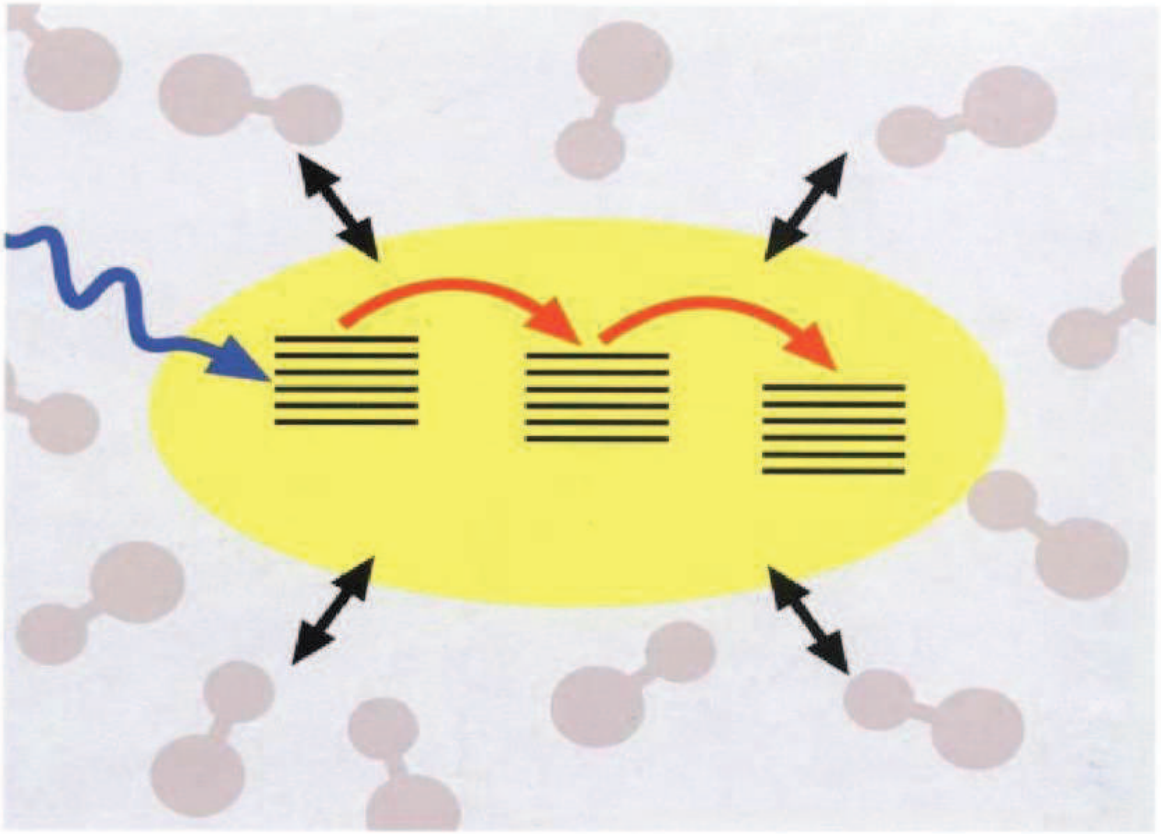
Volkhard May, Oliver Kühn

WILEY-VCH

Charge and Energy Transfer Dynamics in Molecular Systems

Second, Revised and Enlarged Edition



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WILEY-VCH Verlag GmbH & Co. KGaA

Authors

Dr. Volkhard May
Humboldt-Universität Berlin, Germany
e-mail: may@physik.hu-berlin.de

Dr. Oliver Kühn
Freie Universität Berlin, Germany
e-mail: ok@chemie.fu-berlin.de

1st Edition 2004
1st Reprint 2005

Library of Congress Card No.: applied for
British Library Cataloging-in-Publication Data:
A catalogue record for this book is available from the British Library

Bibliographic information published by
Die Deutsche Bibliothek
Die Deutsche Bibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data is available in the Internet at <http://dnb.ddb.de>.

Printed in the Federal Republic of Germany
Printed on acid-free paper

Printing Strauss Offsetdruck GmbH, Mörlenbach
Bookbinding Litges & Dopf Buchbinderei GmbH, Heppenheim

ISBN 3-527-40396-5

Foreword

Our understanding of the elementary processes of charge and energy transfer in molecular systems has developed at an enormous pace during the last years. Time–resolved spectroscopy has opened a real–time look at the microscopic details of molecular dynamics not only in the gas, but also the condensed phase. Atomic scale structures are available for a virtually uncountable number of biological systems which in turn triggers spectroscopic investigations like in the case of photosynthetic complexes or photoactive proteins. The emerging combination of structural and temporal resolution in time–resolved X–ray crystallography bears an unprecedented potential for the understanding of the interrelation between molecular structure and function. On the theoretical side, accurate electronic structure methods are becoming available for systems with hundreds of atoms, thus providing valuable information about interaction potentials governing molecular motions. The combination of quantum and molecular mechanics offers a way to condensed phase systems. Quantum dynamics methods, on the other hand, suffer from exponential scaling. Fortunately, the detailed information contained in the full wave function is quite often not needed and effective model simulations based on quantum chemical, classical molecular dynamical, but also experimental input are appropriate.

"Charge and Energy Transfer Dynamics in Molecular Systems" has been successful in providing an advanced level introduction into modern theoretical concepts of a very active area of research. Here, the quantum statistical density operator approach reveals its full flexibility by facilitating an integrative description of such diverse topics as there are vibrational relaxation, optical excitation, or electron, proton, and exciton transfer. It served the goal set by the authors to contribute to the bridging of the communication gap between researchers with different backgrounds. In addition having this self–contained source proved invaluable for the education of graduate students.

With the enlarged Second Edition V. May and O. Kühn incorporate many of the recent developments in the field. The scope of the introduction into condensed phase dynamics theory has been broadened considerably. It includes a discussion of quantum–classical concepts which emerged with the prospect of being able to describe the approximate quantum time evolution of hundreds of degrees of freedom. The detection of transfer processes by means of ultrafast nonlinear spectroscopy has received a greater emphasis. The timely topic of utilizing tailored laser fields for the active control of charge and energy transfer is introduced in a new chapter. Throughout new illustrative examples have been added which will enhance the appreciation of the mathematical formalism.

I am happy to recommend this Second Edition to an interdisciplinary audience.

Klaus Schulten

Urbana, Illinois, September 2003

Preface

The positive response to the First Edition of this text has encouraged us to prepare the present Revised and Enlarged Second Edition. All chapters have been expanded to include new examples and figures, but also to cover more recent developments in the field. The reader of the First Edition will notice that many of the topics which were addressed in its "Concluding Remarks" section have now been integrated into the different chapters.

The introduction to dissipative quantum dynamics in Chapter 3 now gives a broader view on the subject. Particularly, we elaborated on the discussion of hybrid quantum–classical techniques which promise to be able to incorporate microscopic information about the interaction of some quantum system with a classical bath beyond the weak coupling limit. In Chapter 4 we give a brief account on the state–space approach to intramolecular vibrational energy and the models for treating the intermediate time scale dynamics, where the decay of the survival probability is nonexponential. Chapter 5 now compares different methodologies to compute the linear absorption spectrum of a molecule in a condensed phase environment. Furthermore, basic aspects of nonlinear optical spectroscopy have been included to characterize a primary tool for the experimental investigation of molecular transfer processes. Bridge–mediated electron transfer is now described in detail in Chapter 6 including also a number of new examples. Chapter 7 on proton transfer has been supplemented by a discussion of the tunneling splitting and its modification due to the strong coupling between the proton transfer coordinate and other intramolecular vibrational modes. Chapter 8 dealing with exciton dynamics has been considerably rearranged and includes now a discussion of two–exciton states.

Finally, we have added a new Chapter 9 which introduces some of the fundamental concepts of laser field control of transfer processes. This is a rapidly developing field which is stimulated mostly by the possibility to generate ultrafast laser pulse of almost any shape and spectral content. Although there are only few studies on molecular transfer processes so far, this research field has an enormous potential not only for a more detailed investigation of the dynamics but also with respect to applications, for instance, in molecular based electronics.

Following the lines of the First Edition we avoided to make extensive use of abbreviations. Nevertheless, the following abbreviations are occasionally used: DOF (degrees of freedom), ET (electron transfer), IVR (intramolecular vibrational redistribution), PES (potential energy surface), PT (proton transfer), QME (quantum master equation), RDM (reduced density matrix), RDO (reduced density operator), VER (vibrational energy relaxation) and XT (exciton transfer).

We have also expanded the "Suggested Reading" section which should give a systematic starting point to explore the original literature, but also to become familiar with alternative views on the topics. Additionally, at the end of each Chapter, the reader will find a brief list

of references. Here, we included the information about the sources of the given examples and refer to the origin of those fundamental concepts and theoretical approaches which have been directly integrated into the text. We would like to emphasize, however, that these lists are by no means exhaustive. In fact, given the broad scope of this text, a complete list of references would have expanded the book's volume enormously, without necessarily serving its envisaged purpose.

It is our pleasure to express sincere thanks to the colleagues and students N. Boeijenga, B. Brüggemann, A. Kaiser, J. Manz, E. Petrov, and B. Schmidt, which read different parts of the manuscript and made various suggestions for an improvement. While working on the manuscript of this Second Edition we enjoyed the inspiring atmosphere, many seminars, and colloquia held within the framework of the Berlin Collaborative Research Center (Sfb450) "Analysis and Control of Ultrafast Photoinduced Reactions". This contributed essentially to our understanding of charge and energy transfer phenomena in molecular systems. Finally, we would like to acknowledge financial support from the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie (O.K.).

Volkhard May and Oliver Kühn

Berlin, September 2003

Preface to the First Edition

The investigation of the stationary and dynamical properties of molecular systems has a long history extending over the whole century. Considering the last decade only, one observes two tendencies: First, it became possible to study molecules on their natural scales, that is, with a spatial resolution of some ångström (10^{-10} meters) and on a time scale down to some femtoseconds (10^{-15} seconds). And second, one is able to detect and to manipulate the properties of single molecules. This progress comes along with a steadily growing number of theoretical and experimental efforts crossing the traditional borderlines between chemistry, biology, and physics. In particular the study of molecular transfer processes involving the motion of electrons, protons, small molecules, and intramolecular excitation energy, resulted in a deeper understanding of such diverse phenomena as the photoinduced dynamics in large molecules showing vibrational energy redistribution or conformational changes, the catalysis at surfaces, and the microscopic mechanisms of charge and energy transfer in biological systems. The latter are of considerable importance for unraveling the functionality of proteins and all related processes like the primary steps of photosynthesis, the enzymatic activity, or the details of the repair mechanisms in DNA strands, to mention just a few examples. In a more general context also molecular electronics, that is, the storage and processing of information in molecular structures on a nanometer length scale, has triggered enormous efforts. Finally, with the increasing sophistication of laser sources, first steps towards the control of chemical reaction dynamics have been taken.

The ever growing precision of the experiments requires on the theoretical side to have microscopic models for simulating the measured data. For example, the interpretation of optical spectroscopies in a time region of some tenths of femtoseconds, demands for an appropriate simulation of the molecular dynamics for the considered system. Or, understanding the characteristics of the current flowing through a single molecule in the context of scanning tunneling microscopy, needs detailed knowledge of the electronic level structure of the molecule as well as of the role of its vibrational degrees of freedom. These few example already demonstrate, that advanced theoretical concepts and numerical simulation techniques are required, which are the combination of methods known from general quantum mechanics, quantum chemistry, molecular reaction dynamics, solid state theory, nonlinear optics, and nonequilibrium statistical physics.

Such a broad approach is usually beyond the theoretical education of chemists and biologists. On the other hand, quantum chemistry and chemical reaction dynamics are quite often not on the curriculum of physics students. We believe that this discrepancy quite naturally does not facilitate communication between scientists having different backgrounds. Therefore it is one of the main intentions of the present book to provide a common language for

bridging this gap.

The book starts with an introduction and general overview about different concepts in Chapter 1. The essentials of theoretical chemical physics are then covered in Chapter 2. For the chemistry student this will be mostly a repetition of quantum chemistry and in particular the theory of electronic and vibrational spectra. It is by no means a complete introduction into this subject, but intended to provide some background mainly for physics students. The prerequisites from theoretical physics for the description of dynamical phenomena in molecular systems are presented in Chapter 3. Here we give a detailed discussion of some general aspects of the dynamics in open and closed quantum systems, focusing on transfer processes in the condensed phase.

The combination of qualitative arguments, simple rate equations, and the powerful formalism of the reduced statistical operator constitutes the backbone of the second part of the book. We start in Chapter 4 with a discussion of intramolecular transfer of vibrational energy which takes place in a given adiabatic electronic state. Here we cover the limits of isolated large polyatomic molecules, small molecules in a matrix environment, up to polyatomics in solution. In Chapter 5 we then turn to processes which involve a transition between different electronic states. Special emphasis is put on the discussion of optical absorption, which is considered to be a reference example for more involved electron–vibrational transfer phenomena such as internal conversion which is also presented in this chapter. Chapter 6 then outlines the theoretical frame of electron transfer reactions focusing mainly on intramolecular processes. Here, we will develop the well–known Marcus theory of electron transfer, describe nuclear tunneling and superexchange electron transfer, and discuss the influence of polar solvents. In Chapter 7 it will be shown that, even though proton transfer has many unique aspects, it can be described by adapting various concepts from electron transfer theory. The intermolecular excitation energy transfer in molecular aggregates is considered in Chapter 8. In particular the motion of Frenkel excitons coupled to vibrational modes of the aggregate will be discussed. In the limit of ordinary rate equations this leads us to the well–known Förster expression for the transfer rate in terms of emission and absorption characteristics of the donor and acceptor molecules, respectively.

By presenting a variety of theoretical models which exist for different types of transfer processes on a common formal background, we hope that the underlying fundamental concepts are becoming visible. This insight may prepare the reader to take up one of the many challenging problems provided by this fascinating field of research. Some personal reflections on current and possible future developments are given in Chapter 9.

The idea for writing this book emerged from lectures given by the authors at the Humboldt University Berlin, the Free University Berlin, and at the Johannes Gutenberg University Mainz during the last decade. These courses have been addressed to theoretically and experimentally oriented undergraduate and graduate students of Molecular Physics, Theoretical Chemistry, Physical Chemistry, and Biophysics, being interested in the fast developing field of transfer phenomena. The book is self–contained and includes detailed derivations of the most important results. However, the reader is expected to be familiar with basic quantum mechanics. Most of the chapters contain a supplementary part where more involved derivations as well as special topics are presented. At the end of the main text we also give some comments on selected literature which should complement the study of this book.

Of course this book would not have been possible without the help, the critical com-

ments, and the fruitful discussions with many students and colleagues. In this respect it is a pleasure for us to thank I. Barvik, N. P. Ernsting, W. Gans, L. González, O. Linden, H. Naundorf, J. Manz, S. Mukamel, A. E. Orel, T. Pullerits, R. Scheller, and D. Schirrmeister. We also are grateful for continuous financial support which has been provided by the Deutsche Forschungsgemeinschaft, in particular through the Sonderforschungsbereich 450 "Analysis and Control of Ultrafast Photoinduced Reactions".

Volkhard May and Oliver Kühn

Berlin, September 1999

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