Volkhard May, Oliver Kühn

Charge and Energy Transfer Dynamics in Molecular Systems

Second, Revised and Enlarged Edition

WILEY-VCH

WILEY-VCH Verlag GmbH & Co. KGaA

Volkhard May, Oliver Kühn

Charge and Energy Transfer Dynamics in Molecular Systems

Volkhard May, Oliver Kühn

Charge and Energy Transfer Dynamics in Molecular Systems

Second, Revised and Enlarged Edition

WILEY-
VCH

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 comments, 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

This Page Intentionally Left Blank

Contents

1 Introduction

The understanding of molecular transfer phenomena requires a unified theoretical treatment which should have its foundations in a microscopic definition of the considered molecular system. There are three questions which need to be answered in this respect: First, what is the appropriate theoretical description of the molecular system, second, what is the form of the dynamical equations which describe the transfer process, and third, how can the computed results be related to experimental observations.

From a general point of view, quantum mechanics gives the framework for all phenomena occurring in *molecular systems*. In the following the term "molecular system" shall cover single molecules, simple molecular aggregates, but also larger arrangements of molecules like supra–molecular complexes and, in particular, molecules embedded in different types of environments will be of interest. The definition even encompasses biological macromolecules such as membrane–bound protein complexes. The common link between these molecular systems is that they show *transfer processes*. By "transfer process" we understand the flow of vibrational energy, the dynamics of electrons, protons, and electronic excitation energy. The nature of these processes is intimately related to the kind of preparation of the initial conditions, for instance, by the interaction with an electromagnetic field. In view of this broad scope it is clear that an exact quantum mechanical treatment is impossible if we go beyond the level of simple model systems.

Therefore, we will start in Chapter 2 with a discussion of the steps which lead us from the formally exact to some approximate molecular Hamilton operator. Given a molecule in the gas phase (vacuum) as shown in the upper part of Fig. 1.1, the *Born–Oppenheimer separation* of nuclear and electronic motions can be performed. Here, the molecular wave function is split up into an electronic and a nuclear part, a procedure which is justified by the large mass–difference between both types of particles. This results in a Schrödinger equation for the electronic wave function alone, for given fixed positions of the nuclei. Calculating the electronic energy spectrum for different positions of the nuclei one obtains *potential energy surfaces* which govern the motion of the nuclei. These potential energy surfaces are at the heart of the understanding of stationary molecular spectra and chemical reaction dynamics. If nuclear and electronic motion are adiabatically separable, that is, the coupling between different electronic states is negligible and one can carry out the Born–Oppenheimer approximation. Under certain conditions, however, so–called nonadiabatic transitions between different electronic states as a consequence of the nuclear motions are to be expected.

If we step from the gas to the condensed phase, for example, by considering a molecule in solution as shown in the lower part of Fig. 1.1, the effect of the molecule–environment interaction has to be taken into account. The simplest way to do this is to add an additional

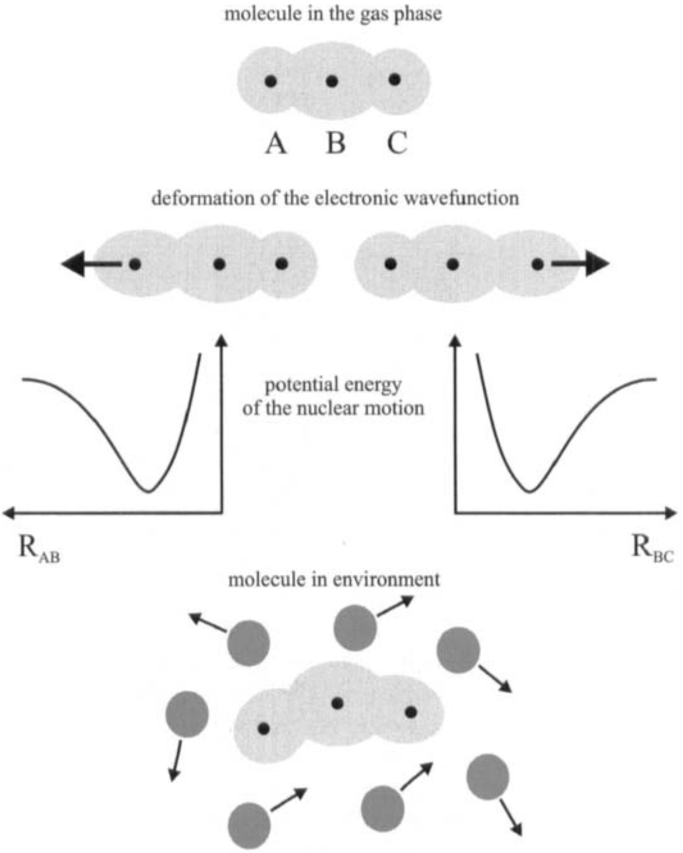

Figure 1.1: The complicated problem of the interaction between electrons and nuclei is reduced to some tractable level by employing the Born–Oppenheimer separation of their motions. Upper panel: Three–atomic molecule with nuclei labelled by A, B, and C. The electronic wave function is indicated by a grey area. Middle panel: The bond length between atom A and B (left part) as well as atom B and C (right part) is increased accompanied by an instantaneous deformation of the electronic wave function. As a result, a potential energy curve is formed determining the dynamics of the bond length. Lower panel: If the molecule is taken from the gas to the condensed phase its stationary properties cannot be calculated without invoking further approximations.

external potential to the molecular Hamiltonian. Often the environment can be described as a macroscopic dielectric and its influence can be judged from its dielectric properties.

Having discussed the stationary molecular properties we turn to the *molecular dynamics* in Chapter 3. Here, the reader will become familiar with concepts ranging from incoherent to coherent transfer events. The connection between these limits is provided by the relevant time scales; of particular importance is the relation between intramolecular relaxation and intermolecular transfer times. In view of experimental advances in ultrafast optical spectroscopy, our treatment reflects the historical evolution of knowledge on molecular dynamics.

open molecular system

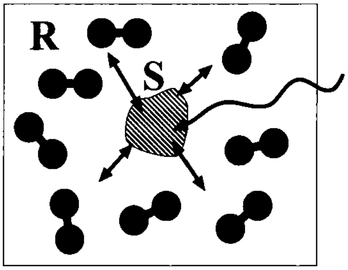

Figure 1.2: Open molecular system S interacting with its environment (reservoir) R. In addition the system may be influenced by external fields (wiggly line).

The essential ingredient for the theoretical modelling is the concept of an *open molecular system* S interacting with its *environment* (reservoir) R by collision processes or via other means of energy exchange. A schematic illustration of this situation is given in Fig. 1.2. The *relevant* system S may represent any type of molecule, but it may also comprise selected so–called *active* degrees of freedom of a particular molecule. In order to study the dynamics of the relevant system in an actual experiment, its response to some external field such as an electromagnetic field is measured.

The most general description of the total system, S plus R, is given by the quantum statistical operator $\hat{W}$ as indicated in the left part of Fig. 1.3. This operator is based on the concept of a *mixed* quantum state formed by S and its macroscopic environment. However, the operator $\hat{W}$ contains much more information than we will ever need, for instance, to simulate a particular experiment. Indeed, it is the relevant system S we are interested in. Making use of a reduction procedure we obtain a *reduced statistical operator* $\hat{\rho}$ which contains the information on the dynamics of S only, but including the influence of the environment R (right–hand part of Fig. 1.3). When deriving equations of motion for the reduced statistical operator, the so–called *Quantum Master Equations*, a number of approximations have to be invoked. Most fundamental in this respect will be the assumption of a weak interaction between the system

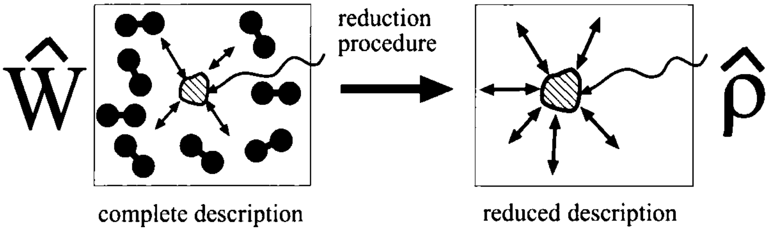

Figure 1.3: The total system $S + R$ is completely described by the quantum statistical operator $\hat{W}$. By means of a reduction procedure one can focus on the relevant system using the reduced statistical operator $\hat{\rho}$.

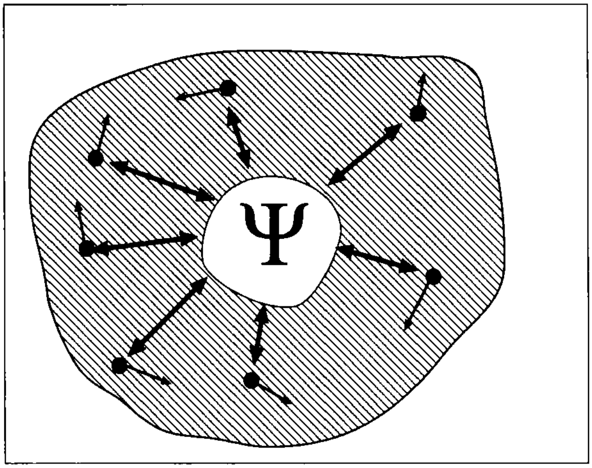

Figure 1.4: Mixed quantum–classical description of condensed phase dynamics. The classical particles move in the mean field generated by the quantum particle described by the wave function Ψ.

S and the reservoir R, which in practice requires a proper separation into relevant and environmental coordinates for the molecular system at hand. If there is no interaction at all, the Quantum Master Equation would be equivalent to the time–dependent Schrödinger equation. This is the regime of *coherent* dynamics. If the interaction is not negligible, however, the system dynamics gradually changes with increasing coupling strength from a *partially coherent* one to an *incoherent* one. The incoherent motion of a quantum system is commonly described using ordinary rate equations which are based on the *Golden Rule* rate expression of quantum mechanics.

The Quantum Master Equation, however, affords a more general frame since it comprises the various dynamical limits. Therefore, it gives a unified description of quantum molecular dynamics of a relevant system and its interaction with some environment.

The concept of the statistical operator provides a *quantum–statistical* description of S and R. However, in many situations it is sufficient to describe R by means of classical mechanics. Then, S can be characterized by a wave function Ψ instead of a statistical operator and the dynamics of the environmental degrees of freedom is governed by Newton's equations. Often the dynamics is split up in such a way that the classical particles move in the mean field of the quantum particle. This situation is visualized in Fig. 1.4.

The formal concepts developed in Chapters 2 and 3 are then applied to describe different transfer phenomena. In principle, the different transfer processes can be classified according to the type of transferred particle. In addition, one can distinguish between intramolecular and intermolecular particle transfer. The common frame is provided by the molecular Schrödinger equation together with the Born–Oppenheimer separation of electronic and nuclear motions as mentioned above.

The coupled nuclear dynamics in polyatomic molecules which might be immersed in some condensed phase environment is treated in Chapter 4. We will show how an initially prepared vibrational state decays while its excitation energy is distributed over all possible environmental modes, as illustrated in the left–hand part of Fig. 1.5. For small polyatomic molecules the reversible energy flow out of the initial state is called *intramolecular vibrational energy redistribution*. For condensed phase situations the irreversible dissipation of energy into the environment is called *vibrational energy relaxation*. In both cases the transferred objects are the quanta of vibrational energy.

As sketched in Fig. 1.5 the preparation of the initial state can be due to an optical transition between two electronic states as a consequence of the interaction between the molecular system and an external electromagnetic field. In Chapter 5 we will discuss the processes of photon absorption and emission sketched in Fig. 1.5. It will be shown that the coupled electron–vibrational dynamics which is responsible for the absorption lineshape can be described by a combined density of states which is the Fourier transform of some correlation function. This theoretical result will turn out to be quite general. In particular we will show that different types of transfer processes can be accommodated into such a framework. For example, the *internal conversion* dynamics of nonadiabatically coupled electronic states (see right–hand part of Fig. 1.5) can, in the incoherent limit, be described by a combined density of states.

The external field interaction, on the other hand, provides the means for preparing nonequilibrium initial states which can act as a donor in a photoinduced electron transfer reaction which is discussed in Chapter 6. The concerted electron–vibrational dynamics accompanying electron transfer reactions can often be modelled in the so–called *curve–crossing* picture of two coupled potential energy surfaces representing two electronic states along a *reaction*

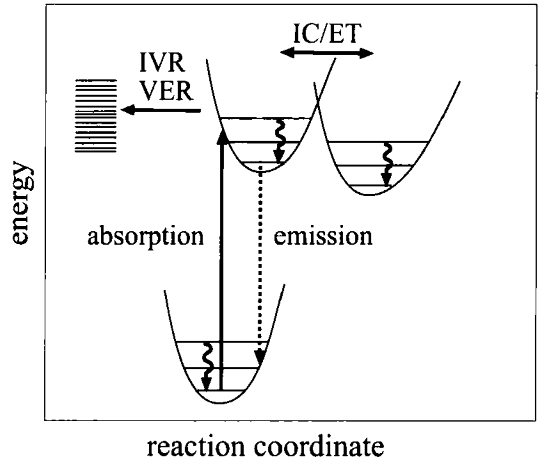

Figure 1.5: After optical preparation of an electronically and vibrationally excited initial state (absorption), different transfer processes can occur. If the electronic state is not changed, but there is a coupling to some manifold of vibrational states, intramolecular energy redistribution (IVR) or vibrational energy relaxation (VER) can be observed. If there is some coupling to another electronic state, intramolecular internal conversion (IC) or electron transfer (ET) take place. At the same time, one has VER as indicated by the wiggly lines. In addition the system may return to the ground state by emitting a photon.

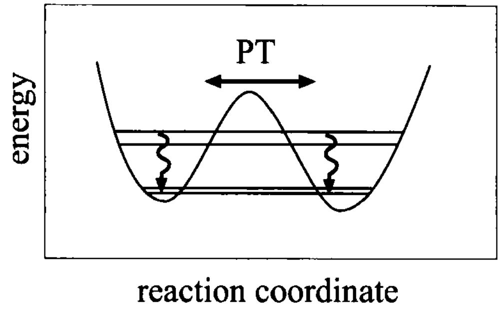

Figure 1.6: Hydrogen bonding which governs the proton transfer (PT) dynamics often leads to a double minimum potential along a reaction coordinate. The interaction between the proton and some environment may cause vibrational relaxation (wiggly lines).

coordinate (see right–hand part Fig. 1.5).

In contrast, the proton or hydrogen atom transfer investigated in Chapter 7 usually does not involve electronic transitions. In Fig. 1.6 we have sketched a typical situation for intramolecular proton transfer which is realized as an isomerization reaction in the adiabatic electronic ground state. Since the proton has a rather small mass, tunneling processes may play an important role for proton transfer. The small mass ratio between the proton and the other heavy atoms provides the background for the introduction of a second Born–Oppenheimer separation. This will enable us to adapt most of the concepts of electron transfer theory to the case of proton transfer.

In Chapter 8 we discuss excitation energy transfer or so–called exciton transfer in molecular aggregates as another example for coupled electron–vibrational motion. In Fig. 1.7 the mechanism of exciton transfer in the limit of localized excitations is shown. The donor (left) is initially excited, for example, by an external field. As a consequence of the Coulomb interaction between the excited molecule and surrounding molecules, excitation energy is transferred to some acceptor (right). Due to the large spatial separation, donor and acceptor are usually described by different sets of nuclear (reaction) coordinates. The process can formally be understood in a picture where the donor emits radiation energy which is in turn absorbed by the acceptor.

A successful analysis of molecular transfer processes triggers the desire to take *active control* of the dynamics. For example, it would be intriguing to have a means for depositing energy into specific bonds or reaction coordinates such as to dissociate a polyatomic molecule into desired products. To utilize electron transfer processes as part of an ultrafast switch is of tremendous importance in the emerging area of molecular electronic. Or controlling the fate of an exciton, for instance, in a photosynthetic light–harvesting complex as well as guiding the motion of protons in enzymatic catalysis would reveal a microscopic picture of biological functions.

Fortunately, many of the theoretical concepts for laser control developed over the last two decades eventually may turn into working schemes because recent years have witnessed an impressive evolution of laser pulse shaping techniques. But the exploration of the potential

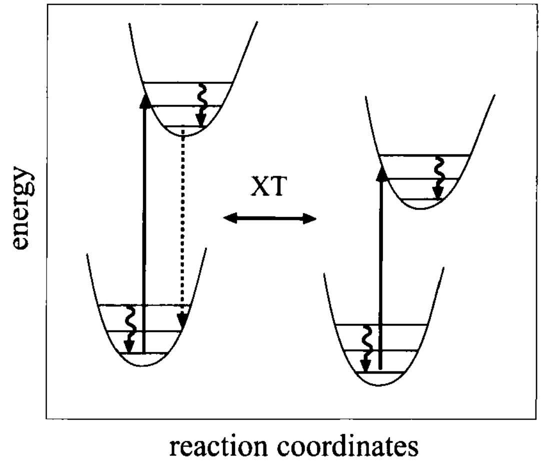

Figure 1.7: Excitation energy transfer (XT) which occurs after optical preparation of an electronically and vibrationally excited initial state (donor, left). The Coulomb interaction is responsible for de-excitation of the donor and excitation of the acceptor (right). The nuclear dynamics may be subject to relaxation processes (wiggly lines). Often two independent nuclear (reaction) coordinates are used for the donor and the acceptor site.

of laser pulse control in the context of molecular transfer processes is still in its infancy. The active control of transfer processes will be discussed in Chapter 9.

This Page Intentionally Left Blank

2 Electronic and Vibrational Molecular States

This chapter provides the background material for the subsequent development of a microscopic description of charge and energy transfer processes in the condensed phase. After introducing the molecular Hamiltonian operator we discuss the Born–Oppenheimer separation of electronic and nuclear motions as the key to the solution of the molecular Schrödinger equation. The Hartree–Fock method which is a simple yet very successful approach to the solution of the ground state electronic structure problem is explained next. It enables us to obtain, for instance, the potential energy surface for nuclear motions. To prepare for the treatment of condensed phase situations we further introduce the dielectric continuum model as a means for incorporating static solvent polarization effects into the electronic structure calculations.

The topology of the potential energy surface can be explored by calculating the first and second derivatives with respect to the nuclear coordinates. Of particular interest are the stationary points on a potential energy surface which may correspond to stable conformations of the molecule. In the vicinity of a local minimum it is often possible to analyze nuclear motions in terms of small amplitude normal mode vibrations. If one wants to model chemical reaction dynamics, however, the shape of the potential energy surface away from the stationary points is required as an input. We present two different approaches in this respect: The minimum energy reaction path and the Cartesian reaction surface model. Particularly the latter will provide the microscopic justification for the generic Hamiltonians used later on to simulate small molecular systems embedded in some environment. Finally, we discuss the diabatic and the adiabatic representation of the molecular Hamiltonian.

2.1 Introduction

The development of quantum theory in the 1920's was to a considerable extent triggered by the desire to understand the properties of atoms and molecules. It was soon appreciated that the Schrödinger equation together with the probabilistic interpretation of its solutions provides a powerful tool for tackling a variety of questions in physics and chemistry. The mathematical description of the hydrogen atom's spectral lines could be given and developed to a textbook example of the success of quantum mechanics. Stepping into the molecular realm one faces a complicated many–body problem involving the coordinates of all electrons and all nuclei of the considered molecule. Its solution can be approached using the fact that nuclei and electrons have quite different masses allowing their motion to be adiabatically separated. This concept was first introduced by Born and Oppenheimer in 1927. Within the Born–Oppenheimer adiabatic approximation the simplest molecule, the hydrogen molecule ion, H_2^+, can be treated.

From the electronic point of view the appearance of one more electron, for instance, in H_2, necessitates the incorporation of the repulsive electronic interaction. Moreover, since one deals with two identical electrons care has to be taken that the wave function has the proper symmetry with respect to an exchange of any two particle labels. In a straightforward way this is accomplished by the *self–consistent field method* according to Hartree, Fock, and Slater. Despite its deficiencies Hartree–Fock theory has played an enormous role in the process of exploring the electronic structure of molecules during the last decades. It still serves as the basis for many of the more advanced approaches used nowadays.

However, it is not only the electronic structure at the equilibrium configuration of the nuclei which is of interest. The form of the potential energy hypersurfaces obtained upon varying the positions of the nuclei proves crucial for an understanding of the vibrational and rotational structure of molecular spectra. Moreover it provides the key to chemical reaction dynamics. While the adiabatic Born–Oppenheimer ansatz is an excellent approximation in the vicinity of the ground state equilibrium configuration, nonadiabatic couplings leading to transitions between electronic states become an ubiquitous phenomenon if the nuclei are exploring their potential surface in processes such as photodissociation and electron transfer reactions, for example.

This chapter introduces the concepts behind the keywords given so far and sets up the stage for the following chapters. Having this intention it is obvious that we present a rather selective discussion of a broad field. We first introduce the molecular Hamiltonian and the respective solutions of the stationary Schrödinger equation in Section 2.2. This leads us directly to the Born–Oppenheimer separation of electronic and nuclear motions in Section 2.3. A brief account of electronic structure theory for polyatomic molecules is given next (Section 2.4). This is followed by a short summary of the dielectric continuum model in Section 2.5 which allows for incorporation of solvent effects into electronic structure calculations. On this basis we continue in Section 2.6 to discuss potential energy surfaces and the related concepts of harmonic vibrations and reaction paths. In Section 2.7 we focus attention to the problem of nonadiabatic couplings which are neglected in the Born–Oppenheimer adiabatic approximation. Finally, the issue of diabatic versus adiabatic pictures which emerges from this discussion is explained and alternative representations of the molecular Hamiltonian are given.