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Comparison of Invariant Manifolds for Model Reduction in Chemical Kinetics

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Abstract. A modern approach to model reduction in chemical kinetics is often based on the notion of slow invariant manifold. The goal of this paper is to give a comparison of various methods of construction of slow invariant manifolds using a simple Michaelis-Menten catalytic reaction. We explore a recently introduced Method of Invariant Grids (MIG) for iteratively solving the invariance equation. Various initial approximations for the grid are considered such as Quasi Equilibrium Manifold, Spectral Quasi Equilibrium Manifold, Intrinsic Low Dimensional Manifold and Symmetric Entropic Intrinsic Low Dimensional Manifold. Slow invariant manifold was also computed using the Computational Singular Perturbation (CSP) method. A comparison between MIG and CSP is also reported.

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1 Introduction

The idea that dissipative systems of chemical kinetics can have a simplified description in terms of fast and slow motions derives from some evidences found out when such systems are integrated numerically. Indeed, a typical behavior of trajectories in the phase space during the relaxation reveals that they quickly move toward a lower dimension manifold and then, when it is reached, do not leave it anymore, proceeding slowly along it toward the equilibrium. Now it is straightforward to understand why, if such a manifold exists, it can be termed the Slow Invariant Manifold (SIM), and that it provides a simplification to the original system. Several methods were proposed to find the SIM:

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Method of Invariant Manifolds (MIM), Method of Invariant Grids (MIG), Computational Singular Perturbation (CSP), as well as constructive approximations to SIM such as the Intrinsic Low Dimensional Manifold (ILDM). In this paper, we want to compare various methods aimed at constructing the SIM for a simple yet non-trivial test-case. In particular, we deal with three essentially different iterative algorithms:

1. *MIG-approach* (based on the Newton method) [2,3,5],
2. *MIG-approach* (based on the relaxation method) [2,3,5],
3. *CSP-approach* [11,12].

Every iterative procedure needs an initial approximation from which it starts a refinement. In general, the quality of this initial step is important for both the convergence toward the solution and for the method efficiency; that is why different initial approximations are considered, too. For our test-case, the following approximations were used:

1. *Quasi-Equilibrium-Manifold* (QEM) [2,3],
2. *Spectral-Quasi-Equilibrium-Manifold* (SQEM),
3. *Intrinsic-Low-Dimensional-Manifold* (ILDM) [8,9],
4. *Symmetric-Entropic-Intrinsic-Low-Dimensional-Manifold* (SEILDM) [2,3].

The paper is organized as follows. In Section 2, for the sake of completeness, we outline the basic notions: invariant manifold, slow manifold and invariant grid, equations of chemical kinetics and the methods of model reduction. In particular, in Section 2.2, the general equations of dissipative reaction kinetics are reviewed and cast in a form which is used throughout the paper. The *Method of Invariant Grid* (MIG) and *thermodynamic projector* concepts are discussed, providing a way to implement the MIG iteratively according to both the *Newton method with incomplete linearization* and the *relaxation method* (Section 2.1, for a general setting, and Section 2.3 for chemical kinetics). Here we also describe the *CSP method* (Section 2.4) and some possible initial approximations of SIM (Section 2.5). In Section 3, we consider a two-step four-component catalytic reaction (Michaelis-Menten mechanism) as a test case. Various initial approximations for that case are found (Sections 3.1, 3.2, 3.3). Starting from these initial approximations, MIG iterations are carried out and compared on the base of both Hausdorff norm and a measure of the invariance defect (Sections 3.4, 3.5). In Section 3.6, the CSP method is used to construct the SIM in this example, and a comparison with MIG is presented. Finally, results are discussed in Section 4.

2 Theoretical background

2.1 Slow invariant manifold (SIM)

In this section, we introduce the notions of (positively) invariant manifold, slow invariant manifold, invariant grid, and slow invariant grid, for a general system of autonomous