Hydrogen/Air Auto-ignition: Algorithmic Identification of QSSA and PEA

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***Abstract*— Algorithmic criteria for the applicability of the Quasi Steady State and Partial Equilibrium approximations are presented and verified in the context of the hydrogen/air auto-ignition.**

I. Introduction

The classical approach in model reduction involves the introduction of the *Quasi Steady State* (QSSA) and the *Partial Equilibrium* (PEA) approximations. Although both approximations have been devised and used for quite a long time, it was only until very recently when their applicability and connection was thorough investigated in [1] in the context of the *CSP method* [2]. Here, the criteria established in [1] for the applicability of QSSA and PEA are presented in a new form and are validated in the case of the Hydrogen/Air autoignition.

II. Statement of the Problem

The evolution of a homogeneous ideal gas mixture where K reversible reactions occur simultaneously among N reacting chemical species obeys the $(N+1)$-dim. system of autonomous ODEs:

$$\frac{d}{dt}\begin{bmatrix}\mathbf{y}\\ T\end{bmatrix}=\begin{bmatrix}\mathbf{S}\\ \mathbf{Q}(\mathbf{y},T)\end{bmatrix}\mathbf{R}(\mathbf{y},T)\equiv\mathbf{g}(\mathbf{y},T) \qquad (1)$$

where $\mathbf{y},\mathbf{g}\in\mathbb{R}^N$ and $\mathbf{y}$ contains the variables relating to the N species (e.g., mass fractions), T is the temperature, $\mathbf{R}\in\mathbb{R}^K$ contains the reaction rates, $\mathbf{S}\in\mathbb{R}^{N\times K}$ is the constant stoichiometric matrix and $\mathbf{Q}\in\mathbb{R}^{1\times K}$ is a row vector depending on the thermodynamic properties of the mixture. We assume that a $(N+1-M)$-dim. *normally hyperbolic slow invariant manifold* $\Omega\subset\mathbb{R}^{N+1}$ develops in phase space as the result of the exhaustion of M fast dissipative time scales τ_i, $(i=1,\ldots,M)$.

Casting (1) in CSP form yields:

$$\frac{d}{dt}\begin{bmatrix}\mathbf{y}\\ T\end{bmatrix}=\mathbf{a}_r(\mathbf{y},T)\mathbf{f}^r(\mathbf{y},T)+\mathbf{a}_s(\mathbf{y},T)\mathbf{f}^s(\mathbf{y},T) \qquad (2)$$

where the M basis vectors in $\mathbf{a}_r$ and the $(N+1-M)$ basis vectors in $\mathbf{a}_s$ span the fast and slow subspaces of the tangent space at the point $\mathbf{y}\in\Omega$ and $\mathbf{f}^r,\mathbf{f}^s$ are the corresponding fast and slow amplitudes in these subspaces. Moreover, Eq. (1) simplifies to the differential-algebraic system:

$$\mathbf{f}^r(\mathbf{y},T)\approx 0 \qquad \frac{d}{dt}\begin{bmatrix}\mathbf{y}\\ T\end{bmatrix}\approx\mathbf{a}_s(\mathbf{y},T)\mathbf{f}^s(\mathbf{y},T) \qquad (3)$$

where the symbol "$\approx$" is indicative of the accuracy by which the fast and slow subspaces are spanned by the basis vectors in $\mathbf{a}_r$ and $\mathbf{a}_s$. Starting from an initial guess, $\mathbf{a}_r^0$ and $\mathbf{a}_s^0$, CSP provides refined fast and slow basis vectors that produce stable (i.e., non stiff) and of increasing accuracy reduced models.

III. Criteria for valid QSSA and PEA

In order to produce a reduced model for Eq. (1) on the basis of QSSA or PEA, M fast variables, say $\mathbf{y}^r$, and M fast reactions, say $\mathbf{R}^r$, must be selected. Under such a choice it was shown in [1] that QSSA and PEA produce specific approximations of the fast and slow subspaces of Ω and that QSSA is a limiting case of PEA. This formulation enables for comparison with the CSP basis vectors and the introduction of the following criteria for the applicability of QSSA and PEA:

A. Stability

The criterion that guarantees stability of the reduced model constructed with QSSA or PEA can be expressed as:

$$\left[\mathbf{D}_{\mathbf{n}_r}(\tilde{\mathbf{f}}^s)\right]\left[\mathbf{D}_{\mathbf{n}_r}(\mathbf{g}^r)\right]^{-1}=\mathcal{O}(\epsilon) \qquad (4)$$

where, ε denotes the fast/slow time scale gap, $\mathbf{D}_{\mathbf{n}_r}[\bullet]$ denotes the directional derivate along the axis of the fast variables, $\tilde{\mathbf{f}}^s$ are the slow amplitudes of the QSSA/PEA reduced model and $\mathbf{g}^r$ is the part of the vector field $\mathbf{g}$ that corresponds to $\mathbf{y}^r$.

B. Accuracy

The criterion that guarantees leading-order accuracy of the reduced model constructed by the PEA can be expressed as:

$$\left[\mathbf{D}_{\mathbf{n}_r}(\mathbf{g}^r)\right]^{-1}\left[\mathbf{D}_{\tilde{\mathbf{a}}_s}(\mathbf{g}^r)\right]=\mathcal{O}(\epsilon) \qquad (5)$$

where $\mathbf{D}_{\tilde{\mathbf{a}}_s}[\bullet]$ denotes the directional derivate along the PEA slow basis vectors $\tilde{\mathbf{a}}_s=\left[-\mathbf{V}_s^r,\ \mathbf{I}_s^s\right]^T$, where $\mathbf{V}_s^r=$

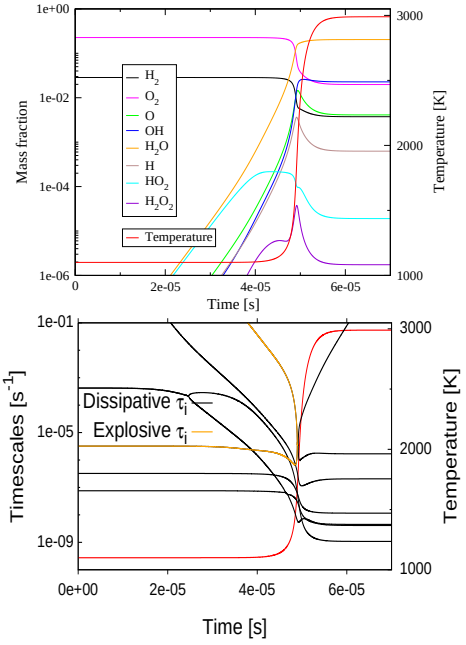

Fig. 1. Top: the evolution of the species mass fractions and of the temperature. Bottom: the evolution of the time scales.

$\left(\frac{\partial \mathbf{R}^r}{\partial \mathbf{y}^r}\right)^{-1}\left(\frac{\partial \mathbf{R}^r}{\partial \mathbf{y}^s}\right)$, $\mathbf{I}_s^s$ is the $(N+1-M)\times(N+1-M)$-dim. identity matrix and $\mathbf{y}^s$ represents the $N+1-M$ variables in $\mathbf{y}$ that do not belong in $\mathbf{y}^r$ [1]. Moreover, if:

$$\mathbf{V}_s^r = \mathcal{O}(\epsilon) \tag{6}$$

the PEA reduces to the QSSA, so that the QSSA provides leading-order accuracy as well.

IV. Hydrogen-Air auto-ignition

To examine the validity of the above criteria, the auto-ignition of a homogeneous hydrogen-air mixture under constant volume is considered [3]. The chemical kinetic mechanism consists of 21 reversible reactions among 8 reacting and one inert (nitrogen) species [4]. Considering a stoichiometric mixture ($\phi = 1$) with initial temperature $T_0 = 1100\,K$ and pressure $P_0 = 2.0\,bar$, Fig. 1 displays the corresponding evolution of the species mass fraction, temperature and time scales.

Before the ignition of the mixture, the two fastest time scales are dissipative followed by an explosive one. The time scale gap between the fast dissipative time scales and the explosive one is $\epsilon = \mathcal{O}(0.10)$. CSP analysis identifies OH and O as the fast variables for the two fast CSP modes and $H_2 + OH \leftrightarrow H_2O + H$ and $H_2 + O \leftrightarrow OH + H$ as the two fast reactions, respectively. This information is sufficient for calculating the quantities in Eqs. (4), (5) and (6) presented in Fig. 2. It is demonstrated that Eqs. (4) and (6) hold but Eq. (5) fails. This implies that the QSSA/PEA reduced models will not provide leading-order accuracy, which is verified by the computed relative errors shown in Fig. 3. Note, that both reduced models produce the same relative errors due to the negligible value of $\mathbf{V}_s^r$.

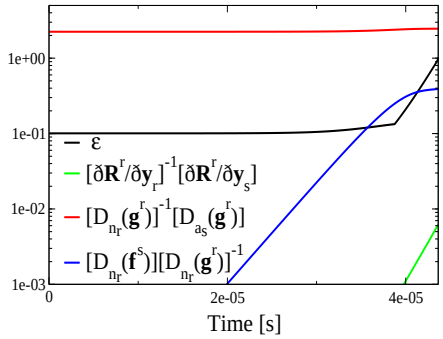

Fig. 2. The evolution of the quantities in Eqs. (4), (5) and (6).

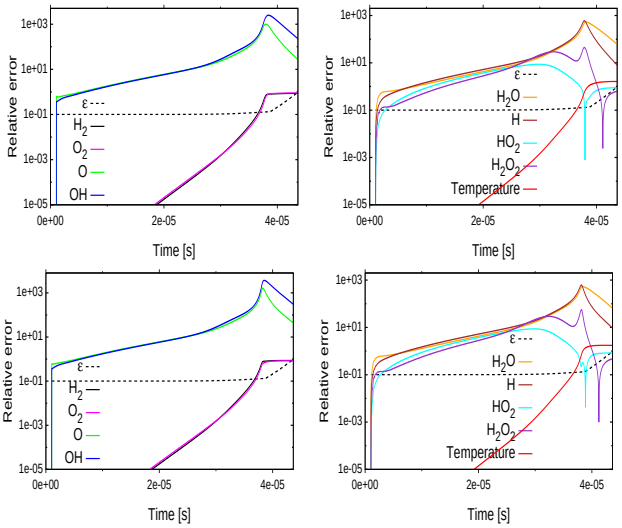

Fig. 3. The relative errors for the reduced models constructed by the PEA (top row) or QSSA (bottom row) approximation.

At the Workshop a detailed analysis and validation of the criteria for the validity of QSSA/PEA will be presented.

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