



# Automated chemical kinetic mechanism simplification with minimal user expertise



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## ABSTRACT

An improved algorithm to generate skeletal mechanisms from the original detailed chemical kinetic mechanisms is proposed. The new algorithm builds on the computational singular perturbation (CSP) framework, by adding an additional layer of automation based on the tangential stretching rate (TSR) and the species' participation index to TSR. The main advantage of the new approach is that it does not require the specification of a set of target species. Instead, the target species set is dynamic and automatically identified through the simplification algorithm, which defines the system's state variables that the skeletal mechanism is required to accurately predict. In this way, the new procedure pursues an optimum set of target species that leads the algorithm to include a minimal number of species/reactions that ensures the replication of global observables, such as ignition delay time, without any *a-priori* knowledge of the chemical pathways. The capabilities and performance of the new simplification algorithm are demonstrated in a test problem employing the 397-species detailed mechanism for C<sub>0</sub>-C<sub>2</sub> species, augmented with polycyclic aromatic hydrocarbon (PAH) soot precursor species. The results are compared with those obtained from the standard CSP-based algorithm in terms of the ignition delay times, main species evolution and their equilibrium state. Subsequent examples also demonstrate the capabilities of the TSR-based algorithm to generate additional sub-mechanisms that, combined with the core mechanism, allow to extend its range of operating conditions and target variables.

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## 1. Introduction

The experimental and kinetic modeling studies of practical fuels, both hydrocarbons and alternative fuels, are continuously growing, providing the scientific community with high fidelity detailed kinetic models for predictive simulations of combustion processes. However, despite the increase in computational resources, such models, which nowadays typically include hundreds or thousands of species, are still impractical for massive computations, especially in computational fluid dynamics (CFD) [1–3]. Model reduction techniques have been proposed in the last decades with the aim of generating smaller/reduced kinetic mechanisms, that are still accurate for the specific applications. A large number of such methods are based on unimportant species/reactions elimination. Among them, algorithms based on sensitivity analysis [4], computational singular perturbation (CSP) [5], sensitivity analysis

within the G-Scheme framework [6], entropy production analysis [7,8], principal component analysis (PCA) [9], path flux analysis (PFA) [10,11] and directed relation graph (DRG) [12] have been successfully employed and improved over time.

Methods such as those based on CSP or DRG require the specification of the system's state variables that the skeletal mechanism is designed to accurately predict. This set of variables, usually referred to as *target species set*, often includes temperature and the major species, such as fuel(s), oxidizer(s) and the major products, and other species that are of interest for specific applications. For example, typical species that are included beyond reactants and products are important pollutants or their precursors, such as NO<sub>x</sub> or polycyclic aromatic hydrocarbons (PAHs). However, global observables such as ignition delay time or equilibrium state cannot be set as target variables, because they are not system's state variables and can only be evaluated *a posteriori*, after a system's evolution has been realized with the reduced model. Additional target variables may be a species known to be important for the ignition dynamics, such as HCO, which is a marker for heat release and

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has been commonly used as a target species in methane skeletal mechanism generation. Although usually successful, this practice requires a prior knowledge of the chemical pathways that are required for retaining accuracy in ignition delay time predictions. Such prior knowledge, however, is often unavailable when dealing with much more complex fuels, such as bio-fuels, synthetic, or other surrogate fuels.

Specifying the set of target species in general is a delicate matter. It is expected that the resulting skeletal mechanisms have a strong dependence on the target set, which acts as a seed for the mechanism construction. Indeed, the more target species are specified, the more species/reactions will be required in the skeletal mechanisms to obtain an accurate prediction of them all. Moreover, if the user is interested in global observables, such as the ignition delay time, the choice of the target species is not trivial.

In the present work, we assume that an optimum target species set exists so as to capture the core kinetics of, say, an ignition problem, with the minimum number of retained species/reactions. This optimum set has always been thought of as a group of reactants, products and other species that are considered important for ignition dynamics. However, even if we have the necessary information to determine them, this set may be redundant, resulting in a larger-than-necessary number of species/reactions in the skeletal mechanisms, with a possibility of even deteriorating the accuracy in predicting the ignition delay time, which is known to exhibit non-monotonic convergent behavior with increasing number of species/reactions of the skeletal kinetic mechanism. This non-monotonicity arises as a consequence of the elimination in total or in part of chain branching/propagation reactions that can promote or postpone the onset of ignition [13], especially when the relevant processes are not correctly targeted by the user.

To summarize, when the investigator is interested in an improved accuracy in predicting global observables, such as the ignition delay time, the specification of the target species (which ones and how many) brings in a considerable number of degrees of freedom, which the investigator have no basis to decide *a priori*. In this work, we propose a modification to the CSP simplification algorithm that aims at removing the need for a user-specified set of target species when global ignition observables are the targets of interest. This is achieved by utilizing a new mathematical quantity called tangential stretching rate (TSR), determined by an automated computational analysis of the chemical system evolution.

In the following, the CSP-based simplification algorithm is recalled, then the TSR-modification is introduced and detailed, followed by a demonstration application.

## 2. Description of algorithm

### 2.1. CSP-based simplification algorithm

In the CSP-based simplification algorithm, the criterion for selecting the subset of reactions and species to be retained is based on their relevance to the fast or slow dynamics of the prescribed set of target species, the concentration of which is desired to be accurately reproduced by the skeletal mechanism. This algorithm relies on the decomposition of the chemical kinetic processes into fast and slow components, using CSP, and on the identification of the processes that produce the most significant contributions in either the fast or slow components [14–18].

Consider a spatially homogeneous chemical kinetic system whose dynamics is described by a Cauchy problem of the form:

$$\frac{d\mathbf{y}}{dt} = \mathbf{g}(\mathbf{y}), \quad \mathbf{y}(0) = \mathbf{y}_0, \quad \mathbf{y} \in \mathbb{R}^N. \quad (1)$$

where  $\mathbf{y}$  is a  $N$ -dimensional state vector and  $\mathbf{g}(\mathbf{y})$  is a generic chemical source term. The Jacobian of the vector field can be always decomposed as  $J_{\mathbf{g}} = A \Lambda B$ , where  $A = \{\mathbf{a}_j\}_{j=1,N}$  and  $B = \{\mathbf{b}^i\}_{i=1,N}$  are the right and left normalized eigenvector matrices of  $J_{\mathbf{g}}$ , respectively, and  $\Lambda = \{\lambda_j^i\}_{i,j=1,N}$  is the eigenvalue matrix of  $J_{\mathbf{g}}$ . Thus, as discussed in [14], Eq. (1) can be recast as an expansion over the kinetic eigen-modes:

$$\frac{d\mathbf{y}}{dt} = \mathbf{g}(\mathbf{y}) = \sum_{i=1,N} \mathbf{a}_i(\mathbf{y}) f^i(\mathbf{y}) \quad f^i := \mathbf{b}^i \cdot \mathbf{g}. \quad (2)$$

The  $N$  CSP-modes in Eq. (2) are ordered so that the first ( $i=1$ ) mode refers to the fastest chemical timescale ( $1/|\lambda_1|$ ), as measured by the modulus of the eigenvalue associated to that mode, the second ( $i=2$ ) mode refers to the second fastest, etc., with  $|\lambda_1| > |\lambda_2| > \dots > |\lambda_N|$ . At any time epoch, one can partition the tangent space into the slow and fast subspaces, so that the first  $M$  timescales and modes are declared to be fast, and the remaining  $N-M$  to be slow. The criterion that determines the dimension of the fast subspace, detailed in [19,20], identifies the first  $M$  modes that offer a negligible contribution to the dynamics over a time period of the order of the fastest of the slow timescales  $1/|\lambda_{M+1}|$ .

As a measure of the degree to which a species contributes to the fast/slow dynamics of the target species, the algorithm adopts the fast/slow CSP Importance Indices, which measure the contribution of each elementary reaction in the detailed mechanism to the fast and slow components of each species production rate [20–23].

For a homogeneous combustion process, the  $N$ -dimensional state vector in Eq. (1) includes the species concentrations and temperature ( $N = N_s + 1$ ), and the chemical source term  $\mathbf{g}(\mathbf{y})$  can be written as:

$$\mathbf{g}(\mathbf{y}) = \sum_{k=1}^{2N_r} \mathbf{S}_k r^k, \quad (3)$$

where  $S$  is a ( $N \times 2N_r$ ) matrix of generalized stoichiometric coefficients,  $\mathbf{r}$  is the vector containing the reaction rates and  $N_r$  is the number of reversible elementary reactions. The relative contribution of a reaction  $k$  in the production/consumption of the species  $i$  in either the fast or slow subspace can be assessed by means of a fast/slow Importance Index defined as:

$$(I)_{k_{\text{slow}}}^i = \frac{\sum_{s=M+1}^N a_s^i(\mathbf{b}^s \cdot \mathbf{S}_k) r^k}{\sum_{kk=1}^{2N_r} \left| \sum_{s=M+1}^N a_s^i(\mathbf{b}^s \cdot \mathbf{S}_{kk}) r^{kk} \right|}, \quad (4)$$

$$(I)_{k_{\text{fast}}}^i = \frac{\sum_{r=1}^M a_r^i(\mathbf{b}^r \cdot \mathbf{S}_k) r^k}{\sum_{kk=1}^{2N_r} \left| \sum_{r=1}^M a_r^i(\mathbf{b}^r \cdot \mathbf{S}_{kk}) r^{kk} \right|}. \quad (5)$$

Given a user-specified tolerance  $\tau$ , the  $k$ th reaction is included in the simplified mechanism if  $(I)_{k_{\text{slow/fast}}}^i > \tau$ , where the species  $i$  is a target species. Once a set of important reactions is identified based on the Importance Indices to the target species, a new set of important species is defined as the one containing the species involved in the important reactions. Then, the Importance Indices are computed for this new set of species. The algorithm loops until this set of important species remains unchanged. This is done in each state of the training database, and the global set of active species/reactions is the union of the local sets of active species/reactions. This approach is very useful in generating a spectrum of simplified mechanisms of different sizes, each associated with a given degree of fidelity, assessed *a posteriori*, specified by the tolerance  $\tau$  on the Importance Indices.

### 2.2. TSR-modified simplification algorithm

The tangential stretching rate (TSR, or  $\omega_{\bar{\tau}}$ ) offers the possibility of removing any user-specified degree of freedom related to

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