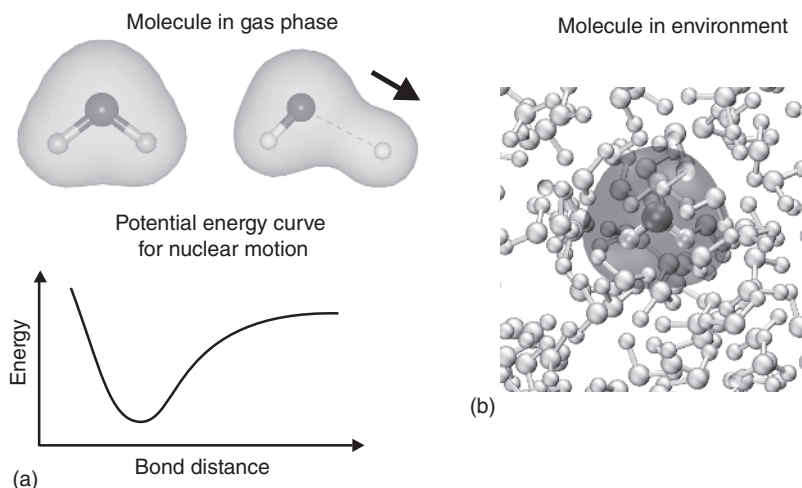# 1

Introduction

The understanding of transfer phenomena in *molecular systems* calls for a unified theoretical treatment that should have its foundation in a microscopic definition of the constituent parts and their interactions. There are three important questions that need to be answered in this regard. *First*, what is the appropriate theoretical description of the molecular system? *Second*, what is the form of the dynamical equations that describe the transfer process? And *third*, how can the computed results be related to experimental observations?

In what follows the term "molecular system" will cover single molecules and simple molecular aggregates as well as larger arrangements of molecules such as supramolecular complexes. In particular, molecules embedded in different types of environments will be of interest. Here, the scope ranges from molecules in solution to 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 and the dynamics of electrons, protons, and electronic excitation energy.

From a general point of view, quantum mechanics gives the framework for all phenomena occurring in molecular systems. Given the broad scope of transfer processes to be discussed, it is clear that an exact quantum mechanical treatment is impossible if we go beyond the level of simple model systems. Therefore, it is a particular challenge for theory to develop versatile models that provide answers to the initially raised three questions.

Chapter 2 addresses the first question discussing the steps that lead us from the formally exact to some approximate molecular Hamilton operator. Given a molecule in gas phase (vacuum) as shown in Figure 1.1a, 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 that 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* that govern the motion of the nuclei. These potential energy surfaces are at the heart of our understanding of stationary molecular spectra and molecular dynamics. If nuclear and electronic

Molecule in gas phase

Molecule in environment

Potential energy curve
for nuclear motion


Energy

Bond distance

(a)

(b)

Figure 1.1 The problem of the interaction between electrons and nuclei is transformed to some tractable level by employing the Born–Oppenheimer separation of their motions. (a) Three-atomic molecule (H_2O) with the electron density shown for the equilibrium distance (left) as well as for a stretched bond (right). The electron density adjusts instantaneously to the configuration of the nuclei. As a result, a potential energy curve is formed determining the dynamics of the bond distance coordinate. (b) If the molecule is taken from the gas into the condensed phase, its stationary and dynamic properties have to take into account the interaction with the surrounding molecules. This may give rise, for instance, to a change in equilibrium geometry and electron density (figure courtesy of Ashour Ahmed).

motion are adiabatically separable, that is if the coupling between different electronic states is negligible, one can carry out the Born–Oppenheimer approximation. Under certain conditions, however, the so-called nonadiabatic transitions between different electronic states as a consequence of the nuclear motions take place.

If we move from the gas to the condensed phase as shown in Figure 1.1b, the effect of the molecule–environment interaction has to be taken into account. The simplest way to do this is to add an additional 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 in Chapter 3 to the second question related to *molecular dynamics*. Here, the reader will become familiar with the 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 spectroscopy, our treatment reflects the historical evolution of knowledge about molecular dynamics from simple transfer rates to quantum mechanical wave packet dynamics.

An important ingredient for the theoretical modeling 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
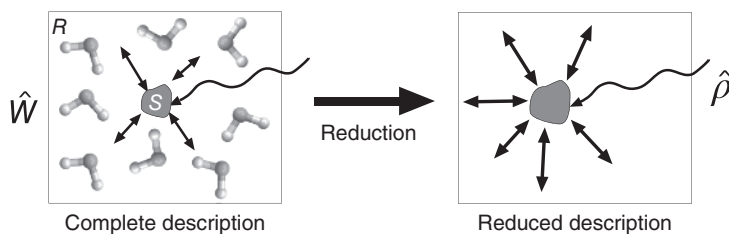
Figure 1.2 The total system consisting of a relevant system (*S*) interacting with a reservoir (*R*) is completely described by the quantum-statistical operator $\hat{W}$. By means of a reduction procedure, one can focus on the relevant system using the reduced statistical operator $\hat{\rho}$. Effects of the *S*–*R* interaction are still accounted for. In addition, the system may be influenced by external fields (wiggly line).

situation is given in Figure 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.

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-hand part of Figure 1.2. 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 will ever be needed, for instance, to simulate a particular experiment. Indeed, it is the relevant system *S* whose properties we are interested in. Making use of a reduction procedure, we obtain a *reduced statistical operator* $\hat{\rho}$ that contains the information on the dynamics of *S* only but including the influence of the environment *R* (right-hand part of Figure 1.2). 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 *S* and the reservoir *R*, which in practice requires a proper separation into relevant and environmental coordinates for the molecular system at hand. Under certain conditions, however, a numerical exact description of the dynamics of the relevant system becomes possible. If there is no interaction at all, the quantum master equation is 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 that are based on the *Golden Rule* rate expression of quantum mechanics.

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, 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 Figure 1.3.

The overwhelming amount of data on transfer processes in molecular systems is obtained by spectroscopic techniques working in the infrared, the visible to
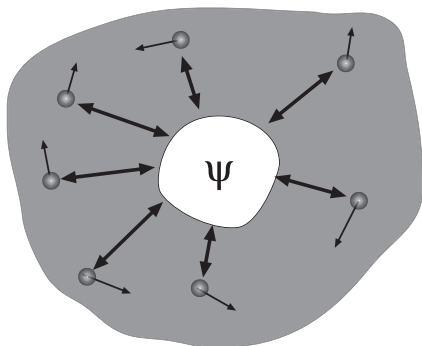
Figure 1.3 Mixed quantum–classical description of condensed phase dynamics. The classical particles move in the mean field generated by the quantum particle described by the wave function Ψ.

ultraviolet, and, more recently, also in the X-ray region. We will discuss the third question related to experimental observation mostly in the context of spectroscopy, with focus on the infrared to ultraviolet domain. As a means of preparation, Chapter 4 gives a brief account on the general theoretical concepts of the interaction of molecular systems with the electromagnetic radiation field. Further, a formulation of linear and nonlinear spectroscopy in terms of correlation functions will be introduced.

The general concepts presented in Chapters 2–4 are then applied to describe different transfer phenomena. In principle, transfer processes can be classified according to the type of transferred particle. In addition, one can distinguish between intra- 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 that might be immersed in some condensed phase environment is treated in Chapter 5. We 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 Figure 1.4. For small polyatomic molecules, the energy flow out of the initial state is called *intramolecular vibrational energy redistribution*. For condensed phase situations, the dissipation of energy into the environment is called *vibrational energy relaxation*. In both cases, the transferred objects are the quanta of vibrational energy.

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 (cf. Figure 1.4). In Chapter 6, we discuss the processes of photon absorption and emission sketched in Figure 1.4. It will be shown that the coupled electron-vibrational dynamics responsible for the absorption line shape can be described by a combined density of states that is the Fourier transform of some correlation function. This theoretical result will turn out to be quite general. In particular, we show that different types of transfer processes can be accommodated in such a framework. For example, the *internal conversion* dynamics of nonadiabatically coupled electronic states (right-hand part of Figure 1.4) 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 that can act as a donor in a photoinduced
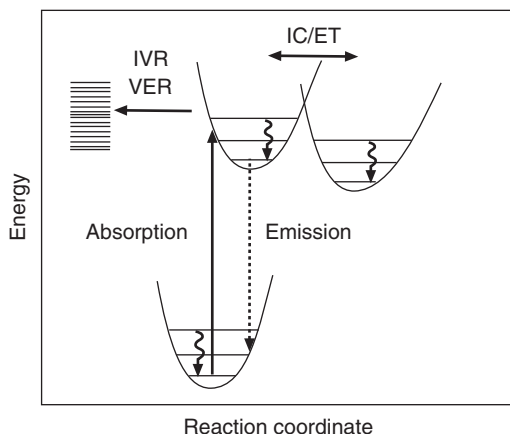
Figure 1.4 Scheme of molecular potential energy surfaces including the levels of the quantized motion of some reaction coordinate. After optical preparation of an electronically and vibrationally excited initial state (absorption), different transfer processes can occur. If the electronic state is not changed, but there is a coupling to some manifold of vibrational states, intramolecular vibrational 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) takes 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.

electron-transfer reaction, which is discussed in Chapter 7. The concerted electron-vibrational dynamics accompanying electron-transfer reactions can often be modeled in the so-called curve-crossing picture of two coupled potential energy surfaces representing two electronic states along a *reaction coordinate* (right-hand part of Figure 1.4). Generalizations of this picture to larger molecular systems and to the case where the molecule is in contact with metal electrodes and a voltage is applied will also be discussed.

In contrast, the proton or hydrogen atom transfer investigated in Chapter 8 usually does not involve electronic transitions. In Figure 1.5, we have sketched a typical situation for intramolecular proton transfer that 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

Figure 1.5 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).
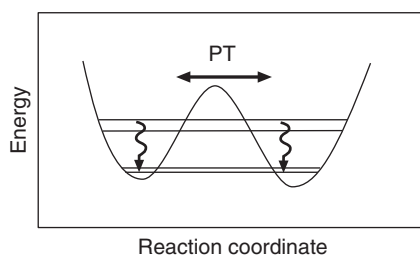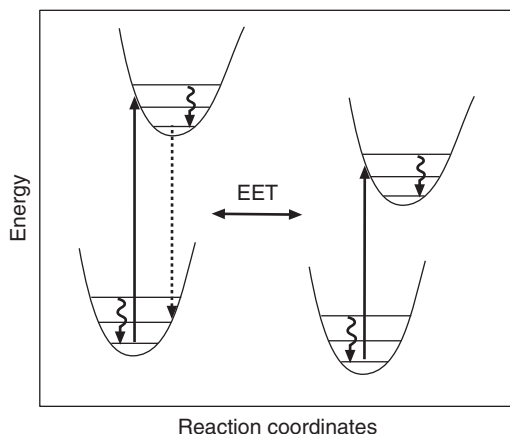
Figure 1.6 Excitation energy transfer (EET), which occurs after optical preparation of an electronically and vibrationally excited initial state (donor, left). The Coulomb interaction is responsible for deexcitation of the donor and excitation of the acceptor (right). The nuclear dynamics may be subject to relaxation processes (wiggly lines). Often, two independent nuclear (reaction) coordinates are used for the donor and the acceptor molecules.

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 9, we discuss excitation energy transfer or the so-called exciton transfer in molecular aggregates as another example of coupled electron-vibrational motion. In Figure 1.6, the mechanism of excitation energy 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, excitation energy is transferred between the excited molecule and some acceptor molecule (right). Often, donors and acceptors retain their chemical identity upon aggregation and, therefore, are usually described by different sets of nuclear (reaction) coordinates. In the incoherent limit, the rate of the process can be expressed in terms of an overlap integral between donor emission and acceptor absorption spectra. If the Coulomb interaction between different molecules becomes large enough, then excitation energy transfer has to be discussed by introducing quantum mechanical superposition states of all excited molecules, the so-called Frenkel excitons. Their introduction gives a new view on excitation energy transfer via the motion of spatially delocalized states. A rigorous nonequilibrium quantum-statistical model can describe both the incoherent and the coherent limits.