

Chapter 2

Theoretical Concepts

This chapter contains an overview of the theoretical methods implemented in this work. Quantum chemical methods, Hartree - Fock and Density Functional theory, are reviewed in section 2.1. Section 2.2 is dedicated to anharmonicity: two approaches are introduced - the Anharmonic Force Field and the Cartesian Reaction Surface method, the former being suitable for describing small amplitude motions, and the later allowing characterization of large displacements, including chemical reactions. A closer look at quantum dynamics calculations is given in Section 2.3 by describing the different treatments of isolated and open systems. The interaction between the system of interest and an external electric field is addressed in Section 2.3.3.

2.1 Quantum Chemistry

The aim of this work is to describe the dynamics of hydrogen bonds. In order to set up the Hamiltonian, quantum chemistry calculations have to be carried out. This chapter contains an overview of quantum chemistry methods used for the present model (for a detailed discussion see [30]-[36]).

By performing a quantum chemical calculation, we mean solving a stationary Schrödinger equation:

$$\hat{H}_{mol}|\psi\rangle = E|\psi\rangle \quad (2.1)$$

with \hat{H}_{mol} being the molecular Hamilton operator. Although this equation has a plain form, it can be solved analytically only for simple systems, like the particle in a box, harmonic oscillator, hydrogen atom, or one-electron ions. A way to solve this eigenvalue problem for a more complex system is not straightforward, but rather comprises different approximate methods. To start with, one usually applies the Born-Oppenheimer approximation, which simplifies the problem by allowing a separate treatment of electronic and nuclear motion. The next approximation con-

cerns the ansatz for the wave function. The simplest form would be to describe it with a single Slater determinant, as in the Hartree-Fock method (section 2.1.1). Although this is the least expensive method, the results are usually not satisfactory, so one has to turn to more sophisticated approaches, like perturbational theory or configuration interaction, that take into account electron correlation. Unfortunately, high accuracy is paid by high computational cost. The compromise is found in the density functional theory, which will be sketched in section 2.1.2.

Born-Oppenheimer Approximation

As already pointed out, solving the time independent Schrödinger equation for a system containing more than two particles is a formidable task. In general, the molecular Hamiltonian describes the motion of N_{el} electrons and N_{nuc} nuclei, which are treated as pointlike particles, whose position is defined by position vectors \mathbf{r} and \mathbf{R} , respectively:

$$\hat{H}_{mol} = \hat{T}_{el}(\mathbf{r}) + \hat{T}_{nuc}(\mathbf{R}) + \hat{V}_{el-el}(\mathbf{r}) + \hat{V}_{nuc-nuc}(\mathbf{R}) + \hat{V}_{el-nuc}(\mathbf{r}, \mathbf{R}). \quad (2.2)$$

The first two terms represent operators of the kinetic energy of the electrons \hat{T}_{el} and the nuclei \hat{T}_{nuc}

$$\hat{T}_{el} = -\frac{1}{2} \sum_{i=1}^{N_{el}} \frac{1}{m_e} \Delta_i, \quad (2.3)$$

$$\hat{T}_{nuc} = -\frac{1}{2} \sum_{I=1}^{N_{nuc}} \frac{1}{M_I} \Delta_I \quad (2.4)$$

with m_e being the electron mass, M_I mass of the I^{th} nucleus, and $\Delta_{i/I}$ the Laplacian operator that contains second derivatives with respect to coordinates of the corresponding particles.

The last three terms stand for the operators of the potential energy, and since they describe charged particles, they contain Coulomb interactions which are repulsive (for electron-electron and nuclear-nuclear interactions, V_{el-el} and $V_{nuc-nuc}$) or attractive (electron-nuclear interactions V_{el-nuc})

$$\hat{V}_{el-el}(\mathbf{r}) = \sum_{i=1}^{N_{el}} \sum_{j>i}^{N_{el}} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}, \quad (2.5)$$

$$\hat{V}_{nuc-nuc}(\mathbf{R}) = \sum_{I=1}^{N_{nuc}} \sum_{J>I}^{N_{nuc}} \frac{Z_I Z_J e^2}{|\mathbf{R}_I - \mathbf{R}_J|}, \quad (2.6)$$

$$\hat{V}_{el-nuc}(\mathbf{r}, \mathbf{R}) = - \sum_{i=1}^{N_{el}} \sum_{I=1}^{N_{nuc}} \frac{Z_I e^2}{|\mathbf{r}_i - \mathbf{R}_I|}. \quad (2.7)$$

At this point we make use of the fact that the mass difference between electrons and nuclei amounts to a few orders of magnitude. According to this, the "light" electrons, which are assumed to move much faster, are able to adjust instantaneously to each new arrangement of the sluggish nuclei. In other words, one can solve the electronic problem for a certain "frozen" configuration of the nuclei. This separate treatment of electronic and nuclear motion is known as *Born-Oppenheimer approximation*.

The electronic Hamiltonian describes electron motion in the field of fixed nuclei and contains the following terms

$$\hat{H}_{el} = \hat{T}_{el} + \hat{V}_{el-el} + \hat{V}_{el-nuc}. \quad (2.8)$$

Solving the stationary Schrödinger equation

$$\hat{H}_{el}\psi_{el,n} = E_{el,n}\psi_{el,n} \quad (2.9)$$

for the electronic problem is the core of all programs that perform quantum chemical calculations. The electronic wave function $\psi_{el,n}$ depends explicitly on electronic (\mathbf{r}) and parametrically on nuclear (\mathbf{R}) coordinates. The corresponding energy $E_{el,n}$ also depends parametrically on \mathbf{R} . This procedure has to be repeated for different nuclear configurations. Having calculated E_{el} for different values of \mathbf{R} , one arrives at the potential hypersurface for nuclear motion (skipping the index n since we are dealing with the ground electronic state only):

$$\hat{V}(\mathbf{R}) = E_{el}(\mathbf{R}) + \hat{V}_{nuc-nuc}(\mathbf{R}). \quad (2.10)$$

This means that the nuclei move in the average field of the electrons, modified by the nuclear repulsion term. Finally, we can define the nuclear Hamiltonian and the corresponding nuclear Schrödinger equation

$$\hat{H}_{nuc}(\mathbf{R})\psi_{nuc}(\mathbf{R}) = [\hat{T}_{nuc} + \hat{V}(\mathbf{R})]\psi_{nuc}(\mathbf{R}) = E_{nuc}\psi_{nuc}(\mathbf{R}). \quad (2.11)$$

The Born-Oppenheimer approximation is well suited for cases when electronic and nuclear Hamiltonians are well separated, i.e., when nuclear motion can not cause a change in the electronic state. As mentioned before, processes described in this work take place in the electronic ground state, that is (for the systems studied in this thesis) well separated from the excited electronic states, which justifies the use of the BOA.

2.1.1 Hartree-Fock Theory

The BOA considerably simplified the problem of solving the molecular stationary Schrödinger equation by a separate treatment of electronic and nuclear motion.

The next obstacle is the electronic problem, since electronic Schrödinger equation is in general a many-body problem. Therefore, the simplest form of a wave function would be a product of functions, each of which represents one electron (those one particle functions are usually denoted as orbitals)

$$\psi(\mathbf{r}_1, \dots, \mathbf{r}_{N_{el}}) = \phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2) \dots \phi_{N_{el}}(\mathbf{r}_{N_{el}}). \quad (2.12)$$

Unfortunately, this wave function does not fulfill the basic requirements for an electronic wave function, i.e., it is not antisymmetric with respect to the exchange of two particles (which are indistinguishable). Additionally, the electron spin has to be taken into account, leading to the definition of a spin-orbital

$$\phi_i(\mathbf{x}) = \phi_i(\mathbf{r})\sigma_i(\omega) \quad (2.13)$$

where $\phi_i(\mathbf{r})$ represents the spatial part of the spin-orbital, that depends only on the electron's spatial coordinates, whereas $\sigma_i(\omega)$ stands for the spin function¹. In order to simplify the calculation, the spin-orbitals are taken to be orthonormal, $\langle \phi_i | \phi_j \rangle = \delta_{ij}$.

We are now able to construct a wave function, ψ^{SD} , that describes the electron distribution

$$\psi^{\text{SD}} = \begin{vmatrix} \phi_1(\mathbf{x}_1) & \phi_2(\mathbf{x}_1) & \dots & \phi_{N_{el}}(\mathbf{x}_1) \\ \phi_1(\mathbf{x}_2) & \phi_2(\mathbf{x}_2) & \dots & \phi_{N_{el}}(\mathbf{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1(\mathbf{x}_{N_{el}}) & \phi_2(\mathbf{x}_{N_{el}}) & \dots & \phi_{N_{el}}(\mathbf{x}_{N_{el}}) \end{vmatrix} \quad (2.14)$$

This is the so-called Slater determinant, which fulfills the conditions of antisymmetry and indistinguishability of the electrons. We restricted ourselves to closed-shell systems, i.e. systems with even number of electrons, which are paired.

Basis Sets

So far, it has been assumed that the spin-orbitals are orthonormal. Since we are not interested in relativistic effects, the Hamiltonian does not depend on the spin, so the spin functions $\sigma_i(\omega)$ do not have to be explicitly defined. They have just been introduced in order to obtain a correct expression for the electronic wave function.

Concerning the spatial part of the spin-orbitals, the most natural choice would be a Slater function

$$\phi_i^s(\zeta_s, \mathbf{r}_i, \mathbf{R}_I) = \left(\frac{\zeta_s^3}{\pi} \right)^{\frac{1}{2}} e^{-\zeta_s |\mathbf{r}_i - \mathbf{R}_I|} \quad (2.15)$$

¹The spin space is spanned by two orthonormal functions σ_α and σ_β that correspond to spin-up and spin-down, respectively.

since it represents an exact solution to the electronic problem of the hydrogen atom in the ground state. The square of the above expression describes the distribution of the i^{th} electron around the I^{th} nucleus, which depends on the *Slater orbital exponent*, ζ_s . However, it turns out that Slater functions are not suitable for further calculations due to the complexity of the evaluation of the integrals they enter. Therefore, they are (e.g., within the *Gaussian* program package [37]) substituted with Gaussian functions

$$\phi_i^G(\zeta_g, \mathbf{r}_i, \mathbf{R}_I) = \left(\frac{2\zeta_g}{\pi}\right)^{\frac{3}{4}} e^{-\zeta_g|\mathbf{r}_i-\mathbf{R}_I|^2}. \quad (2.16)$$

Here, ζ_g is a *Gaussian orbital exponent*. Those functions are also centered at the nuclei and are denoted as *primitive gaussian functions* or 'primitives'. The last equation describes an s-type function. A more general expression

$$\phi_i^G(\zeta_g, \mathbf{r}_i, \mathbf{R}_I) = k_i x^a y^b z^c e^{-\zeta_g|\mathbf{r}_i-\mathbf{R}_I|^2} \quad (2.17)$$

accounts for orbitals with higher values of orbital quantum number, $l = a + b + c$. In order to give the system more flexibility, we define linear combinations of primitive functions, *contracted gaussian functions*,

$$\phi_\mu^{\text{CG}} = \sum_{i=1}^l d_{i\mu} \phi_i^G. \quad (2.18)$$

Actual molecular orbitals $\phi_i(\mathbf{r}_i)$ are linear combinations of contracted gaussian functions.

Fock Equations

Having built the electronic wave function, we turn back to the problem of the electronic stationary Schrödinger equation. Using the normalized wave function in a form of a Slater determinant, Eq. 2.14, the stationary Schrödinger equation is solved by applying the variational principle which states that for the electronic ground state

$$\langle \psi_{el} | \hat{H}_{el} | \psi_{el} \rangle \geq E_{exact}. \quad (2.19)$$

Since, according to the variational theorem, the calculated energy is always greater or equal to the exact one (the equality holds in case ψ_{el} is identical to the exact wave function) the search for the solution of the electronic problem is performed by minimizing the calculated energy. The wave function depends on a set of coefficients, which are optimized in order to give the lowest energy. This procedure leads to the set of Hartree-Fock equations

$$\hat{F}_i(\mathbf{x})\phi_i(\mathbf{x}) = \epsilon_i\phi_i(\mathbf{x}). \quad (2.20)$$

ϵ_i is the energy corresponding to the spin-orbital ϕ_i , and \hat{F}_i is the Fock operator $\hat{F}_i(\mathbf{x}) = h_i(\mathbf{x}) + \sum_{j=1}^{N_{el}/2} (2\hat{J}_j(\mathbf{x}) - \hat{K}_j(\mathbf{x}))$. It is a one-electron operator, consisting of three terms:

$$h_i(\mathbf{x}) = \hat{T}_i(\mathbf{x}) - \sum_{I=1}^{N_{nuc}} \frac{e^2 Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} \quad (2.21)$$

is a single electron Hamiltonian containing the kinetic energy of the electrons, as well as Coulomb interaction with the (fixed) nuclei. The last two terms are two-electron operators that is the Coulomb operator

$$\hat{J}_j(\mathbf{x}_1)\phi_i(\mathbf{x}_1) = \phi_i(\mathbf{x}_1) \int dx_2 \frac{\phi_j^*(\mathbf{x}_2)\phi_j(\mathbf{x}_2)}{r_{12}} \quad (2.22)$$

and the exchange operator

$$\hat{K}_j(\mathbf{x}_1)\phi_i(\mathbf{x}_1) = \phi_j(\mathbf{x}_1) \int dx_2 \frac{\phi_j^*(\mathbf{x}_2)\phi_i(\mathbf{x}_2)}{r_{12}}. \quad (2.23)$$

The Coulomb operator actually represents Coulomb interactions between electrons that occupy orbitals ϕ_i and ϕ_j , whereas the exchange operator has no classical analogue. It vanishes for electrons with opposite spins (due to the orthonormality of the spin functions) and is a consequence of the requirement that the wave function must be antisymmetric.

Hartree-Fock equations are nonlinear equations, since the Fock operator depends on its own eigenfunctions. Therefore, the equations are solved in a self-consistent way: starting with the trial functions, the eigenvalue problem is solved. The obtained single particle functions are used for the construction of the new Fock operator, etc. This procedure is repeated until the difference between two sets of functions obtained in two subsequent steps is negligible. The number of iterations depends on the quality of the initial guess. Finally, taking "the best" single particle functions, the energy is calculated according to

$$E_{el} = 2 \sum_{i=1}^{N_{el}/2} \langle \phi_i | \hat{h}_i | \phi_i \rangle + \sum_{i,j}^{N_{el}/2} (2J_{ij} - K_{ij}). \quad (2.24)$$

J_{ij} and K_{ij} are matrix elements of the Coulomb and the exchange operator, respectively.

In practice, the spin-orbitals are expanded in a certain fixed basis set (see Eq. 2.18) and the expansion coefficients are variationally optimized.

2.1.2 Density Functional Theory

Beyond the Hartree-Fock Method

At the beginning of this chapter, it was noted that the electronic problem consists of solving the time independent Schrödinger equation. Nevertheless, it turned out

that an analytical solution was not attainable for systems containing more than one electron due to the presence of the electron - electron interaction. The electronic wave function $\psi_{el}(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_{N_{el}})$ is a function of $3N_{el}$ spatial and N_{el} spin coordinates. Within the simplest approach, the Hartree-Fock method, the exact wave function was approximated by a Slater Determinant, Eq. 2.14. This method is computationally preferable, but the results are not satisfactory since the mutual interaction between each two electrons is not adequately modelled. The antisymmetric form of the Slater determinant disables two electrons with the same spin to have identical spatial coordinates, which means that the motion of electrons with the same spin is correlated. However, wave functions corresponding to electrons with the opposite spin are allowed to overlap, thereby increasing the calculated energy.

A step forward represent the correlation methods, that approximate the wave function by a linear combination of Slater determinants

$$\psi_{el} = \sum_m c_m \psi_m^{\text{SD}}. \quad (2.25)$$

The wave function is then variationally optimized. This approach improves the quality of the wave function at the price of a drastic increase of the numerical effort.

Another possibility is to turn to perturbative methods. They rest on the partition of the Hamiltonian into a part than can be solved exactly, H_0 ($H_0 \psi_n^0 = E_n^0 \psi_n^0$), and a part that is treated as a perturbation, V , i.e. $H = H_0 + \lambda V$. Thus, the eigenfunctions and the eigenvalues of the total Hamiltonian are given as perturbative expansions

$$\psi_n = \sum_{i=0}^{\infty} \lambda^i \psi_n^{(i)} \quad E_n = \sum_{i=0}^{\infty} \lambda^i E_n^{(i)} \quad (2.26)$$

where the higher order terms are expressed as functions of the zero order terms, ψ_n^0 and E_n^0 . The complexity of those functions increases with increasing the order of expansion, which leads to a high computational cost.

Electron Energy as a Functional of the Electron Density

A search for an economical procedure that would give reliable results led to the Density Functional Theory (DFT). The key DFT quantity that takes the role of the wave function (that is, is able to determine molecular properties) is the electron density $\rho_{el}(x, y, z)$, which depends on the coordinates of the real space. It represents the probability of an electron to be present at a given point, i.e. for the whole space we have

$$\int d\mathbf{r} \rho_{el}(\mathbf{r}) = N_{el}. \quad (2.27)$$

To start with, the electron energy is written as a functional² of the total electron density [36]

$$E_{el}^{\text{DFT}}[\rho_{el}(\mathbf{r})] = T_{el}[\rho_{el}(\mathbf{r})] + V_{el-nuc}[\rho_{el}(\mathbf{r})] + V_{el-el}[\rho_{el}(\mathbf{r})] + V_{xc}[\rho_{el}(\mathbf{r})]. \quad (2.28)$$

The first obstacle is to relate the kinetic energy \hat{T}_{el} to the electron density. Since a simple relationship could not be found, it has been proposed to introduce molecular orbitals, the so - called *Kohn - Sham orbitals*, that form the required electron density

$$\rho_{el}(\mathbf{r}) = \sum_{i=1}^{N_{el}} |\psi_i^{\text{KS}}(\mathbf{r})|^2 \quad (2.29)$$

which leads to the following expression for the expectation value of the kinetic energy

$$T_{el} = \sum_{i=1}^{N_{el}} \int d\mathbf{r} \psi_i^{\text{KS}}(\mathbf{r}) \left(-\frac{1}{2m_e} \Delta_i \right) \psi_i^{\text{KS}}(\mathbf{r}) \quad (2.30)$$

Kohn - Sham orbitals resemble the Hartree - Fock counterpart, a Slater determinant. They represent a reference system of *non-interacting* particles. Although the picture is unphysical, it was necessary to introduce this approximation in order to determine T_{el} . The accuracy of the calculated kinetic energy term depends on the quality of the electron density and corresponding molecular orbitals. Even if the electron density were identical to the exact one, the kinetic energy as given by Eq. 2.30 represents an approximation, since we are dealing with the imaginary non-interacting reference system. Additionally, the Kohn - Sham orbitals are not uniquely defined. Nevertheless, the difference between the exact and the true kinetic term is supposed to be small and included into V_{xc} .

The second and the third term on the right - hand side of Eq. 2.28 are classical Coulomb electron - nuclear and electron - electron interaction, respectively

$$V_{el-nuc} = - \sum_{I=1}^{N_{nuc}} \int d\mathbf{r} \frac{Z_I \rho_{el}(\mathbf{r})}{|\mathbf{r} - \mathbf{R}_I|} \quad (2.31)$$

$$V_{el-el} = \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{\rho_{el}(\mathbf{r}) \rho_{el}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \quad (2.32)$$

The last term, the exchange - correlation energy V_{xc} , takes into account the exchange and the correlation energy, but also includes the *self interaction correction* that arises from the interaction of each electron with itself, Eq. 2.32. The exchange - correlation functional is defined as $\mathcal{V}_{xc}(r) = \delta V_{xc}[\rho(r)] / \delta \rho(r)$. It is often divided into an exchange and a correlation part, $\mathcal{V}_{xc}(\rho_{el}) = \mathcal{V}_x(\rho_{el}) + \mathcal{V}_c(\rho_{el})$. The former term correlates motion of electrons with the same, and the later with the opposite spin. There are different types of exchange - correlation functionals:

²A functional is a function of a function. Electron energy is a function of the electron density, while the electron density is a function of the real space coordinates.

- *Local Density Approximation* functionals depend solely on the value of the electron density at a certain point (and are, therefore, named as *local*), and not on its behavior around it.
- *Local Spin Density Approximation* functionals in addition take into account the spin density.
- *Gradient Corrected* functionals are functions of both the electron density and its gradient.
- *Hybrid* exchange functionals combine the Hartree - Fock (\mathcal{V}_x^{HF}) with the Gradient Corrected (\mathcal{V}_x^{GC}) functional, $\mathcal{V}_x^{hybrid} = \lambda\mathcal{V}_x^{HF} + (\lambda - 1)\mathcal{V}_x^{GC}$. Practice proved their good performance.

It is also common to combine different exchange and correlation functionals. One of the most popular is **B3LYP** (it is composed of Becke's 1988 exchange functional [38] and Lee-Yang-Parr correlation functional [39]).

Having defined the exchange correlation functional, we proceed by optimizing the electron density. According to the Hohenberg - Kohn variational theorem [40], the ground state DFT electron energy is higher than or equal to the true energy. The equality holds if the electron density corresponds to the exact one.

Optimization of the electron density is replaced by actual optimization of the Kohn - Sham molecular orbitals. This procedure leads to a set of Kohn - Sham equations

$$\left[-\frac{1}{2m_e}\Delta_i - \sum_{I=1}^{N_{nuc}} \frac{Z_I}{|\mathbf{r} - \mathbf{R}_I|} + \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \mathcal{V}_{xc}(\mathbf{r}) \right] \psi_i^{KS}(\mathbf{r}) = \epsilon_i^{KS} \psi_i^{KS}(\mathbf{r}) \quad (2.33)$$

that resemble the Fock equations within the Hartree - Fock procedure. Further, the molecular orbitals are expanded in a certain basis set. Since the integrals in 2.33 are calculated numerically, the accuracy of the results depends on the quality of the grid defined around the molecule.

The overall approach resembles the Hartree Fock theory, with the advantage that the exchange - correlation term V_{xc} accounts for correlation of motion of electrons with the opposite spin as well. In addition, the Kohn - Sham potential is local, contrary to the Hartree - Fock procedure where the non - local character of the effective potential arises from the presence of the exchange integral (detailed discussion can be found in [36]).

The quantum chemistry calculations carried out in this work have been performed using the Gaussian 98 program package [37]. In order to obtain reliable results with moderate computational effort, we have applied Density Functional Theory with the B3LYP exchange-correlation functional in combination with the

6-31+G(d,p) basis set. The diffuse and the polarization functions should provide the system enough flexibility for a proper description of the hydrogen bond. This has been demonstrated, for instance, in the work of Tautermann et al. [41] who computed energies for the proton transfer in malonaldehyde and showed that the results obtained with B3LYP/6-31+G(d) and CCSD(T)/aug-cc-pVDZ are comparable. That is, the B3LYP functional and a small basis set give as plausible results as more sophisticated methods, like CCSD(T), with a larger basis set. Further, the calculation of the electronic energy barrier for the double proton transfer in the formic acid dimer [42] showed that the combination B3LYP/6-311G(2d,2p) gives a barrier which is too low. Apparently, the B3LYP functional with a smaller basis set gives reliable results most likely due to a cancellation of errors.

2.2 Anharmonicity

In the early days of quantum dynamics, scientists used simple models like the harmonic oscillator, for example, to describe vibrational motion. However, this is an oversimplification, since fully harmonic systems cannot be found in nature, although often this is a reasonable approximation. Confirmation of anharmonicity in spectroscopy are mode couplings that give rise to combination and overtone transitions, accompanied by red/blue shifts of "harmonically allowed" free vibrations. Moreover, the later bands might become broader and get a substructure. In the language of molecular dynamics, various couplings may lead to intramolecular vibrational redistribution, dissociative processes, etc. As has been emphasized in the Introduction, IR spectra of hydrogen bonded systems verify that their potential is strongly anharmonic. Hence, for an investigation of such systems anharmonicity must be accounted for.

Our aim is to describe the dynamics of molecules that contain intramolecular hydrogen bonds. In general, the Hamiltonian 2.11 that governs nuclear motion contains the kinetic energy of the nuclei, as well as the potential they are moving in. In the case of an N -atomic system, the potential depends on $3N$ nuclear coordinates. Three of them describe translation of the molecule as a whole, while another three (two for linear molecules) characterize rotational motion. This means that the potential hypersurface is a function of $3N-6$ ($3N-5$ in the linear case) nuclear coordinates. Therefore, the total potential energy surface can be obtained only for very small systems, due to the high computational costs. In order to study the properties of polyatomic molecules, one has to incorporate different approximations for setting up the Hamiltonian, which depend on the phenomenon to be obtained. In this work, two types of processes will be considered - namely those that take place in the vicinity of the equilibrium, section 2.2.1 (Anharmonic Force Field method),

and those that require to account large amplitude motions, section 2.2.2 (Cartesian Reaction Surface method).

Choice of Coordinates

In principle, each set of coordinates that includes all degrees of freedom and does not contain redundant coordinates can be used. However, there are some properties that can be (un)desirable.

Cartesian coordinates seem to be appropriate, since each of them corresponds to a motion of a certain atom in a particular direction. Another advantage is that all couplings are part of the potential energy operator, which are much easier to deal with than those in the kinetic energy. However, for an N - atomic system, there are $3N$ cartesian coordinates, while a nonlinear molecule has $3N-6$ internal degrees of freedom. This means that 6 coordinates are redundant. In addition, molecular vibrations do not usually take place along straight lines, which means that the coupling elements in the potential might become larger than those including a single mode, and also more such couplings would occur. In other words, more anharmonic terms should be included. Also, since numerical wave packet propagation with a big number of parameters is difficult, some relatively important terms would have to be neglected.

Internal coordinates comprise bond lengths and bond angles. They can be easily connected with molecular vibrations and also the coupling terms are usually not larger than those including just one mode. The couplings in the potential energy part are in most cases small, thereby leading to better separation of nuclear motion for large displacements. The drawback of using internal coordinates lies in the fact that curvilinear motion introduces strong couplings in the kinetic energy operator, which can have a rather complicated form for larger systems.

Normal mode coordinates are obtained by a linear combination of cartesian coordinates. Thus, there are no couplings in the kinetic part, i.e. they diagonalize the kinetic energy as well the quadratic part of the potential energy operator. They include simultaneous motion of all atoms during the vibration, which leads to a natural description of molecular vibrations. Therefore, they are good candidates for representation of the molecular Hamiltonian.

Since a transformation between different sets of coordinates is possible, the anharmonic terms can be calculated in one representation, and then transformed into another one. However, the difficulty arises from the fact that by using a representation in internal coordinates, the vibrational motion cannot be completely separated from the rotational motion, which results in an effective *Watson* Hamiltonian [43]. Because of the simple form of the kinetic energy operator and the fact that

an analogy can be drawn between them and molecular vibrations that can be experimentally observed, we have used normal mode coordinates in this thesis.

The reference configuration for the normal mode coordinates \mathbf{Q} is usually chosen to be the structure corresponding to the global minimum of the potential energy surface. At this point, the Hessian matrix (i.e., the matrix of partial second derivatives of the potential)

$$\mathbf{K}_{\text{ref}} = \left. \frac{\partial^2 V}{\partial \mathbf{R} \partial \mathbf{R}} \right|_{\mathbf{R}=\mathbf{R}_{\text{ref}}} \quad (2.34)$$

is diagonalized and its eigenvectors are used for transformation from cartesian to normal mode coordinates at each point of the PES

$$\mathbf{R} - \mathbf{R}_{\text{ref}} = \mathbf{m}^{-1/2} \mathbf{U} \mathbf{Q} \quad (2.35)$$

where \mathbf{R} stands for the cartesian coordinates and \mathbf{R}_{ref} are cartesian coordinates at the reference configuration, while \mathbf{m} and \mathbf{U} represent the mass and the transformation matrix. If not emphasized otherwise, it is assumed that the normal mode coordinates are mass - weighted, as in the above formula. Also, **dimensionless normal modes** $\tilde{\mathbf{Q}}$ are often used. They are connected to normal modes \mathbf{Q} (with dimensions bohr (a.m.u.)^{1/2}) via relation

$$\tilde{Q}_i = \gamma_i^{1/2} Q_i \quad (2.36)$$

with $\gamma_i = \lambda_i^{1/2} / \hbar$. λ_i is an eigenvalue of the Hessian at the reference configuration.

Form of the Potential Energy Operator

Having chosen the normal mode representation, we proceed by defining the potential energy operator. Consider a model that includes, for example, four degrees of freedom (in our case four normal modes), $\mathbf{Q} = \{Q_1, Q_2, Q_3, Q_4\}$. For the potential energy surface³ the following form has been proven to be useful (see, e.g., [44])

$$V(\mathbf{Q}) = V^{(1)} + V^{(2)} + V^{(3)} + V^{(4)}. \quad (2.37)$$

The uncoupled motion of each mode is accounted for by the one-dimensional potentials

$$V^{(1)} = \sum_i V(Q_i). \quad (2.38)$$

Couplings between pairs of modes are contained in the two-mode potential

$$V^{(2)} = \sum_{i < j} V(Q_i, Q_j). \quad (2.39)$$

³A "hat" label of the operators corresponding to the potential energy will be omitted in the following.

Three-mode couplings are represented by

$$V^{(3)} = \sum_{i < j < k} V(Q_i, Q_j, Q_k), \quad (2.40)$$

and four-mode couplings by

$$V^{(4)} = V(Q_1, Q_2, Q_3, Q_4). \quad (2.41)$$

Eq. 2.37 represents a full - dimensional potential. Naturally, one would try to obtain an explicit potential on a grid. 1D and 2D potentials are routinely obtainable. However, already calculation of $V^{(3)}$ is computationally too demanding. For the above model, by taking 10 grid points per mode, calculation of three 3D potentials would require 3000 single point energy calculations, which is for large systems and sophisticated quantum chemistry calculations quite ambitious. This prompted a quest for approximate methods, two of which will be described in the remainder of this chapter.

2.2.1 Anharmonic Force Field Approach

In order to describe small changes of nuclear degrees of freedom, it is sufficient to restrict investigations to the vicinity of an equilibrium configuration of the PES. In such situations, the potential can be expanded into Taylor series around an equilibrium point, $\mathbf{Q}^{(0)}$, according to

$$\begin{aligned} V(\mathbf{Q}) = & V(\mathbf{Q}^{(0)}) + \sum_{i=1}^N \left. \frac{\partial V}{\partial Q_i} \right|_{\mathbf{Q}=\mathbf{Q}^{(0)}} (Q_i - Q_i^{(0)}) + \\ & \frac{1}{2!} \sum_{i,j=1}^N \left. \frac{\partial^2 V}{\partial Q_i \partial Q_j} \right|_{\mathbf{Q}=\mathbf{Q}^{(0)}} (Q_i - Q_i^{(0)})(Q_j - Q_j^{(0)}) + \\ & \frac{1}{3!} \sum_{i,j,k=1}^N \left. \frac{\partial^3 V}{\partial Q_i \partial Q_j \partial Q_k} \right|_{\mathbf{Q}=\mathbf{Q}^{(0)}} (Q_i - Q_i^{(0)})(Q_j - Q_j^{(0)})(Q_k - Q_k^{(0)}) + \\ & \dots \end{aligned} \quad (2.42)$$

where \mathbf{Q} comprises all degrees of freedom. Since the expansion is performed around a stationary point, the first derivative is equal to zero. In principle, the expansion given by Eq. 2.42 contains an infinite number of terms. Nevertheless, each subsequent term can be expected to give smaller contribution. The convergence is usually fast, so it is often sufficient to include the elements up to the quartic term. Thus, for setting up the potential energy operator, it is necessary to provide not just the harmonic part, i.e. $V(\mathbf{Q}^{(0)})$ and $\partial^2 V / \partial Q_i \partial Q_j$, but also the anharmonic contributions. This procedure is called **anharmonic force field approach**, with

anharmonic force fields being identified as higher order derivatives of the potential (cubic, quartic, quintic, etc).

The first and the second derivative of the potential energy can be calculated analytically by most program packages, like *Gaussian* [37]. The third derivative can also be determined with lower levels of theory. For large molecules, this would require a large amount of computational time. A compromise is found in analytical calculation of second derivatives, which are then used for numerical computation of higher order derivatives. For example, with the collocation polynomials, derivatives up to the 6th order have been obtained for H₂O by Császár and Mills [45]. This method rests on a search for an expression of a function to be differentiated as a polynomial, and its subsequent differentiation. Suppose the function f is known at collocation points x_0, \dots, x_n and is approximated with the following interpolating polynomial [46]

$$f(x) \approx P_n(x) \quad (2.43)$$

The first derivative at point x_k can be estimated from

$$f'(x_k) \approx \left(\frac{d}{dx} P_n(x_k) \right) \quad (2.44)$$

However, the interpolating polynomials might have rather complicated form. Therefore, for a computation of the first two anharmonic terms, a finite difference approach seems to be more suitable. The simplest version of this procedure would require calculations of the second derivatives for displaced geometries along a single coordinate, Q_k ,

$$\frac{\partial^3 V}{\partial Q_i \partial Q_j \partial Q_k} = k_{ijk} = \frac{k_{ij}^+ - k_{ij}^-}{2\Delta Q_k} + O(V^{(v)}) \quad (2.45)$$

$$\frac{\partial^4 V}{\partial Q_i \partial Q_j \partial Q_k \partial Q_k} = k_{ijkk} = \frac{k_{ij}^+ + k_{ij}^- - 2k_{ij}}{(\Delta Q_k)^2} + O(V^{(vi)}). \quad (2.46)$$

k_{ij} is the second derivative at the reference point, while k_{ij}^+ and k_{ij}^- correspond to the displaced geometries along mode Q_k in the positive and negative direction respectively (cf. Fig. 2.1). O stands for the order of errors, i.e., Eq. 2.45 and 2.46 contain errors of the third and fourth order with respect to k_{ij} (which means that they are proportional to the fifth $V^{(v)}$ and sixth $V^{(vi)}$ derivative of the potential).

Schneider and Thiel [47] have applied this method for calculation of anharmonic force fields in CH₃Br. Also, Breidung et al. [48] have used the same approach for HOF and F₂O. In both cases, the calculations are in a good agreement with the experimental values.

However, the derivatives can be calculated with lower truncation error: A more accurate calculation involves additional double displacements

$$k_{ijk} = \frac{-k_{ij}^{+2} + 8k_{ij}^+ - 8k_{ij}^- + k_{ij}^{-2}}{12\Delta Q_k} + O(V^{(vii)}) \quad (2.47)$$

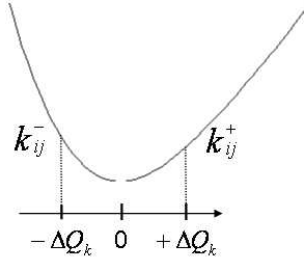


Figure 2.1: One dimensional cut of the PES along mode Q_k . The second derivatives for positive and negative displacements with respect to this mode are computed, which enables calculation of the third and fourth derivatives, k_{ijk} and k_{ijkk} , according to Eq. 2.45 and 2.46.

$$k_{ijkk} = \frac{-k_{ij}^{+2} + 16k_{ij}^+ - 30k_{ij} + 16k_{ij}^- - k_{ij}^{-2}}{12(\Delta Q_k)^2} + O(V^{(viii)}) \quad (2.48)$$

Thus, the results are more accurate, at the price of higher numerical effort. Equation 2.48 enables calculations of quartic derivatives with three different indices. In order to obtain anharmonic terms with four different indices, displacements along two modes have to be performed, as given by the following formulas

$$k_{ijkl} = \frac{k_{ij}^{++} - k_{ij}^{+0} - k_{ij}^{0+} + k_{ij}^{--} - k_{ij}^{-0} - k_{ij}^{0-} + 2k_{ij}}{2\Delta Q_k \Delta Q_l} + O(V^{(vi)}) \quad (2.49)$$

$$k_{ijkl} = \frac{k_{ij}^{++} + k_{ij}^{--} - k_{ij}^{+-} + k_{ij}^{-+}}{4\Delta Q_k \Delta Q_l} + O(V^{(iv)}) \quad (2.50)$$

with the first superscript of the second derivatives corresponding to the displacement along mode Q_k and the second along Q_l . The advantage of the second formula is that it possesses correct symmetry properties [49] : the second derivatives have been calculated symmetrically with respect to the point at which the quartic term is searched for. The former formula lacks displacements along different modes with different signs (+-, -+), while in the latter case all parts of the potential energy surface are treated democratically.

Let us see how those force fields are connected with the spectroscopically observed anharmonicity. The Hamiltonian and the energy levels of a one - dimensional harmonic oscillator are given by [50]

$$H_v^h = -\frac{\hbar^2}{2} \frac{\partial^2}{\partial Q^2} + \frac{1}{2} \frac{\partial^2 V}{\partial Q^2} \Big|_{Q=Q_{eq}} Q^2 \quad (2.51)$$

$$\frac{E_v^h}{hc} = \tilde{\omega} \left(n + \frac{1}{2} \right) \quad (2.52)$$

with the wavenumber $\tilde{\omega} = \nu/c$. The energy levels are equally spaced. Proceeding to an anharmonic potential, which means the one expressed by Eq. 2.42 (in this

case there is only one degree of freedom), presence of anharmonic terms leads to a more complex expression for the energy

$$\frac{E_v^{anh}}{hc} = \tilde{\omega}(n + \frac{1}{2}) + x(n + \frac{1}{2})^2 + y(n + \frac{1}{2})^3 + \dots \quad (2.53)$$

This equation is known as *Dunham expansion* [51]. It is obtained with a perturbative approach, with the anharmonic terms playing the role of the perturbation. The relationship between the anharmonic term x and derivatives of the potential is given by

$$x = -\frac{5}{48\tilde{\omega}} \frac{\partial^3 V}{\partial Q^3} + \frac{1}{16} \frac{\partial^4 V}{\partial Q^4} \quad (2.54)$$

Thus, it can be expressed via cubic and quartic anharmonicities. Similar relationships exist for higher order terms although they are more complicated and less significant, since each subsequent expansion coefficient is about two orders of magnitude smaller than the previous one [49].

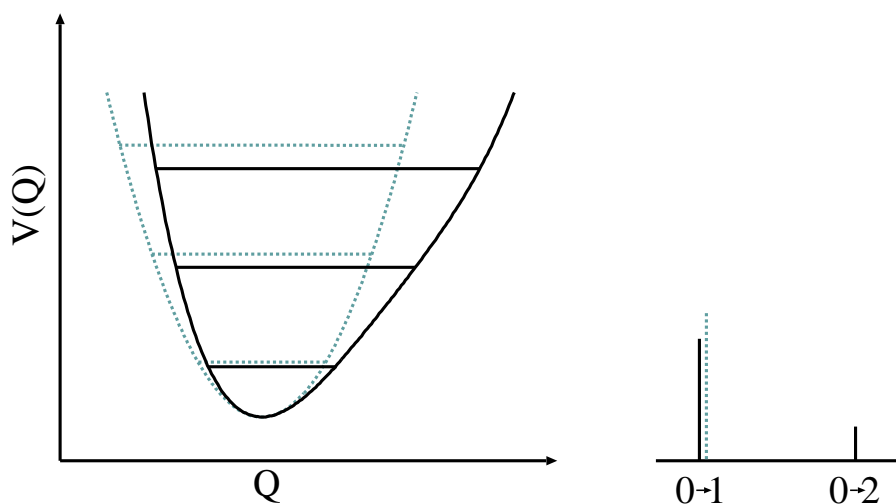


Figure 2.2: Left: Comparison of the harmonic (dotted) and anharmonic (solid) potential energy curve. Right: IR stick spectra for the corresponding systems.

The difference between a harmonic and an anharmonic potential is displayed in Figure 2.2. Anharmonic terms are responsible for the deviation of the anharmonic curve (solid line) with respect to the harmonic one (blue dotted line). Energy levels of the harmonic curve are equally spaced, whereas the spacing between the energy levels of the anharmonic curve decreases with the increase of the quantum number. This leads to the red shift of $0 \rightarrow 1$ transition, as depicted in the stick spectrum. Also, overtone transitions are forbidden in the harmonic picture (for a dipole moment linear in Q), whereas such transitions appear in the anharmonic system, although the intensity of the $0 \rightarrow 2$ line is much lower.

As already mentioned, this method may provide a good agreement with experimental results for small molecules. However, this requires a high level of theory

and a huge basis set (for F₂O, CCSD(T)/cc-pVTZ [48]). With increasing the size of the molecule, the number of anharmonic terms drastically increases, which makes it hard to accomplish both their experimental determination and theoretical calculation.

The Dunham expansion can be generalized for a multidimensional system

$$\frac{E_v^{anh}}{hc} = \sum_{i=1} \tilde{\omega}_i \left(n_i + \frac{1}{2}\right) + \sum_{i \geq j=1} x_{ij} \left(n_i + \frac{1}{2}\right) \left(n_j + \frac{1}{2}\right) + \sum_{i \geq j \geq k=1} y_{ijk} \left(n_i + \frac{1}{2}\right) \left(n_j + \frac{1}{2}\right) \left(n_k + \frac{1}{2}\right) + \dots \quad (2.55)$$

Equations 2.42 and 2.55 contain all possible couplings, between different degrees of freedom. However, for moderate energies it is very seldom that many modes are strongly coupled [52]. Therefore, after the anharmonic force fields have been calculated, only the most important terms will be included in the "dynamical" calculations. This is, of course, an approximation, since some transitions are immediately ruled out.

The anharmonic expansion enables description of combination and overtone bands. Combination transitions include simultaneous excitation of different degrees of freedom, while an overtone transition corresponds to an excitation of a single mode, with the change of vibrational quantum number greater than one (cf. Fig 2.3). Exemplarily, let us take a closer look at the term $k_{ijk} Q_i Q_j Q_k$. It couples the three modes, Q_i , Q_j , and Q_k . If a certain transition is resonant, i.e. if for example the following condition is met

$$\nu_k \approx \nu_i + \nu_j \quad (2.56)$$

this interaction can be studied by examining the IR spectrum. The harmonically forbidden combination band (assuming there is no electrical anharmonicity) centered at $\nu_i + \nu_j$ will appear and will be influenced by the excitation of the Q_k mode. The interaction will lead to a separation between those two peaks, i.e. they will not appear exactly at ν_k and $\nu_i + \nu_j$, but will be slightly shifted. In addition, it will also affect the intensities, since the coupling may lead to oscillator strength borrowing, thus allowing observation of a combination transition. Concerning the dynamics, this term facilitates energy transfer between those three modes. For example, in hydrogen bonded systems that contain an OH bond, the first overtone of the OH bending mode is often close in energy to the OH stretching fundamental transition, Fig. 2.3. Interaction between those vibrations, known as *Fermi resonance*, is described by $k_{bbs} Q_b^2 Q_s$ that couples the stretching and the bending mode (this is a special case of the previous, more general expression, with $i = j$).

Another well known resonance type is the *Darling - Dennison resonance* [51], which describes coupling between two overtone transitions $k_{iijj} Q_i^2 Q_j^2$. The quartic

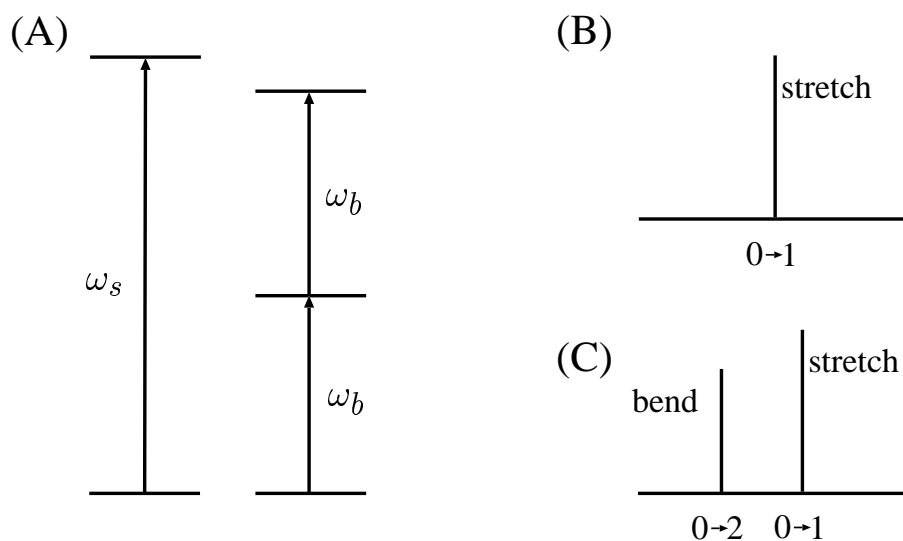


Figure 2.3: (A) Energy levels corresponding to the stretching and bending vibrations. (B) Stick spectrum - fundamental transition of the stretching vibration in the harmonic picture. (C) Stick spectrum for the anharmonic potential energy surface; left line, overtone of the bending vibration, arises as a consequence of anharmonicity. Due to its coupling to the stretching vibration, the later undergoes a blue shift.

force constants usually have much smaller values than the cubic ones, so the former peaks are characterized by a lower intensity. Higher order terms (quintic, etc) usually have negligible importance.

During the discussion so far, the rotation of the molecule as a whole was not considered. Inclusion of ro-vibrational coupling would further complicate all previous expressions. Nevertheless, larger molecules have high moments of inertia, so rotations take place on a much longer time scale than vibrational motion. This means that rotations are very weakly coupled to vibrations and can be safely neglected for ultrafast condensed phase studies.

It has been shown how mechanical anharmonicity can be handled. The same procedure can be used also for the electrical anharmonicity. Starting from the expansion of the dipole moment

$$\begin{aligned} \mu_l(\mathbf{Q}) = & \mu_l(\mathbf{Q}^{(0)}) + \sum_{i=1}^N \left. \frac{\partial \mu_l}{\partial Q_i} \right|_{\mathbf{Q}=\mathbf{Q}^0} (Q_i - Q_i^0) + \\ & \frac{1}{2!} \sum_{i,j=1}^N \left. \frac{\partial^2 \mu_l}{\partial Q_i \partial Q_j} \right|_{\mathbf{Q}=\mathbf{Q}^0} (Q_i - Q_i^0)(Q_j - Q_j^0) + \dots \quad (2.57) \end{aligned}$$

the first and the second derivative can be calculated numerically. In Eq 2.57, μ_l describes the three components of the dipole moment (μ_x , μ_y and μ_z). The second derivative represents the anharmonic term.

The above method enables to explain the origin of the structure of IR spectra. Moreover, this approach allows us to model dynamical processes, like energy flow from the stretching towards the bending mode. Application of the present concepts is given in Chapters 3 and 4.

2.2.2 Cartesian Reaction Surface Approach

If one would like to describe processes that involve large amplitude motions of certain degrees of freedom, for example chemical reactions (photodissociation, hydrogen transfer reactions etc), it is necessary to provide a PES that covers a large region. This can be achieved in different ways, depending on the nature of the system. As has been indicated before, it is not feasible to obtain an exact potential for large systems in full dimensionality. In this section, an overview of a few approaches that deal with this problem will be given, while emphasis will be put on the Cartesian Reaction Surface method.

In general, depending on the *speed* of the investigated process, we distinguish two types of approximations to the reaction surfaces:

- * relaxed potential surface requires partial geometry optimization at each point. This means that the process takes place very slowly, so the whole system always has time to find a locally relaxed configuration. The drawback of this procedure is that it cannot be used for fast processes or for those which are characterized with strong anharmonic intramolecular couplings between more than, for instance, three coordinates. In other words, it is not very likely that the system always has enough time to relax completely. In addition, geometry optimization makes this method computationally demanding.
- * If the reaction takes place very fast, so that the "less important" coordinates have no time to relax, the so called frozen geometry can be employed. This means that after the global minimum has been found, the PES is obtained by scanning along the important degrees of freedom while keeping the rest of the molecule frozen at the equilibrium position. This method gives meaningful results in case the coupling between more and less important coordinates is negligible, at least on the time scale of the investigated process.

On the other hand, both methods can be supplemented by harmonic degrees of freedom for the less important modes to establish a full dimensional reaction surface, as will be discussed in the following.

A quantum chemical investigation starts with the optimization of the stationary points, i.e., the reactants, the products, and the transition state that connects

them. One can proceed by implementing the **reaction path method** [53] - [57], which rests on the fact that during the observed process the changes take place in a way that the system follows the *minimum energy path* which is constructed starting from the transition state and going backward/forward towards the reactants/products, tracing the steepest descent line. It employs geometry optimization, so this procedure is rather expensive. The Hessian is calculated at each point, which enables $3N-7$ normal mode vibrations orthogonal to the path to be taken into account⁴. The final picture is rather simple - it is easy to imagine a one dimensional course (influenced by other internal motions) leading the reaction in the desired direction. If there is only one atom that undergoes drastic changes, this picture is appropriate. Nevertheless, if more particles are strongly involved, the minimum energy path might make many sharp curves, while in reality it is more likely that the system would follow a smooth path, even if that would require slightly higher energy. Therefore, it is recommendable to include large amplitude motions of more degrees of freedom. This extension, known as **reaction surface method** [58]-[60], gives an improved description, owing to the incorporation of the anharmonic corrections whereby the kinetic couplings are on average not so strong. Here, one needs to compute the Hessian at each point in order to get the normal mode vibrations orthogonal to the "surface".

As a starting point, one has to decide which degrees of freedom (DOF) will be described exactly. This depends on a specific system. It is not likely that all DOF are equally important. For example, if a transfer of a light molecule, like hydrogen, takes place between two subgroups of a large molecule, probably only the vicinity of the reactive site will feel the changes, leaving the rest of the molecule unaffected. One possibility would be just to take into account the most important coordinates, usually one - to - three. How the other DOF will be treated depends on the properties of the system and the nature of the process. Concerning the reaction surface method, the other degrees of freedom can be included by calculating the Hessian and comprising the vibrations orthogonal to the surface, as has been mentioned above. The choice of coordinates has already been discussed at the beginning of this chapter. It was pointed out that although the internal coordinates give a natural description, the kinetic couplings might be rather high and difficult to deal with. On the contrary, a model described with cartesian and normal mode coordinates contains couplings in the potential energy part, which makes them good candidates for representing the model system.

⁴If the molecule contains N atoms, there are $3N$ degrees of freedom, 6 of which describe the translational and the rotational motion, as has already been emphasized. Since one degree of freedom is used to describe the motion along the minimum energy path, there are $3N-6-1$ modes that would be neglected if only the minimum energy path would be considered.

Cartesian Reaction Surface

The approach used in this work is the *Cartesian Reaction Surface* (CRS) method [61], which allows a full - dimensional treatment. After the geometry optimization has been performed and the coordinates have been divided into *reactive* \mathbf{r} and *harmonic* \mathbf{R} degrees of freedom, the former are allowed to undergo large amplitude motions and are treated exactly, whereas the later are assumed to stay close to the equilibrium values and are, therefore, described within the harmonic approximation⁵. In other words, for each value of the reaction coordinate, the potential is expanded into Taylor series and truncated at second order

$$V(\mathbf{r}, \mathbf{R}) = V(\mathbf{r}, \mathbf{R}^{(0)}(\mathbf{r})) + \left. \frac{\partial V}{\partial \mathbf{R}} \right|_{\mathbf{R}^{(0)}(\mathbf{r})} (\mathbf{R} - \mathbf{R}^{(0)}(\mathbf{r})) + \frac{1}{2} (\mathbf{R} - \mathbf{R}^{(0)}(\mathbf{r})) \left. \frac{\partial^2 V}{\partial \mathbf{R} \partial \mathbf{R}} \right|_{\mathbf{R}^{(0)}(\mathbf{r})} (\mathbf{R} - \mathbf{R}^{(0)}(\mathbf{r})). \quad (2.58)$$

This means that the first and the second derivative of the potential also have to be calculated at each point. Concerning the reference configuration of the substrate (the remaining degrees of freedom) $\mathbf{R}^{(0)}(\mathbf{r})$, two different cases can be distinguished:

1) If the harmonic coordinates do not undergo large changes throughout the reaction, the skeleton can be considered to perform harmonic motions with respect to a frozen reference, the configuration that corresponds, for instance, to the global minimum $\mathbf{R}^{(0)}(\mathbf{r}_{\text{eq}})$. The molecule PMME [62]-[65] (see also section 3) possesses a medium strong intramolecular hydrogen bond, and has a single minimum along the OH stretching coordinate. The hydrogen atom is hence in the ground electronic state restricted to small amplitude motions, which are not accompanied by drastic change of the molecular scaffold. This allowed the frozen substrate procedure.

2) If the potential energy surface contains a double minimum, like in weak to medium strong hydrogen bonds, the reactant and the product configuration differ considerably, and it is necessary to allow the harmonic modes to relax in a certain way along the whole reaction surface. This *partial optimization* can be done, for example, by optimizing the stationary points, and performing linear interpolation of the intermediate structures along the reaction path, Fig. 2.4. The rest of the reaction surface can be obtained by moving the reactive coordinates and prescribing the molecular scaffold a structure that corresponds to the closest point which lies on the reaction path [66]. Thereby, the configurations at the stationary points would correspond to the optimized ones.

We are interested solely in internal motions, thus the eigenvectors that corres-

⁵For N_r reactive degrees of freedom, there are $3N-6-N_r$ harmonic coordinates.

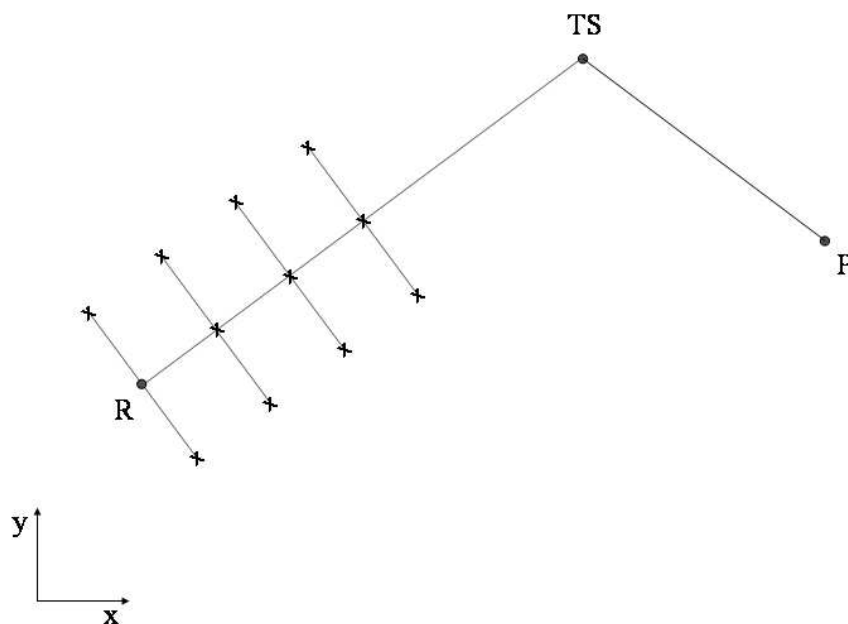


Figure 2.4: Generation of the PES by employing the flexible reference. This model contains two reactive coordinates $\mathbf{r} = \{x, y\}$. First, the stationary points are optimized (the reactant \mathbf{R} , the transition state \mathbf{TS} , and the product \mathbf{P}). Then the points along the path are obtained by changing the coordinates of the skeleton atoms linearly from \mathbf{R} to \mathbf{TS} and from \mathbf{TS} to \mathbf{P} . The rest of the surface is generated by taking the structure of the skeleton and displacing the reactive atom.

pond to infinitesimal rotations and translations are projected out [53]

$$(\mathbf{1} - \mathbf{\Pi})\mathbf{m}^{-1/2}\mathbf{K}_{eq}\mathbf{m}^{-1/2}(\mathbf{1} - \mathbf{\Pi}) \quad (2.59)$$

where \mathbf{K}_{eq} represents the Hessian matrix at the equilibrium configuration, i.e., the global minimum of the PES, which will be used as a reference configuration for the normal mode transformation. $\mathbf{\Pi}$ is the projector onto the rotational and translational degrees of freedom. An assumption is that the molecule does not rotate during the reaction, so the same projection matrix is used for the points on the whole grid. This requirement is fulfilled for processes involving light (reactive) atoms moving with respect to a large skeleton (harmonic). \mathbf{m} is a diagonal matrix, with diagonal elements corresponding to the atomic masses.

Since intramolecular motions do not take place rectilinearly, i.e., along the cartesian coordinates, it is customary to perform normal mode transformation for the substrate coordinates (cf. Eq. 2.35)

$$\mathbf{R} - \mathbf{R}^{(0)}(\mathbf{r}_{\text{ref}}) = \mathbf{m}^{-1/2}\mathbf{U}\mathbf{Q}. \quad (2.60)$$

$\mathbf{R}^{(0)}(\mathbf{r}_{\text{ref}})$ is the reference configuration and can be taken to be the structure at the

equilibrium. The transformation matrix \mathbf{U} diagonalizes the mass - weighted Hessian. Therefore, the following transformation is performed at each point

$$\mathbf{R} - \mathbf{R}^{(0)}(\mathbf{r}) = \mathbf{R}^{(0)}(\mathbf{r}_{\text{ref}}) - \mathbf{R}^{(0)}(\mathbf{r}) + \mathbf{m}^{-1/2}\mathbf{U}\mathbf{Q} \quad (2.61)$$

with $\mathbf{R}^{(0)}(\mathbf{r})$ being the "partially relaxed substrate", which depends on the reaction coordinate. This gives the following form of the potential

$$V(\mathbf{r}, \mathbf{Q}) = V(\mathbf{r}) - \mathbf{f}(\mathbf{r})\mathbf{Q} + \frac{1}{2}\mathbf{Q}\mathbf{K}(\mathbf{r})\mathbf{Q} \quad (2.62)$$

The quantities in the above equation arise straightforwardly from the normal mode transformation of Eq. 2.58

$$\begin{aligned} V(\mathbf{r}) = & V(\mathbf{r}, \mathbf{R}^{(0)}(\mathbf{r})) - \left. \frac{\partial V}{\partial \mathbf{R}} \right|_{\mathbf{R}^{(0)}(\mathbf{r})} [\mathbf{R}^{(0)}(\mathbf{r}) - \mathbf{R}^{(0)}(\mathbf{r}_{\text{ref}})] + \\ & \frac{1}{2}[\mathbf{R}^{(0)}(\mathbf{r}) - \mathbf{R}^{(0)}(\mathbf{r}_{\text{ref}})] \left. \frac{\partial^2 V}{\partial \mathbf{R} \partial \mathbf{R}} \right|_{\mathbf{R}^{(0)}(\mathbf{r})} [\mathbf{R}^{(0)}(\mathbf{r}) - \mathbf{R}^{(0)}(\mathbf{r}_{\text{ref}})], \end{aligned} \quad (2.63)$$

$$\mathbf{f}(\mathbf{r}) = \left\{ - \left. \frac{\partial V}{\partial \mathbf{R}} \right|_{\mathbf{R}^{(0)}(\mathbf{r})} + [\mathbf{R}^{(0)}(\mathbf{r}) - \mathbf{R}^{(0)}(\mathbf{r}_{\text{ref}})] \left. \frac{\partial^2 V}{\partial \mathbf{R} \partial \mathbf{R}} \right|_{\mathbf{R}^{(0)}(\mathbf{r})} \right\} \mathbf{m}^{-\frac{1}{2}}\mathbf{U}, \quad (2.64)$$

$$\mathbf{K}(\mathbf{r}) = \mathbf{U}^+ \mathbf{m}^{-\frac{1}{2}} \left. \frac{\partial^2 V}{\partial \mathbf{R} \partial \mathbf{R}} \right|_{\mathbf{R}^{(0)}(\mathbf{r})} \mathbf{m}^{-\frac{1}{2}}\mathbf{U}. \quad (2.65)$$

$V(\mathbf{r})$ contains the term coming from the normal mode transformation and represents the value of the potential energy for a given configuration of the substrate along the reaction coordinate. It is the effective potential felt by the reaction coordinates. The second term, $\mathbf{f}(\mathbf{r})$, represents a force acting on the normal modes, trying to push them back into a relaxed configuration for a given value of \mathbf{r} . The dependence of forces on reaction coordinates represents coupling between reactive and substrate degrees of freedom. Finally, $\mathbf{K}(\mathbf{r})$ is the Hessian in the normal mode coordinates. It has a diagonal form only at the equilibrium configuration, due to the fact that this is the point at which the normal mode transformation matrix has been defined. The coupling between different normal modes is given by off diagonal elements of the Hessian. Again, the coupling among reactive and harmonic coordinates is given by the fact that \mathbf{K} is a function of \mathbf{r} . Equations 2.63 - 2.65 are derived for the more general case - flexible reference. For the limiting case, of a frozen substrate, they get a simpler form by making use of the fact that $\mathbf{R}^{(0)}(\mathbf{r}) = \mathbf{R}^{(0)}(\mathbf{r}_{\text{ref}})$.

With this potential, the total Hamiltonian can be expressed as

$$H_{\text{CRS}} = [T_{\mathbf{r}} + V(\mathbf{r})] + \frac{1}{2} [\mathbf{P}^2 + \mathbf{Q}\mathbf{K}(\mathbf{r})\mathbf{Q}] - \mathbf{f}(\mathbf{r})\mathbf{Q} \quad (2.66)$$

Vector \mathbf{P} contains the momenta of the normal modes. The first bracket contains terms that govern the motion of the reactive DOF, whereas the second bracket describes the normal mode vibrations. Equation 2.66 has a form of a system (reactive coordinates) coupled to a bath (harmonic coordinates). The last two terms would correspond to the system - bath interaction. All couplings are contained in the potential energy operator. This is a big advantage, since it is often difficult to handle kinetic couplings, due to their complexity.

The difference between the energy at a certain point of the reaction surface and the *totally* relaxed configuration is given by the reorganization energy

$$E_{\text{reorg}}(\mathbf{r}) = \frac{1}{2} \mathbf{f}(\mathbf{r}) [\mathbf{K}(\mathbf{r})]^{-1} \mathbf{f}(\mathbf{r}) \quad (2.67)$$

As indicated above, subtraction of $E_{\text{reorg}}(\mathbf{r})$ from $V(\mathbf{r})$ would give the fully relaxed PES, provided the harmonic approximation is valid.

So far we have outlined a procedure for obtaining the Hamiltonian in full dimensionality. However, treating all DOF is for large systems not feasible. Also, not all modes couple strongly to the reaction coordinates. Hence, the next task is to identify modes that will be taken into account. A useful quantity for this purpose is the reorganization energy corresponding to a single mode, defined as

$$E_{\text{reorg},i}(\mathbf{r}) = \frac{[f_i(\mathbf{r})]^2}{2K_{ii}(\mathbf{r})} \quad (2.68)$$

This expression, comparing to Eq. 2.67 does not include the couplings among different modes. It tells us how much energy is required to shift the system along the i^{th} normal mode coordinate into the configuration relaxed along that mode. Large values for $E_{\text{reorg},i}$ indicate strong couplings with the reaction coordinate and imply that the corresponding mode should be taken into account. Modes that have small values for the reorganization energy do not change much during the course of a reaction, so their inclusion would just increase the computational time, but would not affect the final results.

CRS Method and Anharmonicity

As already described, the Cartesian Reaction Surface approach treats the reaction coordinates explicitly and the substrate coordinates within the harmonic approximation. Normal mode coordinates are defined at the equilibrium configuration. In order to account for the couplings, the forces and the Hessian are represented as functions of reaction coordinates. This means that each displacement from the equilibrium introduces changes in the Hessian and the magnitude of those changes depends on the coupling strength between reaction coordinates and normal mode vibrations. Were there no such couplings, the elements of the Hessian would be

constants for all values of reaction coordinates. In other words, the matrix would always have a diagonal structure, with diagonal elements corresponding to the squares of the frequencies of normal mode vibrations at the reference configuration. The fact that this matrix is a function of reaction coordinates signifies that interactions between reactive and harmonic coordinates do exist. This allows energy flow from reaction towards harmonic coordinates. In addition, appearance of off diagonal elements is a consequence of couplings between different normal modes, which leads to energy exchange between them, as well as their simultaneous excitation. Due to the fact that the force and Hessian are defined for all points of interest, this procedure enables treatment of processes that take place far away from the equilibrium. The drawback is that one has to perform quantum chemistry calculations on the whole grid. Since the second derivatives of the potential have to be computed for each grid point, this step might be limiting for large polyatomic molecules.

It has been described how mechanical anharmonicity is treated within the CRS approach. Yet, the electric dipole moment is also affected by dynamical processes that involve intramolecular motions. By generating a dipole moment as a function of reaction coordinates, the electrical anharmonicity is included as well. Since the dipole moment is a vector, depending on the nature of the vibration that should be excited different vector components have different contributions. This property is important, especially if a molecule is excited with a sequence of pulses that have different polarizations.

2.2.3 CRS versus AFF

Both methods, Cartesian Reaction Surface and Anharmonic Force Field, handle anharmonicity, but in different ways. It has been shown that within the CRS approach the forces and the Hessian are functions of the reaction coordinates. For simplicity, let us consider the case with only one important, r (cartesian), and one harmonic, Q (normal mode), degree of freedom. The potential, the forces⁶ and the Hessian can be expressed as polynomial functions of the reaction coordinate

$$V(r) = V_0 + V_1r + V_2r^2 + V_3r^3 + V_4r^4 + \dots, \quad (2.69)$$

$$f(r) = f_1r + f_2r^2 + f_3r^3 + f_4r^4 + \dots, \quad (2.70)$$

$$K(r) = K_0 + K_1r + K_2r^2 + K_3r^3 + K_4r^4 + \dots. \quad (2.71)$$

With these expansions, the potential 2.62 obtains the following form

$$V_{\text{CRS}} = (V_0 + V_1r + V_2r^2 + V_3r^3 + V_4r^4 + \dots) -$$

⁶Note that $f_0 = 0$, since the expansion is performed around an equilibrium point.

$$(f_1 r + f_2 r^2 + f_3 r^3 + f_4 r^4 + \dots)Q + \frac{1}{2}(K_0 + K_1 r + K_2 r^2 + K_3 r^3 + K_4 r^4 + \dots)Q^2. \quad (2.72)$$

Suppose that within the AFF approach the model system also comprises two degrees of freedom, Q_r (the DOF of interest whose large displacements are considered) and Q_s (a substrate mode strongly coupled to Q_r). We assume that both modes are normal mode coordinates. The AFF potential with (most important) cubic and quartic anharmonicities can be written as

$$\begin{aligned} V_{\text{AFF}} = & V_0(Q_r^{eq}, Q_s^{eq}) + \frac{1}{2!}(k_{rr}Q_r^2 + k_{ss}Q_s^2) + \\ & \left(\frac{1}{3!}k_{rrr}Q_r^3 + \frac{1}{2!}k_{rrs}Q_r^2Q_s + \frac{1}{2!}k_{rss}Q_rQ_s^2\right) + \\ & \left(\frac{1}{4!}k_{rrrr}Q_r^4 + \frac{1}{3!}k_{rrrs}Q_r^3Q_s + \frac{1}{2 \cdot 2!}k_{rrss}Q_r^2Q_s^2\right) \end{aligned} \quad (2.73)$$

The term $k_{rs}Q_rQ_s$ is missing, since in the normal mode representation the Hessian is diagonal, i.e. there is no mixing of second order between the modes.

The difficulty in comparing the above two procedures arises from different nature of coordinates. In order to make the calculations feasible, reactive coordinates in the CRS approach usually comprise cartesian coordinates of a single reactive atom. For an investigation of the dynamics of a hydrogen bonded system, this would be the hydrogen atom which makes the bridge between the proton donor and the proton acceptor. If Q_r from the AFF approach involves only (or mainly) the motion of the "CRS reactive atom", the (non) equivalence between these two methods can easily be viewed, as will be shown in the following. For hydrogen bonded systems, the vibrations of interest (stretching and bending XH vibrations) mainly involve hydrogen motion which makes the two approaches for this family of systems comparable.

In order to simplify the comparison between the two methods, Eq. 2.73 can be rewritten as

$$\begin{aligned} V_{\text{AFF}} = & (V_0(Q_r^{eq}, Q_s^{eq}) + \frac{1}{2!}k_{rr}Q_r^2 + \frac{1}{3!}k_{rrr}Q_r^3 + \frac{1}{4!}k_{rrrr}Q_r^4) + \\ & \left(\frac{1}{2!}k_{rrs}Q_r^2 + \frac{1}{3!}k_{rrrs}Q_r^3\right)Q_s + \\ & \left(\frac{1}{2!}k_{ss} + \frac{1}{2!}k_{rss}Q_r + \frac{1}{2 \cdot 2!}k_{rrss}Q_r^2\right)Q_s^2 \end{aligned} \quad (2.74)$$

Analyzing equations 2.72 and 2.74, it is obvious that the former one is more general - V_{CRS} contains all orders with respect to r , while V_{AFF} represents a special truncation of V_{CRS} . The coefficients in V_{CRS} associated to high order terms usually have small values, so their importance becomes apparent for large Q_r only, far away from the equilibrium. They are negligible for small Q_r . Hence, close to the

equilibrium V_{CRS} can be replaced with V_{AFF} . The anharmonic force field is, therefore, a limiting case of the Cartesian Reaction Surface procedure. Note that some terms in Eq. 2.73 are neglected, like Q_s^3 , $Q_r Q_s^3$, Q_s^4 , because the division of modes into reactive and substrate is done in a way, that the later play a modest role in the dynamics, which allows exclusion of their high powers. This is a desirable property concerning the numerical effort, but may be a disadvantage for high precision spectroscopy.

According to the above discussion, close to the equilibrium the two approaches should in principle give comparable results, provided the lowest anharmonic terms are sufficient for a reasonable description of the PES. Which method would be preferable concerning the numerical effort depends on the character of the investigated system. At first glance, the AFF approach seems to be less demanding. However, owing to the fact that the CRS modes do not include the reactive DOF, they might give a more compact picture. That is, the higher dimensionality of the AFF model could make it less appropriate for certain systems (an example will be given in Chapter 4).

In the following chapters, it will be shown how anharmonicity is utilized for explaining IR spectra, as well as intramolecular vibrational redistribution that takes place after illumination of medium sized molecules with ultrashort laser pulses.

2.2.4 The Diabatic Representation

As already mentioned, we are interested in processes that take place in the electronic ground state that is calculated according to the Born - Oppenheimer approximation (cf. Section 2.1). It assumes that due to the mass difference between the electrons and the nuclei, the former move much faster and are able to follow the motion of the later. In other words - nuclear motion does not cause transitions between electronic levels. The potential energy surfaces calculated employing BOA are called *adiabatic*. However, if the surfaces exhibit, for instance, a conical intersection, the adiabatic representation is not appropriate anymore, and the kinetic couplings between electronic states must be accounted for. Within the *diabatic representation*, these couplings are shifted to the potential energy operator. Which representation will be more useful depends on the nature of the system.

Similar reasoning can be applied to vibrational levels within a single electronic state (e.g. the ground state). Different types of vibrational motion take place on different time scales. Addressing hydrogen - bonded systems, the vibrational period of the XH stretching vibration ν_{XH} might be one or almost two orders of magnitude lower than the one involving the movements of the heavy atoms, ν_{HB} , thereby influencing the hydrogen dynamics. If those modes are coupled, the dy-

namics of this system can be modelled in the spirit of the *second BOA* by treating the excitations of the low frequency mode within each vibrational level of ν_{XH} , as has been mentioned in the Introduction. Due to the relatively small gap between the XH levels, it is likely that the coupling between them can be caused by the heavy atom motion, ν_{HB} . Fig. 1.1 shows such situation: as the arrow indicates, excitation from the overall ground state to $v_{\text{HB}} = 1$ within $v_{\text{XH}} = 1$ might cause a transition to $v_{\text{HB}} = 5$ within $v_{\text{XH}} = 0$. This suggests an employment of the diabatic representation for modelling the hydrogen bond dynamics. Note that this situation resembles that of electron transfer processes [67].

In addition to its natural physical picture, the diabatic representation has an advantage concerning the numerical effort: it is computationally less demanding to handle a limited number of states than to perform calculations on the whole grid (the large grid is mapped onto a few states).

Anharmonic Force Fields and the Diabatic Representation

The diabatic representation can be applied within the AFF approach. Suppose the model consists of n normal mode vibrations, but one DOF, Q_L , has much lower frequency than the others, so that it is reasonable to employ the diabatic representation. The diabatic states $\{|\alpha\rangle\}$ are obtained from the diagonalization of the Hamiltonian at the equilibrium position of Q_L

$$H(Q_1, \dots, Q_{n-1}; Q_L = 0)|\alpha\rangle = E_\alpha|\alpha\rangle. \quad (2.75)$$

Those states can be characterized in terms of zero-order states, $\{|\phi_i\rangle\}$, the eigenstates of one-dimensional Hamiltonians

$$H_{Q_i} = T_{Q_i} + V_{Q_i} = -\frac{\hbar^2}{2} \frac{\partial^2}{\partial Q_i^2} + V^{(1)}(Q_i) \quad (2.76)$$

where the potential $V^{(1)}(Q_i)$ is constructed by displacing the structure along the mode Q_i ($i = 1, \dots, n-1$). Since all other coordinates are fixed at their equilibrium positions, there is no parametric dependence of $\{|\phi_i\rangle\}$ on Q_j which would introduce the kinetic couplings. That is, all couplings are comprised within the potential energy part of the Hamiltonian. The Hamiltonian in the diabatic representation reads

$$H_{\text{AFF}}^{\text{diab}} = \sum_{\alpha\beta} \left[\delta_{\alpha\beta} \left(E_\alpha + \frac{1}{2} P_L^2 + V^{(1)}(Q_L) \right) + \sum_i \langle \alpha | H_L^{(i)} | \beta \rangle Q_L^i \right] |\alpha\rangle \langle \beta|. \quad (2.77)$$

$H_L^{(i)}$ is the part of the Hamiltonian that contains the i^{th} derivative of the potential with respect to Q_L . For example, if $i = 1$ and one takes into account only the

cubic terms that describe the modification of the motion of the j^{th} mode due to its coupling to Q_L , we would have $H_L^{(1)} = \sum_{j=1}^{n-1} k_{jjL} Q_j^2$. As is usually the case, not all matrix elements of the Hamiltonian have the same importance, so it is possible to select the terms that give large contributions and neglect those that are, for instance, off-resonant.

CRS Hamiltonian in the Diabatic Representation

Let us see how the diabatic representation can be incorporated within the CRS method. First, one has to define certain diabatic states and perform an averaging of the matrices that enter Eq. 2.66. Those states can be chosen to be the eigenfunctions of the potential for partially relaxed substrate

$$[T_{\mathbf{r}} + V(\mathbf{r})]\phi_{\alpha}(\mathbf{r}) = E_{\alpha}\phi_{\alpha}(\mathbf{r}) \quad (2.78)$$

Since the CRS method rests on the harmonic expansion of the potential with respect to the skeleton modes, Eq. 2.58, it is to be expected that far away from the equilibrium the harmonic approximation would break down. The diabatic representation enables to account for the points in the relevant region only, where the harmonic approximation should be valid. Besides the fact that the accounted points are reliable, an additional advantage is that the nature of the states being excited is known, since they describe the motion of the important degrees of freedom, for example, whether it is a certain bending/stretching vibration etc. In other words, they can be used as zero-order states, e.g., for the assignment of spectra. The CRS Hamiltonian in the diabatic representation obtains the following form

$$H_{\text{CRS}}^{\text{diab}} = \frac{1}{2}\mathbf{P}^2 + \sum_{\alpha,\beta} [U_{\alpha}(\mathbf{Q})\delta_{\alpha\beta} + V_{\alpha\beta}(\mathbf{Q})(1 - \delta_{\alpha\beta})] |\alpha\rangle\langle\beta| \quad (2.79)$$

The diabatic potential energy curves $U_{\alpha}(\mathbf{Q})$ are defined as

$$U_{\alpha}(\mathbf{Q}) = E_{\alpha} - \mathbf{f}_{\alpha\alpha}\mathbf{Q} + \frac{1}{2}\mathbf{Q}\mathbf{K}_{\alpha\alpha}\mathbf{Q} \quad (2.80)$$

where the forces $\mathbf{f}_{\alpha\alpha}$ and the Hessian $\mathbf{K}_{\alpha\alpha}$ are the average values for the diabatic state α , $\mathbf{f}_{\alpha\alpha} = \langle\alpha|\mathbf{f}|\alpha\rangle$ and $\mathbf{K}_{\alpha\alpha} = \langle\alpha|\mathbf{K}|\alpha\rangle$. They describe normal mode vibrations within a certain diabatic level. Those forces push the normal modes into their locally relaxed configurations. They cause vertical shifts of the potential energy curves (cf. Fig. 2.5), given by Eq. 2.68, but also a displacement Q_{α}^0

$$\mathbf{Q}^0 = -\mathbf{K}^{-1}\mathbf{f} \quad (2.81)$$

The existence of those displacements is a consequence of the dependence of the forces on the actual position of the hydrogen atom (within the harmonic approximation, the forces would be constant, equal to zero, as at the equilibrium). In addition, the curves are characterized by different curvatures, since the Hessian is a

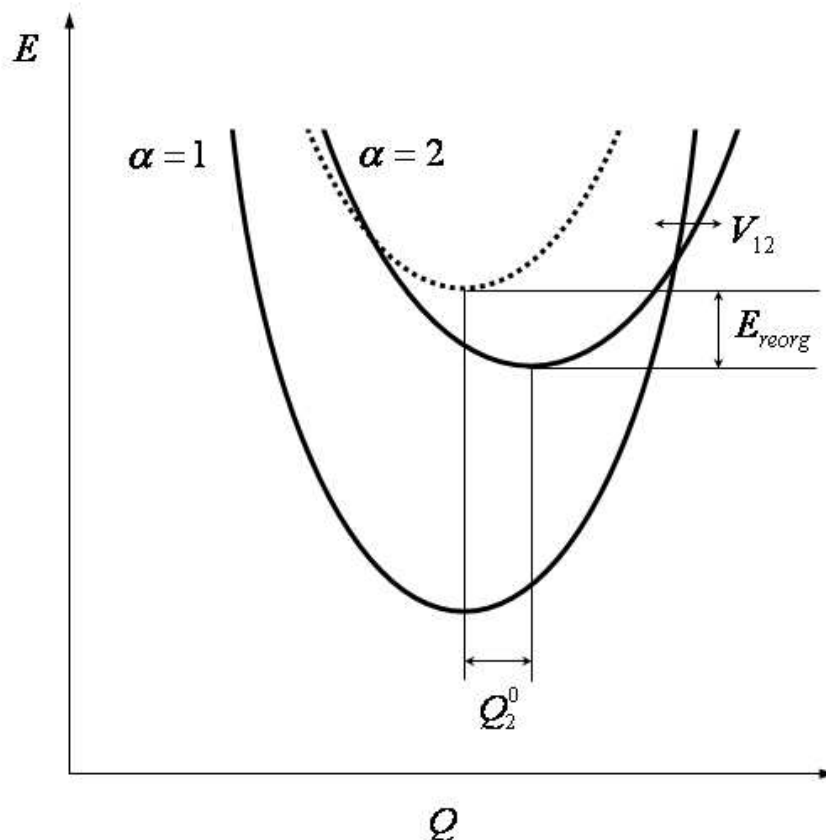


Figure 2.5: The two lowest diabatic levels $|\alpha = 1\rangle$ and $|\alpha = 2\rangle$ within the CRS method. The dotted curve corresponds to the harmonic approximation. The force f_{22} causes a vertical shift of the higher level (characterized by energy change E_{reorg}) and a displacement Q_2^0 . The difference between the force constants K_{11} and K_{22} are reflected in different curvatures of the ground and the excited state. V_{12} is the coupling between the states.

function of the reaction coordinates as well (were the potential harmonic, the diagonal elements of the Hessian would have the values at the reference configuration for all displacements of the hydrogen atom). Owing to their shifts and different curvatures, the curves cross each other, which might lead to a transfer of population between the states. This is an important issue for the dynamics, as will be shown in the next Chapter.

The coupling between the diabatic states is given by

$$V_{\alpha\beta}(\mathbf{Q}) = -\mathbf{f}_{\alpha\beta}\mathbf{Q} + \frac{1}{2}\mathbf{Q}\mathbf{K}_{\alpha\beta}\mathbf{Q} \quad (2.82)$$

Thus, the interaction between different levels is introduced through the matrices $\mathbf{f}_{\alpha\beta}$ and $\mathbf{K}_{\alpha\beta}$. This coupling allows transfer of population between the diabatic levels.

Finally we mention an additional numerical advantage of the diabatic representation. Having defined the CRS Hamiltonian and chosen the important normal modes, it is in principle possible to describe processes that involve arbitrarily large displacements of the reaction coordinates. However, it is likely that the harmonic approximation would break down very far away from the equilibrium. This could imply, for instance, that the reduced Hessian might have negative eigenvalues, so the calculated points would be wrong. This problem is circumvented by employing the diabatic representation, since only the *reliable* points that lie in the relevant region (where the harmonic approximation should be valid) are accounted for.

2.3 Quantum Dynamics

Depending on the nature of the system being investigated, there are different ways for describing dynamical processes. If the process of interest takes place in the gas phase, characterized by low pressure, each particle can be considered as being separated from the rest of the world. Such approach is justified, since the processes we are interested in (vibrational motions, intramolecular vibrational redistribution, chemical reactions) take place on a sub-picosecond timescale, while the average collision time amounts to microseconds, i.e., it is a few orders of magnitude longer. In other words, the dynamics of the relevant system is not influenced by intermolecular interactions, so a description of such **isolated** system with a wave function is sufficient.

On the contrary, reactions taking place in the condensed phase must be modelled by accounting for the influence of the solvent. Due to frequent collisions between the particles, the system initially disturbed by some external force can exchange energy with the environment. The energy flow into the environment is known as dissipation, and the systems interacting with the surrounding - **open** systems. In principle, if the environment is small, the energy can be returned to the system. In certain cases the surrounding forms a so-called bath that is much larger than the system, so the increase in its energy arising from the coupling to the system degrees of freedom is almost instantly redistributed within the bath, leaving it in thermal equilibrium.

An example of an open system is shown in Fig. 2.6. System's degrees of freedom are labelled as Q and q , the former being treated explicitly, and the latter only approximately, by including them into the bath. Z stands for the solvent degrees of freedom. The arrows indicate interactions: coupling of the *important* part of the system, Q , and the *internal bath*, q , leads to internal vibrational redistribution, whereas interaction between Q and the *external bath*, Z , describes dissipation. Release of energy in the direction $Q \rightarrow q$ is further alleviated by the relaxation of the

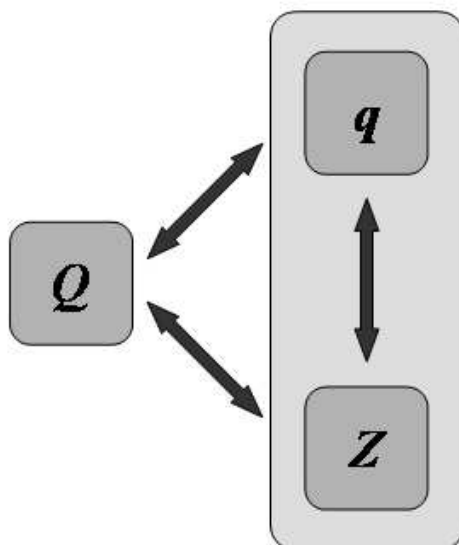


Figure 2.6: Coupling between the system and the reservoir. Q stands for system DOF that play the major role in the investigated process, while q comprises intramolecular modes that influence the dynamics of the system through their coupling to Q . The solvent DOF are labelled by Z .

latter via their coupling to Z . The multidimensionality is the main feature of open systems. The interaction between the system and the bath is usually described using the density matrix approach. The reduced density matrix allows an exact treatment of the system, while approximately incorporating the effects of the environment.

2.3.1 Isolated Quantum Systems

In order to follow the time evolution of an isolated system, one has to find a way to solve the time dependent Schrödinger equation (TDSE) [68], [69]

$$i\hbar \frac{\partial \psi}{\partial t} = \hat{H} \psi \quad (2.83)$$

In the above equation, ψ is a wave function for the nuclear degrees of freedom and \hat{H} is a Hamiltonian. All properties of the system can be extracted from the wave function. For example, the value of any observable is given by an expectation value of the corresponding hermitian operator \hat{O}

$$\langle \hat{O} \rangle = \langle \psi | \hat{O} | \psi \rangle \quad (2.84)$$

With increasing the size of the system, solving Eq. 2.83 becomes a demanding task due to the exponential scaling with the number of DOFs. Therefore, the goal is to find a method that would be suitable for treating large systems.

The *standard approach* for solving the TDSE is based on the expansion of the wave function in a time-independent basis, $\{\chi\}$

$$\psi(\mathbf{Q}, t) = \sum_{i_1=1}^{N_1} \cdots \sum_{i_f=1}^{N_f} C_{i_1, \dots, i_f}(t) \prod_{\kappa=1}^f \chi_{i_\kappa}^{(\kappa)}(Q_\kappa) \quad (2.85)$$

where \mathbf{Q} comprises a set of f degrees of freedom $\{Q\}$, and C are time - dependent expansion coefficients. Application of the Dirac-Frenkel variational principle

$$\langle \delta\psi | \hat{H} - i\hbar \frac{\partial}{\partial t} | \psi \rangle = 0 \quad (2.86)$$

leads to a set of coupled linear differential equations of motion for the coefficients. Although solving this system of equations is straightforward, computational labor increases exponentially with the number of degrees of freedom. That is, when treating larger systems the restriction to small number of basis functions might distort the real picture.

For this reason, it has been proposed to replace this exact propagation with approximate methods. The easiest way would be to represent the wave function as a product of one dimensional time dependent functions, each of them describing one DOF

$$\psi(\mathbf{Q}, t) = C(t) \prod_{i=1}^f \varphi_i(Q_i, t) \quad (2.87)$$

The so - called single particle functions $\{\varphi_i(Q_i, t)\}$ are further expanded in a time - independent primitive basis $\{\chi\}$ adapted to the problem at hand. The expansion given by Eq. 2.3.1 is denoted as *Time Dependent Hartree*, TDH [70], [71]. Application of the Dirac - Frenkel variational principle results in a set of coupled equations of motion for the single particle functions and the expansion coefficients. This approach has the disadvantage that the coupling between different degrees of freedom is treated only in a mean - field way. This is a rather severe approximation, in particular for proton transfer reactions [72]. Hence, it must be improved by using a linear combination of TDH products, which is expected to give a better description of correlation between different modes.

Multi Configuration Time Dependent Hartree

As has been indicated above, the limitations of the TDH approach can be overcome by using more single particle functions for each DOF. This leads to the Multi Configuration Time Dependent Hartree (MCTDH) method [72]-[73], with the following ansatz for the wave function

$$\psi(\mathbf{Q}, t) = \sum_{i_1=1}^{n_1} \cdots \sum_{i_f=1}^{n_f} C_{i_1, \dots, i_f}(t) \prod_{\kappa=1}^f \varphi_{i_\kappa}^{(\kappa)}(Q_\kappa, t) \quad (2.88)$$

As before, \mathbf{Q} stands for a set of f nuclear coordinates (modes), $\varphi_{i_\kappa}^{(\kappa)}$ are single - particle functions (orbitals) for the κ^{th} mode and n_κ is their number. The computational effort strongly depends on n_κ . There are two extreme cases: if n_κ equals 1 (N_κ), one arrives at the TDH (standard) approach. By their proper choice, MCTDH allows more accurate description of mode interactions than the TDH method, with much less effort than the one required for the standard scheme, thanks to the time dependence of the single particle functions.

It goes without saying that the single particle functions are kept orthonormalized throughout the propagation, i.e., $\langle \varphi_i^{(\kappa)}(t) | \varphi_j^{(\kappa)}(t) \rangle = \delta_{ij}$. The projector on the space spanned by them is defined as

$$P^{(\kappa)} = \sum_{i_\kappa=1}^{n_\kappa} |\varphi_{i_\kappa}^{(\kappa)}\rangle \langle \varphi_{i_\kappa}^{(\kappa)}|. \quad (2.89)$$

The wave function given by Eq. 2.88 can be written as

$$\psi = \sum_I C_I \Phi_I \quad (2.90)$$

with the expansion coefficient $C_I = C_{i_1, \dots, i_f}$ and a single Hartree product $\Phi_I = \prod_{\kappa=1}^f \varphi_{i_\kappa}^{(\kappa)}$. A single - hole function, i.e. a wave function with a vacancy (which means it lacks description of one mode, Q_κ for example) is defined as

$$\psi_j^{(\kappa)} = \sum_{i_1} \dots \sum_{i_{\kappa-1}} \sum_{i_{\kappa+1}} \dots \sum_{i_f} C_{i_1 \dots i_{\kappa-1} j i_{\kappa+1} \dots i_f} \varphi_{i_1}^{(1)} \dots \varphi_{i_{\kappa-1}}^{(\kappa-1)} \varphi_{i_{\kappa+1}}^{(\kappa+1)} \dots \varphi_{i_f}^{(f)} \quad (2.91)$$

In the above expression, j can take n_κ values, which means that there are n_κ single - hole functions corresponding to mode Q_κ . Thereby, the total wave function is alternatively given by

$$\psi = \sum_{i=1}^{n_\kappa} \varphi_i^{(\kappa)} \psi_i^{(\kappa)} \quad (2.92)$$

Single - hole functions can be used to define mean - field operators $\langle \hat{H} \rangle_{ij}^{(\kappa)} = \langle \psi_i^{(\kappa)} | \hat{H} | \psi_j^{(\kappa)} \rangle$ that act exclusively on one degree of freedom. Density matrices, whose elements are given by $\rho_{ij}^{(\kappa)} = \langle \psi_i^{(\kappa)} | \psi_j^{(\kappa)} \rangle$, define the one - particle density of mode Q_κ . Since different nuclear modes reflect different types of motion, molecular modes are treated as distinguishable particles.

Having defined the basic quantities, we can employ the Dirac - Frenkel variational principle, which brings us to the following set of equations of motion for the single particle functions and the expansion coefficients [73]

$$\begin{aligned} i\dot{A}_I &= \sum_L \langle \Phi_I | \hat{H} | \Phi_L \rangle A_L \\ i\dot{\varphi}^{(\kappa)} &= (\mathbf{I}_{n_\kappa} - P^{(\kappa)}) (\boldsymbol{\rho}^{(\kappa)})^{-1} \langle \hat{H} \rangle^{(\kappa)} \boldsymbol{\varphi}^{(\kappa)} \end{aligned} \quad (2.93)$$

with $\varphi(\kappa) = \left(\varphi_1^{(\kappa)}, \dots, \varphi_{n_\kappa}^{(\kappa)} \right)^T$ and \mathbf{I}_{n_κ} a unit matrix of dimension n_κ . The expansion coefficients A depend on the single - particle functions, entering through the Hartree products Φ . On the other hand, the single - particle functions depend on the expansion coefficients via the density matrix ρ . This makes the above set a system of non-linear differential equations. In addition, the presence of the projection operator also introduces nonlinearity. The numerical propagation of MCTDH wave packets is incorporated within the MCTDH program package [74].

From the last equation, it is obvious that in order to calculate the matrix elements of the Hamiltonian for a system with f degrees of freedom, it would be necessary to perform an f -fold integration. However, with a proper choice of the form of the Hamiltonian, it is possible to reduce the numerical effort arising from multiple integrations. Assuming that the total Hamiltonian \hat{H} contains a part that operates on a single degree of freedom, $\hat{h}^{(\kappa)}$, and a residual part that describes coupling between different modes, \hat{H}_R , the total Hamiltonian can be written as

$$\hat{H} = \sum_{\kappa=1}^f \hat{h}^{(\kappa)} + \hat{H}_R. \quad (2.94)$$

Further, if the residual part can be represented as a sum of products of single - particle operators

$$\hat{H}_R = \sum_{a=1}^b c_a \prod_{\kappa=1}^f \hat{h}_a^{(\kappa)} \quad (2.95)$$

the problem is simplified to a computation of the integral along one coordinate at a time. Thus, the CRS Hamiltonian described in section 2.2.2 seems to be appropriate for combining with the MCTDH method [74], as will be shown in section 2.3.1.

MCTDH and the Diabatic Representation

The MCTDH program package also enables analysis of systems in the diabatic representation by introducing an additional degree of freedom, k , for labelling the diabatic levels. It can have only positive integer non - zero values, and the number of single particle functions corresponding to this mode equals the number of states. This way for describing the wave function is known as *single - set formulation*. The number of included states is not limited.

In the above example, one set of orbitals is used for all states. In order to give the wave - function more flexibility, different sets of single particle functions can be employed for each level. This also increases the complexity of the working equations, but leads to a more precise description of the process. For this purpose, Eq. 2.88 is used for delineating one diabatic state. In this *multi - set formulation*,

the zero - order states $\{|\alpha\rangle\}$ are used as basis states for the expansion of the overall wave function

$$|\Psi\rangle = \sum_{\alpha=1}^{\sigma} \psi^{(\alpha)} |\alpha\rangle \quad (2.96)$$

where σ denotes number of included diabatic states. The equations of motion now take the following form [75]

$$\begin{aligned} i\dot{A}_I^{(\alpha)} &= \sum_{\beta=1}^{\sigma} \sum_L \langle \Phi_I^{(\alpha)} | \hat{H}^{(\alpha\beta)} | \Phi_L^{(\beta)} \rangle A_L^{(\beta)} \\ i\dot{\varphi}^{(\alpha,k)} &= (\mathbf{I}_{n_k} - P^{(\alpha,k)}) (\boldsymbol{\rho}^{(\alpha,k)})^{-1} \sum_{\beta=1}^{\sigma} \langle \hat{H}^{(\alpha\beta,k)} \rangle \boldsymbol{\varphi}^{(\beta,k)} \end{aligned} \quad (2.97)$$

Therefore, contrary to the single - set formalism, one has to propagate separately single particle functions for each diabatic state. Those equations of motion remind of the set given by Eq. 2.93, being more complicated due to the presence of another degree of freedom. For example, the Hamiltonian matrix elements are given by

$$\hat{H}^{(\alpha\beta)} = \langle \alpha | \hat{H} | \beta \rangle \quad (2.98)$$

and the mean - fields also include the *diabatic* degree of freedom,

$$\langle \hat{H} \rangle_{ij}^{(\alpha\beta,k)} = \langle \psi_i^{(\alpha,k)} | \hat{H}^{(\alpha\beta)} | \psi_j^{(\beta,k)} \rangle \quad (2.99)$$

Although it seems at first glance that the numerical effort is much higher for the multi - set formalism, that is not necessarily the case: in order to achieve the desired convergence, the number of single - particle functions in the single - set formalism might be rather high. Since the effort scales exponentially/linearly with the number of orbitals/states, implementation of the multi - set formalism is in many cases encouraged. For the comparison of results obtained with the single and the multi - set formalism, see Ref. [75]-[77].

Combining the CRS Method with the MCTDH Scheme

In order to make the propagation of the wave packet with the MCTDH method efficient, it is necessary to provide an appropriate (product) form of the Hamiltonian, section 2.3.1. It will be shown in the following that the CRS approach can be successfully combined with the MCTDH method.

Consider Eq. 2.66, the Hamiltonian for a single potential energy surface. Kinetic energy operators T_r and $1/2\mathbf{P}^2$ act exclusively on one degree of freedom, the reactive and the harmonic coordinates respectively. The functions building the potential energy part, the effective potential V , the forces \mathbf{f} as well as the Hessian \mathbf{K} ,

can be expressed as polynomial functions of the reactive coordinates. This kind of Hamiltonian possesses the required product form.

Inspecting the formula for the diabatic system 2.79, we see that it also fulfills the necessary condition, since the potential energy part has a form of a matrix. In this case, the diabatic states correspond to vibrational states with respect to the reactive coordinates within the ground electronic level. That is, the diabatic states reflect solely types of excitations of the reactive coordinates. In principle, one might use either the single - set, or the multi - set formulation.

2.3.2 Open Quantum Systems

Isolated systems investigated in the previous section have been represented by a wave function. This representation is not appropriate for open systems, since the wave function that is supposed to describe the system *and* the environment would depend on a large number of variables. In principle, if it would be possible to include all degrees of freedom of both the system of interest and the surrounding, the wave function approach as described in the previous section would be sufficient. However, if the system of interest is surrounded with a macroscopic reservoir, the representation with a wave function is impossible. This suggests an exact treatment of the system of interest and an approximate treatment of its coupling to the environment. This approach provides all relevant information, since we are not interested in the environment itself, but only on the influence it has on the dynamics of the system of interest. Thus, an interaction between the system and the surrounding is often characterized by using reduced density matrices [78]. In the following, we will only sketch the formalism for treating open systems, which is otherwise fully developed.

Consider a small system of interest **S** embedded in a reservoir **R**. Suppose the reservoir is much larger than the system, so when the system is driven away from the equilibrium by a certain external force and starts interacting with the surrounding, the excess of energy transferred to the surrounding is instantaneously redistributed among its numerous degrees of freedom. Further, let us assume that this excess of energy is negligible compared to the total reservoir's internal energy. If all those conditions are fulfilled, the environment can be treated as a thermal bath, that always stays in equilibrium. In the following, it will be shown how the dynamics of such systems can be studied with the help of density operators.

The Density Operator

Suppose we wish to investigate a certain system by representing it with a wave function Ψ , i.e., a corresponding state vector $|\Psi\rangle$. Let $\{\alpha\}$, comprise a complete

basis set. The calculations are simplified if it is chosen to be orthonormal, $\langle \alpha | \bar{\alpha} \rangle = \delta_{\alpha \bar{\alpha}}$. Since the basis is complete, each state of the system can be represented as a linear superposition

$$|\Psi\rangle = \sum_{\alpha} c_{\alpha} |\alpha\rangle. \quad (2.100)$$

For a condensed phase system, a representation which rests on the density operator is more appropriate

$$\hat{W} = \sum_{\nu} \omega_{\nu} |\Psi_{\nu}\rangle \langle \Psi_{\nu}| \quad (2.101)$$

which is nothing but a linear superposition of projection operators on the quantum states $|\Psi_{\nu}\rangle$, which are eigenstates of a set of commuting operators that correspond to certain physical observables. Those projection operators describe the quantum nature of the system. The expansion coefficients ω_{ν} are the corresponding probabilities for the system to be in a state $|\Psi_{\nu}\rangle$. Thus, a statistical treatment is performed, for a general case when the complete knowledge about the system is not obtainable. This approach enables the investigation of a statistical ensemble. If the above sum collapses into a single projector, say $|\Psi_{\nu}\rangle \langle \Psi_{\nu}|$, the state of the system is said to be **pure**. Such situations can equally well be described by a wave function. On the contrary, if there exists a finite probability for more than one state to enter the expansion 2.101, the state is referred to as **mixed**.

All information about the system are contained in the density operator. For example, the expectation value of any observable can be expressed as

$$\langle \hat{O}(t) \rangle = \text{tr} \left\{ \hat{W}(t) \hat{O} \right\} \quad (2.102)$$

The time evolution of \hat{W} is given by (cf. Appendix A)

$$\hat{W}(t) = \sum_{\nu} \omega_{\nu} U(t, t_0) |\Psi_{\nu}\rangle \langle \Psi_{\nu}| U^{\dagger}(t, t_0) \quad (2.103)$$

The ket vector is propagated with the time evolution operator $U(t, t_0)$, and the bra vector with the corresponding hermitian conjugate, $U^{\dagger}(t, t_0)$. Taking the time derivative of the last equation brings us to the equation of motion for the density operator

$$\frac{\partial}{\partial t} \hat{W}(t) = -\frac{i}{\hbar} \left[\hat{H}, \hat{W}(t) \right]_- \quad (2.104)$$

This equation is known as Liouville-von Neumann equation. The change of the density operator with time is proportional to the commutator of the overall Hamiltonian and the density operator. A more compact form of the above equation is obtained if it is expressed in the Liouville space. The Liouville space is, like the Hilbert space, a linear vector space. Its elements are the operators of the Hilbert

space, so they play the role of Hilbert space vectors. The operators defined in the Liouville space are referred to as *superoperators* in order to distinguish them from Hilbert space operators. Hence, the commutator in the Liouville-von Neumann equation can be replaced with a superoperator \mathcal{L} acting on the density operator

$$\mathcal{L}\hat{W}(t) = \frac{1}{\hbar} [\hat{H}, \hat{W}(t)] \quad (2.105)$$

so the Liouville-von Neumann equation reads

$$\frac{\partial}{\partial t} \hat{W}(t) = -i\mathcal{L}\hat{W}(t) \quad (2.106)$$

The Liouville space is convenient for formal manipulations. However, all calculations have to be performed in the Hilbert space.

The Reduced Density Operator

The state vector, Eq. 2.100, and the density operator, Eq. 2.101, comprise all degrees of freedom of the system **and** the reservoir. If one would propagate the total density operator, it would mean that all degrees of freedom of the reservoir are accounted for. For large environments, this would make the calculations impossible. Therefore, it is convenient to introduce the so-called *reduced density operator* by performing the trace of the total density operator over the reservoir's degrees of freedom

$$\hat{\rho}(t) = \sum_{\alpha_R} \langle \alpha_R | \hat{W}(t) | \alpha_R \rangle = \text{tr}_R \{ \hat{W}(t) \}. \quad (2.107)$$

$\{\alpha_R\}$ is a complete basis defined in the space of the reservoir only. So $\text{tr}_R\{\hat{W}(t)\}$ means that the integration affects only the reservoir degrees of freedom. In this way, the important information about the system's dynamics will be obtained, while accounting for the influence of the environment [79]. The coupling to the environment affects the state of the system. Since the reservoir is not treated exactly, i.e., by including all its DOF, some information is missing. Suppose, for example, that the system is initially in the pure state. If there is no coupling between the system and the reservoir, the system will stay in the pure state throughout the propagation and its evolution can equally well be described with a wave function. However, if the system interacts with the environment, the coupling leaves the system in a mixed state, which cannot be characterized by a single state vector. In addition, the total wave function is not obtainable due to its high complexity and a reduced wave function cannot be constructed, so the reduced knowledge can only be obtained through the probabilities, which are comprised within the reduced density operator.

The total Hamiltonian can be written as

$$\hat{H} = \hat{H}_S + \hat{H}_R + \hat{H}_{SR} = \hat{H}_0 + \hat{H}_{SR} \quad (2.108)$$

with \hat{H}_S and \hat{H}_R being the Hamiltonians that govern solely the dynamics of the system of interest and the reservoir, respectively, and \hat{H}_{SR} represents their coupling. We will assume in the following that \hat{H}_{SR} can be represented as

$$\hat{H}_{SR} = \sum_u g_u \hat{\Theta}_u \hat{\Upsilon}_u \quad (2.109)$$

$\hat{\Theta}$ is an operator that acts on system's degrees of freedom, while $\hat{\Upsilon}$ operates on reservoir's coordinates. g_u is the coupling strength between the system and the reservoir DOFs. Eq. 2.109 can be looked at, for example, as a Taylor expansion with u comprising a set of parameters corresponding to different contributions. Due to the presence of H_{SR} , it is not possible to construct a Hamiltonian which describes the motion of the system of interest only without invoking further approximations, so the reduced density matrix cannot be obtained by performing a unitary transformation of the reduced density matrix at the initial moment, $\hat{\rho}(t_0)$. Inserting the total Hamiltonian in Eq. 2.104, the equation of motion for the reduced density operator reads

$$\frac{\partial}{\partial t} \hat{\rho}(t) = \frac{\partial}{\partial t} \text{tr}_R \{ \hat{W}(t) \} = -\frac{i}{\hbar} \left[\hat{H}_S, \hat{\rho}(t) \right]_- - \frac{i}{\hbar} \text{tr}_R \left\{ \left[\hat{H}_{SR}(t), \hat{W}(t) \right]_- \right\} \quad (2.110)$$

Owing to the fact that \hat{H}_R depends only on the reservoir's degrees of freedom, the trace of the commutator $\left[\hat{H}_R, \hat{\rho}(t) \right]_-$ vanishes. The commutator $\left[\hat{H}_{SR}, \hat{W}(t) \right]_-$ contains the total density operator, whose propagation is impossible. Hence, it is necessary to introduce approximations that lead to an equation of motion that contains only the reduced density operator. A convenient approach would be to turn from Schrödinger to interaction representation, as is given in Appendix B.

The Dissipative Dynamics

The equation of motion for the reduced density operator known as the **Quantum Master Equation** is given by (cf. Appendix B)

$$\begin{aligned} \frac{\partial}{\partial t} \hat{\rho}(t) = & -\frac{i}{\hbar} \left[\hat{H}_S, \hat{\rho}(t) \right]_- \\ & - \sum_{uv} \int_0^{t-t_0} d\tau \left(C_{uv}(\tau) \left[\hat{\Theta}_u, U_S(\tau) \hat{\Theta}_v \hat{\rho}(t-\tau) U_S^\dagger(\tau) \right]_- \right. \\ & \left. - C_{vu}(-\tau) \left[\hat{\Theta}_u, U_S(\tau) \hat{\rho}(t-\tau) \hat{\Theta}_v U_S^\dagger(\tau) \right]_- \right) \end{aligned} \quad (2.111)$$

$C_{uv}(t)$ is the reservoir correlation function. It provides with information about the dynamics of the reservoir. It will be studied in more detail in the following section.

If we turn back to the Liouville space and introduce the Liouville superoperator

$$\mathcal{L}_S \hat{\rho} = \frac{1}{\hbar} [\hat{H}_S, \hat{\rho}]_- \quad (2.112)$$

the compact way of writing Eq. 2.111 would be

$$\frac{\partial}{\partial t} \hat{\rho}(t) = -i\mathcal{L}_S \hat{\rho}(t) - \mathcal{D} \hat{\rho}(t) \quad (2.113)$$

The first term on the right hand side $-i\mathcal{L}_S \hat{\rho}(t)$ according to Eq. 2.106 stands for an evolution of a closed system. The dissipative superoperator \mathcal{D} describes the relaxation dynamics. This is the part which is missing in the Schrödinger equation. It accounts for an irreversible flow of energy from the relevant system towards the reservoir.

We proceed by introducing the eigenstates of the system Hamiltonian \hat{H}_S , $\{|a\rangle\}$. They form a complete basis in the space of the relevant system. The matrix elements of the reduced density operator and the system part of \hat{H}_{SR} read

$$\rho_{ab}(t) = \langle a | \hat{\rho}(t) | b \rangle \quad \Theta_{ab}^{(u)} = \langle a | \hat{\Theta}_u | b \rangle \quad (2.114)$$

The diagonal elements ρ_{aa} represent probabilities of the state $|a\rangle$ to be populated and are known as **populations**. Their sum should, therefore, be equal to 1. The off-diagonal elements ρ_{ab} , the so-called **coherences**, describe a joined evolution of the two states, $|a\rangle$ and $|b\rangle$. Coherences carry information on the relative phase between the two states. If the experiment is performed in a way that the relative phase between those two states is kept constant, the evolution of the system is said to be *coherent*. Otherwise, if it evolves (decreases) in time, the process is *incoherent*. Incoherence represents reduction of knowledge about the system.

Let E_a and E_b be eigenvalues of \hat{H}_S corresponding to eigenstates $|a\rangle$ and $|b\rangle$. Starting from Eq. 2.111 we obtain for the dissipative part of ρ_{ab} after some algebra (full derivation is given in [67])

$$\begin{aligned} \left(\frac{\partial \rho_{ab}(t)}{\partial t} \right)_{\text{diss}} = & - \sum_{cd} \sum_{uv} \int_0^{t-t_0} d\tau \left(C_{-vu}(\tau) \Theta_{db}^{(u)} \Theta_{cd}^{(v)} e^{i\omega_{da}\tau} \rho_{ac}(t-\tau) \right. \\ & + C_{uv}(\tau) \Theta_{ac}^{(u)} \Theta_{cd}^{(v)} e^{i\omega_{bc}\tau} \rho_{db}(t-\tau) \\ & - \left\{ C_{vu}(-\tau) \Theta_{ac}^{(u)} \Theta_{db}^{(v)} e^{i\omega_{bc}\tau} \right. \\ & \left. \left. + C_{uv}(\tau) \Theta_{db}^{(u)} \Theta_{ac}^{(v)} e^{i\omega_{da}\tau} \right\} \rho_{cd}(t-\tau) \right) \end{aligned} \quad (2.115)$$

with ω_{ab} being the transition frequency between the states $|a\rangle$ and $|b\rangle$. The fact that the elements of the density matrix in the integrand depend on the variable τ (i.e., it

is said that the system possess *memory* on the past) make the solution of the above equation troublesome. However, our initial assumption was that the environment is much larger than the system, so the reservoir reaches its equilibrium state within a short period of time, the correlation time τ_{cor} . For $t - \tau > \tau_{cor}$, the correlations become negligible and the integrand approaches zero. That is, the significant time for integration is $t - \tau_{cor} \leq \tau \leq t$. On the other hand, the reduced density matrix changes on a time scale larger than τ_{cor} . The fact that in the interaction representation only the part of the Hamiltonian that describes the coupling, H_{SR} , is treated perturbatively suggests to turn to the interaction picture, replace $\rho_{ab}(t - \tau)$ with $\rho_{ab}(t)$, and get back to the Schrödinger picture. In addition, the upper bound of integration can be set to infinity. This approximation is known as *Markov approximation*. Within the Markov limit, the dissipative part of the Quantum Master Equation reads

$$\left(\frac{\partial \hat{\rho}(t)}{\partial t}\right)_{\text{diss}} = - \sum_{uv} \int_0^{\infty} d\tau \left\{ C_{uv}(\tau) [\Theta_u, \Theta_v^{(I)}(-\tau) \hat{\rho}(t)]_- \right. \\ \left. - [C_{vu}(-\tau) \Theta_u, \hat{\rho}(t) \Theta_v^{(I)}(-\tau)] \right\}. \quad (2.116)$$

Consider the integral

$$\int_0^{\infty} d\tau C_{uv}(\tau) \Theta_u \Theta_v^{(I)}(-\tau). \quad (2.117)$$

It is a complex number whose real part is responsible for the dissipation. The imaginary part modifies the distribution of the energy levels. Those modifications are usually small and do not alter the behavior of the system. Therefore we will neglect them in the following and define the *damping matrix*

$$\Gamma_{ab,cd}(\omega_{dc}) = \text{Re} \sum_{uv} \int_0^{\infty} d\tau C_{uv}(\tau) \Theta_{ab}^{(u)} \Theta_{cd}^{(v)(I)}(-\tau) \quad (2.118)$$

which is actually responsible for the irreversible energy transfer. Further, using the damping matrix, we can define the *relaxation matrix*

$$\mathcal{R}_{ab,cd} = \delta_{ac} \sum_e \Gamma_{be,ed}(\omega_{de}) + \delta_{bd} \sum_e \Gamma_{ae,ec}(\omega_{ce}) - \Gamma_{ca,bd}(\omega_{db}) - \Gamma_{db,ac}(\omega_{ca}) \quad (2.119)$$

which enables to write the equation of motion for the matrix elements of the reduced density matrix in a compact way

$$\left(\frac{\partial \rho_{ab}(t)}{\partial t}\right)_{\text{diss}} = - \sum_{cd} \mathcal{R}_{ab,cd} \rho_{cd}(t) \quad (2.120)$$

Three cases can be distinguished: 1) $a = b, c = d$. $\mathcal{R}_{aa,cc}$ describes population transfer between different eigenstates of the Hamiltonian \hat{H}_S ; 2) $a \neq b, a = c$,

$b = d$. Term $\mathcal{R}_{ab,ab}$ accounts for the loss of coherence; 3) transfer of coherences ($\mathcal{R}_{ab,cd}$), transformation of populations into coherences ($\mathcal{R}_{aa,cd}$) and vice versa ($\mathcal{R}_{ab,cc}$).

Eq. 2.120 includes mixing of different matrix elements of the reduced density matrix. However, under certain conditions some of those couplings can be neglected. In order to justify further approximations, let us rewrite the last equation in the interaction representation[67]

$$\left(\frac{\partial \rho_{ab}^{(I)}(t)}{\partial t} \right)_{\text{diss}} = - \sum_{cd} \mathcal{R}_{ab,cd} e^{i(\omega_{ab} - \omega_{cd})(t-t_0)} \rho_{cd}^{(I)}(t) \quad (2.121)$$

If $1/|\omega_{ab} - \omega_{cd}|$ is much smaller than the time step for which we need to know the density matrix, the contribution of the corresponding term would be negligible, and it can be disregarded. This is the *Secular* or *Rotating Wave Approximation*. Further, if all couplings between the populations and coherences are ruled out, we are in the *Bloch limit*. The Bloch approximation gives good results if it is applied on anharmonic systems. Nevertheless, in order to be on the safe side, it is recommendable to check whether ω_{ab} and ω_{cd} for the neglected terms are off - resonant.

The Reservoir Correlation Function

In order to study the dynamics of an open system, it is necessary to calculate the reservoir correlation function (cf. Eq. 2.111 and B.15). The correlations it describes are usually transient, surviving only for a short period of time, the correlation time τ_{cor} . In order to obtain the exact form of the reservoir correlation function, one would have to perform calculations in the space of the reservoir, which is not viable. Hence, one has to turn to approximate methods.

If the reservoir forms a regular lattice, it is common to introduce the harmonic approximation, i.e., it is assumed that its lattice atoms perform normal mode vibrations around their equilibrium positions and that those vibrations are uncoupled. For weak system - reservoir couplings, often the linear coupling between the active system and the reservoir need to be taken into account. However, depending on the problem at hand it might be necessary to take into account also the nonlinear terms. For example, diatomics in rare gas matrices can be investigated using this approach. Rare gas atoms at low temperature form a regular lattice, which is only marginally distorted by introducing a diatomic molecule, like hydrogen or fluorine, due to their small radii.

If the environment is liquid, the harmonic approximation cannot be applied, although there are attempts to describe the interaction in terms of instantaneous normal modes for a given configuration of the solvent [80].

Alternatively, the reservoir can be represented by fluctuating forces \mathbf{f}_R it exerts on the system DOFs [81]

$$\mathbf{f}_R(\mathbf{Z}) = -\left. \frac{\partial H_{SR}}{\partial \mathbf{Q}} \right|_{\mathbf{Q}=\mathbf{Q}_{eq}}. \quad (2.122)$$

It is common to assume linear coupling with respect to system degrees of freedom, that is (cf. Eq. 2.109)

$$\left. \frac{\partial \hat{\Theta}(\mathbf{Q})}{\partial \mathbf{Q}} \right|_{\mathbf{Q}=\mathbf{Q}_{eq}} = 1 \quad (2.123)$$

The reservoir correlation function is given by

$$C(t) = \langle \mathbf{f}_R(\mathbf{Z}(t)) \mathbf{f}_R(\mathbf{Z}(0)) \rangle_R. \quad (2.124)$$

If in addition linear coupling with respect to a harmonic bath is assumed, i.e.,

$$\hat{Y}(\mathbf{Z}) = \sum_{\lambda} g_{\lambda} Z_{\lambda} \quad (2.125)$$

so we get [67]

$$C(t) = \frac{\hbar}{\pi} \int_0^{\infty} d\omega J(\omega) [\coth\left(\frac{\beta\omega}{2}\right) \cos(\omega t) - i \sin(\omega t)] \quad (2.126)$$

with $J(\omega)$ representing the spectral density

$$J(\omega) = \frac{2}{\pi} \sum_{\lambda} \frac{g_{\lambda}^2}{m_{\lambda} \omega_{\lambda}} \delta(\omega - \omega_{\lambda}). \quad (2.127)$$

Here g_{λ} is the coupling constant for the bath oscillator with frequency ω_{λ} and mass m_{λ} . The significance of the spectral density lies in the fact that it is proportional to the square of the coupling strength g_{λ} between the system and the bath and thereby gives information on the probability of energy transfer from the relevant system to the bath. Looking the other way around, by expressing the spectral density via the reservoir correlation function

$$J(\omega) = \frac{2}{\hbar} \tanh\left(\frac{\hbar\omega\beta}{2}\right) \int_0^{\infty} \text{Re } C(t) \cos(\omega t) dt \quad (2.128)$$

we see that it depends on the real part of $C(t)$ only, and can be replaced by an appropriate classical correlation function, i.e.,

$$\text{Re } C(t) = C_{\text{class}}(t) \quad (2.129)$$

It can be shown [82] that in the limit of the linear response theory, the calculated spectral density can be considered as corresponding to an effective bath which is

harmonic, although the *true* interactions entering $C_{class}(t)$ might be rather anharmonic. In other words, $J(\omega)$ may be considered as being the spectral density of an effective harmonic bath.

To summarize, classical molecular dynamics simulations give information on the reservoir correlation function which is used for the calculation of the spectral density. The spectral density itself provides with the coupling strength between the relevant system and the surrounding.

2.3.3 Interaction with an External Field

We are interested in the dynamics of a system, initiated with an (infrared) electromagnetic field [83], [84]. In principle, both the system of interest and the applied field should be treated quantum mechanically. However, it is common to invoke a *semiclassical approximation* according to which the interaction between a quantum system and a classical field is followed.

Although the electric and the magnetic component constitute the electromagnetic field, the interaction of the magnetic component with the system will be neglected in the following, since its contribution is a few orders of magnitude lower than the term describing the interaction with the electric component. The electric component has the following form

$$\boldsymbol{\varepsilon}(t) = \mathbf{e}E_n(t)S(t) \quad (2.130)$$

with an envelope and a shaping function E_n and S respectively and a polarization \mathbf{e} . Assuming a \sin^2 form of the envelope function, like in Fig. 2.7, the field obtains the form

$$\boldsymbol{\varepsilon}(t) = \mathbf{e} \Theta(t)\Theta(\tau - t) \varepsilon_0 \sin^2(\pi t/\tau) \cos(\Omega t) \quad (2.131)$$

where τ represents the duration of the pulse and Ω the carrier frequency. In Eq. 2.131 we invoked the *semiclassical dipole approximation* [85].

The interaction Hamiltonian between the system of interest and the applied field is given by

$$\hat{H}_{int}(t) = -\boldsymbol{\varepsilon}(t) \cdot \boldsymbol{\mu} \quad (2.132)$$

where $\boldsymbol{\mu}$ represents the dipole moment of the system. It can be expressed via its vector components

$$\boldsymbol{\mu} = \mu_x \mathbf{e}_x + \mu_y \mathbf{e}_y + \mu_z \mathbf{e}_z. \quad (2.133)$$

\mathbf{e}_x , \mathbf{e}_y and \mathbf{e}_z are the unit vectors along the x , y and z axis.

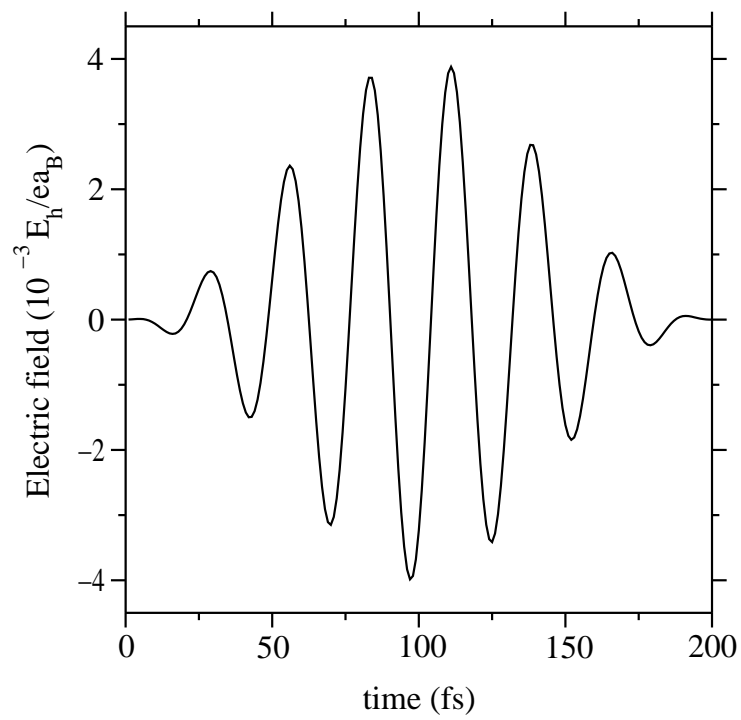


Figure 2.7: The parameters of the \sin^2 pulse are: $\varepsilon_0 = 4 \times 10^3 E_h/ea_B$, $\tau = 200$ fs, and $\Omega = 1200 \text{ cm}^{-1}$.