BOOK REVIEW

The reaction path in chemistry: current approaches and perspectives

One is unable to conceive events occurring in spaces of dimensionality 3N-6, if the number of atoms forming the system, N, is large. In spite of this, chemists describe for a long time the configurational changes in reacting systems by means of a reduced number of geometrical parameters. It became customary to illustrate the main features of the chemical reaction, in terms of transition state theory (TST), as a function of the so-called reaction coordinate (RC). The concepts of reaction coordinate and reaction path (RP) were and are used to provide a simplified description of an event as complicated as a chemical reaction. Good examples for this are the one-variable reaction energy profiles used to represent the amount of energy required by the system in order to allow it to pass from the reagents' to the products' conformations as a function of the reaction coordinate.

Reaction profile, reaction coordinate and reaction path are, from the phenomenological point of view, typically chemical concepts. RP is a fiction of chemical thinking which is, however, extremely valuable in overcoming the dimensionality dilemma. The reaction path is defined as a continuous line in the multidimensional configuration space, connecting the minimum representing the reactants with the minimum representing the products through all intermediate stationary points (saddle points and reaction intermediate minima) along points of lowest energy. In this respect RP describes the minimum energy path (MEP) on the potential energy surface (PES).

This book discusses the mathematical and physical background of the RP concept, it outlines different approaches to the subject and presents new developments. The main fields of research which are dealt with are:

- Analysis of potential energy surfaces, the definition and calculation of reaction paths.
- The further development of reaction theory beyond transition state theory which use the RP concept.
- The theories based on RP and investigations of chemical reactions using these theories.

The volume consists of 12 chapters written by different authors. The first chapter is an introduction to the nomenclature and usage of the reaction path concept (D. Heidrich). In this chapter, definitions related to the RP concept are given and an attempt is made to develop a common language in this field.

The introductory chapter is followed by four others in which basic ideas and new developments of the reaction path theory are outlined. These deal with the following topics:

- Fundamental Groups and Symmetry Rules (P. G. Mezey).
- Loose Definitions of RPs (X. Chapuisat).
- Role of Zero Eigenvalues of Rotation in the Cartesian Force Constant Matrix along RP (A. Tachibana and T. Iwai).
- The Invariance of the RP Description in any Coordinate system (W. Quapp).

Among these, especially the chapter discussing the loose definition of RPs is very helpful for those readers who are less experienced with RP theory.

The next three chapters deal with the calculation of potential energy surfaces and reaction paths:

- Second-Order Methods for the Optimization of Molecular Potential Energy Surfaces (T. Helgaker, K. Rund and P. R. Taylor).
- Gradient Extremals and their Relation to the Minimum Energy Path (W. Quapp, O. Imig and D. Heidrich).
- Density Functional Theory–Calculations of PESs and RPs (G. Seifert and K. Krüger).

These chapters are followed by comprehensive discussions of reaction rate theories based on the RP concept.

- Using the RP concept to Obtain Rate Constants from ab initio Calculations (A. D. Isaacson).
- Direct Dynamics Method of the Calculation of Reaction Rates (D. G. Truhlar).

Both of these chapters provide an up to date description of the reaction rate theories and in addition present some results of their application. These chapters are of importance for all research workers interested in chemical kinetics.

In chapter last but one, ab initio studies of reaction paths in excited-state hydrogen-transfer processes are dealt with by A. L. Sobolewski and W. Domcke. Both the problems and the results of successful applications of the RP concept in this field are presented which is of great importance in photochemistry.

In the last contribution, an excellent short survey of the spectroscopy of the transition state, obtained with time-resolved femtosecond experimental techniques, is presented. (C. Heier and V. Engel). First the so-called pump/probe method is described, then some results are presented for the purpose of illustration.

The book is intended for research workers in theoretical chemistry, molecular modelling, physical chemistry, kinetics and bio-sciences.

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