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Precision of impedance spectroscopy estimates of bulk, reaction rate, and diffusion parameters

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Abstract

Complex least squares fitting and Monte Carlo simulation have been used to generate numerical values for the ultimate precision with which various impedance spectroscopy fitting-model parameters can be estimated by complex nonlinear least squares fitting. Results are presented in terms of normalized relative standard deviations for bulk, reaction-rate, and diffusion parameters. The analysis applies only in the usual case where errors in the data are proportional to the data values themselves (constant percentage error). By using special normalization, we ensure that our results are of universal applicability and may be used for prediction and comparison of data situations with an arbitrary number of data values and for any reasonable error percentage. The results may be used in the design of experiments to predict, before any measurements are carried out, how accurately various fitting parameters can be determined for an assumed amount of error and a particular number of data points. Alternatively, they may be employed to evaluate the minimum expected uncertainty bounds of parameter estimates already obtained from complex nonlinear least squares fitting for comparison with the actual bounds obtained from the fitting. The results apply to several finite-length-diffusion situations, including restricted and ordinary diffusion of charged species and diffusion of neutral entities. We find that, depending on the specific fitting model and parameter values, there are some limiting situations where bulk resistance, reaction resistance, or diffusion exchange rate cannot be estimated with adequate precision by complex nonlinear least squares fitting.

INTRODUCTION

Although data collection is the first step in an impedance spectroscopy (IS) study of a supported or unsupported electrochemical system, the goal of understanding the processes leading to the data requires analysis and interpretation of the data as well. Quantitative analysis is best carried out by complex nonlinear least squares (CNLS) fitting of the data to a theoretical model and/or equivalent electrical circuit [1–3]. Such fitting yields both parameter estimates and estimates of their standard

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deviations (SD). Comparison of a parameter estimate and its estimated SD allows one to quantify the importance of that parameter to the fit and to compare all parameter estimates on this basis. To do so in a scale-invariant way, it is convenient to define the (estimated) relative standard deviation (RSD) or coefficient of variation, of a parameter: the quotient of the estimated SD by the parameter estimate itself. Then fitting results for a parameter A may be written in the forms $A(1 \pm \mathrm{RSD})$ or $A|\mathrm{RSD}$, where the second form may be used for brevity. Clearly, when a RSD value is of the order of or greater than 30%, the parameter is poorly estimated by the data, and one would like to obtain RSD values of 5% or less.

A single CNLS fit is but one from a universe of possibilities and depends directly on the specific errors present in the data. Thus, it may be well or poorly representative of the true situation. Therefore, it is worthwhile using Monte Carlo (MC) simulation methods to derive some universal RSD results for well-specified electrochemical situations important in the IS area. To do so, one picks a theoretical model (usually in the form of an equivalent circuit) representing the situation of interest, derives exact response "data" from it, and then carries out a large number (say K) of CNLS fits of such data after contamination with independent random errors drawn from a known error probability distribution. Each CNLS-fit replication involves a new and independent set of errors, and the final K parameter and RSD estimates are themselves averaged and their own RSD's determined. By picking K sufficiently large, one can ensure that the averaged quantities have as high precision as desired.

Here, we are concerned with RSD results for some bulk, reaction, and diffusion-related equivalent circuit parameters. We use sufficiently small errors that parameter bias, always associated with nonlinear least squares fitting [3,4], is negligible and focus attention on precise RSD results of nearly universal applicability. Since one usually finds for typical IS data that the errors (as mirrored by the residuals between data and model predictions) are, for a good fit, close to a constant percentage of the model predictions, we use this proportional-error assumption in our present MC study. To do so, we draw values randomly from a Gaussian distribution with zero mean and a SD of σ_r, i.e. N(0, $\sigma_r^2 \boldsymbol{I}$), where $\boldsymbol{I}$ is the unit vector. Let $Y_{0i} = Y'_{0i} + \mathrm{j}Y''_{0i}$ represent the exact model prediction (at any immittance level) for the ith data point, where $i = 1,2,\ldots, N$ and $\mathrm{j} = \sqrt{(-1)}$. Then the corresponding synthetic data values are calculated as $y_i = y'_i + \mathrm{j}y''_i$, where $y'_i \equiv y'_{0i}[1 + \sigma_r N(0, I_i)]$ and similarly for the imaginary part. Here, $N(0, I_i)$ is a random sample from the Gaussian distribution of zero mean and unity SD. We use entirely independent Gaussian values for the random error contributions to the real and imaginary parts of y_i, but even using the same values for these contributions makes a negligible difference in SD estimates. As the above shows, the SD σ_r determines the size of the proportional errors in the MC "data".

UNIVERSAL NORMALIZATION

It turns out that for the usual IS data situation, one where $N > 25$ and $\sigma_r < 0.2$, parameter SD estimates are quite closely proportional to $\sigma_r/\sqrt{N}$. Thus, a new quantity, the normalized RSD, $S_N \equiv (\sqrt{N}/\sigma_r)\text{RSD}$, will be essentially independent of N, σ_r, and the parameter magnitude, and is thus of universal utility. Our results are therefore presented in terms of this quantity. In order to compare them with RSD estimates from a single CNLS fit, one needs only the value of N and an estimate of σ_r for the fit. But when proportional errors are indeed present, it is found that S_F, the estimated SD of the CNLS fit, is an excellent estimate of σ_r [1–4] and may be used, along with N, to convert from S_N values to corresponding RSD ones or vice versa. Note that the N data values should be selected so that they span the frequency region of IS response of interest. When N is increased to reduce RSD estimates, the same region should still be so spanned since, of course, data points outside the area of interest will not produce such reduction.

Our MC calculations make use of the general and powerful CNLS program LEVM [1,3,4], which may be obtained from the department of one of the authors (JRM) at nominal cost. In carrying out the fitting, it is important that the weighting (or variance model) match the actual error character of the data as well as possible. Such matching was ensured in the present work by using FPWT: function proportional weighting [3,4]. The LEVM program also may be used to estimate the actual power, ξ, of the model components inherent in the data. When ξ is well determined (small RSD) and its estimate is close to unity, the assumption of proportional errors is verified and the present S_N values may be used with confidence.

BULK AND REACTION PARAMETERS

One of the simplest IS situations, pertinent for either supported or unsupported conditions, is that where only bulk and electrode reaction effects appear in the data over the measured frequency range. Then the relevant equivalent circuit is that

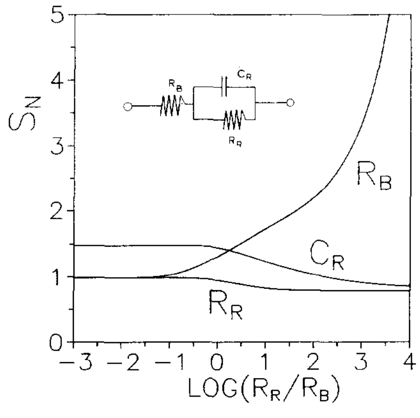

Fig. 1. Dependence of the normalized relative standard deviations, S_N, of R_B, R_R, and C_R on $\log(R_R/R_B)$ for bulk and electrode-reaction response.

shown in the inset of Fig. 1. There R_B is the bulk or solution resistance; R_R is the charge transfer reaction resistance, sometimes written as R_{ct}; and C_R is the reaction capacitance, the double-layer capacitance, C_{dl}. In addition, this and all other IS equivalent circuits must include the geometrical capacitance, $C_g(\ll C_{dl})$, which is connected in the equivalent circuit between the two working electrodes of the system (ref. 2, p. 13ff). Since this capacitance is usually very small, its electrical effects are generally not important until very high frequencies (far above those where reaction effects usually appear); it is correspondingly difficult to determine from the data, and it is often omitted from the equivalent circuit, as is the case in the present work. When the impedance response of the Fig. 1 circuit is plotted in the complex plane, a circular arc begins at $Z' = R_B$ and ends at $Z' = R_B + R_R$, the dc resistance.

Figure 1 shows the dependence of S_N, for each of the three parameters of the circuit, on the ratio R_R/R_B. The various curves are identified by the parameter whose S_N is plotted. Although either R_R or R_B or both of these quantities may be varied here, it is necessary that the frequency range extend over the range of principal variation of the data in order that the present results apply. In particular, one needs a range of the angular frequency ω extending from the frequency of the peak, $\omega_0 \equiv R_R C_R$, to values where $|Z''_{min}|/|Z''_{max}|$ is less than about 0.1. If the complex plane arc is unsymmetrical, data points are needed on both sides of its peak. Although all the RSD results of the present work involved data points taken at equal intervals of $\log(\omega/\omega_0)$, very nearly the same values may be expected with a different spacing of points as long as the main data variation is adequately covered.

As Fig. 1 shows, when R_B is much smaller than R_R CNLS fitting cannot resolve R_B accurately. For example, when $R_R/R_B = 10^4$, $N = 33$, and $\sigma_r = 0.1$, the RSD of R_B is about 15%, and it increases rapidly as the ratio increases further. Interestingly, the situation is different at the other end of the scale where R_R is much smaller than R_B. At first glance the results shown for this region may seem counterintuitive. We see that the S_N's for both R_R and C_R approach limiting values. How is it possible to obtain good estimates of R_R when it is of practically negligible size compared to R_B? The difference between the S_N response for R_B and that for R_R arises because of the presence of C_R in parallel with R_R, leading to Z'' values which involve both C_R and R_R but not R_B. For $R_R/R_B = 10^{-3}$ and the same N and σ_r values as above, the RSD of R_R is only about 1.7%.

Although, as Fig. 1 demonstrates, the S_N of R_R is small and essentially independent of the ratio R_R/R_B for values of this ratio between 0.1 and 0.001, the resolution power of CNLS, while extremely high, is limited. We thus cannot expect constancy of S_N to continue as the ratio approaches sufficiently close to zero when σ_r is non-zero. In fact, when R_R/R_B has decreased to 10^{-6}, adequate estimates of R_R and C_R can no longer be obtained for $\sigma_r = 0.1$, and their RSD's become meaningless. For $R_B = 10^3\ \Omega$, $R_R = 1\ \Omega$, and $C_R = 1\ \mu F$, for example, some actual proportional errors in Z' may be larger than 150 Ω for $\sigma_r = 0.1$, while the magnitude of the parallel $R_R C_R$ combination is less than 1. Although CNLS fitting can still resolve R_R and C_R with this 150:1 situation, it fails for $R_B = 10^6\ \Omega$ where the ratio is 150,000:1 or greater. For a sufficiently small σ_r, however, resolution would still be possible even with such a large ratio.

Because of their normalization, S_N and RSD values are the same for a quantity such as R_R and for its inverse. Since the inverse of R_R is proportional to the product of the equilibrium concentration of the reacting species and its reaction rate constant, the present results show how precisely this product can be determined by CNLS fitting. We see that when all other effects are negligible in the measurement frequency range, so that the circuit shown in Fig. 1 is all that is needed, the RSD of this product will be gratifyingly small. When the uncertainty of the concentration is much less than that of the rate constant, the RSD of R_R given above applies to the rate constant as well, showing that even with a relatively small number of data points and the appreciable σ_r value of 0.1, even a very large rate constant (and a correspondingly small value of R_R/R_B) can still be determined with uncertainty of less than 2%.

The present results represent lower limits to what one would expect, on the average, from fitting a single data set. If such fitting yields appreciably larger RSD values than those calculated from the present S_N results when ξ is found to be close to 1, it implies that there are systematic errors present, and/or the errors are not drawn from a Gaussian distribution in the fashion assumed above. It is worth mentioning, however, that only small changes in the results occur when the errors are samples from a uniform rather than a Gaussian distribution. For example, for $R_R/R_B = 1$, $N = 33$, and $\sigma_r = 0.1$, the RSD's of R_B, R_R and C_R change only in the second or third decimal place from their Gaussian values of 2.3%, 1.6%, and 2.5%, respectively.

Finally, it should be mentioned that in the unsupported binary electrolyte situation, problems may possibly arise in using the present circuit to determine very fast reaction rates [5]. But these problems can be avoided by using the model associated with the exact solution of the response problem [6] rather than the present equivalent circuit. This model is now available as a fitting choice in the LEVM CNLS program mentioned above and includes arbitrary reaction rates and mobilities of the positive and negative charges present.

DIFFUSION EQUATIONS AND RESPONSE

In this section some background on diffusion effects in IS is presented in preparation for the following discussion of S_N results for diffusion-related RSD's. The first analysis of diffusion in a supported electrolyte under small-signal ac conditions appeared in the classic paper of Warburg [7]. He considered the situation implicitly where the diffusion length, l_D, was negligible compared to the extent of the region available for diffusion (e.g., the effective separation between electrodes, L, or the thickness of a diffusion layer at an electrode). Diffusion under such conditions, i.e. the ordinary Warburg response, may be termed, with slight exaggeration, infinite-length diffusion (ILD) as compared with physically realistic finite-length diffusion (FLD). All FLD reduces to ILD when the applied frequency is sufficiently high that $l_D \ll L$.

Since Warburg's pioneering work, much attention has been given to the effects of diffusion of charged species in supported and unsupported liquid or solid electrolytes and of mobile uncharged species in electrolytes and in electrodes [e.g., 3, 8–10]. All AC diffusion response involves a characteristic dimensionless frequency-dependence variable, s, which can be expressed as

$$s = (\mathrm{j})^{1/2}(L_e/l_D) = (\mathrm{j}\omega\tau_D)^{1/2} = (\mathrm{j}\omega/D_e)^{1/2}L_e \qquad (1)$$

where D_e is an effective diffusion coefficient, $l_D \equiv (D_e/\omega)^{1/2}$, and $\tau_D \equiv (\mathrm{L}_e^2/D_e)$. Here, L_e is $L/2$ for diffusion between identical, plane, parallel electrodes, and is L for diffusion in a diffusion layer, half-cell, or in an electrode, each of effective thickness L.

When the diffusing species is either uncharged or charged but present in a supported electrolyte, D_e is just the diffusion coefficient of this species. Note, however, that the diffusion coefficient must be multiplied by the thermodynamic factor [11] when concentrations are sufficiently high that activity coefficients must be used. This, and the following modification, have recently appeared [12] without attribution to earlier work. For a binary electrolyte, where both negative and positive diffusing species are present with diffusion coefficients D_n and D_p and valence numbers z_n and z_p, it has been found that [3,6,10]

$$D_e = D_n D_p(z_n + z_p)/(D_n z_n + D_p z_p) \qquad (2)$$

a result that reduces to just D when $D_n = D_p = D$.

Consider first just the impedance Z_{DG} arising from diffusion of a neutral species in an electrode without electrode reaction or adsorption contributions. The diffusing species is produced by the electrode reaction at the surface of the electrode abutting an electrolyte, diffuses through the electrode of thickness L, and exchanges with the ambient atmosphere at the far side with an exchange rate constant k_G. The present diffusion process is fully analogous electrically to wave motion along an RC transmission line with arbitrary terminating resistance and is thus more general than other diffusion processes discussed below. In the electrode diffusion case, the effective terminating resistance is proportional to $1/k_G$ and the impedance is given by [13]

$$Z_{DG}(\omega) = R_D\left[\frac{\rho + (s)\,\mathrm{ctnh}(s)}{\mathrm{s}^2 + (\rho s)\,\mathrm{ctnh}(s)}\right] = R_D\left[\frac{1 + \rho\{\tanh(s)/s\}}{\rho + (s)\tanh(s)}\right] \qquad (3)$$

where $\rho \equiv (L_e/D_e)k_G$ is a normalized, dimensionless rate constant and R_D is proportional to R_R. Equation (3) shows that $Z_{DG}(0) = (1 + \rho^{-1})R_D$.

Two limiting cases of the eqn (3) result are of particular interest. First, when $\rho \to \infty$ one obtains the usual FLD response result, termed just Z_D here,

$$Z_D(\omega) = R_D[\tanh(s)/s] \qquad (4)$$

which also applies for the important case of diffusion of a charged species in a

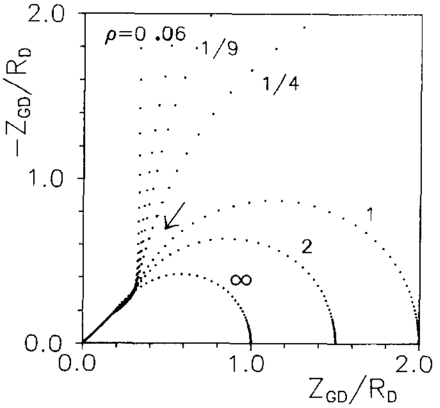

Fig. 2. Complex plane response of the general-diffusion impedance expression, eqn. (3), for several choices of ρ, the normalized exchange rate constant.

supported electrolyte with identical electrodes [2(pp. 60,88,105),3,8,10]. Note that a much more complex result is found when the electrodes are not identical [14]. Equation (4) applies to high accuracy in the identical-electrodes, unsupported binary electrolyte situation as well, so long as both species are mobile [3,5,6,8,10].

The other limiting case is that where $\rho \to 0$; then eqn. (3) reduces to

$$Z_{D0}(\omega) = R_D[\text{ctnh}(s)/s] \tag{5}$$

This expression applies not only for diffusion of a neutral particle without exchange with the ambient atmosphere (complete blocking) [13,15], but also to the diffusion of a charged species in a supported electrolyte where a reaction occurs at one electrode and the other is completely blocking (i.e., restricted diffusion) [14,16,17].

Figure 2 shows the complex-plane response of $Z_{DG}(\omega)/R_D$ for a variety of ρ values. Here, the arrow indicates the direction of increasing frequency, and the frequency ratio between adjacent points is $10^{0.05}$. For $\rho = 0$, the maximum value of $Z_{DG}(\omega)/R_D$, attained at the low-frequency end of the response, where it becomes capacitative, is just 1/3. Note that when ρ is very small but non-zero, the response is primarily a circular arc with a limiting low frequency value of $(1 + \rho^{-1})R_D$, and with a very small ILD region buried at the left corner. In order to distinguish such response from that of a pure circular arc arising from a resistor and capacitor in series, the high-frequency end of the data must be examined carefully. If the data have relatively low errors, CNLS fitting using the full expression for Z_{DG}, available in LEVM, compared to that for a full semicircle should allow the proper choice to be made.

Further ambiguity is possible at the other end of the scale as well. As Fig. 2 shows, when $\rho \geqslant 1$ the response shape is still close to that for $\rho = \infty$. CNLS fitting of exact Z_{DG} response data with the Z_D response function of eqn (4) shows that a pretty good fit can be obtained even with $\rho = 1$, but the difference between the fitted response and the original data would be evident in a complex-plane plot for real data unless their errors were appreciable. But as ρ becomes larger than 1, resolution becomes more and more difficult and will require exceptionally good data for $\rho = 4$ or greater. The result is that if the true Z_{DG} response is confused with the ordinary FLD response and fitted with Z_{D}, the estimated τ_{D} will be larger than it should be by a factor of about 3.7 for $\rho = 1$, reducing to about 1.6 for $\rho = 4$. These results suggest that ρ cannot be well distinguished from ∞ when it is greater than 2 or so. This matter is further investigated quantitatively in the following section.

REACTION AND DIFFUSION PARAMETERS

We now consider parameter uncertainties for CNLS fitting of data that is well represented by a reaction resistance, R_{R}, in series with Z_{DG} or one of its simplifications. For actual data, the resistance in series with Z_{DG} will involve R_{R} and R_{B} in series, and even a series adsorption resistance if adsorption is present, but the present R_{R} may be reinterpreted as necessary. Although C_{R} will always be present, the time constant $R_{\mathrm{R}}C_{\mathrm{R}}$ will usually be much smaller than τ_{D}, since diffusion effects usually occur at very low frequencies. When this is the case, the effect of C_{R} is negligible in the frequency range spanning the diffusion response, and it may thus be neglected just as the effect of $C_{\mathrm{B}} \equiv C_{\mathrm{g}}$ was neglected for the bulk-reaction calculations presented above.

Figure 3 shows results involving the Z_{D0} response. The data covered a frequency range for which $-Z''_{\mathrm{D0}}/R_{\mathrm{D}}$ ranged from a maximum of about 1 to a minimum of about 0.018. The figure shows that the S_N of the series resistance, here R_{R}, rapidly becomes large as $R_{\mathrm{D}}/R_{\mathrm{R}}$ increases, just as it did for the results of Fig. 1, but at an appreciably smaller value of the abscissa ratio. In addition, S_N's of the other two parameters are considerably larger than those in Fig. 1. The corresponding results for the Z_{D} response of Fig. 4 show that R_{D} and τ_{D} can be appreciably better

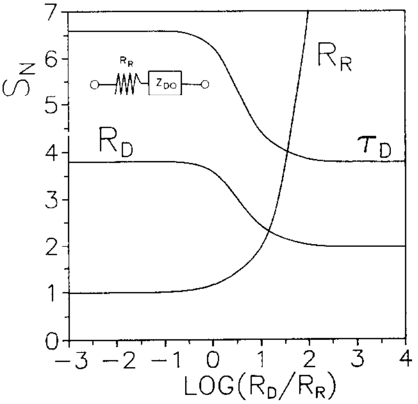

Fig. 3. Dependence of the normalized relative standard deviations, S_N, of R_{R}, R_{D}, and τ_{D} on $\log(R_{\mathrm{D}}/R_{\mathrm{R}})$ for electrode-reaction and restricted-diffusion ($\rho = 0$) response.

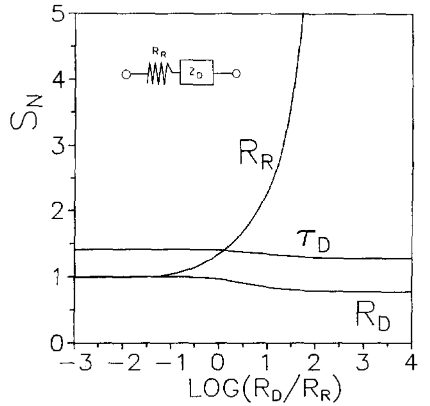

Fig. 4. Dependence of the normalized relative standard deviations, S_N, of R_R, R_D, and τ_D on $\log(R_D/R_R)$ for electrode-reaction and normal, FLD diffusion ($\rho = \infty$) response.

determined for the Z_D, as compared to the Z_{D0}, response. Further, R_R, and so the electrode reaction rate, cannot be determined from CNLS fitting of the present circuits with adequate precision when R_R is less than about 0.01 R_D. Note, however, that when pertinent data are available, it can be determined with good precision for the situation of Fig. 1.

Figure 5 shows how the S_N's of the Z_{DG} parameters vary with the normalized exchange rate ρ when no series resistance is present. Note the use of a logarithmic scale for S_N here. It turns out that it is not always appropriate to use the parameter ρ directly in Eqn. (3) since it depends on both k_G and D_e. Let us define $k_{GN} \equiv \rho/\tau_D \equiv k_G/L_e$, not a dimensionless quantity but one which does not involve D_e. The LEVM program allows either ρ or k_{GN} to be taken as a free or fixed

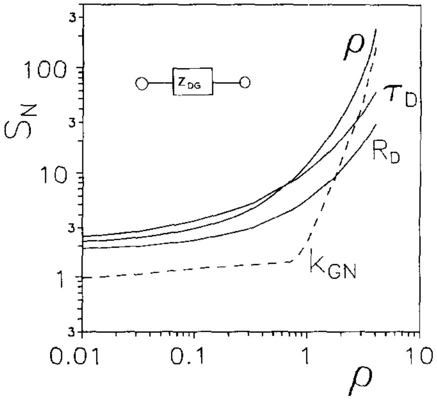

Fig. 5. Dependence of the normalized relative standard deviations, S_N, of R_D, τ_D, k_{GD}, and ρ on ρ for the general diffusion response of eqn. (3).

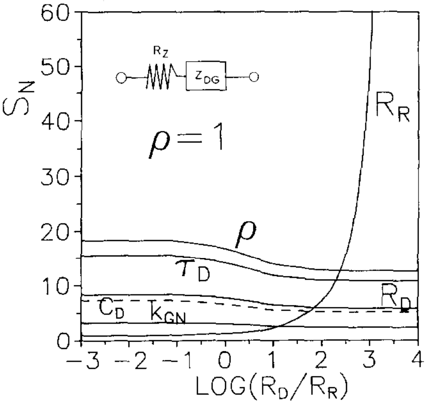

Fig. 6. Dependence of the normalized relative standard deviations, S_N, of R_R, C_D, R_D, τ_D, k_{GD}, and ρ on $\log(R_D/R_R)$ with $\rho=1$ for electrode-reaction and general diffusion response.

parameter in the model defined by eqn. (3). For the MC runs involving k_{GN} free, the τ_D value used in generating the exact response was set to unity; thus ρ and k_{GN} values were numerically the same for any choice of these quantities. The dashed S_N curve for k_{GN} in Fig. 5 shows that k_{GN} can be estimated with far less uncertainty than can ρ. In addition, the correlations between ρ or k_{GN} and other free parameters are appreciably reduced when k_{GN} is used as a free parameter instead of ρ. Nevertheless, the curves of Fig. 5 show that none of the free parameters of a CNLS Z_{DG} fit can usually be estimated with adequate precision when ρ is greater than two or three or so. As an example, with $N=56$ and the probably unrealistically low value of $\sigma_r=0.01$, the RSD's of R_D, τ_D, ρ, and k_{GN} are, respectively, about 4%, 8%, 32%, and 21% for $\rho=4$. When fitting leads to a ρ estimate of two or more whose RSD is large, fitting with Z_D rather than Z_{DG} is then more appropriate.

Finally, Fig. 6 shows S_N results for a circuit involving Z_{DG} in series with R_R for data calculated with ρ fixed at unity. The results are similar to those of Figs. 1, 3, and 4, but note the larger S_N scale here. As before, k_{GN} results for S_N are much superior to ρ ones. The dashed curve below that marked R_D involves yet another reparameterization of eqn. (3), again available in LEVM. For this choice, instead of taking R_D as a free parameter, we use a capacitance C_D instead and calculate the R_D of eqn. (3) as τ_D/C_D. Thus, the dashed line represents S_N results for C_D, and we see that they are 15% to 20% smaller than those for R_D directly.

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