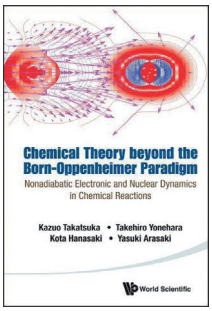

Chemical Theory beyond the Born–Oppenheimer Paradigm
Nonadiabatic Electronic and Nuclear Dynamics in Chemical Reactions. By Kazuo Takatsuka, Takehiro Yonehara, Kota Hanasaki, and Yasuki Arasaki. World Scientific Publishing, New Jersey, 2015. 450 pp., hardcover, $ 138.00.—ISBN 978-9814619646

Chemical Theory beyond the Born–Oppenheimer Paradigm

The development of techniques for the generation of ultra-short, ultra-intense laser pulses allows the creation of fascinating new environments for molecules. The external fields are so strong that they compete with the Coulombic fields of electrons and nuclei within molecules on time-scales of femtoseconds or even attoseconds. These experimental advances have opened a new field of research at the interface between chemistry and physics, revealing a wealth of non-traditional effects, e.g. softening or hardening of chemical bonds, or preferential breaking of strong bonds compared to weak ones. The new phenomena call for the development of new theoretical methods and applications. A special challenge is quantum reaction dynamics of the concerted motion of electrons and nuclei via correlated multiple transitions among many electronic states. The challenge has been taken up by leading groups in Canada, China, Europe, India, Israel, Japan and the USA. The group of Kazuo Takatsuka (Tokyo University) is among the top ten. The book summarizes their accomplishments during the past 15 years or so. For example, they have derived methods that allow tracking of transitions and fluxes from reactants to products via myriads of alternative nonadiabatic paths, much beyond the present popular but empirical (classical) molecular dynamics via "surface hopping".

The book has eight chapters. The first five (186 pages) present the state-of-the-art comprehensively: 1) the aim of the book; 2) basic framework of theoretical chemistry; 3) nuclear dynamics on electronically adiabatic potential energy surfaces; 4) breakdown of the Born–Oppenheimer approximation: classic theories of nonadiabatic transitions and the concepts on which they are based; 5) direct observations of wavepacket bifurcation due to nonadiabatic transitions, in particular at conical intersections. For example, Chapter 4 starts with a survey of one-dimensional problems for avoided curve crossings, covering the traditional Landau–Zener theory as well as the most recent Zhu–Nakamura theory. Next it reviews mixed quantum-classical formulations of electron-nucleus coupled non-adiabatic dynamics for multi-dimensional models. It then presents Tully's fewest-switch surface-hopping method, revealing the deficiencies of this popular technique. Finally Chapter 4 argues why adequate accounts of quantum coherence and decoherence before and after nonadiabatic interactions must be properly described.

The last three chapters (218 pages) contain step-by-step presentations of the major developments of the Takatsuka group, with illuminating applications to model systems from inorganic, organic, and physical chemistry. For example, Chapter 6 replaces the popular surface-hopping method by Takatsuka's novel path-branching representation for electron wavepacket propagation: the sudden hops (Chapter 4) from one electronic state to another are replaced by smooth transitions along paths with multiple branchings that account for quantum effects such as coherence and interferences. Their method can even deal with challenging scenarios involving dense sets of near-degenerate coupled electronic states. Chapter 7 introduces tools for analysis of the results of quantum dynamical computations (e.g., electron fluxes induced by diabatic transitions) or methods for the discrimination of proton versus hydrogen transfer associated with electronic transitions between ground and excited electronic states. The book ends with Chapter 8 on molecular electron dynamics in laser fields, including the generalization of path-branching representations for arbitrary optical and nonadiabatic transitions.

The book is recommended for both experts and novice researchers who are looking for new methods and tools of analysis in the new field of research. The documented developments of concepts, methods and exploratory applications are ingenious and stimulating. It is unfortunate, however, that the book suffers from inadequate proofreading. For example, the text refers repeatedly to colors of figures, even when some of these are printed in black and white or to "future" work, some of which has already been published, and three different spellings of the name of the principal author appear in the bibliography. By extrapolation, the reader may want to check the derivations carefully. As a resume: This is the most up-to-date book in the field, but it deserved a more careful editing.

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International Edition: DOI: 10.1002/anie.201508242
German Edition: DOI: 10.1002/ange.201508242