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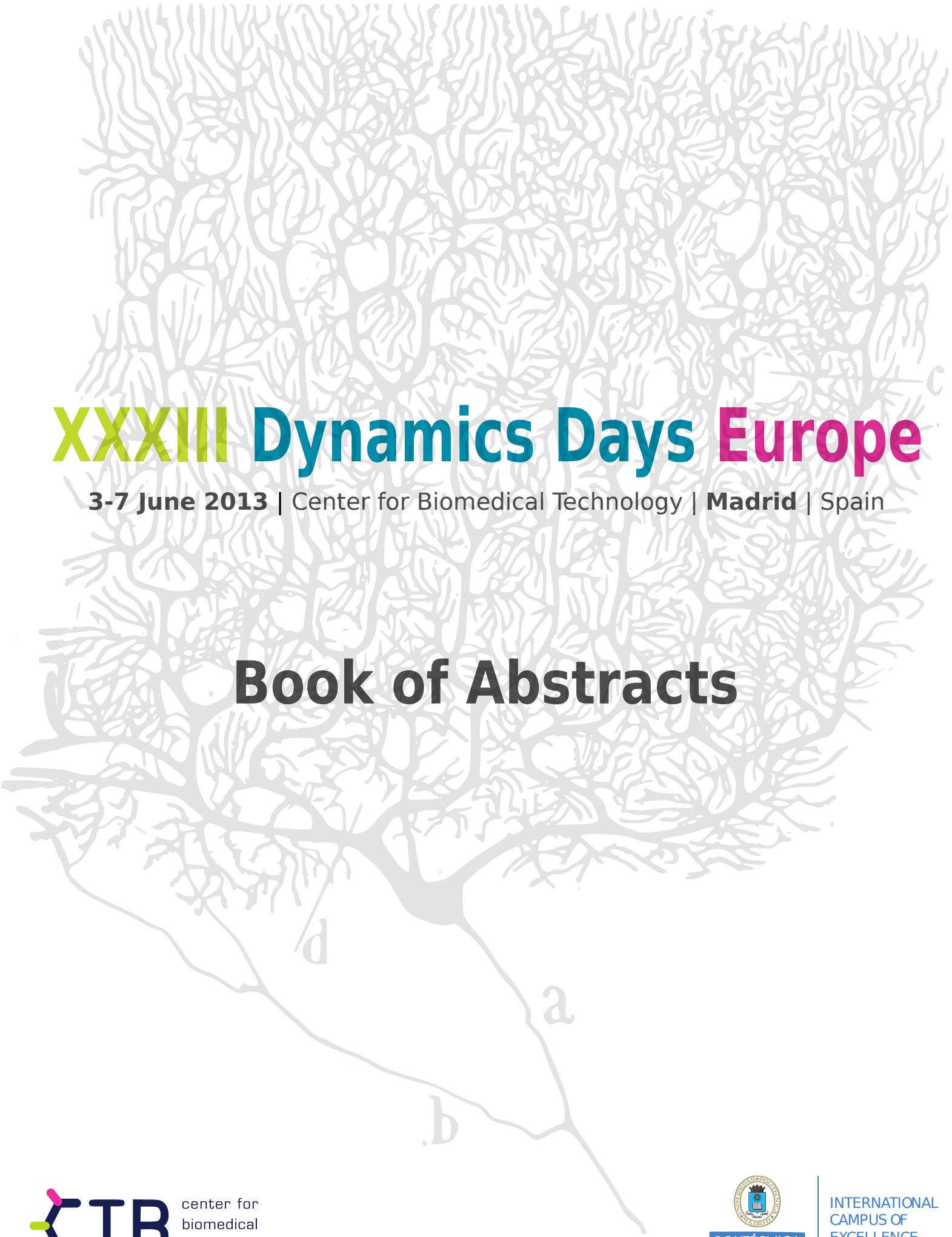
Book of Abstracts



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P57 Reaction rate calculation for dissipative systems using invariant manifolds

Fabio Revuelta[1], *Thomas Bartsch*[2], *Rosa María Benito*[3] *and Florentino Borondo*[4]

[1]Universidad Politécnica de Madrid, Madrid, Spain; fabio.revuelta@upm.es
[2]Loughborough University, Loughborough-Leicestershire, United Kingdom;
T.Bartsch@lboro.ac.uk
[3]Universidad Politécnica de Madrid, Madrid, Spain; rosamaria.benito@upm.es
[4]Universidad Autónoma de Madrid, Madrid, Spain; f.borondo@uam.es

Transition state theory (TST) plays a central role in the study of chemical reactivity since it answers two fundamental questions: the identification of reactive trajectories and the computation of reaction rates [1, 2, 3]. TST is based on the existence of two different states (reactants and products) separated by an energetic barrier, the top of which forms a bottleneck for reactivity; the reaction takes place only if this barrier is crossed. The reaction rate can be computed by simply placing a recrossing-free dividing surface close to this barrier. Nevertheless, the dividing surface usually has recrossings, so the reaction rate is usually overestimated.
In the last years, the application of nonlinear dynamics techniques to study TST has provided a new insight into reactivity, by making a more geometrical description of the phase space. This has allowed the identification of strictly recrossing-free dividing surface in systems with many degrees of freedom [4, 5] as well as in harmonic systems that interact with their environment [6].
In this communication, we report on a new method that allows the identification of reactive trajectories exactly in anharmonic systems that interact with their environments without the need of any computationally costly numerical simulation [7, 8]. The method is based on the existence of geometrical structures (invariant manifolds) that act as separatrices of phase space. Further, we have succeeded in computing exact reaction rates; this has allowed us to calculate analytic corrections to the famous Kramer's formula due to the nonlinearities of the system.

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