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# Investigation of the Effect of Correlated Uncertain Rate Parameters on a Model of Hydrogen Combustion Using a Generalized HDMR method

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## Abstract

The High Dimensional Model Representation (HDMR) method has been applied in several previous studies to obtain global sensitivity indices of uncorrelated model parameters in combustion systems. The method is based on a decomposition of the model output in terms of a hierarchy of cooperative effects among the model inputs, which is unique when the input parameters are independent. However, many combustion systems will contain correlated input parameters. The development of a generalized HDMR method is therefore presented here, which uses the Rosenblatt transformation on a correlated model parameter sample to obtain a sample of independent parameters. The generalized HDMR method is used for the determination of sensitivity indices of a hydrogen combustion model with 33 correlated input parameters for a given set of experimental conditions. The effect of the correlation of rate parameters on the calculated sensitivity indices of ignition delay times is investigated.

## Introduction

Combustion models usually have many parameters and the quantification of each of these parameters will involve a level of uncertainty. Uncertainty analysis is widely used in combustion chemistry [1, 2] to investigate the uncertainty of simulation results knowing the uncertainty of model parameters. A critical step in determining such model output uncertainty is the determination of the extent of the uncertainty of its input parameters. One possibility for the assessment of input uncertainties is the investigation of the parameters one-by-one separately via tracing the source of the value of the parameter. Usually each parameter used in the model is based on one or several measurements. A measurement that aims at the determination of a kinetic or thermodynamic parameter is called a direct one. The evaluation of the systematic and statistical errors of these direct measurements allows an estimation of the uncertainty of each parameter. In most uncertainty analysis studies carried out so far in combustion chemistry (see *e.g.* [3-8]), the parameters were considered to be uncorrelated, since no information was available on their joint distributions.

Indirect measurements can be interpreted only by multi-parameter models. In combustion, such indirect measurements include for example the determination of laminar flame velocities or ignition delay times. Systematic optimization of reaction mechanisms (see *e.g.* [9-12]) means that the highly sensitive model parameters are fitted to indirect experimental data. Sheen and Wang calculated the covariance matrix of the fitted parameters [13, 14], which carries information on the joint uncertainty of the parameters. The rate parameters that Sheen and Wang optimized were Arrhenius  $A$  parameters and 3<sup>rd</sup> body collision efficiency factors. Turányi *et al.* [15-18] extended the methodology of mechanism optimization to the determination of all Arrhenius parameters  $A$ ,  $n$ ,  $E$  of the

important reaction steps together with the fitting of the important 3<sup>rd</sup> body collision efficiency factors. Turányi *et al.* also calculated the covariance matrix of all determined parameters. It follows therefore that the joint distributions of groups of model input parameters are likely to become more widely available as optimization methodologies are applied to more and more systems. Uncertainty and sensitivity analysis techniques therefore need to reflect such developments where correlations between parameters are known.

## HDMR Global Uncertainty Analysis

The aim of sensitivity analysis is to assess how the values of the model parameters influence the modelling results. Local sensitivity analysis [19] is regularly used in combustion modelling practice. The drawback of local methods is that they provide information on the importance of a parameter when all parameters of the model take their nominal value, and therefore cannot easily capture any nonlinear effects. Using another approach, called global sensitivity analysis, all parameters of the model may take any value within their joint domain of uncertainty and the importance of parameters is investigated within this domain. Global sensitivity analysis involves global uncertainty analysis of the model parameters, since the uncertainty domain of the parameters has to be defined. A wide range of global uncertainty analysis methods have been elaborated [2], which differ in computational requirements and the information provided.

The High Dimensional Model Representation (HDMR) method [20-23] has several advantageous features and therefore is summarized below. The HDMR method has several possible variants and the description below concentrates on the random sampling method (RS-HDMR).

First we denote the parameters of a model by  $\mathbf{x} = (x_1, x_2, \dots, x_n)$  and the simulation result  $f(\mathbf{x})$  ( $f: R^n$

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→  $R$ ). The result of the model can be expressed as a hierarchical expansion of the parameters:

$$f(\mathbf{x}) = f_0 + \sum_{i=1}^n f_i(x_i) + \sum_{1 \leq i < j \leq n} f_{ij}(x_i, x_j) + \dots + f_{12\dots n}(x_1, x_2, \dots, x_n), \quad (1)$$

where constant  $f_0$  represents the mean value across the input sample,  $f_i(x_i) : R \rightarrow R$  is the contribution of the  $i$ -th input parameter  $x_i$  to  $f(\mathbf{x})$ ;  $f_{ij}(x_i, x_j) : R^2 \rightarrow R$  is the cooperative contribution of the  $i$ -th and  $j$ -th inputs parameters to  $f(\mathbf{x})$ , etc. The zeroth-order, first-order, second-order, etc. component functions are denoted by  $f_0, f_i, f_{ij}$  etc, respectively. If the expansion is truncated after the third-order component function, the following approximation for the output function is obtained:

$$f(x) \approx f_0 + \sum_{i=1}^n f_i(x_i) + \sum_{1 \leq i < j \leq n} f_{ij}(x_i, x_j) + \sum_{1 \leq i < j < k \leq n} f_{ijk}(x_i, x_j, x_k) \quad (2)$$

If parameters  $x_1, x_2, \dots, x_n$  are independent, then the component functions can be determined uniquely and optimally [24]. This means that the component functions can be expressed using an orthogonal polynomial basis:

$$f_i(x_i) = \sum_{r_i=1}^{O_i} \alpha_i^{r_i} \varphi_i^{r_i}(x_i)$$

$$f_{ij}(x_i, x_j) = \sum_{r_i=1}^{O_i} \sum_{q_j=1}^{O_j} \beta_{ij}^{r_i q_j} \varphi_i^{r_i}(x_i) \varphi_j^{q_j}(x_j) \quad (3)$$

where  $O_i$  and  $O_j$  denote the order and  $\alpha_i, \beta_{ij}$  denote the coefficients of basis functions  $\varphi_i$  and  $\varphi_j$ . These coefficients are determined by fitting the RS-HDMR function to a sample of runs from the full model. It is important to notice that the determination of the orthogonal basis functions depends on the distribution of the input parameters. If optimal basis functions are chosen and the optimal coefficients are calculated (e.g. using a least-squares method), then the sensitivity indices can be determined as detailed below.

Let  $V$  denote the total variance of  $f(x)$ ,  $V_i$  the partial variance of  $f(\mathbf{x})$  due to  $x_i$  alone and  $V_{ij}$  the partial variance of  $f(\mathbf{x})$  due to the interactions between  $x_i$  and  $x_j$ , etc. We can define the first- and second-order sensitivity indices as  $S_i = V_i/V = V(E(f(x)|x_i))/V(f(x))$  and  $S_{ij} = V_{ij}/V = V(E(f(x)|x_i, x_j))/V(f(x))$ , respectively. If an accurate fit is obtained such that Eq. (3) provides a good representation of the expansion in

Eq. (1), then the sum of these indices should be close to 1.

The total order effect for parameter  $x_i$  can be interpreted in the following way:

$$S_i^{total} = S_i + \sum_{j \neq i} S_{ij} + \sum_{j, k \neq i} S_{ijk} + \dots = E(V(f(x)|x_1, \dots, x_{i-1}, x_{i+1}, \dots, x_n))/V(f(x)) \quad (4)$$

The total sensitivity index  $S_i^{total}$  measures the contribution of  $x_i$  to the output variance, including all variances caused by its interactions of any order, with any other input parameters. Note that whilst the sum of all indices, from an accurate RS-HDMR fit should not be greater than 1, perhaps paradoxically  $\sum_i S_i^{total}$  can be higher than 1. For example, sensitivity index  $S_{12}$  is added twice to the sum, since it is counted within the calculation of both  $S_1^{total}$  and  $S_2^{total}$ .

If the input parameters are independent, we can determine the optimal orthogonal polynomial expansion of the component functions. Using Eq. (1), the partial variances can be calculated and the sensitivity indices of the given parameters can be determined:

$$S_i = \sum_{r_i=1}^{O_i} (\alpha_i^{r_i})^2 / V \quad (5)$$

$$S_{ij} = \sum_{r_i=1}^{O_i} \sum_{q_j=1}^{O_j} \beta_{ij}^{r_i q_j} / V \quad (6)$$

This methodology is not applicable when the parameters are dependent, because in this case the polynomial expansion of the component functions is not unique, and coefficients  $\alpha_i$  and  $\beta_{ij}$  cannot be used to calculate sensitivity indices [24].

Li and Rabitz have discussed [24] the application of the HDMR method for the analysis of models with dependent parameters. However, their method is computationally demanding for large, many parameter systems. Here we follow the approach of Mara and Tarantola [25] who, simultaneously with Li and Rabitz, suggested the calculation of sensitivity indices of models with dependent parameters using the HDMR-ANOVA (analysis of variance) method. Mara and Tarantola demonstrated their method on simple examples only. Their method was reproduced, encoded and is applied here to a real combustion chemical model. This methodology is applicable for any distribution, but the since the covariance matrix of optimized combustion mechanisms are assumed to belong to a multivariate normal distribution, here only the case of a normal distribution is discussed.

### Decorrelation Using the Rosenblatt Transformation

Mara and Tarantola [25] suggested the application of the Rosenblatt transformation [26] to create an uncorrelated sample from a correlated one. First, a

sample must be generated based on the joint distribution function of the parameters. The quality of the generated samples can be investigated by checking the positive definite property of the calculated covariance matrix belonging to the sample.

The Rosenblatt transformation consists of the following steps. Let  $\mathbf{x} = (x_1, x_2, \dots, x_n) \in R^n$  denote a random vector with an absolutely continuous distribution function  $F(\mathbf{x}) = F(x_1, x_2, \dots, x_n) : R^n \rightarrow R$ . Consider the following transformation of the vector

$$\begin{aligned} \bar{x}_1 &= F_1(x_1) \\ \bar{x}_2 &= F_2(x_2 | x_1) \\ &\vdots \\ \bar{x}_n &= F_n(x_n | x_1, x_2, \dots, x_{n-1}) \end{aligned} \quad (7)$$

The transformed parameters  $\bar{x}_1, \bar{x}_2, \dots, \bar{x}_n$  are uniformly and independently distributed on interval  $[0,1]$ . This transformation can be expressed explicitly when  $F$  is a normal distribution with mean vector  $\mathbf{m}$  and covariance matrix  $\mathbf{C} = \{c_{ij}\}$ . Let  $C^p = \{\{c_{ij}\}: i, j = 1 \dots p \leq n\}$ ,  $|C^p|$  the cofactor of  $\{c_{ij}\}$  in  $C^p$  and  $|C^p|$  the determinant of  $C^p$ . In this case, the transformed parameters can be calculated using the following equations

$$\begin{aligned} \bar{x}_1 &= \Phi\left(\frac{x_1 - m_1}{\sqrt{c_{11}}}\right) \\ \bar{x}_2 &= \Phi\left(\frac{x_2 - m_2 + \left(\frac{|C_{21}^2|}{|C_{22}^2|}\right)(x_1 - m_1)}{\sqrt{|C_{22}^2|}}\right) \\ &\vdots \\ \bar{x}_n &= \Phi\left(\frac{x_n - m_n + \sum_{j=1}^{n-1} \left(\frac{|C_{nj}^n|}{|C_{nn}^n|}\right)(x_j - m_j)}{\sqrt{|C_{nn}^n|}}\right) \end{aligned} \quad (8)$$

where  $\Phi$  is the standard normal distribution function, which converts a standard normal *pdf* to a standard uniform *pdf*. This means that without applying function  $\Phi$  at the end of the transformation, the obtained transformed parameters are independent ones with standard normal distribution function. Eq. (8) shows that the covariance matrix of the sample must be positive definite.

A Matlab computer code was developed in this work that implements the transformation above. Mara and Tarantola [25] presented several simple examples, which included a 3-parameter linear analytical and a 6-parameter non-linear numerical test case. Using our

code, all the test results of Mara and Tarantola could be reproduced within 1% accuracy.

### Interpretation of the Sensitivity Indices of Transformed Parameters

The transformed parameters  $\bar{x}_1, \bar{x}_2, \dots, \bar{x}_n$  are uniformly and independently distributed. The RS-HDMR method is then applied using samples of these parameters and the corresponding simulated output distributions and sensitivity indices are calculated. Since the first parameter is only transformed and not corrected by the effect of any other parameter, the sensitivity index  $S_1$  of the first parameter is identical to those of the transformed parameter  $S_1^{\text{corr}}$ , which is in fact identical to the sensitivity index  $S_1^{\text{corr}}$  that reflects all possible correlations. The total contribution of  $x_1$  to the variance of the output is indicated by sensitivity index  $S_1^{\text{total}} = S_1^{\text{corr}} = S_1^{\text{corr\_total}}$ . Performing the transformation for each of the indices  $i = 1, 2, 3$ , etc., in turn, sensitivity indices  $S_i^{\text{corr}}$  and  $S_i^{\text{corr\_total}}$  can be calculated for each parameter independently of the later transformations that aim to decorrelate the parameters. This total sensitivity index  $S_i^{\text{corr\_total}}$  reflects the contribution that each parameter makes to the total output variance, taking into account all its possible correlations. If a parameter dominates the output variance, then we would expect this index to be close to 1.

The subsequent transformations aiming to decorrelate the parameters can be performed in any chosen order. Hence, having  $n$  parameters in total, in the second step we may select any of the remaining  $(n-1)$  parameters. We denote the second selected parameter by subscript 2 and hence  $S_2$  represents the contribution of  $x_2$  to the output variance, without its relative contribution with  $x_1$ . Notation  $S_2 = S_{2-1}$  emphasizes this meaning and represents a marginal sensitivity. In a similar way the total effect can be calculated, without the influence of parameter 1, denoted by  $S_2^{\text{total}} = S_{2-1}^{\text{total}}$ . These marginal sensitivities are calculated in sequence and in the last step, we obtain  $S_n^- = S_{n-(n-1)-\dots-2-1} = S_n^{\text{uncorr}}$  which shows the totally uncorrelated contribution of parameter  $x_n$  to the variance of  $f(x)$ . The marginal sensitivity,  $S_n^{\text{total}} = S_{n-(n-1)-\dots-2-1}^{\text{total}} = S_n^{\text{uncorr\_total}}$  is the total sensitivity index of parameter  $n$  without the influence of correlations with any other parameter [25]. While the sensitivity indices of in the middle of the sequence of decorrelation depend on the order of the selection of parameters, the last sensitivity indices  $S_n^{\text{uncorr}}$  and  $S_n^{\text{uncorr\_total}}$  are independent of this order.

|    | reaction  | parameter               | $S_i^{\text{corr}}$ | $S_i^{\text{corr\_total}}$ | $S_i^{\text{uncorr}}$ | $S_i^{\text{uncorr\_total}}$ |
|----|---|-------------------------|---------------------|----------------------------|-----------------------|------------------------------|
| 1  | $\text{H}+\text{O}_2=\text{O}+\text{OH}$                  | $\ln A$                 | 0.088               | 0.089                      | 0.110                 | 0.110                        |
| 2  |   | $n$                     | 0.035               | 0.036                      | 0.109                 | 0.109                        |
| 3  |   | $E/R$                   | 0.259               | 0.260                      | 0.099                 | 0.099                        |
| 4  | $\text{H}+\text{O}_2(+\text{M})=\text{HO}_2(+\text{M})$   | LP $\ln A$              | 0.012               | 0.012                      | 0.000                 | 0.000                        |
| 5  |   | LP $n$                  | 0.000               | 0.001                      | 0.000                 | 0.000                        |
| 6  |   | $m(\text{H}_2)$         | 0.171               | 0.172                      | 0.000                 | 0.000                        |
| 7  |   | $m(\text{H}_2\text{O})$ | 0.039               | 0.041                      | 0.000                 | 0.000                        |
| 8  |   | $m(\text{Ar})$          | 0.044               | 0.044                      | 0.001                 | 0.001                        |
| 9  | $\text{O}+\text{H}_2=\text{H}+\text{OH}$                  | $\ln A$                 | 0.236               | 0.237                      | 0.024                 | 0.024                        |
| 10 |   | $n$                     | 0.229               | 0.229                      | 0.023                 | 0.023                        |
| 11 |   | $E/R$                   | 0.258               | 0.258                      | 0.014                 | 0.014                        |
| 12 | $\text{OH}+\text{H}_2=\text{H}+\text{H}_2\text{O}$        | $\ln A$                 | 0.158               | 0.159                      | 0.004                 | 0.004                        |
| 13 |   | $n$                     | 0.167               | 0.168                      | 0.005                 | 0.005                        |
| 14 |   | $E/R$                   | 0.190               | 0.191                      | 0.002                 | 0.002                        |
| 15 | $\text{H}+\text{HO}_2=\text{H}_2+\text{O}_2$              | $\ln A$                 | 0.149               | 0.150                      | 0.011                 | 0.011                        |
| 16 |   | $n$                     | 0.279               | 0.280                      | 0.012                 | 0.012                        |
| 17 |   | $E/R$                   | 0.131               | 0.133                      | 0.004                 | 0.004                        |
| 18 | $\text{H}+\text{OH}+\text{M}=\text{H}_2\text{O}+\text{M}$ | $\ln A$                 | 0.247               | 0.247                      | 0.000                 | 0.000                        |
| 19 |   | $n$                     | 0.248               | 0.249                      | 0.000                 | 0.000                        |
| 20 |   | $E/R$                   | 0.170               | 0.170                      | 0.000                 | 0.000                        |
| 21 | $\text{HO}_2+\text{H}=2\text{OH}$                         | $\ln A$                 | 0.257               | 0.258                      | 0.000                 | 0.000                        |
| 22 |   | $E/R$                   | 0.237               | 0.238                      | 0.000                 | 0.000                        |
| 23 | $\text{HO}_2+\text{OH}=\text{H}_2\text{O}+\text{O}_2$     | $\ln A$                 | 0.279               | 0.279                      | 0.000                 | 0.000                        |
| 24 |   | $n$                     | 0.280               | 0.281                      | 0.000                 | 0.000                        |
| 25 |   | $E/R$                   | 0.120               | 0.120                      | 0.000                 | 0.000                        |
| 26 | $\text{H}_2\text{O}_2+\text{H}=\text{H}_2+\text{HO}_2$    | $\ln A$                 | 0.250               | 0.250                      | 0.000                 | 0.000                        |
| 27 |   | $n$                     | 0.246               | 0.246                      | 0.000                 | 0.000                        |
| 28 |   | $E/R$                   | 0.234               | 0.235                      | 0.000                 | 0.000                        |
| 29 | $2\text{OH}(+\text{M})=\text{H}_2\text{O}_2(+\text{M})$   | LP $\ln A$              | 0.041               | 0.041                      | 0.000                 | 0.000                        |
| 30 |   | LP $n$                  | 0.140               | 0.140                      | 0.000                 | 0.000                        |
| 31 |   | LP $E/R$                | 0.226               | 0.227                      | 0.000                 | 0.000                        |
| 32 | $2\text{HO}_2=\text{H}_2\text{O}_2+\text{O}_2$            | $\ln A$                 | 0.045               | 0.046                      | 0.000                 | 0.000                        |
| 33 |   | $E/R$                   | 0.126               | 0.127                      | 0.000                 | 0.000                        |

Table 1. The list of important rate parameters (transformed Arrhenius parameters  $\ln A$ ,  $n$ ,  $E/R$ , and third body collision efficiency parameter  $m$ ) and the corresponding elementary reactions, for which correlated posterior uncertainty was determined by Varga *et al.* [18]. The table contains sensitivity indices  $S_i^{\text{corr}}$ ,  $S_i^{\text{corr\_total}}$ ,  $S_i^{\text{uncorr}}$  and  $S_i^{\text{uncorr\_total}}$  (see text) for each parameter. The 2<sup>nd</sup> and 4<sup>th</sup> of these indices are of particular interest and indicated with coloured background. The shift of colours from yellow to red shows increasing importance. LP refers to the low-pressure limit.

For systems with independent parameters, the importance of a parameter can be simply determined by a single total sensitivity measure. For correlated systems however, the picture is not so simple since both the correlated  $S_i^{\text{corr\_total}}$  and uncorrelated  $S_i^{\text{uncorr\_total}}$  total sensitivity indices are available, as well as a large number of marginal sensitivity indices which represent partial correlations. Here for simplicity we restrict the discussion to the correlated  $S_i^{\text{corr\_total}}$  and uncorrelated  $S_i^{\text{uncorr\_total}}$  total sensitivity indices. If both of these indices are close zero, then the investigated parameter is of low importance. If the correlated index  $S_i^{\text{corr\_total}}$  is large (e.g. close to 1), this means that parameter  $x_i$  is important. However, if its uncorrelated total index  $S_i^{\text{uncorr\_total}}$  is small, then its influence on the output variance involves strong correlations with other parameters. Finally, if a parameter has a large uncorrelated index, then it strongly contributes to output variance, without correlated effects with the other parameters.

#### Determination of the Sensitivity Indices of the Rate Parameters of a Hydrogen Combustion System

Varga *et al.* [18] elaborated an optimized hydrogen combustion mechanism based on several thousand experimental data points, including ignition delay time measurements in shock tubes and rapid compression machines, laminar flame velocity determinations and jet stirred reactor (JSR) measurements. They demonstrated that this optimized model reproduces the literature experimental data more accurately (with less deviation), than any of the previously published reaction mechanisms.

The aim of this section is to show typical sensitivity indices of this hydrogen combustion model for a given set of realistic conditions. An important output of the mechanism optimization was the calculation of the posterior uncertainty of 33 rate parameters (Arrhenius parameters  $\ln A$ ,  $n$ ,  $E/R$  and third body collision efficiency parameters  $m$ ) belonging to 11 elementary reactions. The Supplementary material of article [18] contains the covariance matrix of the fitted parameters which illustrates the level of correlation between them.

The mechanism was investigated for the conditions of the experiment of Cheng and Oppenheim [27], who measured ignition delay times in a shock tube using reflected shock waves. The initial gas contained a stoichiometric hydrogen–oxygen mixture, diluted by 90% argon bath gas. The initial conditions were  $T=1252$  K and  $p=1.864$  atm. The single result of the simulation was the ignition delay time, which was defined by the maximum of the time derivative of pressure. The SENKIN simulation code [28] of the CHEMKIN-II package [29] was used for the simulations. Decorrelation of the parameters was carried out with our newly developed Matlab code, while the HDMR sensitivity indices were calculated using the GUI-HDMR code [30].

The first three columns of Table 1 contain the number of the parameter, the corresponding elementary reaction, and the type of the parameter ( $\ln A$ ,  $n$ ,  $E/R$ ,  $m$ ). The last four columns contain sensitivity indices  $S_i^{\text{corr}}$ ,  $S_i^{\text{corr\_total}}$ ,  $S_i^{\text{uncorr}}$  and  $S_i^{\text{uncorr\_total}}$  for each of the 33 parameters of the model.

Comparing the 1<sup>st</sup> and 2<sup>nd</sup> columns of sensitivity indices, little difference is found between the values of  $S_i^{\text{corr}}$  and  $S_i^{\text{corr\_total}}$ . Also, up to 3 decimal digit accuracy, there is no difference between  $S_i^{\text{uncorr}}$  and  $S_i^{\text{uncorr\_total}}$ . This shows that in this case, calculation of the total sensitivities do not provide new information compared to the first-order sensitivities and that few higher-order effects are found. The second column of the sensitivity indices contains the  $S_i^{\text{corr\_total}}$  values. The first thing to note is that no single parameter dominates since none of the indices are close to 1. A large number of the parameters have significant values however, and at first glance the indices seem to indicate that several elementary reactions of species  $\text{HO}_2$  and  $\text{H}_2\text{O}_2$  have high importance. From a chemical perspective this is perhaps surprising, since at such a high temperature and relatively low pressure the reactions of these species are not expected to play a significant role. However, the picture becomes clearer when looking at the  $S_i^{\text{uncorr\_total}}$  values in the 4<sup>th</sup> column. The  $S_i^{\text{uncorr\_total}}$  values belonging to the parameters of the majority of the elementary reactions of  $\text{HO}_2$  and  $\text{H}_2\text{O}_2$  are all close to zero. This indicates that their influence on the output variance is almost entirely related to their correlation with other parameters and that their uncorrelated influence is small. The reaction parameters with the largest  $S_i^{\text{uncorr\_total}}$  values belong to the elementary reaction  $\text{H}+\text{HO}_2=\text{H}_2+\text{O}_2$  (initiation) and chain branching reactions  $\text{H}+\text{O}_2=\text{O}+\text{OH}$ ,  $\text{O}+\text{H}_2=\text{H}+\text{OH}$  and  $\text{OH}+\text{H}_2=\text{H}+\text{H}_2\text{O}$ . Since these parameters have both large correlated and uncorrelated sensitivity indices then they can be classified as important which is consistent with them being typically considered as the most important reactions of hydrogen ignition and explosion below the 2<sup>nd</sup> ignition limit [31].

The sensitivity indices above show that taking into account the correlation of parameters, but carrying out a global sensitivity analysis using only the fully correlated sensitivity indices can lead to misleading results. Many parameters seem to be important, but in many cases the origin of importance is their interaction with other parameters. Unless a parameter is dominant i.e. has an  $S_i^{\text{corr\_total}}$  close to 1, then marginal indices should also be considered. By calculating the uncorrelated sensitivity indices, additional information can be obtained on the independent influence of the parameters. In this case, parameters that exhibited both large correlated and uncorrelated total indices were related to reactions that are typically considered to be important in accordance with chemical intuition.

## Conclusions

Uncertainty analysis investigates the uncertainty of a model output due to the uncertainty of the input parameters. Uncertainty analysis of combustion models has frequently been carried out, but in all cases the parameters were assumed to be uncorrelated. The reason is that most uncertainty analysis methods are not able to cope with correlated parameters and also the uncertainties of model parameters were estimated one-by-one, independently of each other. One result of the optimization of reaction mechanisms is the calculation of the covariance matrix of the important parameters. Also, it is a good assumption that the optimized parameters have multivariate normal distribution.

Mara and Tarantola [25] suggested an extension of the High Dimensional Model Representation (HDMR) method of uncertainty analysis to correlated parameter sets. Their method was reproduced in this work with a newly developed Matlab computer code. Using this code together with the the GUI-HDMR code [30] of Ziehn and Tomlin allows global uncertainty analyses of large, multi-parameter combustion models with correlated inputs.

This method and computer code was used to investigate the ignition of a hydrogen–oxygen mixture for the conditions of a shock tube experiment. The calculations revealed that the sensitivity indices belonging to the correlated parameters can present misleading results when considered in isolation. When coupled with analysis of the uncorrelated sensitivity indices the importance of parameters within the model could be well interpreted.

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