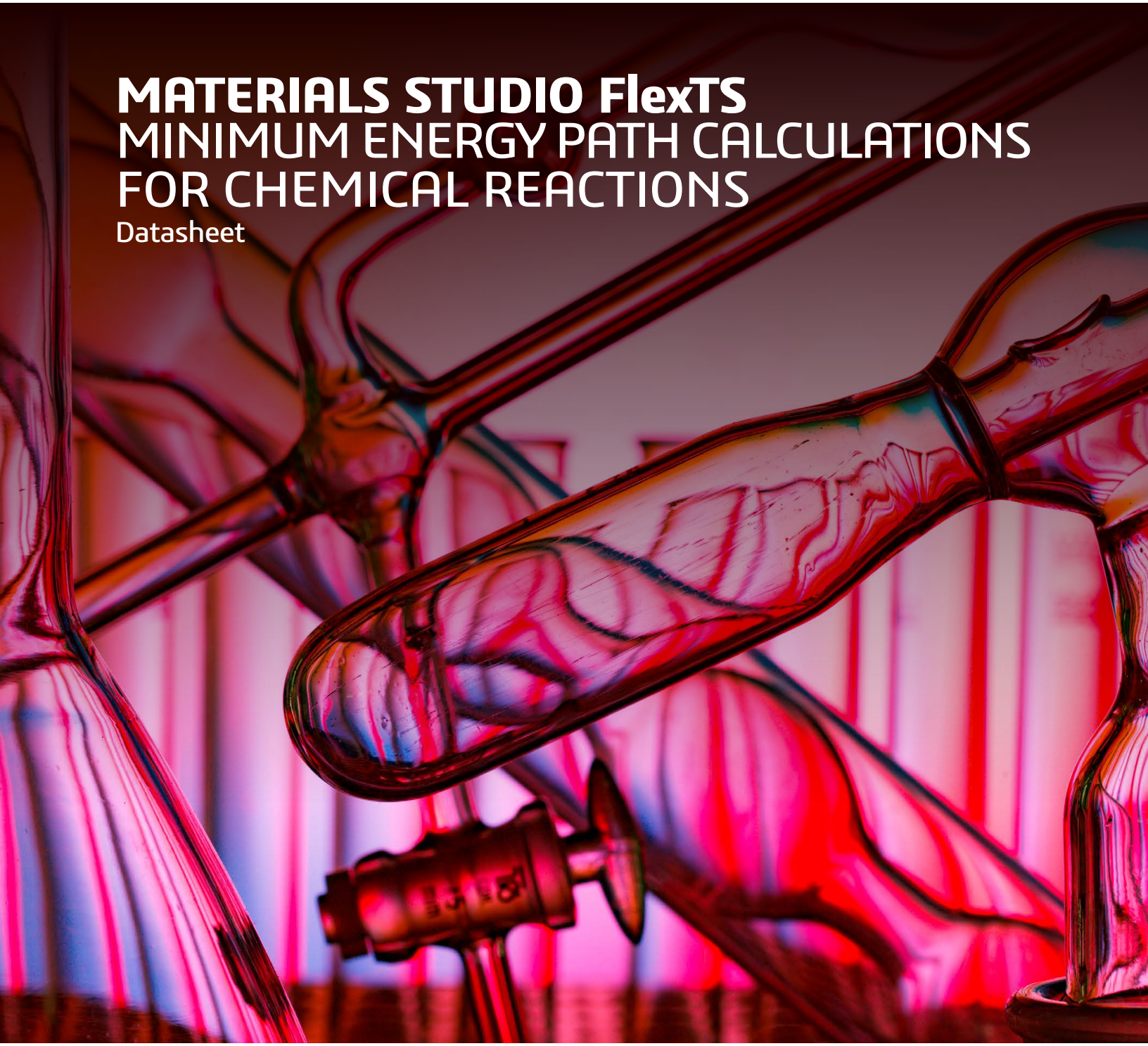
BIOVIA

3DEXPERIENCE®

MATERIALS STUDIO FlexTS
MINIMUM ENERGY PATH CALCULATIONS FOR CHEMICAL REACTIONS

Datasheet



DASSAULT SYSTEMES

OVERVIEW

Transition state theory (TST) is a rather successful approach in theoretical chemistry that underpins studies of chemical reaction kinetics, the quantitative measurement of rates of reactions. This provide insights into reaction mechanisms that allow chemical engineers to design efficient chemical manufacturing processes and to understand chemical mechanisms, such as combustion or material degradation.

The fundamental assumption of TST is the existence of a hypersurface (transition state) in the energy landscape that divides reactants and products (Figure 1). Given the complex interplay between the configurational and electronic contributions composing this energy landscape, the identification of the transition state can be challenging.

BIOVIA Materials Studio FlexTS solves these problems by providing a very efficient route to identify the transition states and their corresponding local minima.

BIOVIA Materials Studio FlexTS provides efficient and robust identification of transition states and local minima on the minimum energy path between reactants and products in chemical reactions.

WHAT IS FlexTS

BIOVIA Materials Studio FlexTS is a general purpose and highly automated implementation for simulating chemical reactions between molecules and between species at surfaces. FlexTS is based on a suite of codes (OPTIM) developed over many years at the University of Cambridge [1-5], and comprises a set of interconnected methods for exploring energy landscapes.

The searching algorithms are agnostic to the source of the potential energy surface. Consequently BIOVIA Materials Studio FlexTS is implemented through a task - Minimum Energy Path - in both DMol^3 and DFTB+. It leverages features of BIOVIA Materials Studio Visualizer to manage the configuration of reactant and product configurations (for which Reaction Preview functionality is used), and jobs are executed using the client-server gateway. The Minimum Energy Path task allows you to compute and extract the relevant energy barriers and reaction pathways graphically or from a single study table document.

Information provided by reaction kinetics measurements can help scientists to propose reaction mechanisms, confirming or contradicting already postulated reaction mechanisms and supporting mathematical modeling of reactions. BIOVIA Materials Studio FlexTS can efficiently identify minimum energy pathways, transition states of both single and multi-step reactions. It automates the use of a hierarchy of methods

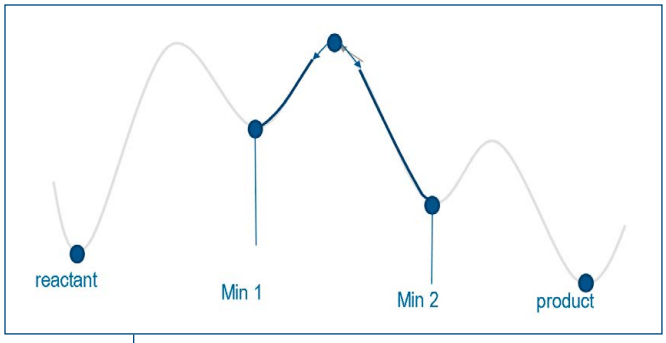


Figure 1: FlexTS constructs the lowest energy route (minimum energy path) across a potential energy surface that involves crossing reaction barriers between chemical reactants and products.

to approximate the minimum energy path, provide a detailed calculation of the transition states and identify the minima corresponding to each transition state. In the case of multi-step reactions, this process repeats until FlexTS finds a pathway connecting the initial and final state of a reaction.

BIOVIA Materials Studio FlexTS supports these calculations by providing a convenient way to define the input molecule geometries for reactants and products; it launches the calculations and then manages, analyzes and displays the results within a single interface. The calculations are highly stable and easy to use, converging even for the most difficult systems. They are significantly more generalized and automated than other implementations of transition state search and optimization in Materials Studio.

By predicting the transition state structure and associated energy, FlexTS links chemistry at the atomistic level to mathematical models of chemical reactor performance such as those provided by BIOVIA Materials Studio Cantera and BIOVIA Materials Studio KINETIX modules by complementing or replacing missing experimental reaction kinetics parameters.

In summary, BIOVIA Materials Studio FlexTS streamlines the task of predicting chemical reaction barriers, enabling scientists and chemical engineers to build a solid understanding of individual chemical reactions, and to build out complex chemical reaction schemes. This provides new efficiencies for characterization and optimization of catalyst materials. It also provides insights into combustion mechanisms, optimization of chemical production, fuel cell material development and fuel reforming, chemistry in battery cells, material deposition and more.

KEY USES OF FLEXTS

New Chemistry & Homogeneous Catalysis

Study chemical reactions of gas phase molecules to understand mechanisms and reaction barriers. Any model requiring reaction barriers such as those for epoxy curing or solid electrolyte interphase development in batteries will benefit from easy identification of the barriers with FlexTS.

Surface Chemistry & Heterogeneous Catalysis

Model surfaces with periodic boundary conditions and model surface reactions. You can use FlexTS calculations for the input to macroscopic reaction kinetics simulations on surfaces using the BIOVIA Materials Studio KINETIX module.

Reactor Design, Optimization & Improvement

With good estimates of the reaction kinetics barriers for individual chemical pathways, you can build realistic chemical reactor models. Then you can model the effects of modified reactor geometry and operating conditions using the BIOVIA Materials Studio Cantera module. By exploring the parameter space, you can quickly identify process trade-offs and optimize the onset of reactions and controllability as a function of reactor conditions.

Identification & Quantification of Emissions

With FlexTS, you can identify combustion byproducts and predict reaction barriers in order to construct chemical reaction mechanisms that may involve competing reactions.

Identification of Sustainable Plastics

With FlexTS, you can identify and understand the degradation of polymers, which is important for developing biodegradable alternatives or maximizing recyclability of synthetics.

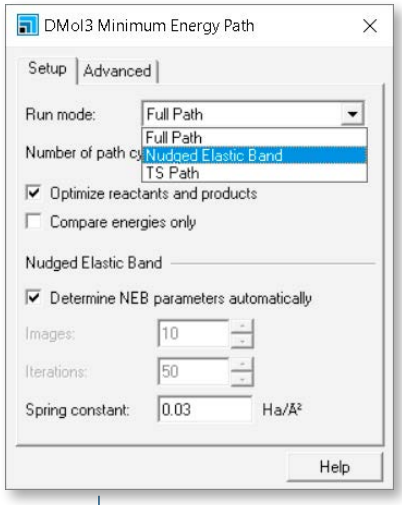


Figure 2: FlexTS is available by selection of Minimum Energy Path Task in either DMol³ or DFTB+ calculation dialogs. See the Minimum Energy Path Task dialogs for DMol³ and DFTB+ respectively.

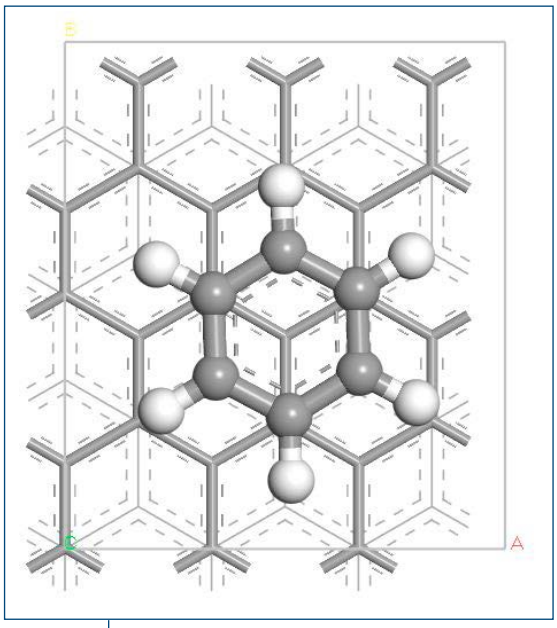


Figure 3: The rotation of benzene on a bilayer of graphene: An example of applying FlexTS to find barriers in very shallow potential energy landscapes

RUNNING FlexTS CALCULATIONS

A Minimum Energy Path task available from the DMol³ and DFTB+ modules allows you to compute energy barriers and reaction pathways using the FlexTS module in Materials Studio.

The BIOVIA Materials Studio User Interface provide a convenient framework for managing the input parameters describing the various transitions and also the solver settings. The following options are exposed on the Minimum Energy Path task dialogs (Figure 2).

FlexTS Minimum Energy Path | Full Path

Full Path is a double-ended task that finds one or more transition states required to connect reactant and product. First, a nudged elastic band calculation runs to approximate the minimum energy path. Next, the tool runs an optimization of the transition state candidates. Finally, the tool performs an optimization of the initial and final structure corresponding to each transition state. This procedure repeats as required until it finds a full minimum energy path.

FlexTS Minimum Energy Path | Nudged Elastic Band

Nudged Elastic Band is a double-ended task that runs a Nudged Elastic Band calculation for a given number of images and iterations or to a convergence threshold provided by the user. This task is useful for studying very small barriers or barrierless reactions.

Structure	Heat of reaction (kcal/mol)	Forward barrier (kcal/mol)	Reverse barrier (kcal/mol)	Reactant energy (kcal/mol)	Transition state energy (kcal/mol)	Product energy (kcal/mol)	Computational Settings
multi-H-trar 1	20.08856420	22.47642473	2.38786053	-7.534709e+004	-7.532461e+004	-7.532700e+004	DFTB+ 2021 Minimum Energy
multi-H-trar 2	11.56005099	18.49756163	6.93751064	-7.532721e+004	-7.530872e+004	-7.531565e+004	DFTB+ 2021 Minimum Energy
multi-H-trar 3	0.09136036	7.71260594	7.62124558	-7.531577e+004	-7.530805e+004	-7.531568e+004	DFTB+ 2021 Minimum Energy
multi-H-trar 4	0.28668774	7.86101319	7.57432545	-7.531573e+004	-7.530786e+004	-7.531544e+004	DFTB+ 2021 Minimum Energy
multi-H-trar 5	-11.61838302	6.82274292	18.44112594	-7.531554e+004	-7.530872e+004	-7.532716e+004	DFTB+ 2021 Minimum Energy
multi-H-trar 6	-20.27364310	2.30866507	22.58230817	-7.532705e+004	-7.532474e+004	-7.534732e+004	DFTB+ 2021 Minimum Energy

Figure 4: FlexTS output study table created from a DFTB+ Minimum Energy Path simulation, providing the thermodynamic property values of interest.

FlexTS Minimum Energy Path | TS Path

TS Path is a single-ended transition state search that starts from the guess for a transition state and refines it. Then the tool calculates the reactant and product minima corresponding to the transition state.

ANALYSIS OF FLEXTS OUTPUT

A study table summarizes the results of the minimum energy path calculation (see Figure 4). The other results files provide background information to understand the results in terms of trajectories and charts.

FlexTS calculation also returns the following documents:

- Text document containing detailed convergence information
- Trajectories and charts for individual reaction steps and the connected path (where available)
- A collection document containing the input structures for the FlexTS calculation

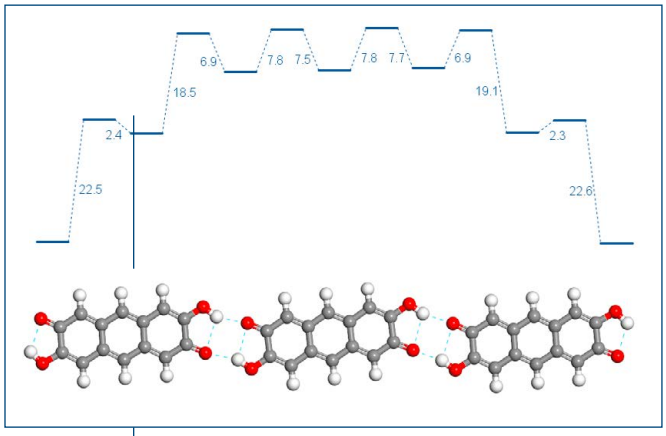


Figure 5: Hydrogen transfer reaction: An example of uncovering a mechanism in a process involving cooperative transitions.

THE BIOVIA MATERIALS STUDIO ADVANTAGE

BIOVIA Materials Studio FlexTS is part of the comprehensive BIOVIA Materials Studio modeling and simulation suite. The integrated model building and editing tools enable you to construct, visualize and manipulate molecular structures. BIOVIA Materials Studio offers a single environment for the calculation of rate coefficients and their deployment in macroscopic chemical reaction simulation by complimenting or replacing missing experimental data with accurate quantum mechanical predicted chemistry.

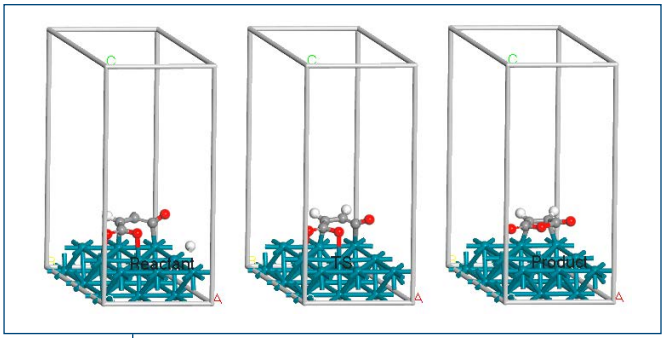


Figure 6: Reactions at surfaces within P1 periodic cells are possible. If present, fixed atom constraints within the periodic cells will be respected.

KEY FEATURES

- FlexTS redefines transition state searches in BIOVIA Materials Studio
  - Numerically stable and easy to use
  - Multiple options for reaction pathways, TS refinements, identification of low barriers
  - Links directly with other Materials Studio tools, e.g., Reaction Kinetics to provide the quantitative reaction rate parameters
- FlexTS Minimum Energy Path | Full Path
  - Finds one or more transition states required to connect reactant and product
- FlexTS Minimum Energy Path | Nudged Elastic Band
  - Doubly-nudged elastic band approach identifying barrierless and ultralow barrier reaction paths
- FlexTS Minimum Energy Path | TS Path
  - Hybrid eigenvector-following, pushoff and optimization of related minima.
- Refinement of transition states with higher order methods

RUNNING JOBS

- All simulation jobs based on BIOVIA Materials Studio FlexTS are run in the background, freeing up the BIOVIA Materials Studio client for other research.
- You can submit all simulation jobs based on BIOVIA Materials Studio FlexTS to remote high performance compute servers.

LEARN MORE

REFERENCES

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