

# ASVDADD algorithm for automatic selection of RCCE constraints

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**Abstract**—The Rate-Controlled Constrained-Equilibrium (RCCE) model reduction scheme for chemical kinetics provides acceptable accuracies with a number of differential equations much lower than the number of species in the underlying Detailed Kinetic Model (DKM). It was originally proposed by James C. Keck (see [1-3] and references therein). To yield good approximations the method requires accurate identification of the rate controlling constraints. Until recently, a drawback of the RCCE scheme has been the absence of a fully automatable and systematic procedure to identify the most effective constraints for a given range of thermodynamic conditions and a required level of approximation. In a recent paper [4], we have proposed a new methodology for such identification based on a simple algebraic analysis of the results of a preliminary simulation of the full underlying DKM, focusing on the behavior of the degrees of disequilibrium (DoD) of the individual chemical reactions. The new methodology is based on computing an Approximate Singular Value Decomposition of the Actual Degrees of Disequilibrium (ASVDADD) obtained as functions of time in the probe DKM simulation. The procedure identifies a low dimensional subspace in DoD space, from which the actual DoD traces do not depart beyond a fixed distance related to the first neglected singular value of the matrix of DoD traces. The effectiveness and robustness of the method has been demonstrated [4-6] for various cases of a very rapid supersonic nozzle expansion of the products of hydrogen and methane oxycombustion and for the case of methane/oxygen ignition.

The RCCE method models the local non-equilibrium states as partially equilibrated states with the local composition  $\mathbf{X}^{\text{CE}} = N_j / \sum_{k=1}^{n_{\text{sp}}} N_k$  that minimizes the Gibbs free energy subject to: (1) the local values of temperature  $T$ , pressure  $p$ , molar amounts of elements  $N_i^{\text{EL}} = \sum_{j=1}^{n_{\text{sp}}} a_{ij}^{\text{EL}} N_j$  (where  $a_{ij}^{\text{EL}}$  represents the number of atoms of element  $i$  in a molecule of species  $j$ ) and (2) the local values of a set of  $n_c$  slowly varying and, hence, rate-controlling (RC) constraints given by linear combinations of the molar amounts,  $c_i(\mathbf{N}) = \sum_{j=1}^{n_{\text{sp}}} a_{ij}^{\text{RC}} N_j$ , where the matrix  $a_{ij}^{\text{RC}}$  is the heart of the model in that it is assumed to fully characterize the rate-controlling bottlenecks of the kinetic mechanism. For ideal gas behavior,  $\mu_j(T, p, \mathbf{X}) = g_{j,\text{pure}}(T, p) + RT \ln X_j$ , the constrained maximization yields the composition  $\ln X_j^{\text{CE}} = -g_{j,\text{pure}}(T, p)/RT - \sum_{i=1}^{n_{\text{el}}} \gamma_i^{\text{EL}} a_{ij}^{\text{EL}} - \sum_{i=1}^{n_c} \gamma_i^{\text{RC}} a_{ij}^{\text{RC}}$ . The Lagrange multipliers  $\gamma_i^{\text{EL}}$  and  $\gamma_i^{\text{RC}}$  are called elemental and constraint potentials, respectively. For the  $\ell$ -th chemical reaction  $\sum_{j=1}^{n_{\text{sp}}} \nu_{j\ell} A_j = 0$ , the stoichiometric balance requires that  $b_{i\ell}^{\text{EL}} = \sum_{j=1}^{n_{\text{sp}}} a_{ij}^{\text{EL}} \nu_{j\ell} =$

0. An advantage of the RCCE approximation is that the composition depends only on the  $n_{\text{el}} + n_c$  parameters  $\gamma_i^{\text{EL}}$  and  $\gamma_i^{\text{RC}}$ , instead of the  $n_{\text{sp}}$  molar amounts of species which can be many more. In the CFD modeling context, this means that in addition to the continuity, Navier-Stokes, and energy balance equations, the  $n_{\text{sp}}$  species balance equations can be effectively substituted by the  $n_{\text{el}} + n_c$  balance equations for the elemental and constraint potentials, thus achieving a substantial model reduction that has a built-in strong thermodynamic consistency and does not require to cut the number of species nor the number of reactions to be taken into account.

The recently proposed ASVDADD algorithm [4] allows the identification of optimal sets of constraints with no need for deep knowledge and understanding of chemical kinetics fundamentals such as chain branching, radical formation, etc., thus making the RCCE method accessible to a broad range of scientists and engineers. The algorithm is based on the following basic observation. The degree of disequilibrium (DoD) of reaction  $\ell$ , defined by  $\phi_\ell = \ln r_\ell^+ / r_\ell^-$  where  $r_\ell^\pm$  are the forward and reverse rates of reaction  $\ell$ , is given in general by  $\phi_\ell = \ln(r_\ell^+ / r_\ell^-) = \sum_{j=1}^{n_{\text{sp}}} \Lambda_j \nu_{j\ell}$  where  $\Lambda_j = -\mu_j / RT$  are the dimensionless entropic chemical potentials that can be viewed as the components of the  $n_{\text{sp}}$ -vector  $\mathbf{\Lambda}$ . Also the  $n_{\text{el}}$  rows of the elemental composition matrix  $a_{ij}^{\text{EL}}$  can be viewed as the components of the  $n_{\text{sp}}$ -vectors  $\mathbf{a}_i^{\text{EL}}$ . Due to relation  $\sum_{j=1}^{n_{\text{sp}}} a_{ij}^{\text{EL}} \nu_{j\ell} = 0$ , the  $n_{\text{el}}$ -dimensional linear span of vectors  $\mathbf{a}_i^{\text{EL}}$  is the left null space of the matrix  $\nu_{j\ell}$  of stoichiometric coefficients, often called the inert subspace.

The projection of vector  $\mathbf{\Lambda}$  onto the inert subspace can be written as  $\mathbf{\Lambda}_{\text{span}(\{\mathbf{a}_i^{\text{EL}}\})} = \sum_{i=1}^{n_{\text{el}}} \gamma_i^{\text{EL}} \mathbf{a}_i^{\text{EL}}$  where the coefficients  $\gamma_i^{\text{EL}}$  can be readily computed (see, e.g., the appendix of Ref. [7]). Since  $\mathbf{\Lambda}_{\text{span}(\{\mathbf{a}_i^{\text{EL}}\})}$  does not contribute to the DoD of any reaction (in fact,  $\sum_{j=1}^{n_{\text{sp}}} \sum_{i=1}^{n_{\text{el}}} \gamma_i^{\text{EL}} a_{ij}^{\text{EL}} \nu_{j\ell} = \sum_{i=1}^{n_{\text{el}}} \gamma_i^{\text{EL}} b_{i\ell}^{\text{EL}} = 0$ ), we call the vector  $\mathbf{\Lambda}_{\text{DoD}} = \mathbf{\Lambda} - \mathbf{\Lambda}_{\text{span}(\{\mathbf{a}_i^{\text{EL}}\})} = \mathbf{\Lambda} - \sum_{i=1}^{n_{\text{el}}} \gamma_i^{\text{EL}} \mathbf{a}_i^{\text{EL}}$  or, equivalently,  $\Lambda_{\text{DoD},j} = \Lambda_j - \sum_{i=1}^{n_{\text{el}}} \gamma_i^{\text{EL}} a_{ij}^{\text{EL}}$  the ‘‘overall DoD vector.’’ In fact, it contains the information about the DoD’s  $\phi_\ell$  of all the reactions,  $\phi_\ell = \sum_{j=1}^{n_{\text{sp}}} \Lambda_{\text{DoD},j} \nu_{j\ell}$ , and it is the null vector if and only if all reactions are equilibrated, in the sense that their DoD’s are all zero. Notice that within

the RCCE model  $\Lambda_{\text{DoD}}^{\text{RCCE}} = \sum_{i=1}^{n_c} \gamma_i^{\text{RC}} \mathbf{a}_i^{\text{RC}}$  or, equivalently,  $\Lambda_{\text{DoD},j}^{\text{RCCE}} = \sum_{i=1}^{n_c} \gamma_i^{\text{RC}} a_{ij}^{\text{RC}}$ .

Now let us consider a CFD numerical simulation in which the index  $z = 1, \dots, Z$  labels the space-time discretization (i.e.,  $z$  labels both the finite volumes or elements of the mesh as well as the time grid). If we adopt the full DKM and solve the full set of balance equations including those for all the species, the resulting overall DoD vectors form an  $n_{\text{sp}} \times Z$  matrix  $\Lambda_{\text{DoD},j}^{\text{DKM}} = \Lambda_{\text{DoD},j}(z)$  that has rank  $r = n_{\text{sp}} - n_{\text{el}}$ . If instead the local states are described according to the RCCE assumption defined above, the  $n_{\text{sp}} \times Z$  matrix  $\Lambda_{\text{DoD},j,z}^{\text{RCCE}} = \Lambda_{\text{DoD},j}^{\text{RCCE}}(z) = \sum_{i=1}^{n_c} \gamma_i^{\text{RC}}(z) a_{ij}^{\text{RC}}$  has rank equal to the (typically much smaller) number  $n_c$  of constraints.

In order to identify the constraint matrix  $a_{ij}^{\text{RC}}$  that allows such approximation, the idea behind the ASVDADD algorithm is to probe the DKM by running a preliminary full DKM computation, possibly on a submesh of the full problem and for a shorter time so as to span a limited range of temperatures, pressures and compositions. The goal of such computation is to obtain the  $r \times Z$  matrix  $\mathbf{D}$  with elements  $\Lambda_{\text{DoD},j,z}^{\text{DKM}}$ . Then we compute its singular value decomposition (SVD). As is well known the result can be written formally in reduced form as  $\mathbf{D} = \mathbf{U} \text{diag}(\boldsymbol{\sigma}) \mathbf{V}$  where  $\mathbf{U}$  is an  $n_{\text{sp}} \times r$  unitary matrix whose  $r$  columns represent an orthonormal basis for the column space of  $\mathbf{D}$ ,  $\mathbf{V}$  is an  $r \times Z$  unitary matrix whose  $r$  rows represent an orthonormal basis for the row space of  $\mathbf{D}$ , and  $\boldsymbol{\sigma}$  is the  $r$ -vector of singular values of  $\mathbf{D}$  in decreasing order. Explicitly, the (reduced form) SVD decomposition of the overall DoD matrix can be written as  $\Lambda_{\text{DoD},j,z}^{\text{DKM}} = \sum_{k=1}^r U_{jk} \sigma_k V_{kz} = \sum_{k=1}^r U_{jk} \gamma_{kz}^{\text{DKM}}$ , where  $\sigma_1 \geq \sigma_2 \geq \dots \geq \sigma_r > 0$  and we defined  $\gamma_{kz}^{\text{DKM}} = \sigma_k V_{kz}$ .

Next, we use the well-known Eckart-Young theorem of linear algebra, whereby if in the SVD of matrix  $\mathbf{D}$  we set to zero the singular values for  $k > n_c$  (i.e., we set  $\sigma_{n_c+1} = \sigma_{n_c+2} = \dots = \sigma_r = 0$ ) then we obtain the ‘‘closest’’ rank  $\leq n_c$  approximation  $\mathbf{D}_{\text{approx}}$  of the original matrix  $\mathbf{D}$  in the sense that the Frobenius norm distance  $\|\mathbf{D}_{\text{approx}} - \mathbf{D}\|_{\text{Fro}}$  between the two matrices is minimal. Such norm distance is equal to  $(\sum_{k=n_c+1}^r \sigma_k^2)^{1/2}$  and can be taken as a measure of the error introduced by the approximation. Therefore, if we accept such level of approximation, we can setup an optimal RCCE model with  $n_c$  constraints by selecting as our constraint matrix the first  $n_c$  columns of the matrix  $\mathbf{U}$ . In fact, by setting (ASVDADD choice of RCCE constraints):  $a_{ij}^{\text{RC}} = U_{ji}$  for  $i = 1, \dots, n_c$  we obtain  $\Lambda_{\text{DoD},j,z}^{\text{RCCE}} = \sum_{k=1}^{n_c} U_{jk} \gamma_{kz}^{\text{RC}} = \sum_{i=1}^{n_c} \gamma_i^{\text{RC}} a_{ij}^{\text{RC}}$ . Interestingly, the  $r$  columns of the matrix  $\mathbf{U}$  provide at once the entire set of optimal RCCE constraints, already ordered in decreasing order of importance. Essentially, in conclusion, the ASVDADD algorithm identifies all the constraints that characterize the kinetic bottlenecks of the underlying DKM in effect in the range of conditions of the chosen probe simulation, and it ranks them in decreasing order of their relative contribution to the overall degree of

disequilibrium. These features make the algorithm suitable for adaptive or tabulation strategies and therefore opens up the advantages of the RCCE method to CFD simulation.

The effectiveness and robustness of the methodology has already been demonstrated in [4-5] for several test cases of increasing complexity in the framework of oxy-combustion of hydrogen (8 species, 24 reactions) and methane (29 species, 133 reactions) as well as in [6] where a demonstration is given for the even more complex full GRI-Mech 3.0 kinetic scheme (53 species, 325 reactions) for methane/air combustion including nitrogen oxidation.

The excellent performance of the ASVDADD constraints confirms the conclusion that the new algorithm essentially resolves the difficulties that have prevented the RCCE method from a more widespread use in model order reduction of detailed combustion kinetic models of hydrocarbon fuels, making it accessible to the non-experts in chemical kinetics.

The RCCE model can be integrated most efficiently by rewriting the balance equations as rate equations for the elemental and constraint potentials (see Eqs. 136-139 of Ref. 3) to obtain  $n_{\text{el}} + n_{\text{nc}} + 2$  implicit differential equations which together with the  $n_{\text{sp}}$  RCCE expressions for the mole fractions can be solved for the  $n_{\text{sp}} + 2$  state variables  $T(t)$ ,  $p(t)$ , and  $N_j(t)$ , and the  $n_{\text{el}} + n_c$  constraint potentials  $\gamma_i^{\text{EL}}(t)$  and  $\gamma_i^{\text{RC}}(t)$ .

## REFERENCES

- [1] J.C. Keck, ‘‘Rate-controlled constrained equilibrium method for treating reactions in complex systems,’’ in: R.D. Levine, M. Tribus (Eds.), *The Maximum Entropy Formalism*, MIT Press, Cambridge, MA, 1979, pp. 219-245.<sup>1</sup>
- [2] G.P. Beretta and J.C. Keck, ‘‘The constrained-equilibrium approach to nonequilibrium dynamics,’’ in: R.A. Gaggioli (Ed.), *Second Law Analysis and Modeling*, ASME Book H0341C-AES, vol.3, ASME, New York, 1986, pp. 135-139.<sup>1,2</sup>
- [3] G.P. Beretta, J.C. Keck, M. Janbozorgi, and H. Metghalchi, ‘‘The rate-controlled constrained-equilibrium approach to far-from-local-equilibrium thermodynamics,’’ *Entropy*, vol. 14, 92-130 (2012).
- [4] G.P. Beretta, M. Janbozorgi, and H. Metghalchi, ‘‘Degree of Disequilibrium Analysis for Automatic Selection of Kinetic Constraints in the Rate-Controlled Constrained-Equilibrium Method,’’ *Combustion and Flame*, vol. 168, 342-364 (2016).
- [5] G.P. Beretta, M. Janbozorgi, and H. Metghalchi, ‘‘Use of Degree of Disequilibrium Analysis to Select Kinetic Constraints for the Rate-Controlled Constrained-Equilibrium (RCCE) Method,’’ *Proceedings of ECOS 2015 – the 28th International Conference On Efficiency, Cost, Optimization, Simulation and Environmental Impact of Energy Systems*, Pau, France, June 30-July 3, 2015.<sup>2</sup>
- [6] L. Rivadossi and G.P. Beretta, ‘‘Validation of the ASVDADD constraint selection algorithm for effective RCCE modeling of natural gas ignition in air,’’ *Proceedings of IMECE2016 – the ASME 2016 International Mechanical Engineering Congress and Exposition*, November 11-17, 2016, Phoenix, Arizona, USA – paper IMECE2016-65323.<sup>2</sup>
- [7] G.P. Beretta, ‘‘Nonlinear Quantum Evolution Equations to Model Irreversible Adiabatic Relaxation With Maximal Entropy Production and Other Nonunitary Processes,’’ *Reports on Mathematical Physics*, vol. 64, 139-168 (2009).

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