

Chapter 2

Theory

In this chapter the theoretical background of the methods used in this work is presented. Section 2.1 will introduce the molecular Schrödinger equation and the Born-Oppenheimer approximation [101] which can be used to separate the nuclear and electronic motions. Section 2.2 deals with the electronic Schrödinger equation; it describes how the wave function is approximated as a single Slater determinant and how the spatial part of the wave function is expanded in terms of basis functions. The variational principle and Hartree-Fock (HF) [102, 103] theory are then reviewed. Two methods, configuration interaction and perturbation theory, are considered to improve the results of the HF theory, by including electron correlation [104, 105]. Density functional theory is presented as an alternative economical method which also considers the electron correlation during the calculation; for more details see Ref. [106, 107]. The concept of a potential energy surface is then introduced and how the anharmonicity in the potential surface may influence the chemical structure of the molecule under investigation. The method applied to solve the time- independent nuclear Schrödinger equation will be outlined in section 2.4. Finally, the time dependent approaches will be presented in section 2.5, as tools for the solution of the time-dependent Schrödinger equation, giving special attention to pure and mixed states.

2.1 The molecular Schrödinger equation

In the following, the time-independent Schrödinger equation will be derived from the the time-dependent one. Moreover, it will be shown how the Born-Oppenheimer approximation can be used to separate the electronic and the nuclear motions. The electronic as well as nuclear Schrödinger equations will be

presented.

According to quantum mechanics, expectation values of observables can be obtained from the molecular wave function which is the solution of the time-dependent Schrödinger equation:

$$i\hbar \frac{\partial}{\partial t} \Phi(\vec{r}, \vec{R}, t) = \hat{H} \Phi(\vec{r}, \vec{R}, t). \quad (2.1)$$

Here, \hat{H} is the Hamiltonian, an operator representing the total energy, $\Phi(\vec{r}, \vec{R}, t)$ is the wave function which depends on the coordinates of all electrons \vec{r} , the coordinates of all nuclei \vec{R} and the time, t .

The Hamiltonian \hat{H} takes the form

$$\hat{H} = \hat{T} + \hat{V}, \quad (2.2)$$

where, for a system with N electrons and M nuclei, the kinetic energy operator \hat{T} is defined as

$$\hat{T} = -\frac{\hbar^2}{2} \sum_{i=1}^N \frac{1}{m_i} \nabla_i^2 - \frac{\hbar^2}{2} \sum_{I=1}^M \frac{1}{M_I} \nabla_I^2. \quad (2.3)$$

The first sum runs over all electrons i and the second sum runs over all nuclei I . m_i is the mass of the electron i and M_I is the mass of the nucleus I . The Laplacian operators ∇_i^2 and ∇_I^2 involve differentiation with respect to the coordinates of the i th electron and the I th nucleus.

The potential energy operator \hat{V} consists of the Coulomb interactions:

$$\hat{V} = \sum_{i=1}^N \sum_{j < i}^N \frac{e^2}{4\pi\epsilon_0 r_{ij}} - \sum_{i=1}^N \sum_{I=1}^M \frac{Z_I e^2}{4\pi\epsilon_0 r_{iI}} + \sum_{I=1}^M \sum_{J < I}^M \frac{Z_I Z_J e^2}{4\pi\epsilon_0 R_{IJ}}, \quad (2.4)$$

where $r_{ij} = |\vec{r}_i - \vec{r}_j|$, $r_{iI} = |\vec{r}_i - \vec{R}_I|$, $r_{ij} = |\vec{R}_I - \vec{R}_J|$, and the double sum is over distinct pairs of particles (electrons or nuclei). Other interactions, such as spin-orbit coupling, are neglected in this approximation.

The time-independent Schrödinger equation can be derived from the time-dependent one. If we write the wave function as a product of spatial and temporal terms:

$$\Phi(\vec{r}, \vec{R}, t) = \Psi_{el,nuc}(\vec{r}, \vec{R})g(t), \quad (2.5)$$

then equation (2.1) becomes, when \hat{H} is time independent,

$$\Psi_{el,nuc}(\vec{r}, \vec{R})i\hbar \frac{\partial g(t)}{\partial t} = g(t)\hat{H}\Psi_{el,nuc}(\vec{r}, \vec{R}). \quad (2.6)$$

or rewritten,

$$\frac{i\hbar}{g(t)} \frac{\partial g(t)}{\partial t} = \frac{1}{\Psi_{el,nuc}(\vec{r}, \vec{R})} \hat{H}\Psi_{el,nuc}(\vec{r}, \vec{R}). \quad (2.7)$$

Since the left-hand side is only a function of t and the right-hand side is only a function of spatial coordinates, the two sides must equal a constant. If one tentatively designates this constant to be E (since the right-hand side clearly must have a dimension of energy), then we extract two ordinary differential equations, namely,

$$\frac{1}{g(t)} \frac{\partial g(t)}{\partial t} = -\frac{iE}{\hbar} \quad (2.8)$$

and

$$\hat{H}\Psi_{el,nuc}(\vec{r}, \vec{R}) = E\Psi_{el,nuc}(\vec{r}, \vec{R}). \quad (2.9)$$

Equation (2.8) can be easily solved and yields

$$g(t) = \exp(-iEt/\hbar). \quad (2.10)$$

Equation (2.9) is the time-independent Schrödinger equation which will be discussed in the following section. Substituting (2.10) in (2.5), one can write the molecular wave function as:

$$\Phi(\vec{r}, \vec{R}, t) = \Psi_{el,nuc}(\vec{r}, \vec{R}) \exp(-iEt/\hbar). \quad (2.11)$$

Thus, the total wave function $\Phi(\vec{r}, \vec{R}, t)$ differs from $\Psi_{el,nuc}(\vec{r}, \vec{R})$ only by a phase factor of constant magnitude. This has some interesting consequences. First of all, the density $|\Phi(\vec{r}, \vec{R}, t)|^2$ is time independent, as can be easily shown:

$$|\Phi(\vec{r}, \vec{R}, t)|^2 = \Phi^*(\vec{r}, \vec{R}, t)\Phi(\vec{r}, \vec{R}, t) \quad (2.12a)$$

$$= \exp(iEt/\hbar)\Psi_{el,nuc}^*(\vec{r}, \vec{R})\exp(-iEt/\hbar)\Psi_{el,nuc}(\vec{r}, \vec{R}) \quad (2.12b)$$

$$= \Psi_{el,nuc}^*(\vec{r}, \vec{R})\Psi_{el,nuc}(\vec{r}, \vec{R}). \quad (2.12c)$$

Secondly, the expectation value for any time-independent operator is also time-independent, if $\Phi(\vec{r}, \vec{R}, t)$ satisfies equation (2.11):

$$\langle A \rangle = \int \Phi^*(\vec{r}, \vec{R}, t)\hat{A}\Phi(\vec{r}, \vec{R}, t) = \int \Psi_{el,nuc}^*(\vec{r}, \vec{R})\hat{A}\Psi_{el,nuc}(\vec{r}, \vec{R}). \quad (2.13)$$

For these two reasons, wave functions of the form (2.11) describe stationary states. Equation (2.11) represents a particular solution of Eq. (2.1). Therefore, the general solution of Eq. (2.1) would be a linear combination of these particular solutions, i.e.

$$\Phi(\vec{r}, \vec{R}, t) = \sum_j \Psi_{el,j}(\vec{r}, \vec{R}) \exp(-iE_j t/\hbar), \quad (2.14)$$

with the eigenfunctions $\Psi_{el,j}(\vec{r}, \vec{R})$ and their corresponding energies E_j .

2.1.1 Born-Oppenheimer separation

In general, it is impossible to solve exactly the time-independent Schrödinger equation, (2.9) for polyatomic systems. A significant simplification arises from the fact that the mass of the electrons is much smaller than that of the nuclei. It follows that one can, as a first approximation, study the two motions separately. This type of approximation is known as the Born-Oppenheimer separation [101]. Within a first step of the Born-Oppenheimer approximation, the kinetic energy of the nuclei can be neglected since it is smaller than the kinetic energy of the electrons by a factor of M_I/M_i , the electrons are then considered as moving in a field of fixed nuclei, where the nuclear-nuclear repulsion is a constant. Therefore, the electronic Hamiltonian reads

$$\hat{H}_{el} = -\frac{\hbar^2}{2} \sum_{i=1}^N \frac{1}{m_e} \nabla_i^2 + \sum_{i=1}^N \sum_{i < j}^N \frac{e^2}{4\pi\epsilon_0 r_{ij}} - \sum_{i=1}^N \sum_{I=1}^M \frac{Z_I e^2}{4\pi\epsilon_0 r_{iI}}, \quad (2.15)$$

and the electronic Schrödinger equation becomes

$$\hat{H}_{el} \Psi_{el}(\vec{r}; \vec{R}) = E_{el}(\vec{R}) \Psi_{el}(\vec{r}; \vec{R}). \quad (2.16)$$

The solution of this equation is the electronic wave function $\Psi_{el}(\vec{r}; \vec{R})$ which describes the motion of the electrons and explicitly depends on the electronic coordinates but parametrically (indicated by the semicolon) on the nuclear coordinates, as does the electronic energy, $E_{el}(\vec{R})$.

Therefore, one can write the wave function $\Psi_{el,nuc}(\vec{r}, \vec{R})$ approximately as

$$\Psi_{el,nuc}(\vec{r}, \vec{R}) = \Psi_{el}(\vec{r}; \vec{R}) \Psi_{el,nuc}(\vec{R}) \quad (2.17)$$

Accordingly, we define the nuclear Schrödinger equation as

$$\hat{H}_{el,nuc} \Psi_{el,nuc}(\vec{R}) = E_{el,nuc} \Psi_{el,nuc}(\vec{R}), \quad (2.18)$$

where

$$\hat{H}_{el,nuc} = -\frac{\hbar^2}{2} \sum_{I=1}^M \frac{1}{M_I} \nabla_I^2 + \hat{V}_{el}(\vec{R}). \quad (2.19)$$

$\hat{V}_{el}(\vec{R})$ provides a potential for the nuclear motion

$$\hat{V}_{el}(\vec{R}) = E_{el}(\vec{R}) + \sum_{I=1}^M \sum_{I < J}^M \frac{Z_I Z_J e^2}{4\pi\epsilon_0 R_{IJ}}, \quad (2.20)$$

depending on the electronic state el .

Thus the nuclei in the Born-Oppenheimer approximation can be considered to move in a potential energy surface $\hat{V}_{el}(\vec{R})$ generated by their mutual Coulomb interaction and the interaction with the electronic charge distribution corresponding to a certain nuclear configuration. This means that as the nuclei start to move, the electrons instantaneously adjust their wave function according to the nuclear motion. This approximation ignores the possibility of having non-radiative transitions between different electronic eigenstates. Transitions can only arise through coupling with an external electric field. Their description involves the solution of the quantum mechanical equation of motion (time-dependent Schrödinger equation) which will be discussed in detail in section 2.5. The main task of the next section is to solve, at least approximately, the electronic Schrödinger equation and hence, find the potential $\hat{V}_{el}(\vec{R})$ for the nuclear motion.

2.2 The electronic Schrödinger equation

In this section we will focus on the solution of the electronic Schrödinger equation, Eq. (2.16). First, we show how to write the wave function approximately as a single Slater determinant consisting of spin orbitals which are a product of spatial and spin functions. Then we express the spatial function as a linear combination of basis functions. The variational method and HF theory as well as its improvement by considering electronic correlation will be introduced. An alternative to the wave function method, density functional theory, will be presented. The concept of potential energy surface will be eventually discussed.

2.2.1 Molecular orbital theory

In the previous section we have defined the Hamiltonian of the electronic Schrödinger equation according to the Born-Oppenheimer separation. At this point, the spin does not appear in the Hamiltonian, but its presence must be recognized in constructing the wave function which must be antisymmetric under an interchange of variables (spatial and spin) for any two electrons. Now we want to define the electronic wave function, Ψ_{el} . For this purpose, we employ the quantum mechanical molecular orbital theory to approximate the wave function. A molecular spin orbital $\chi_i(\vec{x}_i)$ is a function of the spatial and the spin coordinates

of a single electron.

$$\chi_i(\vec{x}_i) = \chi_i(\vec{r}_i, \omega) = \psi_i(\vec{r}_i) \cdot \begin{cases} \alpha(\omega) \\ \beta(\omega) \end{cases} \quad (2.21)$$

where $\psi_i(\vec{r}_i)$ represents the spatial part of the molecular spin orbital, whereas $\alpha(\omega)$ and $\beta(\omega)$ indicate spin up and spin down functions which depend on the spin coordinate ω , respectively. An antisymmetric many-electron wave function of a molecule with N electrons can be written as

$$\Psi^{SD} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(\vec{x}_1) & \chi_2(\vec{x}_1) & \dots & \chi_N(\vec{x}_1) \\ \chi_1(\vec{x}_2) & \chi_2(\vec{x}_2) & \dots & \chi_N(\vec{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(\vec{x}_N) & \chi_2(\vec{x}_N) & \dots & \chi_N(\vec{x}_N) \end{vmatrix} \quad (2.22)$$

where $\frac{1}{\sqrt{N!}}$ is a normalization factor and SD is an abbreviation for Slater determinant. Equation (2.22) can be written in a short hand notation considering only the diagonal elements and including the normalization factor,

$$\Psi^{SD} = |\chi_1(\vec{x}_1)\chi_2(\vec{x}_2)\dots\chi_N(\vec{x}_N)\rangle. \quad (2.23)$$

Assuming that electron 1 occupies spin orbital 1, electron 2 occupies spin orbital 2, ... and so forth, one can write the previous equation more compactly as,

$$\Psi^{SD} = |\chi_1\chi_2\dots\chi_N\rangle. \quad (2.24)$$

This determinant is referred to as a Slater determinant which is an approximation to Ψ_{el} , i.e. $\Psi_{el} \approx \Psi^{SD}$. An interchange of two electrons, what corresponds to interchange two rows of the determinant, changes the sign of the determinant. Thus, Slater determinants meet the requirement of the antisymmetry principle. Slater determinants incorporate exchange correlation, which means that the motion of two electrons with parallel spins is correlated. Since the motion of electrons with opposite spins remains uncorrelated, it is customary to refer to a single determinantal wave function as an uncorrelated wave function (for more details see [105]).

Basis set expansion

A further approximation is imposed, requiring that the individual molecular spatial orbitals $\psi_i(\vec{r}_i)$ are expressed as a linear combination of a finite set of prescribed one-electron functions known as basis functions ϕ_μ . Then an individual orbital ψ_i can be written as

$$\psi_i(\vec{r}_i) = \sum_\mu C_{\mu i} \phi_\mu(\vec{r}_i), \quad (2.25)$$

where $C_{\mu i}$ are the molecular orbital expansion coefficients. These coefficients provide the orbital description a certain flexibility. In molecular orbital theory, atomic orbitals of the constituent atoms are used as basis functions. Such a treatment is known as Linear Combination of Atomic Orbitals (LCAO) theory.

There are two types of atomic basis functions. The first one is the Slater Type Orbitals (STO) which uses functions proportional to $\exp(-\zeta r)$, ζ being the Slater orbital exponent. They are labeled as hydrogen like atomic orbital $1s$, $2s$, and $2p_{xyz}$, etc. The second type of basis functions consists of Gaussian Type Orbital (GTO) atomic basis functions which are proportional to $\exp(-\alpha r^2)$, α being the gaussian orbital exponent. They are less satisfactory than STO's as representations of atomic orbitals since at large distances the atomic orbitals decay as $\exp(-ar)$, where a is a constant, which is of the Slater rather than the gaussian form. Nevertheless, they have the important advantage that all integrals in the computations can be evaluated explicitly without facing the very large numerical computation as STO's do. A compromise is to use linear combinations of gaussian functions as basis functions such as to mimic the Slater-type behavior. Consider the basis function

$$\phi_\mu(\vec{r}_i) = \sum_s d_{\mu s} g_s(\alpha, \vec{r}_i). \quad (2.26)$$

The coefficients $d_{\mu s}$ are fixed; gaussian functions of this type are called contracted basis functions, the individual g_s are termed primitive gaussians. There are many types of contraction schemes but we will describe only those employed in this work:

Split-valence basis sets

Since the inner shells contribute little to most chemical properties they are usually kept contracted and only the valence orbitals are split into two parts: an inner, compact function and an outer, more diffuse, one. During the construction of molecular orbitals the coefficients of these two types of functions can be varied independently as well as those of the core orbitals. 6-31G is an example of a split-valence basis set: the core orbitals consist of six primitive gaussian functions, whereas the inner and outer valence orbitals consist of three and one primitive gaussian functions.

Polarization basis sets

The previous basis set can be improved by adding polarization functions, which are functions of higher angular momentum number. This provides the non-spherical symmetric displacement of electronic charge away from the nuclear center upon molecule formation (charge polarization). For instance, 6-31G(d,p) (used

in sections 3.1, 3.2 and 3.3) is constructed by the addition of a set of gaussian d-type and p-type primitives to the split-valence 6-31G basis set for the description of each heavy (non-hydrogen) atom and hydrogen atom, respectively.

Diffuse basis sets

One can add highly diffuse functions to the basis set for a proper description of the electron density at large distances from the nuclei. This is done by adding a "+", for instance as 6-31+G(d,p) (used in sections 3.1 and 3.6), which indicates that one adds to the 6-31G(d,p) basis set four highly diffuse functions (s, p_x, p_y, p_z) on each non-hydrogen atom of the second row in the periodic table.

2.2.2 Variational method and Hartree-Fock theory

Up to this point, what has been discussed is how a determinantal wave function is constructed from molecular spin orbitals, and how the orbitals may, in turn, be expanded in terms of a set of basis functions. It remains to specify a method for fixing the coefficients of Eq. (2.25). For this purpose, one can use the so called HF theory [105] which is based on the variation principle of quantum mechanics. The variation principle states that for an approximate electronic ground state wave function, the expectation value of the energy, is an upper bound to the exact energy. In this fashion, the HF method is applied to determine the optimum orbitals in single-determinant wave functions. When the determinantal wave function is combined with the variation principle, it turns out that the optimum spin orbitals, must satisfy the HF equations [102]

$$\hat{F}(\vec{x}_i)\chi_i(\vec{x}_i) = \epsilon_i\chi_i(\vec{x}_i), \quad (2.27)$$

where ϵ_i is the energy corresponding to the spin orbital $\chi_i(\vec{x}_i)$ and $\hat{F}(\vec{x}_i)$ is the Fock operator, which has the form:

$$\hat{F}(\vec{x}_i) = \hat{h}(\vec{x}_i) + v^{HF}(\vec{x}_i) = \hat{h}(\vec{x}_i) + \sum_{j=1}^N (\hat{J}_j(\vec{x}_i) - \hat{K}_j(\vec{x}_i)), \quad (2.28)$$

where $\hat{h}(\vec{x}_i)$ is a single electron Hamiltonian containing the kinetic energy of the electron i as well as the Coulomb interaction of the electron i with the fixed nuclei I :

$$\hat{h}(\vec{x}_i) = -\frac{\hbar^2}{2m_i}\nabla_i^2 - \sum_{I=1}^M \frac{Z_I e^2}{4\pi\epsilon_0 r_{iI}}. \quad (2.29)$$

and $v^{HF}(\vec{x}_i)$ is the average potential experienced by the i th electron due to the presence of the other electrons. The Coulomb operator $\hat{J}_j(\vec{x}_i)$ operating on a spin

orbital $\chi_i(\vec{x}_i)$

$$\hat{J}_j(\vec{x}_i)\chi_i(\vec{x}_i) = \left[\int dx_j \chi_j^*(\vec{x}_j) \frac{1}{4\pi\epsilon_0 r_{ij}} \chi_j(\vec{x}_j) \right] \chi_i(\vec{x}_i) \quad (2.30)$$

represents the Coulomb interaction between electrons that occupy orbitals χ_i and χ_j .

The exchange operator $\hat{K}_j(\vec{x}_i)$ operating on a spin orbital $\chi_i(\vec{x}_i)$

$$\hat{K}_j(\vec{x}_i)\chi_i(\vec{x}_i) = \left[\int dx_j \chi_j^*(\vec{x}_j) \frac{1}{4\pi\epsilon_0 r_{ij}} \chi_i(\vec{x}_j) \right] \chi_j(\vec{x}_i) \quad (2.31)$$

exchanges the electron with coordinates \vec{x}_i in spin orbital χ_j and electron with coordinates \vec{x}_j in spin orbital χ_i . It has no classical counterpart and is a consequence of the antisymmetric character of the wave function.

The HF equation is non-linear (see Eq. (2.27)) and must, therefore, be solved iteratively. One can use an initial guess of spin orbitals and solve the eigenvalue equation (2.27) for a new set of spin orbitals. Using these new spin orbitals, one can construct a new Fock operator, Eq. (2.28), and repeat the procedure until self consistency is reached. This procedure is known as the Self Consistent Field (SCF) method. The solution of the HF eigenvalue problem produces a set of orthonormal HF spin orbitals, $\chi_i(\vec{x}_i)$, and their corresponding energies, ϵ_i .

The approximate electronic energy of the electronic ground state ($el = 0$) is then calculated as

$$E_{el}(HF) = \sum_{i=1}^N \epsilon_i - \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N (J_{ij} - K_{ij}), \quad (2.32)$$

where J_{ij} and K_{ij} are the matrix elements of the Coulomb and exchange operators, Eqs. (2.30) and (2.31), respectively. The subtracted term in the previous equation arises from the fact that in the one-electron approach, the repulsion between electrons is accounted for twice. The resulting value will be an upper bound to the exact energy within the limitation imposed by: a) the single determinantal wave function, and b) the particular basis set employed. Hence the best single determinantal wave function is formed by minimizing the expectation value of the energy with respect to the coefficients $C_{\mu i}$.

In practice, one solves the HF equation numerically by introducing a set of known spatial basis functions, Eq. (2.25), then the HF equations can be converted to a set of algebraic equations, the Roothaan-Hall equations [108], which are solved by standard matrix techniques.

$$\mathbf{FC} = \mathbf{SC}\boldsymbol{\epsilon}, \quad (2.33)$$

where, \mathbf{F} is the Fock matrix with elements $F_{\mu\nu} = \int d\vec{r}\phi_\mu^*(\vec{r})\hat{F}(\vec{r})\phi_\nu(\vec{r})$, \mathbf{S} is the overlap matrix with elements $S_{\mu\nu} = \int d\vec{r}\phi_\mu^*(\vec{r})\phi_\nu(\vec{r})$, \mathbf{C} is the matrix of the eigenvectors and ϵ is the diagonal matrix of the orbital energies, ϵ_i .

2.2.3 Electron correlation

The primary deficiency of the HF theory is the insufficient treatment of the correlation between the motion of electrons. In particular, as mentioned in section 2.2.1, single determinant wave functions take no account of correlation between electrons with opposite spin. It must be recognized that the exact wave function, Ψ_{el} , can not generally be expressed as a single determinant. Therefore, calculated HF energies are above the exact values. The difference between the exact and the HF energy is defined as the correlation energy [109]

$$E(exact) = E_{el}(HF) + E(correlation). \quad (2.34)$$

The neglect of correlation between electrons of opposite spin leads to a number of quantitative deficiencies in the description of the electronic structure and energies. There are two methods, which will be briefly outlined, that address this problem. Both involve the use of a linear combination of Slater determinants, each of which represents an individual electronic configuration. In the rest of this section we will drop the subscript "el" for simplicity.

Configuration Interaction (CI)

Configuration interaction (CI) is conceptually the simplest approach to incorporate electron correlation. This method is usually presented as a straightforward consequence of the variation principle applied to a trial wave function chosen as a linear combination of antisymmetrized products of spin orbitals with the coefficients of the linear expansion as the only variational parameters. This method can also be used to calculate the electronically excited states. The history and the evolution of CI has been reviewed in a paper by Shavitt [110].

Consider a system comprising N electrons described by a set of basis functions, ϕ_μ . The ground state HF single-determinant wave function is, in a short notation,

$$\Psi_0 = |\chi_1\chi_2\dots\chi_N\rangle \quad (2.35)$$

Determinantal wave functions, other than the HF function Ψ_0 , can be constructed by replacing one or more of the occupied spin orbitals χ_i, χ_j, \dots in equation (2.35)

by virtual spin orbitals χ_a, χ_b, \dots . The resulting determinants will be denoted as Ψ_s 's with $s > 0$, s is an integer. They are classified into single-substitution (single-excitation) functions, Ψ_i^a in which χ_i is replaced by χ_a , double-substitution functions, Ψ_{ij}^{ab} in which χ_i and χ_j are replaced by χ_a and χ_b , respectively, triple-substitution functions etc. One should use, for the general substitution determinant ($\Psi_{ijk\dots}^{abc\dots}$), the restrictions $i < j < k < \dots$ and $a < b < c < \dots$ to avoid repetition of the same configuration. The expansion of the wave function in terms of these determinantal wave functions is called configuration interaction (CI). When one uses all possible configurations in the expansion, the method is termed full configuration interaction (FCI). In the FCI method, a trial wave function

$$\Psi = a_0 \Psi_0 + \sum_{s>0} a_s \Psi_s \quad (2.36)$$

is used, where the sum runs over all substituted (excited) determinants. The coefficients $a's$ are then determined by the linear variational method.

The FCI method represents the most complete treatment possible within the limitation imposed by the finite basis set. As the basis set becomes infinite, the results of the full configuration interaction treatment will approach the exact solution of the non-relativistic Schrödinger equation. Despite its conceptual simplicity, there are several aspects that give the CI method some difficulties. FCI expansions grow exponentially in length with the size of the molecule and of the one-electron orbital basis set, i.e. it becomes intractable for all but very small molecules and moderate basis sets. To make it tractable, one can truncate the FCI wave function and consider determinants of single excitation, CIS, double-excitation, CID, or both, CISD, and so forth. The disadvantage of this approximation is that one loses the size consistency (the energy of a system is the sum of the energies of its individual non-interacting constituents).

A way to calculate the excited states and to avoid the size inconsistency of a truncated CI expansion is to use a multiconfigurational self-consistent field (MC-SCF) approach. A common form of the MCSCF expansion is the Complete Active Space Self Consistent Field (CASSCF). The orbitals in CASSCF calculations can usually be classified into three groups. The first group consist of the doubly occupied orbitals, those that are fully occupied in all the CASSCF determinants. The second group are the active orbitals, which contain the remaining electrons (called the active electrons); those orbitals can have different distributions of electrons in different CASSCF determinants when describing different electronic states. The third group are the virtual orbitals which are vacant in all the CASSCF determi-

nants. The doubly occupied active orbitals, together, are referred to as internal orbitals, while the virtual orbitals are often called external orbitals. All possible distributions of the active space electrons among the active orbitals are included. Moreover, both the coefficients of the CI expansion as well as the coefficients for constructing the MO's of a given basis functions, Eq. (2.36), are optimized simultaneously. In the multi-configurational CASSCF method, the excitation level of a determinant is given by the number of electrons that have been moved from internal to external orbitals. The inactive orbitals remains unchanged during the calculations. An FCI calculation is performed for the active orbitals. Typically, the active orbitals should be composed of, at least, the Highest Occupied Molecular Orbital (HOMO) and the Lowest Unoccupied Molecular Orbital (LUMO) obtained from the HF method. Since a full CI is performed for the active molecular orbitals, the size inconsistency of the truncated CI is overcome.

Møller-Plesset perturbation method

The perturbation theory of Møller and Plesset [111] is an alternative approach to take into account the correlation between electrons. The approach is to treat the Hamiltonian as the sum of two parts, the second being a perturbation on the first.

The Møller-Plesset model is formulated first by introducing a generalized electronic Hamiltonian, \hat{H}_λ , according to

$$\hat{H}_\lambda = \hat{H}_o + \lambda \hat{V}, \quad (2.37)$$

where, \hat{H}_o is the unperturbed Hamiltonian whose matrix representation, with elements $\langle \Psi_i | \hat{H}_o | \Psi_j \rangle$, is diagonal. The perturbation, $\lambda \hat{V}$ is defined by

$$\lambda \hat{V} = \lambda (\hat{H} - \hat{H}_o), \quad (2.38)$$

where \hat{H} is the exact Hamiltonian and λ is a dimensionless parameter.

In Møller-Plesset theory, the zero-order Hamiltonian, \hat{H}_o , is taken to be the sum of the one-electron Fock operators. The eigenvalue corresponding to a particular determinant Ψ is the sum of the one-electron energies, ϵ_i , for the spin orbitals which are occupied in Ψ .

Since \hat{H} depends on λ , the eigenfunctions and eigenvalues of \hat{H} must also depend on λ . Ψ_λ and E_λ , the exact ground state wave function and the exact electronic energy for a system described by the Hamiltonian \hat{H} , can be expanded

in a power series with respect to λ ,

$$\Psi_\lambda = \Psi^{(0)} + \lambda\Psi^{(1)} + \lambda^2\Psi^{(2)} + \dots \quad (2.39a)$$

$$E_\lambda = E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \dots \quad (2.39b)$$

Practical correction methods may now be formulated by setting $\lambda=1$ and by truncating the series in equations (2.39) to various orders. Accordingly, the method is referred by the highest order energy term allowed, that is, truncation after the second-order is termed as MP2, after the third-order as MP3 and so forth.

Inserting equations (2.39) as well as the Hamiltonian (Eq. (2.37)) in the electronic Schrödinger equation, Eq. (2.16), leads to the following energy expressions (up to the second-order):

$$E^{(0)} = \langle \Psi^{(0)} | \hat{H}_o | \Psi^{(0)} \rangle \quad (2.40a)$$

$$E^{(1)} = \langle \Psi^{(0)} | \hat{V} | \Psi^{(0)} \rangle \quad (2.40b)$$

$$E^{(2)} = \langle \Psi^{(0)} | \hat{V} | \Psi^{(1)} \rangle \quad (2.40c)$$

The leading terms in equations (2.39) are $\Psi^{(0)} \equiv \Psi_0$ and $E^{(0)} = \sum_{i=1}^N \epsilon_i$, where Ψ_0 is the HF wave function and ϵ_i are the one-electron orbital energies. Since $E^{(0)} + E^{(1)} = \langle \Psi^{(0)} | \hat{H} | \Psi^{(0)} \rangle$, the Møller-Plesset energy to the first-order is thus the HF energy. As a consequence a correction to the HF energy starts with MP2 [111] which is considered in this work. Inclusion of higher order terms may improve the energy but this demands for a higher computational effort.

It is noteworthy that MP2, MP3, MP4, etc energy expressions are well-defined and can be applied quite widely. They do satisfy the size consistency requirement. In this respect, the perturbation expressions are more satisfactory than the CID or CISD methods for determining correlation energies. On the other hand, perturbation theory terminated at any order is no longer variational.

2.2.4 Density functional theory (DFT)

So far we discussed the HF method which calculates the electronic wave functions and their corresponding energies. The HF wave functions lack electronic correlation, therefore, one can use Møller-Plesset perturbation or Configuration interaction methods to recover the electronic correlations. These methods are computationally demanding. An economical method, Density Functional Theory (DFT) based on the electronic density, will be introduced. DFT calculations include at least approximately the correlation energy. This technique has gained a considerable ground in recent years to become one of the most widely used techniques

for the calculation of the ground state electronic energy. Its advantages include less demanding computational effort, i.e. less computer time, and - in some cases - better agreement with experimental values than the one obtained from other ab initio procedures.

The central focus of the DFT is the electron density, $\rho(\vec{r})$, rather than the wave function, Ψ . The term density means the number of electrons per unit volume in a given electronic state, $\rho(\vec{r})$, which depends only on the coordinates. A functional is a rule which makes a correspondence between a number (E) and a function ($\rho(\vec{r})$), i.e. $E[\rho]$.

Given a system with N electrons and M nuclei : The total Hamiltonian of the electronic Schrödinger equation is defined as $\hat{H}_{el} = \hat{T} + \hat{V}_{ee} + \hat{V}$, where $\hat{V} = v(\vec{r})$ is the external potential due to M nuclei. \hat{T} , \hat{V}_{ee} and \hat{V} are all written explicitly in Eq. (2.15).

Modern DFT is based on the following two statements (Hohenberg-Kohn theorems [112]):

1) The ground state density $\rho(\vec{r})$ uniquely determines the ground state wave function Ψ and the external potential $v(\vec{r})$, this implies that any observable of a static many-particle system is a functional of its ground state electron density $\rho(\vec{r})$. The functional $F = \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle$ is then universal and has no dependence on $v(\vec{r})$, it is the same for all electronic systems (with \hat{V}_{ee} interaction).

2) The total energy functional corresponding to the external potential $v(\vec{r})$, $E_v[\rho^t] = \langle \Psi | \hat{T} + \hat{V}_{ee} + \hat{V} | \Psi \rangle$ (superscript t means trial), is equal to the exact ground state energy, $E_v[\rho]$, if and only if the exact ground state density ρ_o is considered (this is equivalent to the variational principle introduced in section 2.2.2), $E_v[\rho] < E_v[\rho^t]$ for $\rho^t \neq \rho_o$.

Applying the variational principle to get the electronic energy, $E_v[\rho]$:

$$E_v[\rho] = \text{Min}_\rho(E_v[\rho^t]) \quad (2.41a)$$

$$= \text{Min}_\rho(\langle \Psi | \hat{T} + \hat{V}_{ee} + \hat{V} | \Psi \rangle) \quad (2.41b)$$

$$= \text{Min}_\rho(\langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle + \int v(\vec{r})\rho(\vec{r})d\vec{r}) \quad (2.41c)$$

$$= \text{Min}_\rho(F + \int v(\vec{r})\rho(\vec{r})d\vec{r}). \quad (2.41d)$$

Equation (2.41) is exact but F is unknown. The following procedure was developed to solve the problem of the Schrödinger equation in general, and to help finding appropriate approximations to the universal functional F in particular.

To find a form of the functional F , suppose we have a system with non-

interacting electrons, i.e. $\hat{V}_{ee} = 0$. Hence, one can write

$$\hat{H}_s = \hat{T}_s + \hat{V}_s. \quad (2.42)$$

where \hat{H}_s , \hat{T}_s and \hat{V}_s are the Hamiltonian, kinetic energy and potential energy operators, respectively, for a system of non-interacting electrons.

In this case F reduces to T_s , the kinetic energy functional. The ground state wave function of this non-interacting system is exactly the determinant composed of orbitals ϕ_i , $\Psi_s(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) = |\phi_1\phi_2\dots\phi_N|$. Therefore the kinetic energy functional can be defined as follows:

$$T_s = \sum_{i=1}^N \langle \phi_i | -\frac{\hbar^2}{2m_i} \nabla^2 | \phi_i \rangle. \quad (2.43)$$

Then one can write

$$\frac{\delta F}{\delta \rho(\vec{r})} + v(\vec{r}) = \frac{\delta T_s}{\delta \rho(\vec{r})} + v_s(\vec{r}). \quad (2.44)$$

One always has to keep in mind that Ψ_s is not the wave function of the real system, nor are the ϕ 's related to the real electrons, except that they yield the same density through the sum $\rho(\vec{r}) = \sum_{i=1}^N |\phi_i(\vec{r})|^2$.

The true system can be treated as a non-interacting system with an effective external potential:

$$v_s(\vec{r}) = v_{eff}(\vec{r}) = \frac{\delta T}{\delta \rho(\vec{r})} - \frac{\delta T_s}{\delta \rho(\vec{r})} + \frac{\delta V_{ee}}{\delta \rho(\vec{r})} + v(\vec{r}) \quad (2.45)$$

Therefore,

$$E_v[\rho] = T_s[\rho] + V_{ee}[\rho] + T[\rho] - T_s[\rho] + \int v(\vec{r})\rho(\vec{r})d\vec{r}, \quad (2.46)$$

where $V_{ee}[\rho] = J[\rho] + \text{exchange term}$, with classical Coulomb term

$$J[\rho] = \frac{1}{2} \int \frac{\rho(\vec{r})\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}d\vec{r}'. \quad (2.47)$$

Then one can write

$$E_v[\rho] = T_s[\rho] + J[\rho] + E_{XC}[\rho] + \int v(\vec{r})\rho(\vec{r})d\vec{r}, \quad (2.48)$$

with $E_{XC}[\rho]$ contains the exchange-correlation energy plus a correlation kinetic term. If one supposes that E_{XC} is known, the total energy, $E_v[\rho]$, can be minimized with respect to the density ρ , yielding the Kohn-Sham equations that can be solved self-consistently.

$$[-\frac{\hbar^2}{2m_i} \nabla^2 + \int \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' + v(\vec{r}) + v_{XC}(\vec{r})] \phi_i(\vec{r}) = \epsilon_i \phi_i(\vec{r}), \quad (2.49)$$

where

$$v_{XC}(r) = \frac{\delta E_{XC}[\rho]}{\delta \rho}. \quad (2.50)$$

These equations are exact but the exact XC functional of ρ is unknown. The most pragmatical way is to build approximate XC functionals of ρ and solve these equations iteratively. In the following, some of the approximations to construct functionals will be sketched:

- 1) Local density approximation and local spin density approximation. They depend on the value of the electron density at a certain point only. Moreover, the latter approximation takes into account the spin density [112, 113, 114].
- 2) Gradient corrected functionals, which are functionals of both the electron density and its gradient [115, 116].
- 3) Hybrid exchange functionals, which combine the correct HF exchange expression with the gradient corrected functional [117].

Common functionals are a combination of different exchange and correlation functionals. An example is the B3LYP functional (composed of Beck's 1988 exchange functional [117] and Lee-Yang-Parr correlation [118] functional). This functional is combined by three parameters, which are derived by fitting the results of DFT calculations for test systems to experimental data. The B3LYP functional has the mathematical form [118]

$$E_{XC} = a_o E_X^{HF} + (1 - a_o) E_X^{LDA} + a_x \delta E_X^B + (1 - a_c) E_C^{VWN} + a_c \delta E_C^{LYP}. \quad (2.51)$$

The exchange-correlation terms are parameterized by a_o , a_x and a_c , with fixed values of 0.20, 0.72 and 0.81 respectively. These values are derived from fitting thermodynamic and spectroscopic properties of various systems.

Once E_{XC} is approximated, the Kohn-Sham equations, Eq. (2.49), can be solved to get the best orbitals. Eventually the total electronic energy can be calculated and then used in the construction of the potential energy surface for the nuclear motion.

2.3 Potential energy surface (PES)

In the following we are going to introduce the concept of the potential energy surface (PES) and its properties. Different coordinates, which can be used in the construction of the PES, will be presented. Moreover, the anharmonicity in the PES will be briefly introduced with the distinction between the large amplitude motions and the motion occurring in the vicinity of the equilibrium geometry.

Different methods to calculate the PES will be discussed with emphasis on the advantages and disadvantages of each method.

The PES is a consequence of the separation of the nuclear and electronic motions as proposed by Born and Oppenheimer (see section 2.1.1). The nuclei are considered to move under the influence of a potential determined by their mutual electrostatic repulsion and by the total energy of the electrons, an energy which is determined for every possible static configuration of the nuclei, cf. Eq. (2.20). Thus, the change of the molecular configurations can be visualized, within Born-Oppenheimer approximation, in terms of a multi-dimensional PES. The relative thermodynamic stabilities of molecules, their bond lengths and angles, and the rate of stereochemical outcomes of chemical reactions are all determined by the shape of this potential surface. The PES, Eq. (2.20), is a function of $3N$ nuclear coordinates. The negative of its gradient, derivative with respect to the nuclear coordinates, represents the force acting on the atoms:

$$\nabla \hat{V}_{el}(\vec{R}) = \left(\frac{\partial \hat{V}_{el}(\vec{R})}{\partial R_1}, \dots, \frac{\partial \hat{V}_{el}(\vec{R})}{\partial R_{3N}} \right). \quad (2.52)$$

The point in the configuration space with zero gradient is called a stationary point at which an important quantity, the Hessian matrix (K_{mn}), can be calculated

$$K_{mn} = \frac{\partial^2 \hat{V}_{el}(\vec{R})}{\partial R_m \partial R_n} \quad (m, n = 1, \dots, 3N). \quad (2.53)$$

At the stationary points, there are $3N$ eigenvalues of the Hessian matrix, six of them being equal to zero corresponding to three translational and three rotational motions. The remaining $(3N - 6)$ normal modes correspond to the vibrational degrees of freedom ($3N - 5$ for linear molecule). If all the eigenvalues are positive, this will correspond to a minimum in the PES. On the other hand, vibrational degrees of freedom with M negative eigenvalue indicate stationary saddle point of order M .

From the diagonalized Hessian matrix (harmonic approximation¹), one can get information about the PES with full-dimensionality. However, part of the present work is dealing with large amplitude motions which are not captured within the harmonic approximation. Therefore, different approximations should be introduced to manipulate the large amplitude motions, as well as decreasing the di-

¹In the harmonic approximation, only the first and the second derivatives of the potential are considered, i.e. the higher order derivatives with respect to the nuclear coordinates are not included.

mensionality of the PES in larger systems, and to keep the computational problem tractable.

In the present work, we are dealing with two types of coordinates: (a) internal coordinates and (b) Cartesian coordinates.

(a) Internal coordinates

Internal coordinates comprise bond lengths, bond angles, and torsional angles. The potential couplings are usually small which lead to better separation of the nuclear motion for large displacements. The disadvantage of using internal coordinates is that the kinetic couplings may be difficult to deal with. In certain cases one can avoid this kind of coupling by transforming these internal coordinate system to another coordinate system where the kinetic coupling vanishes, see e.g. Appendix D.

(b) Cartesian coordinates

For this kind of coordinates, the couplings in the kinetic energy vanish and the coupling is only in the potential part. In a polyatomic molecule of N atoms, there are $3N$ independent Cartesian coordinates, x , y , and z for each atom. The motion of the atoms in a chemical reaction might not take place along a straight line, but in a curved path e.g. in a plane. Therefore, a special kind of Cartesian coordinates known as reaction plane coordinates would be relevant to such reactions, since they represent a collective motion of the Cartesian coordinates in all directions. Another kind of Cartesian coordinates is the normal coordinates which are composed of linear combinations of the Cartesian displacements of each atom.

2.3.1 Anharmonicity in the PES and large amplitude motions

The fact that springs eventually lose their elasticity and break leads to a conclusion that the harmonic approximation is not a realistic model for large amplitude motions. As a consequence, it is beneficial to devise an approximation that goes beyond the limits of the harmonic approximation for a reasonable description of the potential energy surface.

Before doing any business with the anharmonicity in the PES, one has to distinguish between two types of changes. First, the changes occurring in the vicinity of an equilibrium point. Second, the changes associated with large amplitude motions. For the former we employ the so-called Anharmonic Force Field approximation in which the normal coordinates have been used. For the latter, other kinds of approximations are considered for describing the large amplitude motions; one of them is the Cartesian reaction surface approximation.

2.3.2 Anharmonic Force Field (AFF)

Anharmonic Force Fields (AFF) are often used to describe changes in the vicinity of an equilibrium configuration of the PES. Therefore, the normal coordinates are relevant to describe these changes. Suppose we have a system with $\vec{Q} = Q_1, Q_2, \dots, Q_{3N-6}$ degrees of freedom. The PES of such system would be [119]:

$$\hat{V}_{el}(\vec{Q}) = V_{el}^{(1)} + V_{el}^{(2)} + \dots + V_{el}^{(3N-6)}. \quad (2.54)$$

$V_{el}^{(1)}$ represents a one-mode potential for the uncoupled motion of each mode:

$$V_{el}^{(1)} = \sum_i V_{el,i}^{(1)}(Q_i). \quad (2.55)$$

$V_{el}^{(2)}$ represents a two-mode potential for the coupling between every two modes:

$$V_{el}^{(2)} = \sum_{i < j} V_{el,ij}^{(2)}(Q_i, Q_j). \quad (2.56)$$

and so forth until $V_{el}^{(3N-6)}$ which represents a $(3N - 6)$ -mode potential for the coupling between all modes:

$$V_{el}^{(3N-6)} = V_{el}^{(3N-6)}(Q_1, Q_2, \dots, Q_{3N-6}). \quad (2.57)$$

Equation (2.54) is the full-dimensional PES. In the AFF the PES is expanded in Taylor series around the equilibrium point, Q^o ,

$$\begin{aligned} \hat{V}_{el}(\vec{Q}) = & V_{el}(\vec{Q}^o) + \sum_{i=1}^{3N} \frac{\partial V_{el}}{\partial Q_i} \Bigg|_{\vec{Q}=\vec{Q}^o} (Q_i - Q_i^o) + \\ & \frac{1}{2!} \sum_{i,j=1}^{3N} \frac{\partial^2 V_{el}}{\partial Q_i \partial Q_j} \Bigg|_{\vec{Q}=\vec{Q}^o} (Q_i - Q_i^o)(Q_j - Q_j^o) + \\ & \frac{1}{3!} \sum_{i,j,k=1}^{3N} \frac{\partial^3 V_{el}}{\partial Q_i \partial Q_j \partial Q_k} \Bigg|_{\vec{Q}=\vec{Q}^o} (Q_i - Q_i^o)(Q_j - Q_j^o)(Q_k - Q_k^o) + \dots \end{aligned} \quad (2.58)$$

This expansion comprises a large number of terms. However, the subsequent terms can be expected to give smaller contribution. Therefore, it is often sufficient to include elements up to cubic terms. Moreover, the second term in the previous expansion is equal to zero because the first derivative of the potential at the stationary point is zero. In order to construct the PES in the AFF, one needs the potential $V_{el}(\vec{Q}^o)$ as well as the second derivative of the potential $\frac{\partial^2 V_{el}}{\partial Q_i \partial Q_j}$. The anharmonicity will be reflected in the higher order derivatives of the potential, i.e. higher order

force constants. The harmonic potential and the second derivative of the potential can be calculated analytically using quantum chemical *ab initio* calculations (see section 2.2.2). The higher order force constants can be calculated with less sophisticated methods like the finite difference method. This approach requires calculation of the second order derivatives for a displaced geometry along a single mode, Q_k , then the third order force constant can be calculated as [120, 121]:

$$\frac{\partial^3 V_{el}}{\partial Q_i \partial Q_j \partial Q_k} = k_{ijk} = \frac{k_{ij}^+ - k_{ij}^-}{2\Delta Q_k} \quad (2.59)$$

where k_{ij}^+ and k_{ij}^- are the second derivative matrices (cf. Eq. 2.53) corresponding to the displaced geometries along Q_k in the positive and negative directions, respectively.

This approach cannot be used for large amplitude motions, i.e. tunneling or laser control of chemical reactions, because the Taylor expansion is considered to be around an equilibrium point. Other procedures will be then introduced that can be used to describe the large amplitude motions.

2.3.3 Frozen molecular geometry

First-of-all the equilibrium geometry has to be detected. Then one or more internal coordinate(s) (bond length, bond angle, torsion angle) is(are) allowed to vary from the equilibrium position, simultaneously. The corresponding energies of the new geometries are then calculated giving rise to a PES. For practical reasons the number of coordinates that are allowed to vary should be kept as small as possible to make the procedure tractable. This method is suitable for reactions where motions along the varying coordinates are relatively fast compared the other coordinates, or some coordinates are effectively decoupled on the considered time scale. Since the other degrees of freedom are kept frozen, the resulting PES will have no information about those degrees of freedom. This method needs only calculations of single point energies without any need to calculate the forces or the Hessian matrix. This means, one can construct the PES without too much effort. The disadvantage of this method is that the kinetic coupling is sometimes difficult to handle. This problem can be solved by using a set of Cartesian coordinates for which the kinetic coupling vanishes.

2.3.4 Relaxed potential energy

In this method, one localizes the stationary points, the reactant, the product and the transition state which connects the reactant and the product. The minimum energy path starts from the transition state and follows the path of steepest descent in mass-weighted Cartesian coordinates towards the local energy minima (reactant and product) that are separated by this point. All molecular coordinates, except the reaction path, are allowed to relax to their minimum energy configuration. This path is one-dimensional by definition which allows a simplistic description of the PES. Since this method requires geometry optimization for each point and is still one-dimensional, the computational efforts are moderate. When there is a large difference between the masses of the atoms involved in the large amplitude motions, the minimum energy path may possess sharp curvatures. An extension of the minimum energy path is the reaction surface method [122, 123, 124], which treats the problem of the curvature in the minimum energy path. Calculation of the Hessian is needed in the reaction surface method to get the normal modes orthogonal to the reaction surface. Moreover, it can give some information about the coupling to the relaxed degrees of freedom. This method is suitable for describing the slow dynamics of the large amplitude motions, when there is enough time for the other degrees of freedom to relax. Therefore, this method may not be suitable for the fast motion of the reactive degrees of freedom (degrees of freedom allowed to vary during the reaction course). Since one needs partial geometry optimization, this method requires more computational efforts than the method of frozen molecular geometry. Both methods have the same disadvantage, namely the kinetic coupling.

2.3.5 Cartesian reaction surface

In this approach one employs Cartesian coordinates to avoid the kinetic coupling at the expense of neglecting rotation and rotation-vibration coupling. In the Cartesian reaction surface [125], the total set of coordinates are divided into reactive (atomic Cartesian coordinates), \vec{z} , and harmonic (substrate), \vec{Z} , degrees of freedom. The reactive coordinates are allowed to vary significantly (large amplitude motion), while the other degrees of freedom are treated within the harmonic approximation (small amplitude motion). Thus one can expand the potential energy

surface, $V_{el}(\vec{z}, \vec{Z})$, in a Taylor series to second order:

$$\begin{aligned} V_{el}(\vec{z}, \vec{Z}) = & V_{el}(\vec{z}, \vec{Z}^o(\vec{z})) + \frac{\partial V_{el}}{\partial \vec{Z}} \Big|_{\vec{Z}^o(\vec{z})} (\vec{Z} - \vec{Z}^o(\vec{z})) \\ & + \frac{1}{2} (\vec{Z} - \vec{Z}^o(\vec{z})) \frac{\partial^2 V_{el}}{\partial \vec{Z} \partial \vec{Z}} \Big|_{\vec{Z}^o(\vec{z})} (\vec{Z} - \vec{Z}^o(\vec{z})), \end{aligned} \quad (2.60)$$

where $\vec{Z}^o(\vec{z})$ is a reference configuration at which one calculates the first and the second derivatives of the potential. However, there may be significant couplings between small amplitude collective coordinates and large amplitude atomic coordinates just because a complete separation between these two does not necessarily yield the most compact representation of the potential energy surface.

According to $\vec{Z}^o(\vec{z})$, one can distinguish two cases:

1) Fixed reference:

When the harmonic degrees of freedom do not change significantly throughout the reaction, the skeleton can be considered to perform harmonic motions with respect to a fixed reference configuration $\vec{Z}^o(\vec{z}_{ref})$. This corresponds to a reference configuration that is independent of the reactive coordinates. Therefore, the reaction surface becomes a plane. This approximation is suitable for systems with strong intramolecular hydrogen bonds whose potential energy surface possesses a single minimum and the motions take place around the equilibrium configuration, i.e. it is a special case of the anharmonic expansion. However, it will be shown in section 2.3.6 that one can use the fixed reference in case of double minimum potential surface; here the special case $\vec{Z}^o(\vec{z}) \equiv 0$ should be considered.

2) Flexible reference:

Systems with medium strong hydrogen bonds possess a double minimum potential energy surface. In this case the reactant and the product are considerably different that leads to a significant change in the harmonic modes which should be left to relax during the reaction course. The reactive coordinates are considered to be the Cartesian coordinates of the atoms that represent a large amplitude motion, for instance the hydrogen atom in proton transfer reactions. The $\vec{Z}^o(\vec{z})$ can be generated by performing partial geometry optimization of all harmonic coordinates for each value of \vec{z} . Since one is interested in internal motions, i.e. the overall rotational and translational motions are not of interest, one projects out the infinitesimal rotation and translation [126]:

$$(1 - \mathbf{P}) \mathbf{m}^{-1/2} \mathbf{K}_e \mathbf{m}^{-1/2} (1 - \mathbf{P}), \quad (2.61)$$

where \mathbf{K}_e is the Hessian matrix calculated at the equilibrium configuration, \mathbf{P} is the projector onto the space spanned by the rotational, translational and reactive

degrees of freedom. The \mathbf{m} is the diagonal matrix with elements corresponding to atomic masses. Next, normal mode coordinates are introduced for the substrate coordinates according to the transformation:

$$\vec{Z} - \vec{Z}^o(\vec{z}_{ref}) = \mathbf{m}^{-1} \mathbf{U} \vec{Q}, \quad (2.62)$$

where $\vec{Z}^o(\vec{z}_{ref})$ is a suitable reference configuration and \mathbf{U} is the transformation matrix at this reference point. Thus we have

$$\vec{Z} - \vec{Z}^o(\vec{z}) = \vec{Z}^o(\vec{z}_{ref}) - \vec{Z}^o(\vec{z}) + \mathbf{m}^{-1} \mathbf{U} \vec{Q}, \quad (2.63)$$

with $\vec{Z}^o(\vec{z})$ being the partially relaxed substrate. Using this normal mode transformation, one gets (for the flexible reference):

$$V_{el}(\vec{z}, \vec{Z}) = V_{eff}(\vec{z}) - \vec{f}(\vec{z}) \vec{Q} + \frac{1}{2} \vec{Q} \mathbf{K}(\vec{z}) \vec{Q}. \quad (2.64)$$

where

$$\begin{aligned} V_{eff}(\vec{z}) = & V_{el}(\vec{z}, \vec{Z}^o(\vec{z})) - \left. \frac{\partial V_{el}}{\partial \vec{Z}} \right|_{\vec{Z}^o(\vec{z})} [(\vec{Z}^o(\vec{z})) - \vec{Z}^o(\vec{z}_{ref})] + \\ & \frac{1}{2} [(\vec{Z}^o(\vec{z})) - \vec{Z}^o(\vec{z}_{ref})] \left. \frac{\partial^2 V_{el}}{\partial \vec{Z} \partial \vec{Z}} \right|_{\vec{Z}^o(\vec{z})} [(\vec{Z}^o(\vec{z})) - \vec{Z}^o(\vec{z}_{ref})], \end{aligned} \quad (2.65)$$

$$\vec{f}(\vec{z}) = \left\{ - \left. \frac{\partial V_{el}}{\partial \vec{Z}} \right|_{\vec{Z}^o(\vec{z})} + [(\vec{Z}^o(\vec{z})) - \vec{Z}^o(\vec{z}_{ref})] \left. \frac{\partial^2 V_{el}}{\partial \vec{Z} \partial \vec{Z}} \right|_{\vec{Z}^o(\vec{z})} \right\} \mathbf{m}^{-1/2} \mathbf{U} \quad (2.66)$$

and

$$\mathbf{K}(\vec{z}) = \mathbf{U}^+ \mathbf{m}^{-1/2} \left. \frac{\partial^2 V_{el}}{\partial \vec{Z} \partial \vec{Z}} \right|_{\vec{Z}^o(\vec{z})} \mathbf{m}^{-1/2} \mathbf{U}. \quad (2.67)$$

Equation (2.65) represents the value of the potential energy for a given configuration of the substrate along the reaction coordinate. The second and third terms of the right hand side of Eq. (2.65) represent the contributions introduced by the particular choice of the reference configuration for the normal mode transformation. Equation (2.66) represents the forces acting on the normal modes, trying to push them back into a relaxed configuration for a given value of the reactive coordinate. This reflects the coupling between the reactive and substrate degrees of freedom. Equation (2.67) represents the Hessian in the normal mode coordinates. The coupling between different normal modes is represented by its off-diagonal elements. The coupling between the reactive and substrate degrees of freedom is given by the fact that \mathbf{K} is a function of \vec{z} .

Equation (2.64) represents a full-dimensional potential energy surface. However, if the substrate modes adjust themselves adiabatically with the reactive degree(s) of freedom, the kinetic coupling will be neglected and the potential energy

surface can be reduced to the first term of the right hand side of Eq. (2.60). However, some modes can be coupled strongly to the reaction coordinate. Some of these modes might promote the reaction and then one can call them promoting modes. A convenient measure for this coupling is the substrate oscillator's displacement, $\vec{Q}^{(0)}(\vec{z})$, from their equilibrium value taken at the selected reference geometry:

$$\vec{Q}^{(0)}(\vec{z}) = -[\mathbf{K}(\vec{z})]^{-1} \vec{f}(\vec{z}). \quad (2.68)$$

This quantity can also be used to define the reorganization energy required to equilibrate the substrate at a given position of the reactive atom(s), i.e.

$$E_{reorg}(\vec{z}) = 1/2 \vec{Q}^{(0)}(\vec{z}) \mathbf{K}(\vec{z}) \vec{Q}^{(0)}(\vec{z}). \quad (2.69)$$

Note that at a stationary point, the reorganization energy compensates the additional potential due to the special choice of the reference configuration. The larger the value of the substrate oscillator's displacement, $\vec{Q}^{(0)}(\vec{z})$, the stronger the coupling with the reaction coordinate, and then these modes should be incorporated in the potential energy surface. Modes that have small values of $\vec{Q}^{(0)}(\vec{z})$ do not experience a large force during the reaction course. These modes will nevertheless contribute to the potential energy surface by their zero point energies .

2.3.6 Cartesian reaction plane

In the Cartesian reaction surface (section 2.3.5), reactive coordinates are defined by atomic positions. The separation of the reactive coordinates from the substrate coordinates is not a natural separation in case of a large coupling between both. An alternative approach is to consider collective Cartesian reactive coordinates. This is similar, in spirit, to normal modes, since they represent collective motions of several atoms. These collective coordinates can be used to build a potential as in the Cartesian reaction surface approach, section 2.3.5.

In order to formulate the Cartesian reaction plane, consider a molecule with two tautomeric structures, say left (L) and right (R). Each tautomer has a vector with $3N$ mass-weighted Cartesian coordinates, i.e. \vec{X}_L for left and \vec{X}_R for right. These vectors are assumed to be transformed to one another by permutation of all atoms and subsequent rotation. One can define two vectors in the multidimensional configuration space as follows, [127, 128]:

$$\vec{d}_1 = \frac{\vec{X}_R - \vec{X}_L}{|\vec{X}_R - \vec{X}_L|}, \quad (2.70)$$

and

$$\vec{d}_2 = \frac{\vec{X}_C - \vec{X}_{TS}}{|\vec{X}_C - \vec{X}_{TS}|}, \quad (2.71)$$

where $\vec{X}_C = 1/2(\vec{X}_R + \vec{X}_L)$ represents the center geometry and \vec{X}_{TS} is the vector of $3N$ mass-weighted Cartesian coordinates of the transition state (TS). The vectors \vec{d}_1 and \vec{d}_2 are characterized by their orthogonality as well as their anti-symmetric and symmetric motions, respectively. The plane spanned by the two vectors \vec{d}_1 and \vec{d}_2 is uniquely defined and is called the reaction plane [129]. This is why this approach is called Catesian reaction plane. These two $3N$ -dimensional vectors, \vec{d}_1 and \vec{d}_2 , do not necessarily coincide with Cartesian coordinates of a certain atom, with large amplitude motion, or any other special atom, instead these vectors describe cooperative motions of the reactive atom together with the remaining atoms. As a simple model, the rest of the $3N$ coordinates ($3N - 2$) orthogonal to the reaction plane can be treated in the harmonic approximation.

Assuming that these two vectors (coordinates) perform the large amplitude motions (reactive coordinates), the full dimensional PES can be expanded as a Taylor series to second order

$$\begin{aligned} V_{el}(d_1, d_2, \vec{Z}) = & V_{el}(d_1, d_2, \vec{0}) + \sum_{i=1}^{3N-2} \frac{\partial V_{el}(d_1, d_2, \vec{0})}{\partial Z_i} Z_i + \\ & \frac{1}{2} \sum_{i,j=1}^{3N-2} \frac{\partial^2 V_{el}(d_1, d_2, \vec{0})}{\partial Z_i \partial Z_j} Z_i Z_j, \end{aligned} \quad (2.72)$$

where $d_1 \equiv |\vec{d}_1|$, $d_2 \equiv |\vec{d}_2|$ and \vec{Z} is the vector comprising the complementary $3N - 2$ coordinates. Equation (2.72) is similar to Eq. (2.60) with d_1 and d_2 considered as the reactive coordinates and the choice $Z=0$ is equivalent to the special fixed reference case. The quality of this approximation depends strongly on the system at hand. The next step is to project out the three rotational, three translational, d_1 and d_2 coordinates, for a fixed reference,

$$(1 - \mathbf{P}) \mathbf{K}_e (1 - \mathbf{P}), \quad (2.73)$$

where \mathbf{P} is the projector onto the eight dimensional space spanned by the rotational, translational and reactive degrees of freedom. Diagonalization of the projected Hessian results in $3N - 8$ eigenvectors, denoted as \vec{Q}_j , with non-vanishing eigenvalues. The coordinates, Q_j , corresponding to these eigenvectors in addition to the reactive coordinates form a full-dimensional potential energy surface.

2.4 The stationary nuclear Schrödinger equation

In this section, the Fourier grid Hamiltonian will be outlined as a method for the calculation of the vibrational eigenfunctions. Separation of the total wave function into vibrational, rotational and translational ones will be considered. The disadvantage of this method together with an alternative technique, namely the relaxation technique, will be presented. The relaxation technique will be introduced in section 2.5.3.

2.4.1 Fourier Grid Hamiltonian (FGH)

The methods discussed so far were used to construct the potential energy surface on which the atoms are moving. Once the potential is obtained, one can make use of it to solve the time independent nuclear Schrödinger equation, Eq. (2.18), and get the corresponding eigenfunctions and eigenvalues. Actually, $\Psi_{el,nuc}(\vec{R})$ comprises all nuclear degrees of freedom (translational, rotational and vibrational). Since we are interested in the vibrational degrees of freedom, we have to separate the translational and rotational degrees of freedom. This can be achieved by transforming the laboratory fixed coordinates to the center of mass fixed coordinates. Therefore, one can write

$$\Psi_{el,nuc}(\vec{R}) = \Psi_{transrot}(\vec{R}) \cdots \Psi_{el,vib}(\vec{R}), \quad (2.74)$$

and Eq. 2.18 is then written for the vibrational degrees of freedom as

$$\hat{H}_{el,nuc} \Psi_{el,vib}(\vec{R}) = E_{el,vib} \Psi_{el,vib}(\vec{R}), \quad (2.75)$$

whose solutions give the vibrational eigenfunctions and eigenstates.

One way to solve Eq. (2.75) numerically is the Fourier Grid Hamiltonian method [130, 131, 132]. It is characterized by its simplicity and accuracy. This method requires only the evaluation of the potential at equally spaced grid points, and yields directly the amplitude of the eigenfunctions at the same grid points. It relies on the fact that the kinetic energy operator is best represented in momentum space, while the potential energy is best given in coordinate space.

Assume a single particle of mass m moving in one linear dimension, e.g. x , under the influence of a potential V_{el} . Since all terms in the time independent nuclear Schrödinger equation are obviously nuclear coordinate dependent, we will drop the nuclear coordinate dependence in the following. The system Hamiltonian

can be then written as

$$\hat{H}_{el,nuc} = \hat{T}_{nuc} + \hat{V}_{el}(x) = \frac{\hat{p}^2}{2m} + V_{el}(x) \quad (2.76)$$

The principle representation used in this method is the coordinate representation. The basic vectors of this representation, $|x\rangle$, are eigenfunctions of the position coordinate operator, \hat{x} :

$$\hat{x}|x\rangle = x|x\rangle \quad (2.77)$$

These basis vectors fulfill the orthogonality and completeness relationships:

$$\langle x|x'\rangle = \delta(x - x') \quad (2.78)$$

$$\hat{I}_x = \int_{-\infty}^{\infty} |x\rangle\langle x| dx. \quad (2.79)$$

As the potential is diagonal in the coordinate representation, one can write

$$\langle x'|V_{el}(\hat{x})|x\rangle = V_{el}(x)\delta(x - x'). \quad (2.80)$$

On the same footing, the eigenvectors of the momentum operator are

$$\hat{p}|k\rangle = k\hbar|k\rangle, \quad (2.81)$$

and the orthogonality as well as the completeness relations are written as

$$\langle k|k'\rangle = \delta(k - k') \quad (2.82)$$

$$\hat{I}_k = \int_{-\infty}^{\infty} |k\rangle\langle k| dk. \quad (2.83)$$

Therefore, the kinetic energy operator can be written in the momentum space as

$$\langle k'|\hat{T}_{nuc}|k\rangle = T_{nuc,k}\delta(k - k') \equiv \frac{\hbar^2 k^2}{2m}\delta(k - k'). \quad (2.84)$$

One can transform from the coordinate space to the momentum space and vice versa through the following relation

$$\langle k|x\rangle = \frac{1}{\sqrt{2\pi}} \exp(-ikx) \quad (2.85)$$

The Hamiltonian can then be written in the coordinate representation as

$$\langle x|\hat{H}_{el,nuc}|x'\rangle = \langle x|\hat{T}_{nuc}|x'\rangle + V_{el}(x)\delta(x - x') \quad (2.86)$$

By inserting the identity operator Eq. (2.83) to the right of the kinetic energy operator, one obtains

$$\langle x | \hat{H}_{el,nuc} | x' \rangle = \langle x | \hat{T}_{nuc} \left\{ \int_{-\infty}^{\infty} |k\rangle \langle k| \right\} |x' \rangle dk + V_{el}(x) \delta(x - x') \quad (2.87a)$$

$$= \int_{-\infty}^{\infty} \langle x | k \rangle T_{nuc,k} \langle k | x' \rangle dk + V_{el}(x) \delta(x - x') \quad (2.87b)$$

$$= \frac{1}{2\pi} \int_{-\infty}^{\infty} \exp(ik(x - x')) T_{nuc,k} dk + V_{el}(x) \delta(x - x'). \quad (2.87c)$$

Now one can replace the continuous representation, x , by a grid of discrete values x_i :

$$x_i = i\Delta x, \quad i = 1, \dots, N. \quad (2.88)$$

where Δx is the uniform spacing between the grid points. The orthogonality and the identity operator can then be written as

$$\Delta x \langle x_i | x_j \rangle = \delta_{ij}, \quad (2.89)$$

and

$$\hat{I}_x = \sum_{i=1}^N |x_i\rangle \Delta x \langle x_i|. \quad (2.90)$$

The Hamiltonian operator matrix elements, Eq. 2.87, becomes

$$H_{ij} = \langle x_i | \hat{H}_{el,nuc} | x_j \rangle \quad (2.91a)$$

$$= \frac{1}{2\pi} \sum_{l=-n}^n \exp(il\Delta k(x_i - x_j)) \left\{ \frac{\hbar^2}{2m} (l\Delta k)^2 \right\} \Delta k + \frac{V_{el}(x_i)\delta_{ij}}{\Delta x} \quad (2.91b)$$

$$= \frac{1}{2\pi} \left(\frac{2\pi}{N\Delta x} \right) \sum_{l=-n}^n \exp[il(2\pi/N\Delta x)] \quad (2.91c)$$

$$\times (i-j)\Delta x] \{T_l\} + \frac{V_{el}(x_i)\delta_{ij}}{\Delta x} \quad (2.91d)$$

$$= \frac{1}{\Delta x} \left\{ \sum_{l=-n}^n \frac{\exp(il2\pi(i-j)/N)}{N} \{T_l\} + V_{el}(x_i)\delta_{ij} \right\}, \quad (2.91e)$$

where

$$T_l = \frac{\hbar^2}{2m} (l\Delta k)^2 \quad \& \quad \Delta k = \frac{2\pi}{N\Delta x}. \quad (2.92)$$

Having the Hamiltonian matrix elements, one can write an expression for the expectation value of the energy corresponding to an arbitrary state function, which is expressed as a linear combination of the basis functions $|x_i\rangle$.

$$|\Psi\rangle = \hat{I}_x |\Psi\rangle = \sum_i |x_i\rangle \Delta x \Psi_i. \quad (2.93)$$

Therefore, the expectation value becomes

$$E = \frac{\langle \Psi | \hat{H}_{el} | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \frac{\sum_{ij} \Psi_i^* \Delta x H_{el,ij} \Delta x \Psi_j}{\Delta x \sum_i |\Psi_i|^2}. \quad (2.94)$$

After renormalization of the Hamiltonian matrix ($H_{el,ij}^0 = \Delta x H_{ij}$) the expectation value may be written as

$$E = \frac{\langle \Psi | \hat{H}_{el} | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \frac{\sum_{ij} \Psi_i^* H_{el,ij}^0 \Psi_j}{\sum_i |\Psi_i|^2}. \quad (2.95)$$

Minimizing this energy with respect to the coefficients, Ψ_i , yields a set of secular equations

$$\sum_i [H_{el,ij}^0 - E_\lambda \delta_{ij}] \Psi_j^\lambda = 0. \quad (2.96)$$

The eigenvalues E_λ of this equation are the vibrational state energies of the system and Ψ_j^λ are the corresponding vibrational eigenfunctions.

Since the FGH method involves matrices of the order $L \times L$, where L is the number of the employed grid points, one may face the problem of the growing order of the matrices which must be diagonalized when a multidimensional case is considered. This can be handled easily nowadays for one or two dimensional problems due to fast computer development. Nevertheless, the multidimensional problem is best treated using the relaxation technique which will be discussed in section (2.5.3).

2.5 Time dependent nuclear Schrödinger equation

In the previous section, we have seen how one calculates the vibrational eigenfunctions as solutions of the time independent Schrödinger equation. To know how the state of the system evolves in time after some perturbation is introduced, one has to solve the quantum mechanical equation of motion, the time dependent Schrödinger equation, but this is impossible to do analytically for the systems treated here. Therefore, this has to be done numerically. Since we are interested in the interaction of the molecular system with an external field, the Hamiltonian consists of a molecular part, $\hat{H}_{el,nuc} = \hat{T}_{nuc} + \hat{V}_{el}$, and a time dependent interaction $\hat{W}(t)$ of the molecule with the electric field

$$\hat{H}(t) = \hat{H}_{el,nuc} + \hat{W}(t) = \hat{T}_{nuc} + \hat{V}_{el} + \hat{W}(t). \quad (2.97)$$

The kinetic energy operator \hat{T}_{nuc} in its simplest form is:

$$\hat{T}_{nuc} = -\frac{1}{2m_1} \frac{\partial^2}{\partial q_1^2} - \frac{1}{2m_2} \frac{\partial^2}{\partial q_2^2} - \cdots - \frac{1}{2m_n} \frac{\partial^2}{\partial q_n^2}, \quad (2.98)$$

with coordinates q_i and the corresponding masses, m_i . The coordinates q_i can be Cartesian, normal or internal coordinates. In many cases, however, the kinetic energy operator can have a more complicated form if there exist kinetic couplings, e.g. a product of momenta corresponding to different coordinates. We will see later an example of how to avoid this kind of coupling by transforming the coordinates into other ones where the kinetic coupling vanishes, see Appendix D. The potential energy operator \hat{V}_{el} in Eq. (2.97) is the potential energy surface obtained with traditional quantum chemical calculations (see section 2.2.2).

The molecular wave function, Eq. (2.17), can be generally written as

$$\Phi(\vec{r}, \vec{R}, t) = \sum_{el} \Psi_{el}(\vec{r}; \vec{R}) \Psi_{el,nuc}(\vec{R}, t). \quad (2.99)$$

Therefore, Eq. (2.1) becomes

$$\begin{aligned} i\hbar \frac{\partial}{\partial t} \Phi(\vec{r}, \vec{R}, t) &= \sum_{el} \Psi_{el}(\vec{r}; \vec{R}) i\hbar \frac{\partial}{\partial t} \Psi_{el,nuc}(\vec{R}, t) \\ &= \sum_{el} \hat{H}(t) \Psi_{el}(\vec{r}; \vec{R}) \Psi_{el,nuc}(\vec{R}, t). \end{aligned} \quad (2.100)$$

Left-multiplying both sides by $\Psi_{el'}^*(\vec{r}; \vec{R})$ and integration over \vec{r} , we get

$$i\hbar \frac{\partial}{\partial t} \Psi_{el,nuc}(\vec{R}, t) = \int d\vec{r} \sum_{el} \Psi_{el'}^*(\vec{r}; \vec{R}) \hat{H}(t) \Psi_{el}(\vec{r}; \vec{R}) \Psi_{el,nuc}(\vec{R}, t). \quad (2.101)$$

The formal solution of Eq. (2.101), in terms of an operator that describes the dynamics of the system, will be simply of the form:

$$\Psi_{el,nuc}(\vec{R}, t) = \hat{U}(t, t_o) \Psi_{el,nuc}(\vec{R}, t_o), \quad (2.102)$$

where $\hat{U}(t, t_o)$ is the time evolution operator which propagates the wavefunction, $\Psi_{el,nuc}(\vec{R}, t)$, from time t_o to time t . If the Hamiltonian operator is time independent and neglecting the non-adiabatic coupling, the form of the time evolution operator becomes (for a single electronic state) [133]:

$$\hat{U}(t, t_o) = \exp\left(-\frac{i}{\hbar} \hat{H}_{el,nuc}(t - t_o)\right). \quad (2.103)$$

Since our simulations are concerned with the electronic ground state as well as the first electronic excited state, it is necessary to rewrite the time dependent Schrödinger equation for both electronic (ground and first excited) states as:

$$i\hbar \frac{\partial}{\partial t} \begin{pmatrix} |\Psi_0(t)\rangle \\ |\Psi_1(t)\rangle \end{pmatrix} = \begin{pmatrix} \hat{H}_{00} & \hat{H}_{01} \\ \hat{H}_{10} & \hat{H}_{11} \end{pmatrix} \begin{pmatrix} |\Psi_0(t)\rangle \\ |\Psi_1(t)\rangle \end{pmatrix}, \quad (2.104)$$

where $|\Psi_0(t)\rangle$ and $|\Psi_1(t)\rangle$ are the time dependent nuclear wave functions in the electronic ground and first excited states, respectively. The subscripts 0 and 1 stand for the electronic states. Neglecting kinetic couplings the matrix representation of the Hamiltonian is given by

$$\begin{pmatrix} \hat{H}_{00} & \hat{H}_{01} \\ \hat{H}_{10} & \hat{H}_{11} \end{pmatrix} = \begin{pmatrix} \hat{T}_{00} & 0 \\ 0 & \hat{T}_{11} \end{pmatrix} + \begin{pmatrix} \hat{V}_{00} & 0 \\ 0 & \hat{V}_{11} \end{pmatrix} + \begin{pmatrix} \hat{W}_{00} & \hat{W}_{01} \\ \hat{W}_{10} & \hat{W}_{11} \end{pmatrix}. \quad (2.105)$$

There are several numerical methods to solve the quantum-mechanical equation of motion, Eq. (2.104). Before we go through its solution, we will see a brief description of the electric field, $\hat{W}(t)$, mentioned above.

Laser field

The time dependent molecule-electric field interaction mentioned in Section 2.5 was described by an operator $\hat{W}(t)$ which in the semiclassical dipole approximation takes the form:

$$\hat{W}_{ij}(t) = -\vec{\mu}_{ij} \cdot \vec{\epsilon}(\vec{R}, t) \quad (2.106)$$

where $\vec{\mu}_{ij}$ is the transition dipole moment² between different electronic states i and j and $\vec{\epsilon}(\vec{R}, t)$ is the time-dependent field in fixed laboratory coordinates \vec{R} . The transition dipoles can be obtained from the quantum chemical calculations (see Section 2.2.2). The field, $\vec{\epsilon}(\vec{R}, t)$, that has been used throughout this work is expressed as:

$$\vec{\epsilon}(\vec{R}, t) = \vec{e}_{x,y,z} \epsilon^o \cos(\omega t + \eta) s(t) \quad (2.107)$$

where $\vec{e}_{x,y,z}$ is the polarization vector, ϵ^o is the field amplitude, ω is the carrier frequency, η is the phase and $s(t)$ is the pulse shape, which is considered, in the present work, to be a \sin^2 -function [134] within the pulse duration and zero otherwise:

$$s(t) = \sin^2\left(\frac{\pi t}{t_p}\right) \quad 0 \leq t \leq t_p, \quad (2.108)$$

with t_p being the pulse duration.

2.5.1 Split Operator Method

In the following we will present an approximation to solve the quantum-mechanical equation of motion, Eq. (2.104). One might distinguish two classes of

²The permanent dipole moments, $\vec{\mu}_{ii}$, are neglected, since we are dealing with electronic transitions

approximations: the first focuses on the Hamiltonian (the split operator method, discussed in this section) and the second approximates the wave function (mean-field and multiconfiguration methods, discussed in section 2.5.2).

The split operator method, introduced by Feit and Fleck [135, 136], is one of the most popular methods to solve the time dependent Schrödinger equation numerically. It begins by representing the time evolution operator, Eq. (2.103), over the global time interval $[0, \mathfrak{T}]$ as a product of propagators over short time intervals, Δt , where $N\Delta t = \mathfrak{T}$ (\mathfrak{T} stands for the final time). Thus

$$\hat{U}(\mathfrak{T}, 0) = \exp\left(\frac{-i\Delta t \hat{H}(\tilde{t}_N)}{\hbar}\right) \exp\left(\frac{-i\Delta t \hat{H}(\tilde{t}_{N-1})}{\hbar}\right) \cdots \exp\left(\frac{-i\Delta t \hat{H}(\tilde{t}_1)}{\hbar}\right), \quad (2.109)$$

where \tilde{t}_i chosen in the time interval $[t_{i-1}, t_i]$, $t_i = i\Delta t$, and we assume that $\hat{H}(t)$ is approximately time independent in the short time interval $[t_{i-1}, t_i]$. The strategy is then to approximate each short time propagator by splitting of the kinetic and potential energy operators:

$$\begin{aligned} \exp\left(\frac{-i\Delta t \hat{H}}{\hbar}\right) &= \exp\left(\frac{-i\Delta t(\hat{T} + \hat{V} + \hat{W})}{\hbar}\right) \\ &\approx \exp\left(\frac{-i\Delta t \hat{T}}{\hbar}\right) \exp\left(\frac{-i\Delta t(\hat{V} + \hat{W})}{\hbar}\right) + O(\Delta t)^2. \end{aligned} \quad (2.110)$$

However, \hat{T} and \hat{V} do not commute, i.e. $[\hat{T}, \hat{V}] \neq 0$, hence we have an error of a second order in Δt . Nevertheless, one can make the error smaller by approximating each short time propagator by a symmetric splitting of the kinetic and potential energy operators in the following way:

$$\begin{aligned} \exp\left(\frac{-i\Delta t \hat{H}}{\hbar}\right) &\approx \exp\left(\frac{-i\Delta t \hat{T}}{2\hbar}\right) \exp\left(\frac{-i\Delta t(\hat{V} + \hat{W})}{\hbar}\right) \\ &\quad \times \exp\left(\frac{-i\Delta t \hat{T}}{2\hbar}\right) + O(\Delta t)^3 \end{aligned} \quad (2.111)$$

The error in such a splitting is of a third order in Δt .

The propagation of the wave function involves the following steps: Fourier transforming the wave function to the momentum space, multiplying it by the propagator $\exp\left(\frac{-i\Delta t \hat{T}}{2\hbar}\right)$ and transforming back to the coordinate space, where it is multiplied by $\exp\left(\frac{-i\Delta t \hat{V}}{\hbar}\right)$. The resulting function is transformed to the momentum space, multiplied by $\exp\left(\frac{-i\Delta t \hat{T}}{2\hbar}\right)$ and transformed again back to the

coordinate space in order to complete one time-step propagation. This procedure should be repeated until the final time \mathfrak{T} . Fourier transform is performed very efficiently using forward and backwards fast fourier transform [137].

2.5.2 The multi-configuration time dependent Hartree (MCTDH)

Another approach can be used in the solution of the time dependent Schrödinger equation for nuclear motion (Here: the electronic ground state and the case of no laser are considered), Eq. (2.101), that is the mean-field approximation. In this approximation, one considers the wave function to be a Hartree product of wave functions for the individual nuclear coordinate. The main idea of this approximation is to reduce all interactions of a particle with all the others to an average or effective interaction. This replaces the multi-particle problem to many effective one-body problems. This means that the time evolution of the total system can be solved at a relatively low cost.

For illustration, consider the simple situation when the total system has only two degrees of freedom, for instance a reaction coordinate X coupled to a harmonic vibrational mode Q . The potential energy surface in this case reads

$$V(X, Q) = V_X^{(1)}(X) + V_Q^{(1)}(Q) + V^{(2)}(X, Q). \quad (2.112)$$

The extension to larger systems is straightforward. The wave function can be written as Hartree product [138, 139]:

$$\Psi(X, Q; t) = \varphi^{(X)}(X; t)\varphi^{(Q)}(Q; t), \quad (2.113)$$

where, $\varphi^{(X)}(X; t)$ and $\varphi^{(Q)}(Q; t)$ are single particle functions whose equations of motion, derived from the Dirac-Frenkel variational principle [138, 140]

$$\langle \delta\Psi | H - i\hbar \frac{\partial}{\partial t} | \Psi \rangle = 0, \quad (2.114)$$

become

$$i\hbar \frac{\partial}{\partial t} \varphi^{(X)}(X; t) = [T_X + V_{SCF,X}(X; t)]\varphi^{(X)}(X; t), \quad (2.115)$$

and

$$i\hbar \frac{\partial}{\partial t} \varphi^{(Q)}(Q; t) = [T_Q + V_{SCF,Q}(Q; t)]\varphi^{(Q)}(Q; t). \quad (2.116)$$

The $V_{SCF,X}(X, t)$ and $V_{SCF,Q}(Q, t)$ are the mean-field potentials representing the coupling between the two coordinates which, in the time dependent self consistent

field approach, read

$$V_{SCF,X}(X, t) = V_X^{(1)}(X) + \int dQ \varphi^{(Q)*}(Q; t) V^{(2)}(X, Q) \varphi^{(Q)}(Q; t) \quad (2.117)$$

$$V_{SCF,Q}(Q, t) = V_Q^{(1)}(Q) + \int dX \varphi^{(X)*}(X; t) V^{(2)}(X, Q) \varphi^{(X)}(X; t). \quad (2.118)$$

In general, dimensionality plays a strong role in determining whether the mean-field approach will work for a particular problem. In this approach, many interactions are replaced by one effective interaction. Then it naturally follows that if the particle exhibits many comparable interactions in the original system, the mean-field approach will be more accurate for such a system. This is true in case of high dimensionality. Therefore, the quality of the mean-field approach depends on the number of spatial dimensions in the system of interest.

This approach was found to work well in some applications as shown in Ref. [141]. Makri and Miller showed a poor performance of this approach in case of proton transfer reactions [142]. In order to improve the mean-field approach, one may take several configurations into account. The multi-configurational time-dependent self-consistent field approach (MC-TDSCF) was first proposed by Makri and Miller [142] and Kosloff et al. [143]. These important early investigations were developed by H.-D. Meyer and coworkers to a more applicable approach known as Multi-Configurational Time Dependent Hartree (MCTDH) [144, 145, 132]. The ansatz for the wave function reads

$$\Psi(q; t) = \sum_{\nu_1=1}^{n_1} \cdots \sum_{\nu_N=1}^{n_N} A_{\nu_1, \dots, \nu_N}(t) \varphi_{\nu_1}^{(1)}(q_1; t) \cdots \varphi_{\nu_N}^{(N)}(q_N; t), \quad (2.119)$$

where ν_j refer to the number of single particle functions corresponding to a certain degree of freedom q_j . Equations of motion for the coefficient matrix $A_{\nu_1, \dots, \nu_N}(t)$ and the single particle functions $\varphi_{\nu_j}^{(j)}(q_j; t)$ can be derived by the Dirac-Frenkel variational principle, Eq. (2.114) [144]. For the numerical integration of the equations of motion the single particle function are often expressed in a discrete variable representation grid [146, 147]. For more details see Refs. [145, 148]. The time-dependent single particle functions can follow the wave packet during the propagation, making the ansatz, Eq. (2.119), more efficient than using the same number of time-independent basis functions, see Fig. 2.1.

In this thesis, we used combined modes constraint for e.g. four dimensional model in which the wave functions ansatz reads

$$\Psi(Q_1, Q_2, Q_3, Q_4; t) = \sum_{\nu_1=1}^4 \sum_{\nu_2=1}^4 A_{\nu_1, \nu_2}(t) \varphi_{\nu_1}^{(1)}(Q_1, Q_2; t) \cdot \varphi_{\nu_2}^{(2)}(Q_3, Q_4; t), \quad (2.120)$$

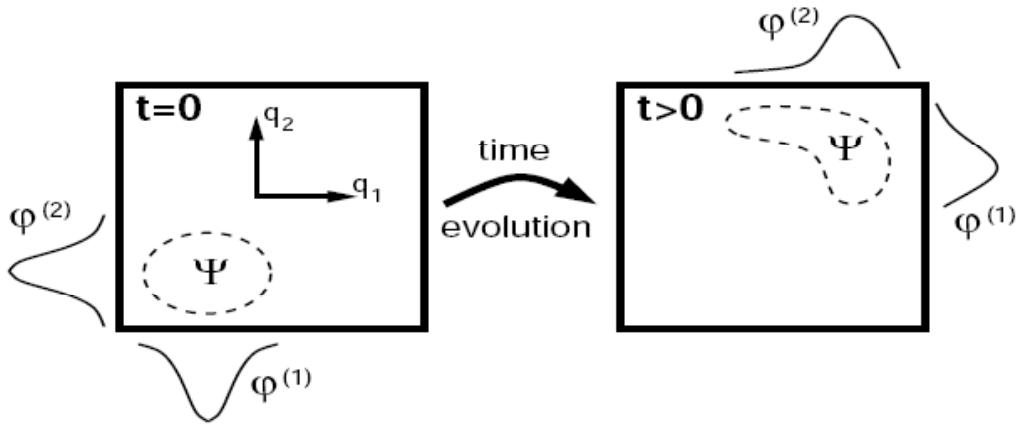


Figure 2.1: The initial wave packet, $\Psi(t = 0)$ moves and spreads during the time evolution. The time-dependent single particle functions $\varphi^{(j)}$ can follow the motion of Ψ (only one single particle function per degree of freedom is shown); this is adapted from Ref. [20].

2.5.3 Imaginary time propagation method

The relaxation technique [149] provides an elegant and efficient way to solve the time-independent nuclear Schrödinger equation, i.e. to calculate the stationary vibrational wavefunctions. The key point of this method is to replace the time in the time-dependent Schrödinger equation (2.101) by an imaginary one, $t = -i\tau$. The solution of Eq. (2.101) then becomes:

$$\Psi_0(\tau) = \exp(-\hat{H}_0\tau/\hbar)\Psi_0(0), \quad (2.121)$$

where $\Psi_0(0)$ is an initial wave function. Expanding the initial wave function in eigenfunctions Ψ_j of the Hamiltonian:

$$\Psi_0(\tau) = \exp(-\hat{H}_0\tau/\hbar) \sum_n c_n \Psi_n(0) = \sum_n c_n \exp(-E_{0,n}\tau) \Psi_{0,n}(0). \quad (2.122)$$

Equation (2.122) reveals that each eigenfunction relaxes to zero at a rate proportional to its eigenvalue. This means that the vibrational ground state will be present finally.

To get the excited state wave functions, one has to remove the ground state wave function from the Hilbert space; this makes the first excited state the ground state in the new space. If $\hat{P}_0 = |\Psi_0\rangle\langle\Psi_0|$ is the projection operator of the ground state, then the resulting state of the operator:

$$\hat{H}_1 = (I - \hat{P}_0)\hat{H}(I - \hat{P}_0) \quad (2.123)$$

is the first excited state. One can repeat this procedure by removing the first excited state from the Hilbert space to get the second excited state, and so forth. Generally the resulting state from the operator:

$$\hat{H}_n = (\hat{I} - \sum_{m=0}^{n-1} \hat{P}_m) \hat{H} (\hat{I} - \sum_{m=0}^{n-1} (\hat{P}_m)) \quad (2.124)$$

is the n th excited state, after removing the $n-1$ state from the calculations, where $\hat{P}_m = |\Psi_m\rangle\langle\Psi_m|$.

2.6 Pure and mixed state dynamics

So far we have dealt with pure quantum states where the system can be characterized by a wave function which can be expanded in eigenfunctions of the Hamiltonian, Eq. (2.122). This is not the most general case we can think of. For instance, in order to talk about enantiomers in a racemate one has to think in terms of a mixture of states. We can consider a probability distribution of pure states, such as $|0\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$ with probability 1/2 and $|1\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$ with probability 1/2.

Another possibility are the states (with probability 1/2 for each):

$$|+\rangle = \frac{1}{\sqrt{2}}(|0\rangle + |1\rangle) \quad (2.125)$$

$$|-\rangle = \frac{1}{\sqrt{2}}(|0\rangle - |1\rangle) \quad (2.126)$$

In general, one can think of mixed states as a collection of pure states $|\Psi_i\rangle$, each with probability p_i , with the condition $0 \leq p_i \leq 1$ and $\sum_i p_i = 1$.

Accordingly, we will consider the result of measuring a mixed quantum state. Consider a system composed of a mixture of quantum states $|\Psi_i\rangle$ with probability p_i . Each $|\Psi_i\rangle$ can be represented as a vector $\begin{pmatrix} a_1 & a_2 & \dots & a_N \end{pmatrix}^T$ and thus we can write the outer product $|\Psi_i\rangle\langle\Psi_i| = \Psi_i\Psi_i^*$, when we have N basis functions, as

$$\begin{pmatrix} a_1 \\ a_2 \\ \vdots \\ a_N \end{pmatrix} \left(\begin{matrix} a_1^* & a_2^* & \dots & a_N^* \end{matrix} \right) = \begin{pmatrix} a_1a_1^* & a_1a_2^* & \dots & a_1a_N^* \\ a_2a_1^* & a_2a_2^* & \dots & a_2a_N^* \\ \vdots & \vdots & \ddots & \vdots \\ a_Na_1^* & a_Na_2^* & \dots & a_Na_N^* \end{pmatrix} \quad (2.127)$$

where a_i and a_i^* represent the coefficients of the basis functions. The density matrix of the mixture can be obtained by taking the average of these matrices:

$$\rho = \sum_i p_i |\Psi_i\rangle\langle\Psi_i|. \quad (2.128)$$

Suppose we have the mixed state which consists of $|0\rangle$ with probability 1/2 and $|1\rangle$ with probability 1/2. Then the operator density matrix reads:

$$\rho = \frac{1}{2}|0\rangle\langle 0| + \frac{1}{2}|1\rangle\langle 1|. \quad (2.129)$$

Now we consider the mixed states $|+\rangle$ and $|-\rangle$. Then we have:

$$\rho = \frac{1}{2}|+\rangle\langle +| + \frac{1}{2}|-\rangle\langle -|. \quad (2.130)$$

One can notice that if we substitute from Eq. (2.125) in Eq. (2.130), we shall get Eq. (2.129), i.e. Eqs. (2.129) and (2.130) are equivalent. In chapter 4, we shall see how to apply this result for the case of enantiomers in a racemate whose density matrix can be composed of different mixed states.

A differential equation for the time evolution of the density operator may be derived by taking the time derivative of Eq. (2.128) and using the time dependent Schrödinger equation to replace the time derivative of the wave function with the Hamiltonian operating on the wave function. This results in the Liouville von Neumann equation:

$$i\hbar \frac{\partial \rho(t)}{\partial t} = [\hat{H}(t), \rho(t)], \quad (2.131)$$

where the time-dependent density matrix is given by:

$$\rho(t) = \begin{pmatrix} \rho_{00}(t) & \rho_{01}(t) \\ \rho_{10}(t) & \rho_{11}(t) \end{pmatrix}, \quad (2.132)$$

with the densities $\rho_{ij} = |\psi_i(t)\rangle\langle\psi_j(t)|$, assuming non-dissipative environment. The indices i and j represent the electronic states 0 and 1. The Hamiltonian is written as

$$\hat{H}(t) = \begin{pmatrix} \hat{H}_{00}(t) & \hat{H}_{01}(t) \\ \hat{H}_{10}(t) & \hat{H}_{11}(t) \end{pmatrix} = \begin{pmatrix} \hat{T}_{nuc}(t) + V_0(t) & -\vec{\mu}_{01}\vec{\epsilon}(t) \\ -\vec{\mu}_{10}\vec{\epsilon}(t) & \hat{T}_{nuc}(t) + V_1(t) \end{pmatrix}. \quad (2.133)$$

This Liouville von Neumann equation, Eq. (2.131), can be used to describe the evolution of an ensemble of molecules such as a mixture of enantiomers. The density of the initial mixture of enantiomers can be written as

$$\rho(t=0) = \begin{pmatrix} \rho_{00}(t=0) & 0 \\ 0 & 0 \end{pmatrix}, \quad (2.134)$$

which is, using Eqs. (2.129) and (2.130), given by

$$\rho(t=0) = \begin{pmatrix} \frac{1}{2}|0\rangle\langle 0| + \frac{1}{2}|1\rangle\langle 1| & 0 \\ 0 & 0 \end{pmatrix}, \quad (2.135)$$

or

$$\rho(t=0) = \begin{pmatrix} \frac{1}{2}|+\rangle\langle+| + \frac{1}{2}|-\rangle\langle-| & 0 \\ 0 & 0 \end{pmatrix}. \quad (2.136)$$