

Non-linear Kinetics Parameter Identification by HDMR Map Inversion

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Abstract

A new method for parameter identification in non-linear kinetic systems is presented. Parameter identification is achieved through the use of HDMR, (High Dimensional Model Representations) which can reduce greatly the computational cost of high dimensional function inversion. This technique is applied to two previously studied kinetic systems in order to verify its accuracy. In addition, modifications to the existing algorithm are discussed which could increase both the efficiency and generality of HDMR.

Introduction

Kinetic experiments are routinely performed to determine values of reaction rate constants. The data obtained from such experiments often take the form of species' concentrations as a function of time of reaction. This target data must then be deconvoluted to yield the parameters of interest. If the reaction model is a system of ordinary differential equations, this inversion can be accomplished in a number of ways. Most straightforward is a simple non-linear fitting approach which varies the rate constants of interest in order to minimize the error-squared value between the target data and the model data. However, this method involves the repeated integration of systems of potentially stiff ODEs, which can be resource intensive and numerically difficult. In addition, because each of the parameters can be varied independently, the searchable parameter space grows exponentially with the number of parameters. Thus, the number of points which must be sampled to obtain a good fit can quickly become unmanageable, an obstacle which is often referred to as the "curse of dimensionality".¹

The difficulties of high dimensionality can be palliated by the judicious use of HDMR.² HDMR is based upon the assumption that most multi-dimensional functions display relatively low-order correlation between input variables. HDMR can be expressed mathematically by the following equation:³

$$f(\mathbf{x}) = f(\bar{x}) + \sum_i f_i(\bar{x}^i, x_i) + \sum_{i,j} f_{ij}(\bar{x}^{ij}, x_i, x_j) + \dots + f(x_1, x_2, \dots, x_N)$$

Thus, one need only consider low-order correlation to obtain a reasonable approximation of the function's overall behavior. For instance, a first order HDMR would consist of the sum of functions depending only on a single variable; a second order HDMR would consist of the sum of functions depending on every possible combination of two variables. By neglecting higher order correlation, the number of sample points needed to describe a function's behavior is greatly reduced. An HDMR map which accurately approximates the function of interest can be generated with a relatively low overhead. In the case of non-linear kinetics, this function takes as input the rate constants of the system and returns the concentration of a given species at a specified time. Rather than inverting

¹ Rabitz, Herschel and Omer Alis. "Managing the Tyranny of Parameters in Mathematical Modelling of Physical Systems." Preprint. May 16, 1999.

² *ibid.*

³ H. Rabitz, O. Alis, J. Shorter, K. Shim, "Efficient input-output model representations," *Computer Physics Communications.* (1999) 11-20.

the actual function, the evaluation of which can be computationally expensive, we can invert the HDMR map, which can be evaluated with much less cost.

The primary goal of our research was to prove that parameter evaluation of non-linear kinetic systems is amenable to the HDMR technique.

Technique

Integration of the ODEs which describe the kinetics of the system was initially attempted using a 4th-order Runge-Kutta algorithm.⁴ However, this method was unsuccessful due to the stiffness of the equations. Eventually, the equations were successfully integrated using the lsode integration package, a "canned" routine which is adapted to the solution of stiff ODEs.

The first system to be studied was the formation of HBr from H₂ and Br₂ in gas phase. This reaction occurs by a free-radical mediated mechanism, which has been well studied and has been firmly established experimentally.⁵ Because six reactions are involved in the mechanism, there are six rate constants which govern the system's behavior. Test data was then generated by using the literature values for the rate constants and using the lsode package to integrate the system over 100 seconds.⁶ The concentration of each of the five species at a series of fixed time intervals was recorded, just as real laboratory data would be collected during an experiment. In several trials, we included random error in our generated data to simulate the experimental error associated with real laboratory measurements. To test the HDMR inversion scheme, we then fed this target data into the inversion algorithm and compared the best-fit parameters to the known parameters with which the data was generated.

The first issue that needed to be addressed was the size of the parameter space for which the HDMR was to be constructed. HDMRs using small windows displayed greater accuracy, but limited the possible values of the rate constants to narrow ranges. It is assumed that at least some rough estimate of the real values of the parameters is known; in this case, the ranges were centered on the literature values of each rate constant. The second issue that was considered was whether a first order HDMR would be sufficient to model the function, or whether a second order HDMR would have to be constructed to obtain the desired accuracy.

To determine the optimal window size and HDMR order, several HDMR maps were constructed and tested by conducting 1000 random trials and comparing the real function values with the HDMR approximation. If we were using real laboratory data, we would try to ensure that the error in the HDMR model is no larger than the experimental measurement error. In general, we tried to ensure that the HDMR error was less than 10 percent. The results of the trials are shown in Table 1. The largest window that was found to yield sufficiently accurate HDMR maps was a window spanning one order of magnitude on each axis: in other words, each rate constant was allowed to vary over a range of an order of magnitude. Furthermore, in order to achieve the desired level of accuracy for a reasonably sized HDMR window, a second order HDMR was required.

⁴W. Press, S. Teukolsky, W. Vetterling, and B. Flannery, *Numerical Recipes in C*. Cambridge: Cambridge University Press, 1992. 710-714

⁵J. Espenson, *Chemical Kinetics and Reaction Mechanisms*. New York: McGraw-Hill, 1981. 139

⁶A compilation of accepted rate constant values can be found in *The Handbook of Bimolecular and Termolecular Gas Reactions*. CRC Press, 1981

Once the HDMR map was constructed, the actual inversion process was implemented using the galib2.44 genetic algorithm package⁷. Though a simulated annealing or gradient descent algorithm could have been used, we chose a genetic algorithm because it offered the option of propagating a family of acceptable solutions rather than a single solution. Previous studies have shown that many non-linear kinetic systems have multiple solutions⁸. This tendency is even more pronounced if experimental error (not to be confused with HDMR error) is taken into account. Thus, it was hoped that a genetic algorithm would locate all sets of rate constants which yielded the test data within the specified experimental error.

Results

Initially, an inversion run was performed on data generated by observing the concentration of HBr over the course of 2000 seconds with samples taken every 100 seconds. As expected, multiple solutions were located by the genetic algorithm, all of them generating curves that fit the target data extremely well. We had hoped that the distribution of solutions found would be concentrated around the real rate constants used to generate the data, but unfortunately, this was not the case. Only k_3 displayed a sharp distribution around its truth value; the distributions of the other rate constants were broad and spanned the entire inversion window (see figures 1 and 2). If random error was introduced into the target data, the distributions of all rate constants became even less sharp (see figure 3). By adding more information to the system, the rate constants could be determined with greater specificity. For instance, when the concentration of H was monitored along with the concentration of HBr, rate constants k_3 , k_4 , and k_5 all showed sharp distributions centered around their truth values.

To further test the generality and the accuracy of HDMR map inversion, a second non-linear kinetic system was modeled. The oxidation of formaldehyde had previously been studied by Rabitz et al., who used a mechanism containing 17 reactions, and hence 17 rate constants⁹. Rather than generate the target data computationally as we did in the HBr case, real laboratory data reported by Rabitz was used along with the reported experimental error associated with the measurements. Again, a window of 1 order of magnitude for each rate constant, centered on its truth value (as reported by the Rabitz paper) proved to be optimal. The HDMR maps generated were of comparable accuracy to the HBr system, despite the greater dimensionality of the formaldehyde system, and a second-order HDMR yielded acceptable accuracy.

Inversion of the target data was accomplished using the same genetic algorithm as in the HBr system. Because only the concentration of the hydroxyl radical had been monitored in the experiment, it was found that only k_1 through k_5 were well-specified; the best-fit values of the other rate constants were distributed evenly over the inversion window. Furthermore, the well-defined behavior of k_2 and the ill-defined behavior of k_{17} , which had previously been reported by Rabitz, was confirmed by our analysis as well. The traditional method of inversion employed by Rabitz and the HDMR map inversion both determined the value of k_2 with a high degree of accuracy. In general, the

⁷ <http://lancet.mit.edu/ga/>

⁸ Park, S.W. "Parameter Estimation and Unique Identifiability," *The Chemical Engineering Journal*, **25** (1982). 163-174

⁹ H. Rabitz, R. Yetter. "Evaluation of the rate constant for the reaction OH+H₂CO," *J. Chem. Phys.*, **91** (1989)

HDMR inversion of the formaldehyde system behaved very similarly to the inversion of the HBr system.

Summary

Thus far, the application of the HDMR map inversion technique to parameter identification in non-linear kinetic systems has been successful. Though it was found that not all of the rate constants could be identified with great accuracy, this uncertainty was a result of multiple solutions present in the systems themselves. Traditional methods of inversion, such as those used by Rabitz et al., also reported this uncertainty. On the other hand, specification of well-defined parameters was accomplished very effectively and accurately, as evinced by the comparison of the results of traditional and HDMR map identification of the k2 rate constant in the formaldehyde system. However, the increased efficiency and decreased computational cost of HDMR map inversion relative to traditional inversion, makes HDMR map inversion a desirable alternative.

Though the usefulness of HDMR map inversion has been demonstrated in the case of two non-linear systems, there are still problems with the technique. Obtaining an accurate HDMR map is an absolute necessity for accurate inversion. Currently, the accuracy of an HDMR map of an intractable function -for instance, a function with strong higher order correlations- can be improved only by decreasing the size of the inversion window, an operation which limits the generality of the inversion or increasing the order of the HDMR. However, by reworking the basic mathematical foundations of HDMR, we can increase its accuracy and generality without simply shrinking the size of the window or increasing the HDMR order. For instance, preliminary work suggests that if HDMR is redefined such that:

$$g(f(\mathbf{x})) = g(f(\bar{x})) + \sum_i g(f_i(\bar{x}^i, x_i)) + \sum_{i,j} g(f_{ij}(\bar{x}^{ij}, x_i, x_j)) + \dots + g(f(x_1, x_2, \dots, x_N))$$

the non-linear function $g()$ can be used to remove some of the higher order function correlations and thereby increase HDMR accuracy without sacrificing window size. Other ideas, such as the rotation of the HDMR axes or the use of non-orthogonal HDMR bases, also show promising results. It is also possible that accuracy could be increased to such a degree that a first order HDMR would be sufficient when previously a second- or third- order HDMR was necessary. Hopefully, continued research will yield an algorithm which can model previously intractable functions with great accuracy and with a minimum number of function evaluations.

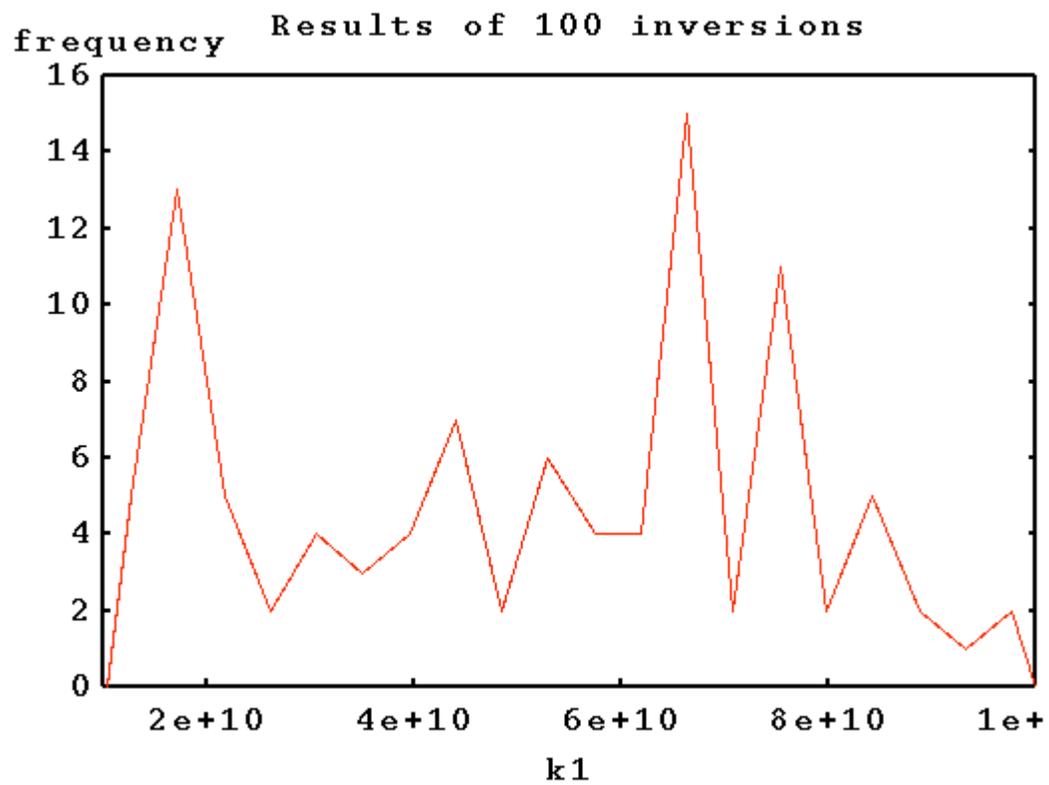


Figure 1 - Solutions obtained for k_1 in 100 separate inversion trials. The output data was not sensitive to rate constant k_1 , and hence k_1 is not well-specified, as is shown by the very broad distribution.

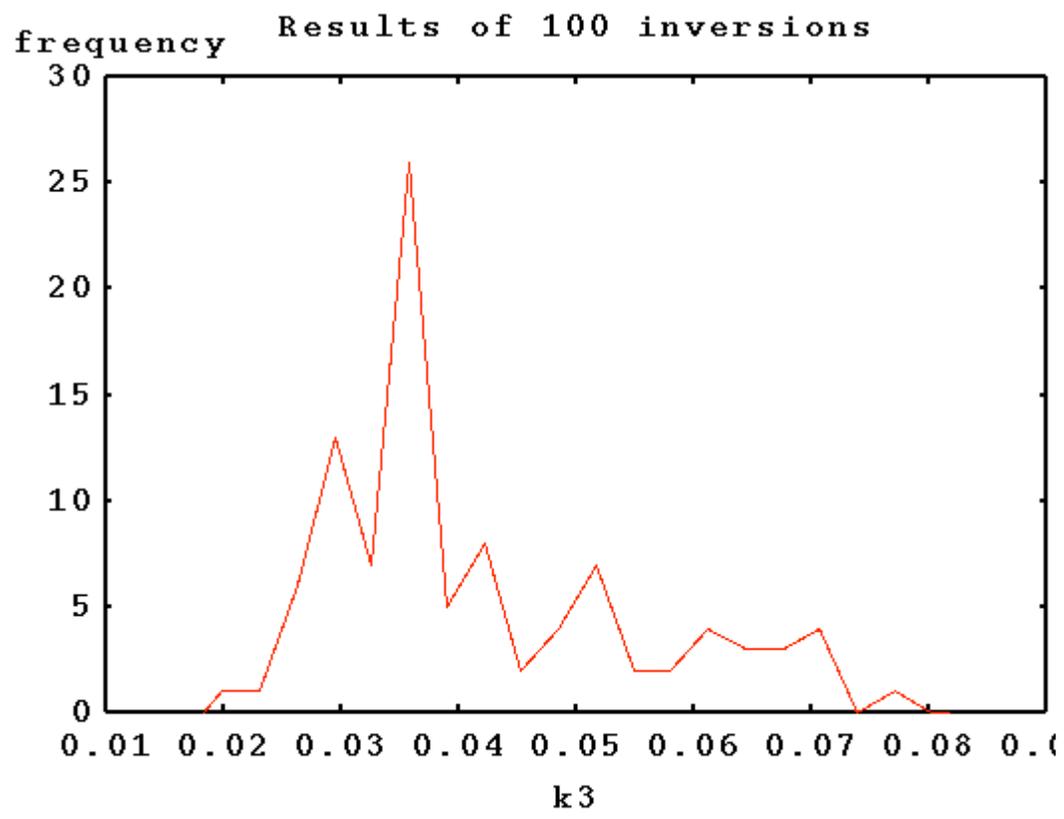


Figure 2 - Values obtained for k3 for 100 separate inversion trials. Each solution found modeled the target data within $\pm 5\%$

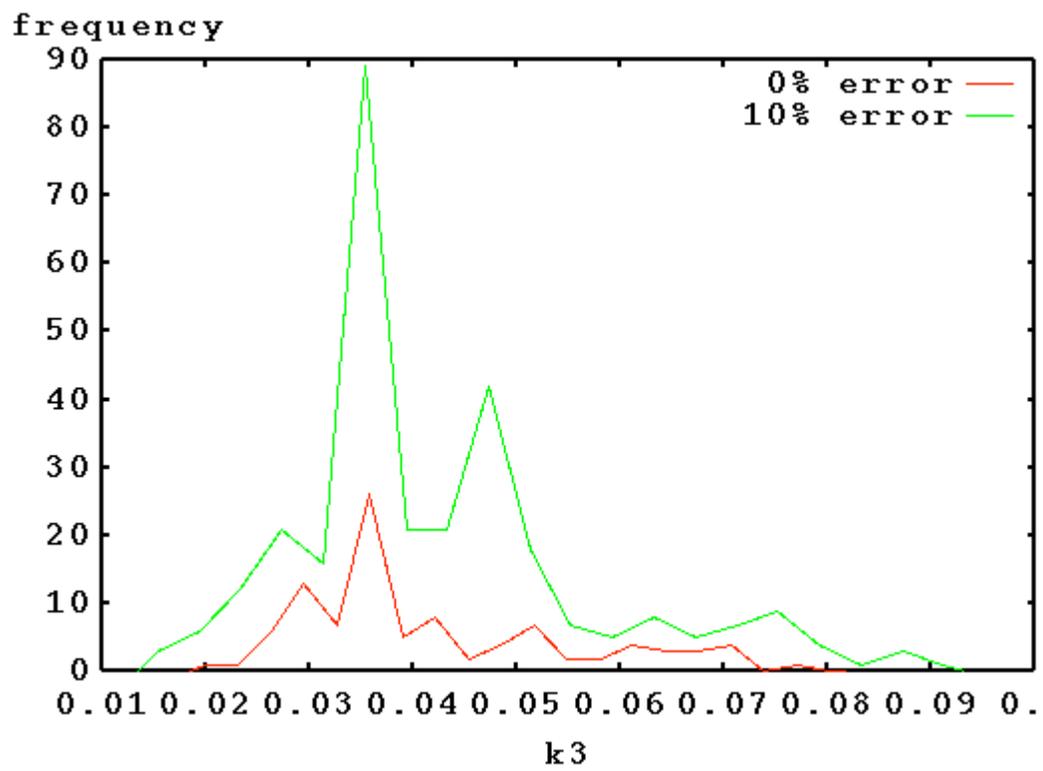


Figure 3 - Solutions for k_3 which modeled the target data within $\pm 10\%$

Orders of magnitude	0th order	1st order	2nd order
2	556.8576	488.1731	180.062
1.5	280.3485	192.6781	56.1079
1	119.3876	50.1730	9.5417
.5	43.4858	8.4946	.8183

Table 1 - Standard deviation of HDMR values of 1000 test points from real values (in percent). Orders of magnitude lists the size of HDMR window used.