

A CSP-based automatic procedure to identify reactions leading to hyper-fast timescales in reacting systems

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Abstract

A computational singular perturbation (CSP) based tool is shown to be able to identify the reactions mostly participating to a kinetic eigen-mode. This tool is effectively employed to determine which reactions are causing the existence of extremely fast, unphysical timescales in auto-ignition problems involving a large and complex kinetic mechanism, consisting of 2484 species and 10368 reactions. This mechanism, in fact, triggers the presence of very large eigenvalues, which drastically reduce the solver computational efficiency and possibly prevent an accurate fast/slow subspaces decomposition for model reduction purposes.

1. Introduction

Chemical kinetics mechanisms design is a complex and challenging process, that involves the definition of stoichiometries and thermochemical data for each of the reaction steps. Several computer codes and automated procedures have been developed in the last decades to improve and possibly replace the complicated manual generation of mechanisms that historically represented the state of the art in this field [1]. However, today's fuels used both in aircraft and car engines are composed of a multitude of different molecular components, whose physical and chemical properties are not fully known, and such fuels are often represented by surrogates. The kinetic mechanisms that are used to model such fuels are designed to reproduce certain physical or chemical properties of the blend, such as ignition delay times, laminar burning velocities or pollutants formation [2]. Mechanisms of this kind, typically including thousands of species, may generate chemical dynamics characterized by unphysical timescales, arising from extremely fast kinetics eigen-modes. In this paper, we show how the reactions that cause such unphysical scales can be identified, relying on the computational singular perturbation (CSP) method [3]. In particular, we employ a CSP-based participation index that points the reactions mostly participating to a given kinetic eigen-mode, effectively revealing those responsible of the modes associated to the extremely fast timescales.

2. Theoretical formulation

2.1. The CSP method

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

$$\frac{dy}{dt} = g(y), \quad y(0) = y_0, \quad x \in \mathbb{R}^N. \quad (1)$$

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

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

where $\hat{\mathbf{S}}$ is the $(N_s \times 2N_r)$ generalized matrix of the stoichiometric coefficients, \mathbf{r} is the vector containing the reaction rates and N_r is the number of reversible elementary reactions (see [3] for further details). The Jacobian \mathbf{J}_g of the vector field $\mathbf{g}(\mathbf{y})$ can be always decomposed as $\mathbf{J}_g = \mathbf{A} \Lambda \mathbf{B}$, where $\mathbf{A} = \{\mathbf{a}_j\}_{j=1,N}$ and $\mathbf{B} = \{\mathbf{b}^i\}_{i=1,N}$ are the right and left normalized eigenvector matrices of \mathbf{J}_g , respectively, and $\Lambda = \{\lambda_j^i\}_{i,j=1,N}$ is the eigenvalue matrix of \mathbf{J}_g . Thus, as discussed in [4], Eq. (1) can be recast as an expansion over the kinetics eigen-modes:

$$\frac{d\mathbf{y}}{dt} = \mathbf{g}(\mathbf{y}) = \sum_{i=1,N} \mathbf{a}_i(\mathbf{y}) f^i(\mathbf{y}) \quad f^i := \mathbf{b}^i \cdot \mathbf{g}. \quad (3)$$

The N CSP-modes in Eq. (3) are ordered so that the first ($i = 1$) mode refers to the fastest chemical timescale, the second ($i = 2$) mode refers to the second fastest, etc.

2.1.1. Fast/Slow decomposition

At any time epoch and space location, one can partition the tangent space into the slow and fast subspaces. The criterion that determines the dimension of the fast subspace M , is based on the definition of an error vector \mathbf{y}_{error} defined as $y_{err}^i = \epsilon_{rel}^i y^i + \epsilon_{abs}^i$, $i = 1, N$, where ϵ_{rel}^i and ϵ_{abs}^i are the maximum relative and absolute errors on the i -th element of the state vector \mathbf{y} respectively. The number M of timescales which - within the limits of accuracy specified by the given error vector - are considered exhausted (in near equilibrium), is defined as the largest integer lying between 1 and N that satisfies the following inequality for each $i = 1, N$:

$$\delta y_{fast}^i \approx \int_0^{\tau^{M+1}} \left(\sum_{r=1}^M a_r^i f^r(t) \right) < y_{error}^i = \epsilon_{rel}^i y^i + \epsilon_{abs}^i, \quad (4)$$

where $\tau^{M+1} = 1/\lambda_{M+1}$ is the fastest of the slow chemical timescales. An estimate of this integral is built retaining the functional dependence of f^r with time, and then approximating the amplitude evolution $f^r(t)$ with $f_0^r e^{\lambda_r t}$, thus assuming an exponential decay of $f^r(t)$ according to its corresponding -negative- eigenvalue. Hence, the contribution to the change of the state variables due to the fast subspace becomes:

$$\delta y_{fast}^i \approx \int_0^{\tau^{M+1}} \left(\sum_{r=1}^M a_r^i f^r(t) \right) = \int_0^{\tau^{M+1}} \left(\sum_{r=1}^M a_r^i f_0^r e^{\lambda_r t} \right) < y_{error}^i = \epsilon_{rel}^i y^i + \epsilon_{abs}^i, \quad (5)$$

where f_0^r are the values of the fast mode amplitudes at the beginning of the time interval of duration τ^{M+1} . The last integral can be solved in closed form to yield the criterion that determines the dimension of the fast subspace M as the largest integer that satisfies the following inequality for each component i of the state vector:

$$\delta y_{fast}^i \approx |\tau^{M+1} \sum_{r=1}^M a_r^i f_0^r \frac{1 - e^{\lambda_r \tau^{M+1}}}{\lambda_r}| < y_{error}^i = \epsilon_{rel}^i y^i + \epsilon_{abs}^i. \quad (6)$$

When the amplitudes of the M fastest modes have vanished, i.e., when the following relations hold:

$$f^r \approx 0 \quad r = 1, M \quad (7)$$

then we will declare “exhausted” the chemical timescales τ_r ($r = 1, M$) and “fast” the corresponding modes. Equation (7) defines the slow invariant manifold. The remaining $N - M$ timescales and modes are declared as being “slow”. The fast and slow modes span the fast and slow subspaces, respectively. The separate examination of fast and slow subspaces allows to distinguish the fast processes mostly participating to the emergence of the slow invariant manifold and the slow processes driving the solution along the manifold itself, as demonstrated in [3], and is crucial for model reduction purposes, as shown in [5, 6].

2.2. Diagnostics tools to identify hyper-fast reactions

In the general framework of the CSP theory, various algorithmic mathematical tools have been developed for diagnostics [4, 7, 8, 9] and mechanism simplification purposes [3, 10], and their validity has been widely tested.

The CSP participation index, in particular, provides an estimate of the participation of a given reaction to a mode. This index is built considering that the amplitude of the i -th mode f^i can be expanded as:

$$f^i = \mathbf{b}^i \cdot \mathbf{g}(\mathbf{y}) = \sum_{k=1}^{2N_r} \mathbf{b}^i \cdot \hat{\mathbf{S}}_k R^k = \sum_{k=1}^{2N_r} \beta_k^i, \quad (8)$$

then the CSP participation index P_k^i can be introduced in order to measure the relative contribution of the k -th reaction to the i -th mode amplitude [11, 12]:

$$P_k^i = \frac{\beta_k^i}{\sum_{j=1}^{2N_r} |\beta_j^i|}. \quad (9)$$

With this tool in hand, it is straightforward to identify the reactions that contribute the most to the modes associated to unphysical, hyper-fast timescales.

3. Application to a complex auto-ignition problem

The investigation of hyper-fast timescales and their mostly contributing chemical reactions is tested on an auto-ignition problem of an homogeneous, isobaric reactor. The mixture is a stoichiometric air-gasoline-butanol blend whose fuel composition - in % mole - is summarized in Table 1 and whose initial condition is $T=900$ K, $p = 10$ bar.

Table 1: Mixture composition

Component	% mole
iso-octane	35.19
n-heptane	8.02
toluene	29.23
n-butanol	27.56

The detailed mechanism employed for the auto-ignition problem is a 2484-species, 10368-reactions, referred to as “TRF+dodecane+butanol”, built on the Aramcomech 1.3 base chemistry [13], whose development is still in progress. We obtain time accurate solutions of the auto-ignition problem by means of the CSPTk package [14], which integrates in time Eq. 1 using CVODE and where the thermokinetic databases are parsed and handled using the TChem package [15].

We define a logarithmic version of the system eigenvalues $\Lambda_i = \text{Sign}(\lambda_i) \cdot \text{Log}_{10}|\lambda_i|$, following [9], so as to appreciate the order of magnitude of both the positive and negative eigenvalues in the same figure.

Figure 1(a) shows the evolution of eigenvalues Λ_i and temperature against the number of integration timestep, computed with the aforementioned mechanism. The most concerning issue is the presence of eigenvalues with high or very high modulus, which reaches the order of 10^{27} in the first part of the ignition. We define as hyper-fast those timescales that correspond to eigenvalues, both positive and negative, whose modulus is greater than 10^{15} . These large eigenvalues, corresponding to extremely fast timescales, are unphysical and may be the cause of prohibitively small integration time steps or, in the vast majority of the cases, may prevent the convergence to a solution. Also, they may be the root cause of a wrong identification of the fast/slow subspaces in a CSP context, *i.e.* for analysis and/or model reduction purposes. As an example, it may happen that the fast subspace is confined to these extremely fast modes only, loosing the opportunity to take advantage of any sort of model reduction. Moreover, the noisy behavior in the positive half-plane of Fig. 1(a) can be attributed to the Jacobian ill-conditioning in presence of such large eigenvalues. With the help of the CSP participation indices, defined in Eq. (9), we are able to identify the reactions that contribute the most to the modes associated to the hyper-fast timescales, which are summarized in Table 2.

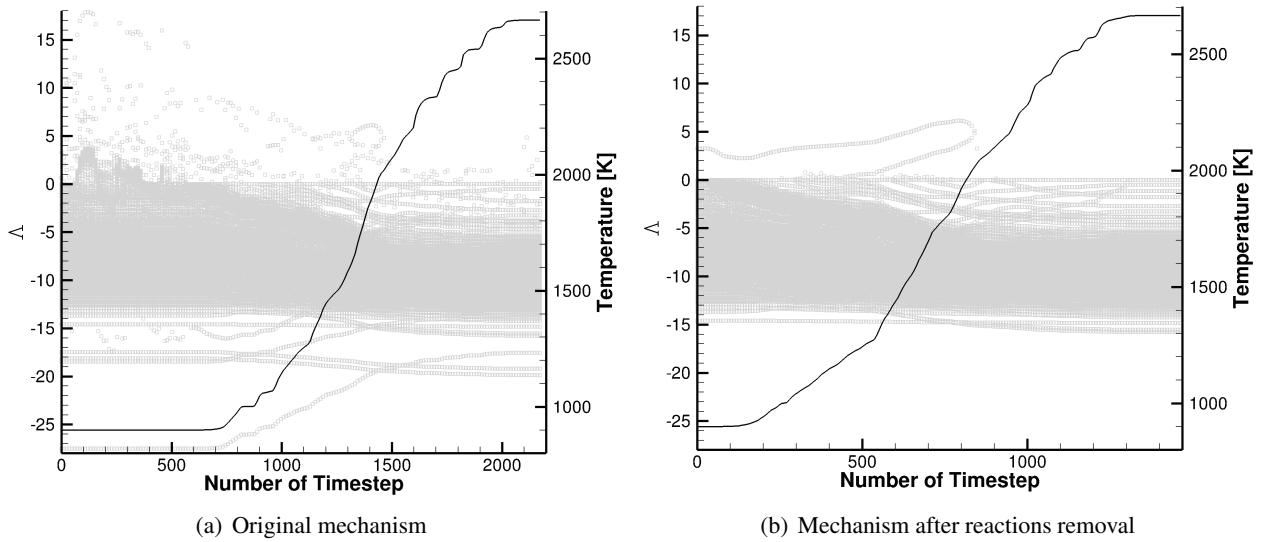


Figure 1: Eigenvalues (in Λ formulation) and temperature evolution against number of integration timestep

The same auto-ignition problem is solved again after the removal of the 7 reactions of Table 2 from the detailed mechanism. Figure 1(b) shows the resulting evolution of eigenvalues Λ_i and temperature against the number of integration timestep. The eigenvalues in modulus are always smaller than 10^{15} . This, in turn, allows the solver to take less timesteps to converge. Moreover, the eigenvalues evolution appears smoother, especially in the positive half-plane, where a couple of merging positive eigenvalues is clearly distinguishable among all the other -negative- eigenvalues, resembling a well-known behavior in auto-ignition problems [16].

The removal of the reactions does not appear to be pivotal in the replication of the physical behavior of the system: fig. 2 shows the temperature evolution in time obtained with the two mechanisms, highlighting a negligible difference in the ignition delay time.

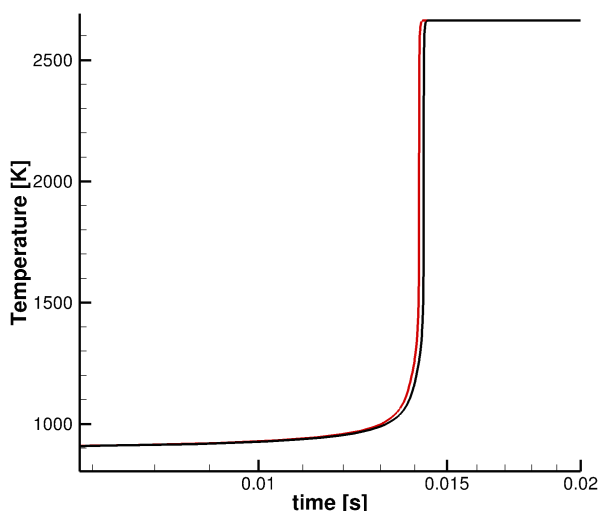


Figure 2: Temperature evolution in time with the original mechanism (red) and cleaned mechanism (black)

Table 2: Reactions mostly contributing to hyper-fast modes

$\text{CH}_2\text{O} + \text{HO}_2 \leftrightarrow \text{OCH}_2\text{O}_2\text{H}$
$\text{C}_5\text{H}_9\text{2-4} + \text{HO}_2 \leftrightarrow \text{C}_5\text{H}_9\text{O}_2\text{-4} + \text{OH}$
$\text{C}_5\text{H}_9\text{2-4} + \text{CH}_3\text{O}_2 \leftrightarrow \text{C}_5\text{H}_9\text{O}_2\text{-4} + \text{CH}_3\text{O}$
$\text{C}_5\text{H}_9\text{2-4} + \text{C}_2\text{H}_5\text{O}_2 \leftrightarrow \text{C}_5\text{H}_9\text{O}_2\text{-4} + \text{C}_2\text{H}_5\text{O}$
$\text{C}_5\text{H}_9\text{2-4} + \text{O}_2 \leftrightarrow \text{C}_5\text{H}_9\text{2O}_2\text{-4}$
$\text{C}_3\text{H}_6\text{OH-3OOH-1} + \text{O}_2 \leftrightarrow \text{C}_3\text{H}_6\text{OH-3OOH-1O}_2$
$\text{C}_3\text{H}_6\text{OH-1OOH-3} + \text{O}_2 \leftrightarrow \text{C}_3\text{H}_6\text{OH-1OOH-3O}_2$

The solver performance are also evidently affected by the stiffness removal: CVODE performed the second integration with less than 40% of the CPU time required for the original mechanism, employing 67% of the number of iterations.

It should be stressed that the key feature of the present strategy is the identification of the reactions which are responsible for the unphysical scales. The removal of these reactions is a brute-force solution to the problem. A wiser approach would be to revise the Arrhenius parameters associated to those reactions in order to get a well-behaving system, without losing the affected chemical pathways.

It is also important to highlight that a comprehensive analysis campaign on different initial conditions and/or other model problems is needed to inspect all the possible pathways that the detailed mechanism offers.

4. Conclusions

A CSP-based tool was presented to identify the reactions mostly contributing to unphysically large eigenvalues that may appear when using very large and complex detailed mechanisms. A test case was presented in which a 2484-species mechanism was employed in a constant pressure, homogeneous reactor,

auto-ignition problem. The systems eigenvalues appeared to be as large as 10^{27} during the ignition, causing stiffness in the time integration due to the very fast timescales, and possibly a wrong identification of the fast/slow subspaces in the CSP context, *i.e.* for the generation of skeletal mechanisms. The CSP importance index was able to identify the 7 reactions that were contributing to the extremely large eigenvalues. The removal of those reactions proved that they were actually causing the presence of such eigenvalues. Future development will be towards the updating of the Arrhenius parameters associated to the reactions triggering unphysical timescales.

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