product of \( \alpha, \beta, \gamma \) and \( \delta \) can be ignored.
or \[ v_1 = \alpha \left[ \frac{\partial N(t)}{\partial N_1} \right] + \beta \left[ \frac{\partial N(t)}{\partial N_2} \right] + \gamma \left[ \frac{\partial N(t)}{\partial \lambda_1} \right] + \delta \left[ \frac{\partial N(t)}{\partial \lambda_2} \right] \]

\[ + N'(t_1) - N(t_1) \]  

(21)

Let

\[
\begin{align*}
  r_1 &= N'(t_1) - N(t_1) \\
  r_2 &= N'(t_2) - N(t_2) \\
  \vdots \\
  r_n &= N'(t_n) - N(t_n)
\end{align*}
\]

(22)

The quantities \( r_1, r_2, \ldots, r_n \) are the residuals for the approximation curve \( N'(t) = f(t, N_1', N_2', \lambda_1', \lambda_2') \), since they are the differences between the observed ordinates and the ordinates to this curve.

Then the residual becomes

\[
\begin{align*}
v_1 &= \alpha X_1 + \beta Y_1 + \gamma Z_1 + \delta p_1 + r_1 \\
v_2 &= \alpha X_2 + \beta Y_2 + \gamma Z_2 + \delta p_2 + r_2 \\
\vdots \\
v_n &= \alpha X_n + \beta Y_n + \gamma Z_n + \delta p_n + r_n
\end{align*}
\]

(23)

where

\[
\begin{align*}
X_i &= \left[ \frac{\partial N(t_i)}{\partial N_1} \right] \\
Y_i &= \left[ \frac{\partial N(t_i)}{\partial N_2} \right] \\
Z_i &= \left[ \frac{\partial N(t_i)}{\partial \lambda_1} \right] \\
p_i &= \left[ \frac{\partial N(t_i)}{\partial \lambda_2} \right]
\end{align*}
\]
The eqn. (22) is linear in corrections to $\alpha$, $\beta$, $\gamma$ and $\delta$. To obtain the best values of $\alpha$, $\beta$, $\gamma$ and $\delta$ from this set of equations, method of least square is applied. According to this method

$$\sum v^2 = v_1^2 + v_2^2 \ldots \ldots \ldots v_n^2$$

must be minimum

i.e. $F = \sum \left( (\alpha x_1 + \beta y_1 + \gamma z_1 + \delta p_1 + r_1)^2 \right)$

must be minimum

For this to be minimum

$$\frac{\partial F}{\partial \alpha} = 0, \quad \frac{\partial F}{\partial \beta} = 0, \quad \frac{\partial F}{\partial \gamma} = 0, \quad \frac{\partial F}{\partial \delta} = 0$$

i.e.

$$\alpha \sum x_1^2 + \beta \sum x_1 y_1 + \gamma \sum x_1 z_1 + \delta \sum p_1 x_1 + \Sigma r_1 x_1 = 0$$

$$\alpha \sum x_1 y_1 + \beta \sum y_1^2 + \gamma \sum y_1 z_1 + \delta \sum p_1 y_1 + \Sigma r_1 y_1 = 0 \quad (24)$$

$$\alpha \sum x_1 z_1 + \beta \sum y_1 z_1 + \gamma \sum z_1^2 + \delta \sum p_1 z_1 + \Sigma r_1 z_1 = 0$$

$$\alpha \sum x_1 p_1 + \beta \sum y_1 p_1 + \gamma \sum z_1 p_1 + \delta \sum p_1^2 + \Sigma r_1 p_1 = 0$$

These are four linear equations in $\alpha$, $\beta$, $\gamma$ and $\delta$, and can be solved simultaneously to obtain unique best values of $\alpha$, $\beta$, $\gamma$ and $\delta$. After correcting the $N_1$, $N_2$, $\lambda_1$ and $\lambda_2$. 
a better set of values for $N_1, N_2, \lambda_1,$ and $\lambda_2$ can be obtained using eqn. (13). The whole procedure is repeated again and again, until the desired degree of convergence is attained.

The computer programme for these two methods (Non-iterative and iterative) are given below.

**Computer program for non-iterative method:**

1 REM-COMPUTER PROGRAM FOR THE SUM-OF-TWO EXPONENTIAL FUNCTION BY NON-ITERATIVE METHOD.
3 REM- (N) IS NUMBER OF DATA POINTS.
4 REM- (T1(I)) IS TIME INTERVAL.
5 REM- (Y(I)) IS CORRESPONDING DATA VALUE.
6 OPEN "S1" \ PRINT #1
7 DIM T1(100), Y1(100)
8 INPUT N
9 FOR I=1 TO N
10 INPUT T1(I), Y1(I)
20 NEXT I
30 FOR I=1 TO N-2
40 A1=A1+Y1(I+1)*Y1(I+2)
50 A2=A2+Y1(I+1)*Y2
60 A3=A3+Y1(I)*Y1(I+1)
70 B1=B1+Y1(I)*Y1(I+2)
80 B2=B2
90 B3=B3+Y1(I+1)*2
100 NEXT I
105 D1=A2*B3-A3*B2
110 U1=A1*B3-A3*B1
120 U2=(A1*B2-A2*B1)/B1
130 U3=U1+(U1*2-4*U2)^.5
140 X1=U1+(U1*2-4*U2)^.5
150 X2=U1+(U1*2-4*U2)^.5
160 L1=-LOG(X1/2)
170 L2=-LOG(X2/2)
180 L1=L1/(T1(2)-T1(1))
190 L2=L2/(T1(2)-T1(1))
195 PRINT #1, "L1="L1,"L2="L2
290 FOR I=1 TO N-2
300 C1=C1+Y1(I)*EXP(-L1*T1(I))
310 C2=C2+EXP(-2*L1*T1(I))
320 C3=C3+EXP(-L1*L2*T1(I))
330 G1=G1+Y1(I+1)*EXP(-L2*T1(I))
340 G2=C3
350 G3=G3+EXP(-2*L2*T1(I))
360 G4=G4+EXP(-L1*L2*T1(I))
370 G5=G5+EXP(-2*L1*T1(I))
380 G6=G6+EXP(-2*L2*T1(I))
390 PRINT #1, "N1=",N1,"N2=",N2
395 STOP
Computer program for iterative method:

1 REM- COMPUTER PROGRAM FOR FITTING THE SUM-OF-TWO EXPONENTIAL
FUNCTION BY ITERATIVE METHOD.
3 REM- (M) IS NUMBER OF COEFFICIENTS PLUS ONE (=5)
5 REM- (N) IS NUMBER OF DATA POINTS.
7 REM- (M1(I)) ARE THE COEFFICIENTS, WHOSE VALUES ARE TO BE IMPROVED,
NAMELY, (M1(1),M1(2),LAMBDA(1),LAMBDA(2))
9 REM- TO REPEAT THE ITRATION GIVE VALUES OF (M,N)
10 OPEN "SI" \ PRINT #1
15 REM- (M) IS NUMBER OF COEFF.+1 (=5 IN THIS CASE)
16 REM- (N) IS NUMBER OF DATA POINTS.
20 INPUT M,N
30 FOR I=1 TO M-1
40 INPUT M1(I)
50 NEXT I
60 FOR I=1 TO N
70 INPUT X1(I),Y1(I)
80 NEXT I
90 INPUT M,N
100 FOR I=1 TO N
110 Z7(I)=M1(1)*(EXP(M1(2)*X1(I)))
120 P7(I)=M1(3)*(EXP(M1(4)*X1(I)))
130 Y2(I)=Z7(I)+P7(I)
140 R(I)=Y2(I)-Y1(I)
150 C2=R(I)/Y1(I)*100
160 PRINT #1,"Y1(I)="Y1(I),"Y2(I)="Y2(I),"R(I)="R(I),"PER="C2
170 NEXT I
180 K9=0 \ G9=0
190 FOR I=1 TO N
200 K9=K9+R(I)^2
210 NEXT I
220 PRINT #1,"VALUE OF SUM OF SQRS OF DEVN="K9
230 FOR I=1 TO N
240 G9=G9+((R(I)/Y1(I))^2)
250 NEXT I
260 PRINT #1,"PERCENT DEVN="G9
270 FOR I=1 TO N
280 V(I,1)=EXP(M1(2)*X1(I))
290 V(I,2)=M1(1)*X1(I)*EXP(M1(2)*X1(I))
300 V(I,3)=EXP(M1(4)*X1(I))
310 V(I,4)=M1(3)*X1(I)*EXP(M1(4)*X1(I))
320 NEXT I
330 FOR I=1 TO N
340 FOR J=1 TO M-1
350 A(I,J)=V(I,J)
360 NEXT J
370 NEXT I
380 FOR I=1 TO N
390 A(I,M)=R(I)
226
400 NEXT I
410 FOR K = 1 TO M-1
420 FOR J=1 TO N
430 FOR I=1 TO N
440 C(I,J)=A(I,K)*A(I,J)
450 NEXT I
460 NEXT J
470 FOR J=1 TO M
480 FOR I=1 TO N-1
490 C(I+1,J)=C(I,J)+C(I+1,J)
500 NEXT I
510 U(K,J)=C(N,J)
520 NEXT J
530 NEXT K
540 A1=U(1,1) \ B1=U(1,2) \ C1=U(1,3) \ D1=U(1,4) \ P1=U(1,5)
550 A2=U(2,1) \ B2=U(2,2) \ C2=U(2,3) \ D2=U(2,4) \ P2=U(2,5)
560 A3=U(3,1) \ B3=U(3,2) \ C3=U(3,3) \ D3=U(3,4) \ P3=U(3,5)
570 A4=U(4,1) \ B4=U(4,2) \ C4=U(4,3) \ D4=U(4,4) \ P4=U(4,5)
580 P1=-P1 \ P2=-P2 \ P3=-P3 \ P4=-P4
600 V1=(A2*C1-C2*A1)
610 U1=(A2*B1-D2*A1)
620 K1=(A2*P1-P2*A1)
630 U2=(A3*B2-B3*A2)
640 V2=(A3*C2-C3*A2)
650 W2=(A3*D2-D3*A2)
660 K2=(A3*P2-P3*A2)
670 U3=(A4*B3-B4*A3)
680 V3=(A4*C3-C4*A3)
690 W3=(A4*D3-D4*A3)
700 K3=(A4*P3-P4*A3)
710 G1=(U2*V1-V2*U1)
720 H1=(U2*W1-W2*U1)
730 I1=(U2*W1-W2*U1)
740 G2=(U3*V2-V3*U2)
750 H2=(U3*W2-W3*U2)
760 I2=(U3*W2-W3*U2)
770 T=(G2*I2-G1*I2)/(G2*H1-H2*G1)
780 Z=(I1-H1*T)/G1
790 Y=(K1-U1*T-V1*Z)/U1
800 X=(P1-D1*T-C1*Z-B1*Y)/A1
810 M(1)=M(1)+X \ M(2)=M(2)+Y \ M(3)=M(3)+Z \ M(4)=M(4)+T
820 PRINT M1,"M1(1)="M1(1),"M1(2)="M1(2),"M1(3)="M1(3),"M1(4)="M1(4)
830 GO TO 90