

# Chapter 2

## Theory

This chapter reviews the theoretical concepts of this work: First, the Hamiltonian describing a molecule coupled with an external electric field is introduced in section 2.1. In section 2.2 the adiabatic and diabatic representation of the time dependent Schrödinger equation are introduced. The topics of the following sections are rotational averaging (section 2.3), time dependent calculation of spectra (section 2.4), pump-probe ionization spectroscopy (section 2.5), and the calculation of the initial nuclear wave function (section 2.6). In section 2.7 the applied propagation schemes are described and section 2.8 deals with methods for finding an approximate solution of the electronic Schrödinger equation. Finally, our approach of calculating the kinetic couplings is presented in section 2.9.

### 2.1 Schrödinger equation, molecular Hamiltonian and coupling with the laser field

#### Time dependent Schrödinger equation

The time evolution of a state vector  $|\Psi(t)\rangle$  is governed by the Schrödinger equation,

$$i\hbar\frac{\partial}{\partial t}|\Psi(t)\rangle = \hat{H}(t)|\Psi(t)\rangle, \quad (2.1)$$

where  $\hat{H}(t)$  is the Hamilton operator of the system. In this work the Hamilton operator consists of two parts: The first part describes the molecule without any external field and neglecting relativistic effects. The second part expresses the influence of the electric field (laser pulses in this work).

#### Molecular Hamilton operator

Assuming no interaction with the environment the non-relativistic time-independent Hamilton operator of a molecule,  $\hat{H}_{mol}$ , with  $N$  nuclei and  $n$

electrons is given by

$$\hat{H}_{mol}(\{\hat{P}_A\}, \{\hat{R}_A\}, \{\hat{p}_a\}, \{\hat{r}_a\}) = \hat{T}(\{\hat{P}_A\}, \{\hat{p}_a\}) + \hat{V}(\{\hat{R}_A\}, \{\hat{r}_a\}), \quad (2.2)$$

where

$$\hat{T}(\{\hat{P}_A\}, \{\hat{p}_a\}) = -\sum_{A=1}^N \frac{\hbar^2}{2M_A} \hat{P}_A^2 - \sum_{i=a}^n \frac{\hbar^2}{2m_e} \hat{p}_a^2 \quad (2.3)$$

describes the kinetic energy of the nuclei and electrons and

$$\hat{V}(\{\hat{R}_A\}, \{\hat{r}_a\}) = \frac{1}{4\pi\epsilon_0} \left( -\sum_{a=1}^n \sum_{A=1}^N \frac{Z_A e^2}{|\hat{r}_a - \hat{R}_A|} + \sum_{a<b}^n \frac{e^2}{|\hat{r}_a - \hat{r}_b|} + \sum_{A<B}^N \frac{Z_A Z_B e^2}{|\hat{R}_A - \hat{R}_B|} \right) \quad (2.4)$$

accounts for the electron-nuclei, electron-electron and nuclei-nuclei interactions, respectively, and represents the potential energy of the molecule in the absence of external time-dependent fields. In the above equations  $\hat{R}_A$  is the position operator,  $\hat{P}_A$  the momentum operator,  $M_A$  the mass and  $Z_A$  the atomic number of the nucleus  $A$ . Likewise  $\hat{r}_a$  and  $\hat{p}_a$  are the operators of the position and momentum of the electron  $a$  and  $m_e$  is the electron mass.

### Coupling with the Laser Field

The applied laser pulses used in this work can be described classically for they have a high photon density. The electric field is a function of time  $t$  and space  $\underline{R}$  and can be written as

$$\underline{\epsilon}(\underline{R}, t) = \underline{e} \cdot \epsilon_0 \cdot s(t) \cdot \frac{e^{i(\underline{k} \underline{R} - \omega t)} + e^{-i(\underline{k} \underline{R} - \omega t)}}{2}, \quad (2.5)$$

where  $\underline{e}$  denotes the polarization vector,  $\epsilon_0$  is the amplitude,  $s(t)$  defines the shape of the pulse,  $\underline{k}$  is the wave vector and  $\omega$  is the central frequency of the field. The term  $e^{i\underline{k} \underline{R}}$  can be expanded in a Taylor series:

$$e^{i\underline{k} \underline{R}} = 1 + i\underline{k} \underline{R} + \dots \quad (2.6)$$

Since the spatial extension of a typical molecule is of the order of  $\approx 10 \text{ \AA}$  whereas the wave lengths of the applied lasers are around 400 nm (= 4000  $\text{\AA}$ ) the Taylor expansion (2.6) can be truncated after the first term turning the electric field independent of  $\underline{k}$  and  $\underline{R}$ :

$$\underline{\epsilon}(t) = \underline{e} \cdot \epsilon_0 \cdot s(t) \cdot \frac{e^{i\omega t} + e^{-i\omega t}}{2}. \quad (2.7)$$

$$\text{or: } \underline{\epsilon}(t) = \underline{\epsilon}_0 \cdot s(t) \cdot \cos(\omega t), \quad \text{where } \underline{\epsilon}_0 = \underline{e} \cdot \epsilon_0. \quad (2.8)$$

It can be shown that, if the wave length of the electromagnetic field is much smaller than the extension of the molecule, the light-molecule interaction consists of an electric dipole, a magnetic-dipole and an electric-quadrupole part [50]. The latter two are by the order of the dimensionless factor  $1/137$  smaller than the electric-dipole term [50]. This means that the electric-dipole term - if it does not vanish at all - is the dominant one and the other two can be neglected. In this so-called electric-dipole approximation [50, 51] the operator,  $\hat{W}(t)$ , describing the interaction of the molecule with the electric field is given by

$$\hat{W}(t) = -\underline{\epsilon}(t) \cdot \overset{\leftrightarrow}{D} \cdot \underline{\hat{\mu}}, \quad (2.9)$$

where  $\hat{\mu}$  is the electric dipole operator and  $\overset{\leftrightarrow}{D}$  is the rotation matrix that connects the space-fixed coordinate system of  $\underline{\epsilon}(t)$  with the molecule-fixed coordinate system of  $\underline{\hat{\mu}}$ . In this work it will be approximated by classical averaging (see section 2.3).

To describe the molecule-laser interaction the total Hamiltonian  $\hat{H}$  is written as a sum of the molecular Hamiltonian  $\hat{H}_{mol}$  and the coupling with the external electric field  $\hat{W}(t)$ :

$$\hat{H}(t) = \hat{H}_{mol} + \hat{W}(t). \quad (2.10)$$

Describing the electric field classically (*cf* equation (2.9)) and the molecule quantum-mechanically (*cf* equation 2.2) is often referred to as the semiclassical dipole approximation.

## 2.2 Adiabatic and diabatic representation of the time-dependent Schrödinger equation

For a numerical treatment of the Mn-CO photodissociation the time-dependent Schrödinger equation will be represented in the adiabatic basis in section 2.2.1 and 2.2.2. In section 2.2.3 the time-dependent equations of an alternative representation, the diabatic picture, will be derived. The probability of dissociation can be used to determine life times of excited states. It will be defined in section 2.2.6 after the Born-Oppenheimer approximation has been introduced in section 2.2.5.

### 2.2.1 Derivation of the adiabatic representation

It is assumed that the eigenvectors  $|\Phi_j\rangle$  and eigenvalues  $E_j^{el}$  of the electronic Schrödinger equation

$$\hat{H}_{el}|\Phi_j\rangle = E_j^{el}|\Phi_j\rangle, \quad (2.11)$$

where

$$\hat{H}_{el} = -\sum_{a=1}^n \frac{\hbar^2}{2m_e} \hat{p}_a^2 + \frac{1}{4\pi\epsilon_0} \left( -\sum_{i=a}^n \sum_{A=1}^N \frac{Z_A e^2}{|\hat{r}_a - \hat{R}_A|} + \sum_{a<b}^n \frac{e^2}{|\hat{r}_a - \hat{r}_b|} \right) \quad (2.12)$$

is the electronic Hamiltonian, are known for fixed positions of the nuclei  $A = 1 \dots N$ . In reality, exact solutions of (2.11) exist only for very simple systems. In section 2.8 methods for an approximate solution of the electronic Schrödinger equation are discussed.

Since the repulsion between nuclei,

$$\frac{1}{4\pi\epsilon_0} \left( \sum_{A<B}^N \frac{Z_A Z_B e^2}{|\hat{R}_A - \hat{R}_B|} \right),$$

is a constant for fixed nuclear coordinates it can be added to the electronic Hamiltonian

$$\hat{H}'_{el} = \hat{H}_{el} + \frac{1}{4\pi\epsilon_0} \left( \sum_{A<B}^N \frac{Z_A Z_B e^2}{|\hat{R}_A - \hat{R}_B|} \right), \quad (2.13)$$

or to the electronic energy yielding the adiabatic potential energy  $V_j$ :

$$V_j(\{\hat{R}_A\}) = E_j^{el}(\{\hat{R}_A\}) + \frac{1}{4\pi\epsilon_0} \left( \sum_{A<B}^N \frac{Z_A Z_B e^2}{|\hat{R}_A - \hat{R}_B|} \right). \quad (2.14)$$

With these definitions the molecular Hamiltonian reads as

$$\hat{H}_{mol} = -\sum_{A=1}^N \frac{\hbar^2}{2M_A} \hat{P}_A^2 + \hat{H}'_{el}. \quad (2.15)$$

In the adiabatic representation the total wavefunction  $|\Psi(t)\rangle$  is expanded in the basis of the electronic wavefunctions  $|\Phi_\nu\rangle$  which diagonalize the electronic Hamiltonian  $\hat{H}_{el}$ :

$${}_{nu}\langle \{\underline{R}_A\} | \Psi(t) \rangle = \sum_j \chi_j(\{\underline{R}_A\}, t) |\Phi_j(\{\underline{R}_A\})\rangle_{el}. \quad (2.16)$$

The multiplication of  $|\Psi(t)\rangle$  with  ${}_{nu}\langle \{\underline{R}_A\} |$  on the left side of equation (2.16) describes a projection of the total wavefunction on the basis of the nuclear coordinates. The index "el" in (2.16) denotes the dependence of the electronic wavefunctions  $|\Phi_j\rangle$  on the electronic coordinates. This index will be skipped in the following equations. In equation (2.16) - the so called Born-Oppenheimer ansatz - the time-dependent coefficients  $\chi_j(t)$  can be interpreted as the nuclear wave functions. Equation (2.16) is exact as long as the electronic basis  $\{|\Phi_j(\{\underline{R}_A\})\rangle\}$  is not truncated. Inserting (2.16) in the time dependent Schrödinger equation (2.1) with the total Hamiltonian (2.10) leads to:

$$i\hbar \frac{\partial}{\partial t} \sum_j \chi_j(\{\underline{R}_A\}, t) |\Phi_j(\{\underline{R}_A\})\rangle =$$

$$\begin{aligned}
& - \sum_{A=1}^N \frac{\hbar^2}{2M_A} \Delta_A \sum_j \chi_j(\{\underline{R}_A\}, t) |\Phi_j(\{\underline{R}_A\})\rangle \\
& + \hat{H}'_{el}(\{\underline{R}_A\}) \sum_j \chi_j(\{\underline{R}_A\}, t) |\Phi_j(\{\underline{R}_A\})\rangle \\
& - \underline{\epsilon}(t) \cdot \overleftrightarrow{D} \cdot \hat{\underline{\mu}}(\{\underline{R}_A\}) \sum_j \chi_j(\{\underline{R}_A\}, t) |\Phi_j(\{\underline{R}_A\})\rangle.
\end{aligned}$$

Multiplying by  $\langle \Phi_i(\{\underline{R}_A\}) |$  on the left and integrating over the electronic coordinates, one obtains

$$\begin{aligned}
& i\hbar \frac{\partial}{\partial t} \sum_j \chi_j(\{\underline{R}_A\}, t) \underbrace{\langle \Phi_i(\{\underline{R}_A\}) | \Phi_j(\{\underline{R}_A\}) \rangle}_{\delta_{ij}} = \\
& \sum_j \left( \underbrace{\langle \Phi_i(\{\underline{R}_A\}) | \Phi_j(\{\underline{R}_A\}) \rangle}_{\delta_{ij}} \sum_{A=1}^N \left( -\frac{\hbar^2}{2M_A} \Delta_A \chi_j(\{\underline{R}_A\}, t) \right) \right) \\
& + \not\partial \cdot \sum_j \sum_{A=1}^N -\frac{\hbar^2}{2M_A} \left( \underbrace{\langle \Phi_i(\{\underline{R}_A\}) | \nabla_A | \Phi_j(\{\underline{R}_A\}) \rangle}_{T_{ij,A}^{(1)}(\{\underline{R}_A\})} \cdot \nabla_A \chi_j(\{\underline{R}_A\}, t) \right) \\
& + \sum_j \left( \chi_j(\{\underline{R}_A\}, t) \cdot \sum_{A=1}^N \left( -\frac{\hbar^2}{2M_A} \underbrace{\langle \Phi_i(\{\underline{R}_A\}) | \Delta_A | \Phi_j(\{\underline{R}_A\}) \rangle}_{T_{ij,A}^{(2)}(\{\underline{R}_A\})} \right) \right) \\
& + \sum_j \left( \underbrace{\langle \Phi_i(\{\underline{R}_A\}) | \hat{H}'_{el}(\{\underline{R}_A\}) | \Phi_j(\{\underline{R}_A\}) \rangle}_{V_j(\{\underline{R}_A\}) \cdot \delta_{ij}} \cdot \chi_j(\{\underline{R}_A\}, t) \right) \\
& - \underline{\epsilon}(t) \cdot \overleftrightarrow{D} \cdot \sum_j \left( \underbrace{\langle \Phi_i(\{\underline{R}_A\}) | \hat{\underline{\mu}}(\{\underline{R}_A\}) | \Phi_j(\{\underline{R}_A\}) \rangle}_{\underline{\mu}_{ij}(\{\underline{R}_A\})} \cdot \chi_j(\{\underline{R}_A\}, t) \right),
\end{aligned}$$

where

$$\langle \Phi_i(\{\underline{R}_A\}) | \nabla_A | \Phi_j(\{\underline{R}_A\}) \rangle \tag{2.17}$$

and

$$\langle \Phi_i(\{\underline{R}_A\}) | \Delta_A | \Phi_j(\{\underline{R}_A\}) \rangle \quad (2.18)$$

are the matrix elements of the kinetic coupling matrices  $\underline{\underline{T}}^{(1)}$  and  $\underline{\underline{T}}^{(2)}$ , respectively.  $V_i$  corresponds to the adiabatic potential of the  $i$ -th electronic state, forming a diagonal element of the adiabatic potential matrix  $\underline{\underline{V}}$  that is diagonal in the adiabatic picture. Finally,  $\underline{\underline{\mu}}_{ij}(\{\underline{R}_A\})$  are the matrix elements of the adiabatic dipole matrix  $\underline{\underline{\mu}}$ . With these notations the resulting adiabatic time dependent Schrödinger equation becomes:

$$\begin{aligned} i\hbar \frac{\partial}{\partial t} \chi_i(\{\underline{R}_A\}, t) = & \left( - \sum_{A=1}^N \frac{\hbar^2}{2M_A} \Delta_A + V_i(\{\underline{R}_A\}) \right) \chi_i(\{\underline{R}_A\}, t) \\ & + \sum_j \left( \sum_{A=1}^N - \frac{\hbar^2}{M_A} T_{ij,A}^{(1)}(\{\underline{R}_A\}) \cdot \nabla_A \cdot \chi_j(\{\underline{R}_A\}, t) \right) \\ & + \sum_j \left( \sum_{A=1}^N - \frac{\hbar^2}{2M_A} T_{ij,A}^{(2)}(\{\underline{R}_A\}) \right) \cdot \chi_j(\{\underline{R}_A\}, t) \\ & - \underline{\underline{\epsilon}}(t) \cdot \overleftrightarrow{D} \cdot \sum_j \underline{\underline{\mu}}_{ij}(\{\underline{R}_A\}) \cdot \chi_j(\{\underline{R}_A\}, t). \end{aligned} \quad (2.19)$$

## 2.2.2 Adiabatic description of the Mn-CO<sub>ax</sub> photodissociation

Taking into account the Mn-CO<sub>ax</sub> stretching coordinate  $q_a$  with the corresponding reduced mass  $\mu_a$ ,

$$\mu_a = \frac{m_{CpMn(CO)_2} \cdot m_{CO}}{m_{CpMn(CO)_2} + m_{CO}}, \quad (2.20)$$

and neglecting all other nuclear degrees of freedom, equation (2.19) gets

$$\begin{aligned} i\hbar \frac{\partial}{\partial t} \chi_i(q_a, t) = & \underbrace{\left( \underbrace{- \frac{\hbar^2}{2\mu_a} \frac{\partial^2}{\partial q_a^2} + V_i(q_a)}_{H_i(q_a)} \right)}_{\text{Born-Oppenheimer dynamics (section 2.2.5)}} \chi_i(q_a, t) \\ & - \underbrace{\frac{\hbar^2}{\mu_a} \sum_j T_{ij}^{(1)}(q_a) \cdot \frac{\partial}{\partial q_a} \cdot \chi_j(q_a, t) - \frac{\hbar^2}{2\mu_a} \sum_j T_{ij}^{(2)}(q_a) \cdot \chi_j(q_a, t)}_{\text{kinetic coupling terms}} \end{aligned}$$

$$\underbrace{-\underline{\epsilon}(t) \cdot \overleftrightarrow{D} \cdot \sum_j \underline{\mu}_{ij}(q_a) \cdot \chi_j(q_a, t)}_{\text{coupling by electric field}}, \quad (2.21)$$

where

$$T_{ij}^{(1)}(q_a) = \langle \Phi_i(q_a) | \frac{\partial}{\partial q_a} | \Phi_j(q_a) \rangle \quad (2.22)$$

and

$$T_{ij}^{(2)}(q_a) = \langle \Phi_i(q_a) | \frac{\partial^2}{\partial q_a^2} | \Phi_j(q_a) \rangle. \quad (2.23)$$

The last equation describes the nuclear motion of a (pseudo-)diatomic molecule along the internuclear bonding coordinate  $q_a$ , where  $\chi_j(q_a, t) = \chi_j^{vib}(q_a, t)$  is the vibrational part of the nuclear wave function. The rotational and translational molecular degrees of freedom are separated by a product ansatz,

$$\chi(\underline{q}_a, \underline{R}_S) = \chi^{vib}(q_a) \cdot \chi^{rot}(\theta_a, \varphi_a) \cdot \chi^{trans}(\underline{R}_S), \quad (2.24)$$

where  $\underline{q}_a$  is the relative and  $\underline{R}_S$  is the center of mass coordinate.

It is helpful to write equation (2.21) in matrix notation,

$$i\hbar \frac{\partial}{\partial t} \underline{\chi} = -\frac{\hbar^2}{2\mu_a} \underline{\underline{1}} \frac{\partial^2}{\partial q_a^2} \underline{\chi} + \underline{\underline{V}} \underline{\chi} - \frac{\hbar^2}{\mu_a} \underline{\underline{T}}^{(1)} \frac{\partial}{\partial q_a} \underline{\chi} - \frac{\hbar^2}{2\mu_a} \underline{\underline{T}}^{(2)} \underline{\chi} - \underline{\epsilon}(t) \cdot \overleftrightarrow{D} \cdot \underline{\underline{\mu}} \underline{\chi}. \quad (2.25)$$

In the adiabatic representation the potential matrix  $\underline{\underline{V}}$  is diagonal with the potential energy curves  $V_i(q_a)$  of the  $i$ -th electronic state as diagonal elements:

$$\underline{\underline{V}} = \begin{pmatrix} V_1(q_a) & 0 & \dots \\ 0 & V_2(q_a) & \\ \vdots & & \end{pmatrix}. \quad (2.26)$$

$\underline{\underline{T}}^{(1)}$  and  $\underline{\underline{T}}^{(2)}$  define the off-diagonal part of the kinetic energy operator in the adiabatic representation. In section 2.9 it is shown that  $\underline{\underline{T}}^{(1)}$  is antisymmetric with diagonal elements equal to zero,

$$\underline{\underline{T}}^{(1)} = \begin{pmatrix} 0 & T_{12}^{(1)}(q_a) & \dots \\ T_{21}^{(1)}(q_a) & 0 & \\ \vdots & & \end{pmatrix}, \quad \text{with } T_{ij}^{(1)}(q_a) = -T_{ji}^{(1)}(q_a), \quad (2.27)$$

whereas  $\underline{\underline{T}}^{(2)}$  is neither symmetric nor anti-symmetric:

$$\underline{\underline{T}}^{(2)} = \begin{pmatrix} T_{11}^{(2)}(q_a) & T_{12}^{(2)}(q_a) & \dots \\ T_{21}^{(2)}(q_a) & T_{22}^{(2)}(q_a) & \\ \vdots & & \end{pmatrix}. \quad (2.28)$$

Finally, the coupling with the laser is given by (2.9). In the symmetric matrix  $\underline{\underline{\vec{\mu}}}$  the diagonal elements are the dipole moments of the molecule on the corresponding potentials and the off-diagonal elements are the transition dipole moments connecting the electronic states:

$$\underline{\underline{\vec{\mu}}} = \begin{pmatrix} \underline{\underline{\mu}}_{11}(q_a) & \underline{\underline{\mu}}_{12}(q_a) & \cdots \\ \underline{\underline{\mu}}_{21}(q_a) & \underline{\underline{\mu}}_{22}(q_a) & \\ \vdots & & \end{pmatrix}, \text{ with } \underline{\underline{\mu}}_{ij}(q_a) = \underline{\underline{\mu}}_{ji}(q_a). \quad (2.29)$$

### 2.2.3 An alternative description: The diabatic picture

Starting with the adiabatic time dependent Schrödinger equation (2.25) the derivation of the diabatic representation follows mainly the paper by Baer [52]. Yet, in opposition to the latter article the equations are formulated one-dimensional and time-dependent including interaction with an electric field in the electric dipole approximation. The diabatic basis can be obtained from the adiabatic one by a unitary transformation,  $\hat{U}$ , of the electronic wave functions  $|\Phi_i\rangle$ :

$$|\xi_i\rangle = \hat{U}^\dagger |\Phi_i\rangle. \quad (2.30)$$

The kets  $|\xi_i\rangle$  form the diabatic basis, and equation (2.30) defines the unitary transformation  $\hat{U}$  of the adiabatic into the diabatic basis set. Both, the total wavefunction expressed in the diabatic basis,

$${}_{nu}\langle \{\underline{R}_A\} | \Psi(t) \rangle = \sum_i \eta_i(\{\underline{R}_A\}, t) |\xi_i(\{\underline{R}_A\})\rangle \quad (\underline{\underline{\text{diabatic}}}), \quad (2.31)$$

and the total wavefunction in the adiabatic basis,

$${}_{nu}\langle \{\underline{R}_A\} | \Psi(t) \rangle = \sum_i \chi_i(\{\underline{R}_A\}, t) |\Phi_i(\{\underline{R}_A\})\rangle \quad (\underline{\underline{\text{adiabatic}}}), \quad (2.32)$$

have to be identical. This defines the relation between the diabatic nuclear wavefunction  $\underline{\underline{\eta}}$  and the adiabatic one,  $\underline{\underline{\chi}}$ :

$$\underline{\underline{\chi}} = \underline{\underline{U}} \underline{\underline{\eta}}, \quad (2.33)$$

From equation (2.33) it follows that

$$\frac{\partial}{\partial q_a} \underline{\underline{\chi}} = \frac{\partial}{\partial q_a} \underline{\underline{U}} \underline{\underline{\eta}} + \underline{\underline{U}} \frac{\partial}{\partial q_a} \underline{\underline{\eta}}, \quad (2.34)$$

and

$$\frac{\partial^2}{\partial q_a^2} \underline{\underline{\chi}} = \frac{\partial^2}{\partial q_a^2} \underline{\underline{U}} \underline{\underline{\eta}} + 2 \frac{\partial}{\partial q_a} \underline{\underline{U}} \frac{\partial}{\partial q_a} \underline{\underline{\eta}} + \underline{\underline{U}} \frac{\partial^2}{\partial q_a^2} \underline{\underline{\eta}}. \quad (2.35)$$

Substitution of the last three equations, (2.33), (2.34) and (2.35), in the adiabatic representation of the time-dependent Schrödinger equation (2.25) yields

$$\begin{aligned}
i\hbar \frac{\partial}{\partial t} \underline{\underline{U}} \underline{\underline{\eta}} &= -\frac{\hbar^2}{2\mu_a} \underline{\underline{1}} \left( \frac{\partial^2}{\partial q_a^2} \underline{\underline{U}} \underline{\underline{\eta}} + 2 \frac{\partial}{\partial q_a} \underline{\underline{U}} \frac{\partial}{\partial q_a} \underline{\underline{\eta}} + \underline{\underline{U}} \frac{\partial^2}{\partial q_a^2} \underline{\underline{\eta}} \right) + \underline{\underline{V}} \underline{\underline{U}} \underline{\underline{\eta}} \\
&- 2 \frac{\hbar^2}{2\mu_a} \underline{\underline{T}}^{(1)} \left( \frac{\partial}{\partial q_a} \underline{\underline{U}} \underline{\underline{\eta}} + \underline{\underline{U}} \frac{\partial}{\partial q_a} \underline{\underline{\eta}} \right) - \frac{\hbar^2}{2\mu_a} \underline{\underline{T}}^{(2)} \underline{\underline{U}} \underline{\underline{\eta}} - \epsilon(t) \overset{\leftrightarrow}{D} \overset{\rightarrow}{\mu} \underline{\underline{U}} \underline{\underline{\eta}} \\
&= -\frac{\hbar^2}{2\mu_a} \underline{\underline{1}} \underline{\underline{U}} \frac{\partial^2}{\partial q_a^2} \underline{\underline{\eta}} + \underline{\underline{V}} \underline{\underline{U}} \underline{\underline{\eta}} - 2 \frac{\hbar^2}{2\mu_a} \left( \frac{\partial}{\partial q_a} \underline{\underline{U}} + \underline{\underline{T}}^{(1)} \underline{\underline{U}} \right) \frac{\partial}{\partial q_a} \underline{\underline{\eta}} \\
&- \frac{\hbar^2}{2\mu_a} \left( 2 \underline{\underline{T}}^{(1)} \frac{\partial}{\partial q_a} \underline{\underline{U}} + \underline{\underline{T}}^{(2)} \underline{\underline{U}} + \frac{\partial^2}{\partial q_a^2} \underline{\underline{U}} \right) \underline{\underline{\eta}} - \epsilon(t) \overset{\leftrightarrow}{D} \overset{\rightarrow}{\mu} \underline{\underline{U}} \underline{\underline{\eta}}. \tag{2.36}
\end{aligned}$$

By definition, the kinetic coupling terms are replaced by potential coupling in the diabatic representation. It will be proved that, if  $\underline{\underline{U}}$  fulfills the differential equation (2.37):

$$\frac{\partial}{\partial q_a} \underline{\underline{U}} + \underline{\underline{T}}^{(1)} \underline{\underline{U}} = 0, \tag{2.37}$$

also the term

$$2 \underline{\underline{T}}^{(1)} \frac{\partial}{\partial q_a} \underline{\underline{U}} + \underline{\underline{T}}^{(2)} \underline{\underline{U}} + \frac{\partial^2}{\partial q_a^2} \underline{\underline{U}} \tag{2.38}$$

vanishes.

To prove the last statement, equation (2.37) is differentiated,

$$\frac{\partial^2}{\partial q_a^2} \underline{\underline{U}} = -\frac{\partial}{\partial q_a} \underline{\underline{T}}^{(1)} \underline{\underline{U}} - \underline{\underline{T}}^{(1)} \frac{\partial}{\partial q_a} \underline{\underline{U}}, \tag{2.39}$$

and substituted into equation (2.38):

$$2 \underline{\underline{T}}^{(1)} \frac{\partial}{\partial q_a} \underline{\underline{U}} + \underline{\underline{T}}^{(2)} \underline{\underline{U}} - \frac{\partial}{\partial q_a} \underline{\underline{T}}^{(1)} \underline{\underline{U}} - \underline{\underline{T}}^{(1)} \frac{\partial}{\partial q_a} \underline{\underline{U}} = 0 \tag{2.40}$$

$$\Rightarrow \underline{\underline{T}}^{(1)} \frac{\partial}{\partial q_a} \underline{\underline{U}} + \underline{\underline{T}}^{(2)} \underline{\underline{U}} - \frac{\partial}{\partial q_a} \underline{\underline{T}}^{(1)} \underline{\underline{U}} = 0. \tag{2.41}$$

Inserting (2.37) into the last expression leads to

$$-\underline{\underline{T}}^{(1)} \underline{\underline{T}}^{(1)} \underline{\underline{U}} + \underline{\underline{T}}^{(2)} \underline{\underline{U}} - \frac{\partial}{\partial q_a} \underline{\underline{T}}^{(1)} \underline{\underline{U}} = 0. \tag{2.42}$$

It can be shown that the term

$$-\underline{\underline{T}}^{(1)} \underline{\underline{T}}^{(1)} \underline{\underline{U}} + \underline{\underline{T}}^{(2)} \underline{\underline{U}} - \frac{\partial}{\partial q_a} \underline{\underline{T}}^{(1)} \underline{\underline{U}} \tag{2.43}$$

vanishes identically. The proof is given in section 2.9.3. It is therefore shown that, if  $\underline{U}$  satisfies the differential equation (2.37) the kinetic coupling terms  $\underline{T}^{(1)}$  and  $\underline{T}^{(2)}$ , defined in equations (2.22) and (2.23), respectively, vanish and the time dependent Schrödinger equation (2.36) is expressed as:

$$i\hbar \frac{\partial}{\partial t} \underline{U} \underline{\eta} = -\frac{\hbar^2}{2\mu_a} \underline{1} \underline{U} \frac{\partial^2}{\partial q_a^2} \underline{\eta} + \underline{V} \underline{U} \underline{\eta} - \underline{\epsilon}(t) \cdot \overset{\leftrightarrow}{D} \cdot \underline{\underline{\mu}} \underline{U} \underline{\eta}. \quad (2.44)$$

By multiplication of the last expression with  $\underline{U}^\dagger$  the final result is obtained:

$$i\hbar \frac{\partial}{\partial t} \underline{\eta} = -\frac{\hbar^2}{2\mu_a} \underline{1} \frac{\partial^2}{\partial q_a^2} \underline{\eta} + \underbrace{\underline{U}^\dagger \underline{V} \underline{U}}_{\underline{V}^{dia}} \underline{\eta} - \underline{\epsilon}(t) \cdot \overset{\leftrightarrow}{D} \cdot \underbrace{\underline{U}^\dagger \underline{\underline{\mu}} \underline{U}}_{\overset{\rightarrow}{\underline{\mu}}^{dia}} \underline{\eta}. \quad (2.45)$$

In the last expression

$$\underline{\eta} = \underline{U}^\dagger \underline{\chi}$$

is the diabatic nuclear wavefunction,

$$\underline{U}^\dagger \underline{V} \underline{U} = \underline{V}^{dia} \quad (2.46)$$

denotes the diabatic potential matrix which is in general not diagonal and

$$\underline{U}^\dagger \overset{\rightarrow}{\underline{\mu}} \underline{U} = \overset{\rightarrow}{\underline{\mu}}^{dia} \quad (2.47)$$

defines the diabatic dipole matrix.

## 2.2.4 Comparison between the adiabatic and the diabatic representation

In the adiabatic representation the potential matrix is diagonal, whereas the kinetic energy has coupling terms,  $T^{(1)}$  and  $T^{(2)}$ . In the diabatic picture the kinetic couplings are replaced by potential couplings, therefore, the diabatic potential matrix has off-diagonal elements which couple the different states. Both representations are equivalent in the physical sense [53] and are connected by the unitary matrix  $U$  that defines the transformation of the nuclear and electronic wavefunction, the potential and kinetic energy and the transition dipole moment (see previous section). In this work, the adiabatic potentials and transition dipole moments come from quantum chemistry calculations and the kinetic coupling terms  $T^{(1)}$  and  $T^{(2)}$  have been numerically evaluated from the ab initio data (chapter 3).

The physical interpretation of the adiabatic representation is straightforward: The potentials and transition dipole moments are computed for fixed positions of the nuclei using approximate methods for the solution of the electronic

Schrödinger equation (section 2.8). The kinetic couplings are only large around avoided crossings which mark the break-down of the Born-Oppenheimer approximation (= a strict separation of the electron and nuclear motion). The Franck-Condon principle implies that electronic transitions are vertical transitions meaning that the electronic (adiabatic) potentials do not change during the transition. This principle allows the calculation of the absorption spectra.

In the diabatic case, the potentials and consequently the excitation energies differ from the adiabatic ones. Therefore, it is not clear how the diabatic excitation energies can be interpreted (*i.e.* if they can be related to experiment). For that reason the adiabatic representation in dynamics simulations was used throughout this work. This was possible because the kinetic couplings are smooth enough to use them as non-adiabatic couplings in the numerical calculations. Nevertheless, the use of the potential couplings (*i.e.* diabatic picture) is inevitable in all cases where the kinetic couplings defined by (2.22) and (2.23) are very sharply peaked around avoided crossings causing numerical difficulties. These computational problems of the adiabatic representation can be avoided by transforming into the diabatic basis, where the kinetic couplings are replaced by potential coupling functions which are usually smooth [54].

The problem of transforming the adiabatic into the diabatic representation has been treated in recent studies [55, 56, 57]. The diabatic representation has been used to treat atom-atom collisions [54, 58], atom-molecule interactions [52, 59], photodissociation of OH [60], photodesorption [61] and photodissociation of organometallic compounds [34], amongst some applications. In the latter two articles by Saalfrank and coworkers a diabatization procedure is applied which makes use of the fact that the kinetic coupling terms can be approximated by Lorentzians [62] if numerical results are not available.

### 2.2.5 Born-Oppenheimer dynamics

In the Born-Oppenheimer approximation [63] the kinetic coupling terms  $T^{(1)}$  and  $T^{(2)}$  in equation (2.21) are neglected. The first term of the left-hand side of equation (2.21) defines the Born-Oppenheimer dynamics (without coupling due to the electric field). Within this approximation the one-dimensional time-dependent Schrödinger equation is given by:

$$i\hbar\frac{\partial}{\partial t}\chi_i(q_a, t) = \left( \underbrace{-\frac{\hbar^2}{2\mu_a}\frac{\partial^2}{\partial q_a^2} + V_i(q_a)}_{H_i(q_a)} \right) \chi_i(q_a, t). \quad (2.48)$$

The infinitesimal change of the electronic wavefunction when changing the internuclear distance,  $\frac{\partial}{\partial q_a}|\Phi_j\rangle$ , vanishes when the electrons follow the nuclei instantaneously. The Born-Oppenheimer approximation breaks down in the case of avoided crossings of electronic potential curves of the same symmetry and spin. The kinetic couplings are the larger the smaller the reduced mass is, *i.e.* when light particles are involved (for example hydrogen atoms), and the higher the momentum,  $-i\hbar\frac{\partial}{\partial q_a}\chi_j$ , of the particles is.

## 2.2.6 Population and probability of dissociation

The normalization condition for a wave function in one dimension, for example in the Mn-CO stretching coordinate  $q_a$ , is

$$\langle\Psi|\Psi\rangle_{q_a} = 1. \quad (2.49)$$

In the adiabatic picture the total wave function,  $|\Psi(t)\rangle$ , is expanded in terms of the electronic wave functions  $|\Phi_i\rangle$ :

$$\langle q_a|\Psi(t)\rangle = \sum_i \chi_i(q_a, t)|\Phi_i\rangle_{el}. \quad (2.50)$$

Under the assumption that the electronic wave functions are orthonormal,

$$\langle\Phi_i|\Phi_j\rangle = \delta_{ij}, \quad (2.51)$$

the normalization condition gets:

$$1 = \sum_i \int_{-\infty}^{\infty} dq_a \chi_i^*(q_a, t)\chi_i(q_a, t). \quad (2.52)$$

The population  $P_i$  of the  $i$ -th electronic state can be then defined as the part of the total norm (which is equal to one) calculated by:

$$P_i(t) = \int_{-\infty}^{\infty} dq_a \chi_i^*(q_a, t)\chi_i(q_a, t). \quad (2.53)$$

Furthermore, the vibrational part of the nuclear wave functions  $\chi_i^{vib}$  can be expanded in terms of the vibrational eigenfunctions  $\Theta_{v_i}^{vib}$  (a numerical method for calculating them is given in section 2.6):

$$\chi_i^{vib}(q_a, t) = \sum_{v_i} c_{v_i}(t)\Theta_{v_i}^{vib}(q_a). \quad (2.54)$$

Then the population of the  $i$ -th electronic state is given by the sum of the populations on the different vibrational eigenstates:

$$P_i(t) = \int_{-\infty}^{\infty} dq_a \sum_{w_i} c_{w_i}^*(t)\Theta_{w_i}^{vib*}(q_a) \sum_{v_i} c_{v_i}(t)\Theta_{v_i}^{vib}(q_a)$$

$$= \sum_{w_i} \sum_{v_i} c_{w_i}^*(t) c_{v_i}(t) \int_{-\infty}^{\infty} \Theta_{w_i}^{vib^*}(q_a) \Theta_{v_i}^{vib}(q_a) dq_a. \quad (2.55)$$

Assuming that the eigenfunctions form an orthonormal set,

$$\int_{-\infty}^{\infty} \Theta_{w_i}^{vib^*}(q_a) \Theta_{v_i}^{vib}(q_a) dq_a = \delta_{w_i v_i}, \quad (2.56)$$

equation (2.55) becomes

$$P_i(t) = \sum_{v_i} c_{v_i}^*(t) c_{v_i}(t) = \sum_{v_i} |c_{v_i}(t)|^2 \quad (2.57)$$

and the population of the  $v$ -th vibrational level of the  $i$ -th electronic state is defined by the coefficients  $c_{i,v}$ :

$$P_{iv}(t) = |c_{iv}(t)|^2. \quad (2.58)$$

Similarly, in one dimension it is possible to define the probability of dissociation of the system in a certain electronic state as the part of the population which lies between a defined dissociation point  $b$  and the asymptotic region of the considered potential:

$$P_i^{(b)}(t) = \int_b^{\infty} \chi_i^*(q_a, t) \chi_i(q_a, t) dq_a. \quad (2.59)$$

Usually a pragmatic, yet reasonable, choice for the dissociation point  $b$  is a value of three times the equilibrium distance of the reaction coordinate. An alternative way to define  $b$  is to choose the point at which the orbitals of the fragments are pure, meaning that no orbitals with contributions centered at both fragments at the same time are present. If the wavepacket or a part of it can move towards dissociation (and is not trapped by a barrier) the probability of dissociation yields a rising signal from which a decay time  $\tau$  of the excited state can be calculated. It must be pointed out that a computation of  $\tau$  using (2.59) only makes sense if the applied laser pulses are much shorter than  $\tau$ . In this work, dissociation probabilities and corresponding life times have only been calculated for infinitesimal short  $\delta$ -pulses (see section 4.3).

## 2.3 Rotational averaging

In this work freely rotating (*i.e.* not oriented) molecules are considered. The dipole moment and the electric field are defined in two different coordinate systems: The space fixed coordinate system is chosen such that the  $z$ -axis is parallel to the electric field vector  $\underline{\epsilon}(t)$ , whereas the dipole moment is given in the molecule or body-fixed coordinate system with the  $z$ -axis pointing in a different direction (*e.g.* parallel to the dissociation coordinate [41]). The rotation matrix (2.61) connects the body-fixed coordinate system (which rotates with the molecule) with the space fixed one. In the semiclassical dipole approximation the interaction of two electronic states  $i$  and  $j$  is given by

$$W_{ij}(\underline{q}_a, t)\chi_j(\underline{q}_a, t) = -\underline{\epsilon}(t) \cdot \overleftrightarrow{D} \cdot \underline{\mu}_{ij}(\underline{q}_a) \cdot \chi_j(\underline{q}_a, t), \quad (2.60)$$

where  $\overleftrightarrow{D}$  is the rotation matrix [64]

$$\overleftrightarrow{D} = \begin{pmatrix} D_{xx} & D_{xy} & D_{xz} \\ D_{yx} & D_{yy} & D_{yz} \\ D_{zx} & D_{zy} & D_{zz} \end{pmatrix} \quad (2.61)$$

connecting both coordinate systems, in this work, approximated by rotational averaging of  $\overleftrightarrow{D}$ . To derive the working equations three electronic states will be considered ( $i = 0, 1, 2$ ). Only transitions from the ground state ( $i = 0$ ) to the excited states ( $i = 1, 2$ ) are taken into account. Therefore, the transition dipole matrix reads as:

$$\underline{\underline{\mu}} = \begin{pmatrix} 0 & \underline{\mu}_{01} & \underline{\mu}_{02} \\ \underline{\mu}_{10} & 0 & 0 \\ \underline{\mu}_{20} & 0 & 0 \end{pmatrix}. \quad (2.62)$$

The Born-Oppenheimer dynamics of this three-state-system is governed by the following set of three coupled differential equations:

$$i\hbar \frac{\partial}{\partial t} \chi_i(\underline{q}_a, t) = \left( -\frac{\hbar^2}{2\mu_a} \frac{\partial^2}{\partial q_a^2} + V_i(\underline{q}_a) \right) \chi_i(\underline{q}_a, t) - \underline{\epsilon}(t) \cdot \overleftrightarrow{D} \sum_j \underline{\mu}_{ij}(\underline{q}_a) \cdot \chi_j(\underline{q}_a, t),$$

$$i = 0, 1, 2. \quad (2.63)$$

Consider an  $x$ -polarized laser pulse which propagates along the  $z$ -axis. Then,

$$W_{ij}(\underline{q}_a, t)\chi_j(\underline{q}_a, t) =$$

$$- \left( \epsilon_x, \underbrace{\epsilon_y}_{=0}, \underbrace{\epsilon_z}_{=0} \right) \cdot \begin{pmatrix} D_{xx} & D_{xy} & D_{xz} \\ D_{yx} & D_{yy} & D_{yz} \\ D_{zx} & D_{zy} & D_{zz} \end{pmatrix} \cdot \begin{pmatrix} \mu_{ij,x} \\ \mu_{ij,y} \\ \mu_{ij,z} \end{pmatrix} \cdot \chi_j$$

$$= -(\epsilon_x \cdot D_{xx}, \epsilon_x \cdot D_{xy}, \epsilon_x \cdot D_{xz}) \cdot \begin{pmatrix} \mu_{ij,x} \\ \mu_{ij,y} \\ \mu_{ij,z} \end{pmatrix} \cdot \chi_j$$

$$= -(\epsilon_x \cdot D_{xx} \cdot \mu_{ij,x} \cdot \chi_j + \epsilon_x \cdot D_{xy} \cdot \mu_{ij,y} \cdot \chi_j + \epsilon_x \cdot D_{xz} \cdot \mu_{ij,z} \cdot \chi_j). \quad (2.64)$$

Let us now assume that the system is photodissociated by a  $\delta$ -pulse, *i.e.* we use

$$\underline{\epsilon}(t) = \underline{\epsilon} \text{ for } 0 \leq t \leq \delta t$$

$$\underline{\epsilon}(t) = 0 \text{ else,} \quad (2.65)$$

where  $\delta t$  is a sufficiently short time interval, such that it allows one to approximate the time derivative in equation (2.63) by a finite difference:

$$\frac{\partial}{\partial t} \chi_i \approx \frac{\chi_i(\delta t) - \chi_i(t=0)}{\delta t}. \quad (2.66)$$

Using the last expression with the initial conditions,

$$\chi_0(t=0) = \Theta_{00},$$

$$\chi_1(t=0) = 0,$$

$$\chi_2(t=0) = 0,$$

where  $\Theta_{00}$  is the vibrational and electronic ground state, in equation (2.63) one obtains (neglecting the term  $\propto \mu_{00}$ ):

$$\frac{1}{i\hbar} \left( -\frac{\hbar^2}{2\mu_a} \frac{\partial^2}{\partial q_a^2} + V_0 \right) \Theta_{00} \approx \frac{\chi_0(\delta t) - \Theta_{00}}{\delta t} \Rightarrow \chi_0(\delta t) = \Theta_{00} - \delta t \cdot \frac{i}{\hbar} \cdot E_{00} \cdot \Theta_{00} \approx \Theta_{00},$$

$$\frac{1}{i\hbar} \left( -\underline{\epsilon} \cdot \overleftrightarrow{D} \cdot \underline{\mu}_{10} \right) \Theta_{00} \approx \frac{\chi_1(\delta t)}{\delta t} \Rightarrow \chi_1(\delta t) = \delta t \cdot \frac{i}{\hbar} \cdot \underline{\epsilon} \cdot \overleftrightarrow{D} \cdot \underline{\mu}_{10} \cdot \Theta_{00},$$

$$\frac{1}{i\hbar} \left( -\underline{\epsilon} \cdot \overleftrightarrow{D} \cdot \underline{\mu}_{20} \right) \Theta_{00} \approx \frac{\chi_2(\delta t)}{\delta t} \Rightarrow \chi_2(\delta t) = \delta t \cdot \frac{i}{\hbar} \cdot \underline{\epsilon} \cdot \overleftrightarrow{D} \cdot \underline{\mu}_{20} \cdot \Theta_{00}. \quad (2.67)$$

Substituting equation (2.64) into equation (2.67), the population at time  $t = \delta t$  is:

$$\text{For } i = 0 : P_0(\delta t) \approx \int dq_a \Theta_{00}^* \Theta_{00} = 1.$$

$$\text{For } i = 1, 2 : P_i(\delta t) \approx$$

$$\begin{aligned}
& \epsilon_x^2 \cdot \int dq_a (D_{xx}D_{xx}|\mu_{i0,x}\Theta_{00}|^2 + D_{xx}D_{xy}(\mu_{i0,x}\Theta_{00})^*(\mu_{i0,y}\Theta_{00}) + D_{xx}D_{xz}(\mu_{i0,x}\Theta_{00})^*(\mu_{i0,z}\Theta_{00})) \\
& + D_{xy}D_{xy}|\mu_{i0,y}\Theta_{00}|^2 + D_{xy}D_{xx}(\mu_{i0,y}\Theta_{00})^*(\mu_{i0,x}\Theta_{00}) + D_{xy}D_{xz}(\mu_{i0,y}\Theta_{00})^*(\mu_{i0,z}\Theta_{00}) \\
& + D_{xz}D_{xz}|\mu_{i0,z}\Theta_{00}|^2 + D_{xz}D_{xx}(\mu_{i0,z}\Theta_{00})^*(\mu_{i0,x}\Theta_{00}) + D_{xz}D_{xy}(\mu_{i0,z}\Theta_{00})^*(\mu_{i0,y}\Theta_{00})).
\end{aligned}$$

Averaging over angles:

$$\begin{aligned}
\overline{D_{xx}D_{xy}} &= \overline{D_{xx}D_{xz}} = \overline{D_{xy}D_{xz}} = 0, \\
\overline{D_{xx}D_{xx}} &= \overline{D_{xy}D_{xy}} = \overline{D_{xz}D_{xz}} = \frac{1}{3},
\end{aligned} \tag{2.68}$$

leads to

$$P_1(\delta t) \approx \epsilon_x^2 \cdot \int dq_a \frac{1}{3} (|\mu_{10,x}\Theta_{00}|^2 + |\mu_{10,y}\Theta_{00}|^2 + |\mu_{10,z}\Theta_{00}|^2) \tag{2.69}$$

$$P_2(\delta t) \approx \epsilon_x^2 \cdot \int dq_a \frac{1}{3} (|\mu_{20,x}\Theta_{00}|^2 + |\mu_{20,y}\Theta_{00}|^2 + |\mu_{20,z}\Theta_{00}|^2). \tag{2.70}$$

Therefore, the initial excited state wave packet is given by the ground state wave function  $\Theta_{00}$  multiplied by the corresponding transition dipole moment function. After the  $\delta$ -pulse, the populations of the electronic states do not change and the wave packet in each excited state is governed by equation (2.63) (Born-Oppenheimer dynamics).

## 2.4 Time dependent calculation of absorption spectra

According to Heller [65] the total absorption spectrum  $\sigma_{tot}(\omega)$ , which measures the capability of the molecule to absorb radiation with a frequency  $\omega$  is obtained from the Fourier transformation of the total autocorrelation function,

$$\sigma_{tot}(\omega) \propto \int_{-\infty}^{\infty} e^{i(E_{00} + \hbar\omega)t/\hbar} S_{tot}(t) dt, \tag{2.71}$$

where  $E_{00}$  is the energy of the vibrational ground state of the electronic ground state and  $\hbar\omega$  is the energy of the absorbed photon [41]. The total autocorrelation function  $S_{tot}(t)$  is defined as the sum of the individual autocorrelation functions  $S_f(t)$  of the electronic states  $f$ .

$$S_{tot}(t) = \sum_f S_f(t) = \sum_f \langle \chi_f(t=0) | \chi_f(t) \rangle \tag{2.72}$$

The autocorrelation function describes the overlap between the wave function  $\chi_f(t)$  and the initial wavefunctions  $\chi_f(t = 0)$  as a function of time  $t$ . In this work, the initial wave function of the excited states  $f$  is calculated by multiplying the vibrational ground state wave function of the electronic ground state  $\Theta_{0_0}^{vib}$  with the transition dipole moment that connects the ground state with the state  $i$ :

$$|\chi_f^{vib}(t_0 = 0)\rangle = \mu_{0f,x/y/z} \cdot |\Theta_{0_0}^{vib}\rangle \quad (2.73)$$

A derivation of equation (2.71) is given in the appendix A.

## 2.5 Pump-probe ionization spectroscopy

Two steps are involved in a pump-probe ionization scheme. In a first step a laser pulse, called pump pulse, excites the molecule. In a second step, after a certain time delay, another laser pulse, the probe pulse, is employed to ionize the molecule. The theoretical pump-probe signal of the parent ion is determined here as the part of the population which is trapped in a certain ionic state, whereas the yield of the parent and the daughter ions correspond to the non-dissociative and the dissociating parts of the ionic states population, respectively. The pump-probe ionization spectrum reflects the nuclear dynamics of the electronic excited state as a function of the delay between the pulses.

In this work the vibrational ground state of the electronic ground state,  $\Theta_{0_0}^{vib}$ , is chosen as the initial wavefunction. Since this is an eigenstate of the system, the corresponding expectation values (for example of the position operator) do not change with time (stationary state). The pump pulse, however, creates a wave packet in the excited state which is a coherent superposition of stationary states [41]. Being not an eigenstate, the wave packet moves governed by the time-dependent Schrödinger equation. Consequently, the wave packet is located at different areas of space at different times. That is the reason why the ionization probability will depend on the delay time [66].

The electron removed during the ionization process has a continuous spectrum of allowed kinetic energies of the detached electron [67, 68, 69, 70, 71, 72, 73, 74]. However, for a numerical treatment the kinetic energy spectrum has to be discretized. As pointed out in refs. [75, 76] the ionization occurs very rapidly with approximate conservation of the nuclear kinetic energy and the contribution of a single optimal selected photon energy already defines the dominant features of the total transient ionic signal. Hence, in the approach of this work it is assumed that the electron removed during the ionization process has zero-kinetic-energy (ZEKE). The laser-induced transitions to ionic states are then treated in the

same way as to neutral states. However, it is important to avoid unphysical back-transformation (dump) of ionic state population by the applied lasers. This can be achieved by means of small intensities of the pump and (more importantly) the probe pulse. (*e.g.*: In this work the intensities were chosen such that the pump pulse transfers about 10 % of the ground state population to an electronic excited state and the probe pulse produces an ionic state population of less than 1 %.)

## 2.6 Calculation of the initial wave function: The Fourier Grid Hamiltonian (FGH) method

Within the Born-Oppenheimer approximation (equation (2.48)) the one-dimensional time-independent nuclear Schrödinger equation is:

$$\underbrace{\left(-\frac{\hbar^2}{2\mu_a}\frac{\partial^2}{\partial q_a^2} + V_i(q_a)\right)}_{=H_i(q_a)} \Theta_{v_i}^{vib}(q_a) = E_{v_i} \Theta_{v_i}^a(q_a). \quad (2.74)$$

The nuclear wavefunctions  $\Theta_{v_i}^{vib}(q_a)$  are the vibrational eigenfunctions of the Hamiltonian  $H_i(q_a)$ . The eigenvalues  $E_{v_i}$  are the allowed total energies (neglecting the rotational and translational contributions) of the one-dimensional system. Both, the energies  $E_{v_i}$  and the wavefunctions  $\Theta_{v_i}^{vib}$  of the  $i$ -th electronic state are labeled by the index  $v_i$ , the vibrational level corresponding to state  $i$ .

By solving the nuclear Schrödinger equation (2.74) for the electronic ground state potential  $V_0(q_a)$  the stationary states  $\Theta_{v_0}(q_a)$  and corresponding energies  $E_{v_0}$  in the Born-Oppenheimer approximation are obtained. The *Fourier Grid Hamiltonian method* [77], whose principles are described in this section, has been employed to solve the above equation. An alternative method to get at least the energetically lowest eigenfunction, not applied in this thesis though, is the so-called "propagation in imaginary time" from Kosloff and Tal-Ezer [78].

In equation (2.74)  $H_i$  is represented in coordinate space:

$$\langle q'_a | \hat{H}_i | q_a \rangle = \langle q'_a | \hat{T}_i | q_a \rangle + \langle q'_a | \hat{V}_i | q_a \rangle. \quad (2.75)$$

The potential operator  $V_i$  is a function of the position operator  $\hat{Q}$  with eigenvalues  $q_a$  and eigenvectors  $|q_a\rangle$ :

$$\hat{Q}_a |q_a\rangle = q_a |q_a\rangle. \quad (2.76)$$

Its "matrix elements" in the coordinate representation are then [51]:

$$\langle q'_a | \hat{V}_i | q_a \rangle = V_i(q_a) \delta(q'_a - q_a). \quad (2.77)$$

The action of  $\hat{V}_i$  in coordinate space is a simple multiplication of the wave function  $\Theta(q_a)$  with the potential energy function  $V_0(q_a)$ , as expressed in equation (2.74). On the other hand, the matrix elements of the kinetic energy operator  $\hat{T}_i$  in the momentum representation are given by,

$$\langle k' | \hat{T}_i | k \rangle = \frac{\hbar k^2}{2\mu_a} \delta(k' - k), \quad (2.78)$$

where  $|k\rangle$  are the eigenvectors and  $k$  the eigenvalues of the momentum operator  $\hat{K}$ :

$$\hat{K} | k \rangle = k | k \rangle. \quad (2.79)$$

The completeness relation holds for the coordinate and momentum eigenstates:

$$\int_{-\infty}^{\infty} |q_a\rangle \langle q_a| dx = \hat{1} \quad (2.80)$$

and

$$\int_{-\infty}^{\infty} |k\rangle \langle k| dk = \hat{1}. \quad (2.81)$$

Inserting (2.81) and (2.77) in equation (2.75) yields

$$\begin{aligned} \langle q'_a | \hat{H}_i | q_a \rangle &= \int_{-\infty}^{\infty} \langle q'_a | \hat{T}_i | k \rangle \langle k | q_a \rangle dk + V_i(q_a) \delta(q'_a - q_a) \\ &= \int_{-\infty}^{\infty} \langle q'_a | k \rangle \frac{\hbar k^2}{2\mu_a} \langle k | q_a \rangle dk + V_i(q_a) \delta(q'_a - q_a) \end{aligned} \quad (2.82)$$

The transformation matrix elements between the coordinate and the momentum representation are

$$\langle q'_a | k \rangle = \frac{1}{\sqrt{2\pi}} e^{ikq'_a} \quad (2.83)$$

and

$$\langle k | q_a \rangle = \frac{1}{\sqrt{2\pi}} e^{-ikq_a}. \quad (2.84)$$

Therefore, (2.82) gets

$$\langle q'_a | \hat{H}_i | q_a \rangle = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{ik(q'_a - q_a)} \frac{\hbar k^2}{2\mu_a} dk + V_i(q_a) \delta(q'_a - q_a). \quad (2.85)$$

The last equation is the heart of the FGH method. To get the eigenfunctions of  $\hat{H}_i$  the position operator  $\hat{Q}$  is discretized by substituting the continuous coordinate values  $q_a$  by a discrete set  $q_a^n$ :

$$q_a^n = n\Delta q_a, \quad n = 1, \dots, N. \quad (2.86)$$

$\Delta q_a$  denotes the spacing in coordinate space and  $N$  is the number of grid points. Finally, the following expression for the matrix elements of  $\hat{H}_i$  is obtained [77]:

$$H_{lm} = \frac{1}{\Delta q_a} \left\{ \sum_{l=-N}^N \frac{e^{il2\pi(n-m)/N}}{N} \cdot T_l + V_i(q_a^n) \delta_{nm} \right\}, \quad (2.87)$$

with

$$T_l = \frac{\hbar^2}{2m} \cdot (l\Delta k)^2, \quad \Delta k = 2\pi/N\Delta q_a. \quad (2.88)$$

Diagonalizing the  $N \cdot N$  matrix of the Hamilton operator (2.87) yields the eigenvectors and eigenvalues of  $\hat{H}_i$  on the chosen grid.

## 2.7 Propagation schemes for the time dependent Schrödinger equation

The commonly used propagation schemes are critically analyzed in a review article by Leforestier et al. [79] and recapitulated by Balakrishnan et al. [80]. Nonetheless, for the sake of completeness, the basic equations are presented in this section. In addition, it will be shown how the kinetic coupling terms introduced in section 2.2 can be included in the second order differencing (SOD) algorithm.

The Hamilton Operator in equation (2.2) is a sum of the kinetic energy operator  $\hat{T}$  and the potential energy operator  $\hat{V}$ . The evaluation of  $\hat{V}\Psi$  in coordinate space is straightforward, since  $\hat{V}$  is diagonal in this representation and its action consists of a simple multiplication. The bottleneck of all quantum time-dependent propagations is the calculation of  $\hat{T}\Psi$ , which is diagonal only in the momentum representation. Kosloff and Kosloff [81] introduced the fast Fourier transformation technique (FFT), in combination with a second order differencing scheme, to evaluate the action of the kinetic energy part of the Hamiltonian in the momentum space. Using the fast Fourier transformation algorithm the second derivative of the wave function is calculated in three steps:

1. Inverse Fourier transformation (IFT) to momentum space:

$$\tilde{\Psi}(k) = \sqrt{\frac{1}{2\pi}} \int_{-\infty}^{\infty} \Psi(q_a) e^{-ikq_a} dq_a \quad (\text{IFT}),$$

2. Multiplication with  $-k^2$  ( $k$  = wave number),
3. Fourier transformation (FT) to coordinate space:

$$\Psi(q_a) = \sqrt{\frac{1}{2\pi}} \int_{-\infty}^{\infty} \tilde{\Psi}(k) e^{ikq_a} dk \quad (\text{FT}).$$

If the Hamilton Operator is time-independent, the formal solution of (2.1) is [51]:

$$|\Psi(t)\rangle = \hat{U}(t, t_0) |\Psi(t_0)\rangle = e^{-\frac{i}{\hbar} \hat{H}(t-t_0)} |\Psi(t_0)\rangle, \quad (2.89)$$

where  $U(t, t_0)$  is the time-evolution operator. An electric field makes the Hamilton Operator time dependent. If, however, the time step is chosen so small that the change of the electric field is negligible, the Hamilton operator can be treated time independent and (2.89) is still valid. In this work the split operator [82, 83, 84] and the second order differencing scheme [81] were used to solve the time dependent Schrödinger equation numerically. Since both methods require short time steps (which are also needed for handling time-dependent Hamiltonians) they are a good

choice in the presence of molecule-laser-interactions. Both algorithms are unitary and norm preserving. The SOD method conserves the energy whereas the split operator does not. Moreover, the split operator technique cannot be applied when space-momentum mixed terms - for example kinetic coupling terms - appear in the Hamiltonian [79]. Therefore, in this work, the split operator was used when the kinetic couplings were neglected as a first approximation, while when these couplings were included, the time dependent Schrödinger equation was integrated by means of the second order differencing scheme.

### 2.7.1 Second Order Differencing (SOD)

One way of solving the time dependent Schrödinger equation numerically is to expand the time dependent wavefunction in a Taylor series [85, 86]:

$$\Psi(t + \Delta t) = \Psi(t) + \Delta t \cdot \frac{\partial}{\partial t} \Psi(t) + \frac{\Delta t^2}{2!} \cdot \frac{\partial^2}{\partial t^2} \Psi(t) + \frac{\Delta t^3}{3!} \cdot \frac{\partial^3}{\partial t^3} \Psi(t) \dots \quad (2.90)$$

or

$$\Psi(t - \Delta t) = \Psi(t) - \Delta t \cdot \frac{\partial}{\partial t} \Psi(t) + \frac{\Delta t^2}{2!} \cdot \frac{\partial^2}{\partial t^2} \Psi(t) - \frac{\Delta t^3}{3!} \cdot \frac{\partial^3}{\partial t^3} \Psi(t) \dots \quad (2.91)$$

Subtracting equation (2.91) from equation (2.90) yields

$$\Psi(t + \Delta t) - \Psi(t - \Delta t) = 2 \cdot \Delta t \cdot \frac{\partial}{\partial t} \Psi(t) + 2 \cdot \frac{\Delta t^3}{3!} \cdot \frac{\partial^3}{\partial t^3} \Psi(t) \dots \quad (2.92)$$

The resulting propagation scheme with a third order error in  $\Delta t$  is

$$\Psi(t + \Delta t) = \Psi(t - \Delta t) + 2 \cdot \Delta t \cdot \frac{\partial}{\partial t} \Psi(t) + O(\Delta t^3). \quad (2.93)$$

This algorithm requires both the initial wave function  $\Psi(0)$  and the wave function at the first step  $\Psi(\Delta t)$ . The initialization scheme used in this work is the Runge-Kutta propagation with the same accuracy (second order) as the SOD method:

$$\Psi(\Delta t) = \Psi(0) + \Delta t \cdot \frac{\partial}{\partial t} \Psi(0) + \frac{\Delta t^2}{2!} \cdot \frac{\partial^2}{\partial t^2} \Psi(0). \quad (2.94)$$

According to (2.1) the term  $\frac{\partial \Psi}{\partial t}$  reads, in atomic units,

$$\frac{\partial \Psi}{\partial t} = -i\hat{H}\Psi = \left( -i\frac{1}{2\mu_a} \frac{\partial^2}{\partial q_a^2} - iV(q_a) - \frac{1}{\mu_a} T^{(1)}(q_a) \cdot \left( -i\hbar \frac{\partial}{\partial q_a} \right) + i\frac{1}{2\mu_a} T^{(2)}(q_a) \right) \Psi, \quad (2.95)$$

where the potential operator  $\hat{V}$  contains the coupling with the electric field. The kinetic energy operator  $\hat{T}$  and the momentum operator  $\hat{P}$  act in momentum-space as multiplications with  $\frac{1}{2\mu_a}k^2$  and  $k$  respectively. The following scheme can be applied:

1. Inverse Fourier transformation to momentum space:

$$\Psi(q_a) \xrightarrow{\text{IFT}} \tilde{\Psi}(k),$$

2. Calculate the action of  $\hat{T}$  and  $\hat{P}$  in momentum space:

$$\begin{aligned} &\xrightarrow{-i \cdot \frac{1}{2\mu_a} k^2} -i \left( \hat{T} \tilde{\Psi}(k) \right), \\ &\xrightarrow{\cdot k} \left( \hat{P} \tilde{\Psi}(k) \right), \end{aligned}$$

3. Fourier transformation of  $\hat{T}\tilde{\Psi}$  and  $\hat{P}\tilde{\Psi}$  to coordinate space

$$\begin{aligned} &\xrightarrow{\text{FT}} -i \left( \hat{T} \Psi(q_a) \right) \text{ (term I),} \\ &\left( \hat{P} \Psi(q_a) \right), \end{aligned}$$

4. Calculate the action of all other operators in coordinate space:

$$\begin{aligned} &\Psi(q_a) \xrightarrow{-iV(q_a)} -iV(q_a)\Psi(q_a) \text{ (term II),} \\ &\left( \hat{P} \Psi(q_a) \right) \xrightarrow{-\frac{1}{\mu_a} T^{(1)}(q_a)} -\frac{1}{\mu_a} T^{(1)}(q_a) \left( \hat{P} \Psi(q_a) \right) \text{ (term III),} \\ &\Psi(q_a) \xrightarrow{i \frac{1}{2\mu_a} T^{(2)}(q_a)} i \frac{1}{2\mu_a} T^{(2)}(q_a) \Psi(q_a) \text{ (term IV),} \end{aligned}$$

5. Sum up terms I to IV to get  $-iH\Psi = \frac{\partial \Psi}{\partial t}$ .

In accord with the uncertainty principle, the time step must not exceed the critical time step

$$\Delta t_{crit} = \frac{\hbar}{E_{max}}, \quad (2.96)$$

where the maximum energy

$$E_{max} = T_{max} + V_{max}. \quad (2.97)$$

In the last equation  $V_{max}$  is the maximum potential energy and  $T_{max}$  the maximum kinetic energy of the grid defined as

$$T_{max} = \frac{\hbar^2 \pi^2}{2\mu_a (\Delta x)^2}. \quad (2.98)$$

For practical calculations a time step five times smaller than the critical one is recommended [79].

### 2.7.2 Split Operator

In this method the time propagation operator  $\hat{U}(t, t_0)$  of equation (2.89) is approximated as [82, 83, 84]:

$$\hat{U}(t + \Delta t, t) = e^{-\frac{i}{\hbar}\hat{H}\Delta t} = e^{-\frac{i}{2\hbar}\hat{T}\Delta t} e^{-\frac{i}{\hbar}\hat{V}\Delta t} e^{-\frac{i}{2\hbar}\hat{T}\Delta t} + O(\Delta t^3). \quad (2.99)$$

The propagator (2.99) leads to an error of third order in the time step as a consequence of the noncommutability of the kinetic and potential energy operators. A slightly larger time step than that of the SOD method specified in section 2.7.1 can be used [80].

This method involves the following steps: The wave function is transformed to momentum space and multiplied with  $\exp(-\frac{i\hbar}{4\mu_a}k^2\Delta t)$ . After transformation to coordinate space it is multiplied with  $\exp(-\frac{i}{\hbar}V(q_a)\Delta t)$ . The resulting wave function is again transformed to the momentum space and multiplied by  $\exp(-\frac{i\hbar}{4\mu_a}k^2\Delta t)$ . A following Fourier transformation to coordinate space completes one evolution step. Since the factor  $\exp(-\frac{i\hbar}{4\mu_a}k^2\Delta t)$  is independent of the step of the propagation, the left and the right part in (2.99) of two successive propagation steps can be combined.

## 2.8 Solution of the electronic Schrödinger equation using *ab initio* and DFT methods

Deriving the adiabatic representation in section 2.2 it was assumed that the solutions of the electronic Schrödinger equation

$$\hat{H}_{el}|\Phi_\nu\rangle = E_\nu^{el}|\Phi_\nu\rangle, \quad (2.100)$$

where

$$\hat{H}_{el} = -\sum_{a=1}^n \frac{\hbar^2}{2m_e} \Delta_a + \frac{1}{4\pi\epsilon_0} \left( -\sum_{i=a}^n \sum_{A=1}^N \frac{Z_A e^2}{|r_a - R_A|} + \sum_{a<b}^n \frac{e^2}{|r_a - r_b|} \right) \quad (2.101)$$

is the electronic Hamiltonian in Cartesian coordinates, are known. In practice only a limited number of electronic eigenfunctions are calculated and used as a basis to describe the adiabatic behaviour of the molecule. How many electronic wave functions are needed depends on the process to be described. In this work the photodissociation under a femtosecond laser pulse excitation is investigated; therefore, a sufficient representation must contain all states which are, directly or indirectly, significantly populated after the applied pulse.

Nowadays, many sophisticated methods for an approximate solution of (2.100) exist. In this section those which have been applied in this work will be explained

in subsections 2.8.1 (*ab initio* methods) and 2.8.2 (DFT methods). Before, some general remarks about the applied strategy concerning the quantum chemistry calculations will be made.

The first step of modern quantum chemical applications is usually to determine the geometry by an optimization of all degrees of freedom. Compared with single point energy calculations the geometry can normally be obtained at a rather low level of treatment [87], (e.g. in this work the CASSCF method was used for geometry optimizations but the MS-CASPT2 - a more sophisticated method - was employed for energy computations.) In a second step, the vertical excitation energies are calculated at the optimized geometry. (Here, MS-CASPT2 and TD-DFT calculations have been performed.) These energies can be compared with the experiment and the accuracy of the applied quantum chemistry method can be judged. For a correct description of the quantum dynamics the accurate computation of potential energy curves, which are obtained in the adiabatic representation (e.g. equation (2.21)), is an essential requirement. The potential energy curves of big molecules like organometallic compounds can only be described by highly-developed quantum chemistry methods in a restricted number of degrees of freedom (because of computational cost). Usually, only the reactive coordinates leading to dissociation are taken into account (here, the Mn-CO<sub>ax</sub> stretching coordinate). Besides, on an ultrafast time scale the rest of the molecule is supposed to stay at a fixed geometry, supporting that very few degrees of freedom are necessary and IVR can be neglected. The choice of the reaction coordinates is guided by the structure of the primary products which can be obtained via geometry optimizations of the molecule in the ground state and relevant electronic excited states.

### 2.8.1 Standard quantum chemical (*ab initio*) methods

Standard quantum chemical (*ab initio*) methods are based on a Hartree-Fock (HF) [88] treatment. The molecular ground state  $|\Phi_0\rangle$  of stable molecules (if the system has an even number of electrons) is usually well-described by a single closed shell Slater-determinant,  $|D_0\rangle$ , containing the  $n$  (= total number of electrons) energetically lowest spin orbitals  $\varphi$  (determined in a HF calculation):

$$|\Phi_0\rangle \xrightarrow{\text{HF-ansatz}} |D_0\rangle = \frac{1}{\sqrt{n!}} \begin{vmatrix} \varphi_1(1) & \varphi_2(1) & \dots & \varphi_n(1) \\ \varphi_1(2) & \varphi_2(2) & \dots & \varphi_n(2) \\ \dots & \dots & \dots & \dots \\ \varphi_1(n) & \varphi_2(n) & \dots & \varphi_n(n) \end{vmatrix}, \quad (2.102)$$

where the rows are labeled by electrons and the columns are labeled by spin orbitals. Using this ansatz for the electronic wavefunction to minimize the electronic energy  $E_v^{el}$  variationally leads to the Hartree-Fock equations. In a Restricted

Hartree Fock (RHF) calculation [88] the spin orbitals  $\varphi$  are a product of the spatial orbitals  $\phi$  (depending on the spatial coordinate  $\underline{r}$ ) and the spin function (depending on the spin coordinate  $\omega$ ),  $\alpha$  or  $\beta$ :

$$\varphi(\underline{r}, \omega) = \begin{cases} \phi(\underline{r}) \cdot \alpha(\omega) \text{ or} \\ \phi(\underline{r}) \cdot \beta(\omega) . \end{cases} \quad (2.103)$$

With this ansatz the spin functions  $\alpha$  and  $\beta$  can be integrated out. For a numerical treatment the remaining spatial orbitals  $\phi$  are linearly expanded in a finite basis set  $\{\varrho_j\}$  of dimension  $M$ :

$$\phi_i(\underline{r}) = \sum_j^M k_{ij} \varrho_j(\underline{r}), \quad (2.104)$$

leading to the Roothaan-Hall equations [89]:

$$\underline{\underline{F}} \underline{\underline{K}} = \underline{\underline{S}} \underline{\underline{K}} \underline{\underline{\varepsilon}}, \quad (2.105)$$

where  $\underline{\underline{F}}$  is the Fock matrix,  $\underline{\underline{S}}$  is the overlap matrix,  $\underline{\underline{K}}$  is coefficient matrix and  $\underline{\underline{\varepsilon}}$  is the orbital energy matrix. The iterative solution of equation (2.105) is called the Self-Consistent-Field (SCF) procedure.

The difference between the exact solution of the electronic Schrödinger equation (2.11),  $E^{(\text{Schr.})}$ , and the Hartree-Fock-limit energy,  $E^{(\text{HF-Limit})}$ , which is the solution of the Hartree-Fock equations [88] when using a complete basis expansion, is defined as the correlation energy  $E_{\text{corr}}$ :

$$E_{\text{corr}} = E^{(\text{Schr.})} - E^{(\text{HF-Limit})}. \quad (2.106)$$

The obvious way to account for the correlation energy is to use Configuration Interaction (CI). For a given basis set a Full Configuration Interaction (FCI) calculation constitutes a benchmark by which computations of the correlation energy with the same basis set can be judged, i. e. "full CI is the best that one can do" [88]. If the basis set reaches completeness, the FCI result will be the exact solution  $E^{(\text{Schr.})}$ . The FCI expansion of an electronic state reads as [88]:

$$|\Phi^{FCI}\rangle = c_0 |D_0\rangle + \sum_{ar} c_a^r |D_a^r\rangle + \sum_{a<b, r<s} c_{ab}^{rs} |D_{ab}^{rs}\rangle + \dots \quad (2.107)$$

In equation 2.107,  $|D_0\rangle$  stands for the ground state configuration and  $|D_a^r\rangle$  denotes a single excitation, *i.e.* a Slater determinant where the spin orbital  $\varphi_a$  which is occupied in the ground state is replaced by the unoccupied (=virtual) spin orbital  $\varphi_r$ . Similarly,  $|D_{ab}^{rs}\rangle$  is a doubly excited determinant where the orbitals  $\varphi_a$  and  $\varphi_b$  are

replaced by the virtual orbitals  $\varphi_r$  and  $\varphi_s$ . The number of  $i$ -tuply excited determinants for  $n$  electrons and  $2M$  spin orbitals,  $M$  being the number of spatial basis functions  $\phi$ , is given by

$$\binom{M}{i} \binom{2M-N}{i}. \quad (2.108)$$

From this formula it is clear that the number of configurations in the expansion (2.107) grows very rapidly with the number of electrons and basis functions making the FCI method only applicable for very small molecules and reduced basis sets. Only truncated CI methods like CIS or CISD, where Single (S) and Double (D) excitations are considered, can be used in general, but they suffer from size-consistency (*e.g.* a CISD calculation of two  $\text{H}_2$  molecules separated by a large distance (say 100 Å) does not give twice the CISD energy of one  $\text{H}_2$  molecule (which is lower)). Furthermore, CIS gives poor excitation energies.

Due to their multiconfigurational character, electronic excited states can not be described by a single Slater determinant and, therefore, a multiconfigurational procedure is needed. A solution for computing electronic excited states or for cases where a single determinant is not even a good zeroth order reference wavefunction is the so-called Multi-Configuration Self-Consistent Field (MCSCF) approach, which consists of a truncated CI expansion where not only the CI coefficients  $C_i$  in front of the Slater-determinants  $|D_i\rangle$

$$|\Phi^{MCSCF}\rangle = \sum_i C_i |D_i\rangle \quad (2.109)$$

are variationally optimized, but also the Molecular Orbital (MO) coefficients  $k_{ij}$  in the basis set expansion [90]. The practical problem lies on the choice of the relevant configurations,  $|D_i\rangle$ . A popular solution consists of partitioning the molecular orbitals in active and inactive spaces. This is the way how the selection of the configurations is chosen in the Complete Active Space Self Consistent Field Method (CASSCF) [91]. The inactive orbitals stay either doubly occupied or empty during the calculation. Typically the active space orbitals consist of the highest occupied and lowest unoccupied orbitals of a RHF wave function. In addition, calculations of excited states of transition metal compounds containing metal atoms of the first transition row have to deal with the problem of the  $3d$  double shell effect: Two sets of  $d$  orbitals ( $3d$  and  $4d$ ) must be included in the reference space in order to obtain accurate results [92]. Within the active orbitals a Full Configuration Interaction (FCI) calculation is performed (figure 2.1). Therefore, the CASSCF method is on the one hand a special MCSCF method, meaning that not only the CI coefficients but also the orbital coefficients in (2.109) are optimized, and on the other hand a

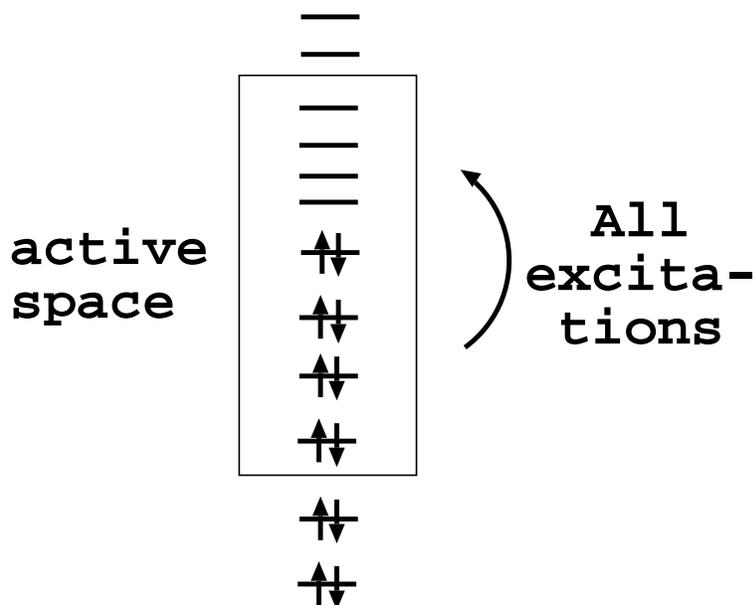


Figure 2.1: *All the possible excitations within the active space define the configurations in a CASSCF calculation.*

special case of the FCI method, meaning that all possible excitations within the active space are taken into account.

The correlation energy (2.106) can be divided into two different contributions: The static and the dynamical parts. The static part of the correlation energy accounts for the effect of allowing the orbitals to be partly singly occupied, like in the CASSCF description, instead of forcing double occupation, like in the HF approximation. This allows the description of near-degeneracy effects of molecular orbitals which are especially important for organometallic compounds. The remaining correlation energy is the dynamic correlation which describes the correlated motion of the electrons. The latter part is normally taken into account by subsequent perturbation treatment, CASPT2 or by the Multi-Reference Configuration Interaction (MRCI) method [93]. Conventional CI methods like CISD consider only configurations generated by exciting electrons from a single determinant [94], usually the ground state RHF wave function. A MRCI calculation is based on a previous MCSCF treatment, for example CASSCF. The critical step in this method is the choice of the reference wavefunctions, which has to be consistent along the process investigated [95]. The externally contracted version of the MRCI method called MR-CCI, introduced by Siegbahn [96], was applied in this work to calculate the potential energy curves, transition dipole moments and kinetic couplings.

The CASPT2 method applies second order perturbation theory to a CASSCF reference wavefunction [97, 98]. This treatment includes a large amount of the

dynamical correlation leading to very accurate results for excitation energies (normally the error is in the range 0.0-0.3 eV [92, 99]). However, the original version of the CASPT2 method allowed the calculation of a single state at a time, which made the description of curve crossing problems impossible. Recently, it was replaced by the Multi-State CASPT2 (MS-CASPT2) [100] method which make the simultaneous treatment of more than one state possible.

Near-degeneracies in the zeroth-order Hamiltonian lead to the problem of intruder states. The solution of this problem is to increase the active space. However, this is not always possible, since a larger active space increases the number of configurations and therefore, the computational cost. A remedy to avoid intruders is to introduce a level shift [101, 92], but then the amount of the correlation energy included decreases.

For the chosen basis set and active space the CASPT2 method was not able to describe dissociation correctly in  $\text{CpMn}(\text{CO})_3$ . For that reason the MS-CASPT2 method was used in this work to calculate the vertical excitation spectrum, whereas the CASSCF/MR-CCI method was applied for the calculation of the potential energy curves.

## 2.8.2 DFT methods

An alternative approach to the Hartree-Fock based methods is the Density Functional Theory (DFT) which is based on the Hohenberg-Kohn theorems [102]. The first Hohenberg-Kohn theorem (HK-I) states that there is a one-to-one mapping between the external potential  $v$  (*i.e.* the Coulomb attraction of an electron by all nuclei), the electron density  $\rho$  and the ground state wave function  $\Phi_0$ :

$$\rho \leftrightarrow v \leftrightarrow \Phi_0 \text{ (HK-I)}. \quad (2.110)$$

This implies that all properties are functionals of the ground state density due to the fact that they are calculated as expectation values of operators for the state vector  $\Phi_0[\rho]$  corresponding to the density  $\rho$ . The second Hohenberg-Kohn theorem (HK-II) states that the functional  $E[\rho] = \langle \Phi_0[\rho] | \hat{H} | \Phi_0[\rho] \rangle$ ,  $\hat{H}$  being the Hamiltonian, will have the exact ground state energy  $E_0^{exact}$  as a lower bound:

$$E[\rho] \geq E_0^{exact} \text{ (HK-II)}. \quad (2.111)$$

HK-II is equivalent to the variational principle. The so-called Kohn-Sham Hamiltonian  $H_s$ , which is applied in virtually all DFT applications, is just a sum of one-electron operators (without electron-electron interaction):

$$\hat{H}_s = \sum_i \left( -\frac{1}{2} \nabla^2(i) + v_s(i) \right). \quad (2.112)$$

Using ansatz (2.112) assumes that *noninteracting* electrons move in an external local potential, called  $v_s$ , which has the property that its wave function - a single Slater determinant of the lowest  $n$  (= number of electrons) orbitals - yields exactly the same electron density as the exact interacting electron system with potential  $v$ . This is correct, since the HK-I theorem states that  $v_s$  must be unique and this is clearly independent of the form of the two electron interaction - totally neglected in (2.112). The Kohn-Sham one-electron equations are:

$$\left(-\frac{1}{2}\nabla^2(i) + v_s(i)\right)\varphi_i^{KS} = \varepsilon_i\varphi_i^{KS}. \quad (2.113)$$

It is not clear if the Kohn-Sham orbitals  $\varphi_i^{KS}$  have any other physical significance than the property that the sum of their squares adds up to the exact electron density. Their orbital energies can not be related to the ionization energies like the Hartree-Fock orbital energies (previous subsection) - except for the energy of the highest occupied orbital which equals the negative of the exact ionization energy. It is therefore hazardous to compare DFT and Hartree-Fock calculations at molecular orbital level.

For details about the DFT method the reader is referred to refs [102, 103, 104]. The Time Dependent DFT (TD-DFT) method which can be applied to calculate excited states is based on "the fact that frequency dependent linear response of a finite system with respect to a time-dependent perturbation has discrete poles at the exact, correlated excitation energies of the unperturbed system." [103] The mean polarizability  $\alpha(\omega)$  is frequency dependent and describes the response of the dipole moment to a time-dependent electric field with frequency  $\omega$ . Its relation to the electronic excitation energies  $\omega_i = E_i^{el} - E_0^{el}$  and corresponding oscillator strength  $f_i$  is given by:

$$\alpha(\omega) = \sum_i \frac{f_i}{\omega_i^2 - \omega^2}. \quad (2.114)$$

It can be seen from equation (2.114) that the mean polarizability  $\alpha(\omega)$  has poles at  $\omega = \omega_i$  (= the excitation energy). In the Kohn-Sham formalism the exact linear response to the time-dependent perturbation with frequency  $\omega(t)$  is expressed as the linear density response. The ordinary Kohn-Sham orbitals (2.113) obtained in a regular ground state calculation are involved. Their energy differences are shifted towards the excitation energies (the poles in equation (2.114)) by a systematic change in the perturbation frequency  $\omega$ . "Hence, excitation energies are expressed in terms of ground state properties and the problem whether density functional theory can be applied to excited states is most elegantly circumvented." [103] As long as only low-lying valence states (not Rydberg states) are involved, the error of the TD-DFT method is within a few tens of eV. Therefore, the TD-DFT approach may

rival more sophisticated and much more costly wave function based approaches (like CASPT2). Yet, comparison between these two approaches is not often in the literature and the real performance of TD-DFT is difficult to judge.

The TD-DFT method has been applied in this work for the calculation of excitation energies to compare them with the corresponding MS-CASPT2 excitation spectrum. Furthermore, CASSCF optimized ground state geometries have been compared with DFT optimizations. The applied particular functionals and basis sets applied in this work will be described in chapter 3.

## 2.9 Calculation of the kinetic coupling terms $\mathbf{T}^{(1)}$ and $\mathbf{T}^{(2)}$

This section deals with the numerical computation of the kinetic coupling terms  $\mathbf{T}^{(1)}$  and  $\mathbf{T}^{(2)}$  using the CI and MO coefficients of a multiconfigurational wave function. In section 2.9.1 some general properties of  $\mathbf{T}^{(1)}$  and  $\mathbf{T}^{(2)}$  are reviewed. In section 2.9.2 our method of calculating  $\mathbf{T}^{(1)}$  is presented and compared with different approaches found in literature. Finally, in section 2.9.3 it is described how  $\mathbf{T}^{(2)}$  can be calculated using  $\mathbf{T}^{(1)}$ .

### 2.9.1 General Properties of $\mathbf{T}^{(1)}$ and $\mathbf{T}^{(2)}$

The one-dimensional Schrödinger equation (2.21) with coupling elements defined by equations (2.22) and (2.23) is considered. It is assumed that the electronic wave functions  $|\Phi_\nu\rangle$  are real and orthonormal

$$\langle \Phi_\mu | \Phi_\nu \rangle = \delta_{\mu\nu}. \quad (2.115)$$

If  $\mu$  is equal to  $\nu$  it follows:

$$\begin{aligned} \frac{\partial}{\partial q_a} \langle \Phi_\mu | \Phi_\mu \rangle &= \langle \Phi_\mu | \frac{\partial}{\partial q_a} \Phi_\mu \rangle + \langle \frac{\partial}{\partial q_a} \Phi_\mu | \Phi_\mu \rangle = 2 \cdot \langle \Phi_\mu | \frac{\partial}{\partial q_a} \Phi_\mu \rangle = 0 \\ \Rightarrow \langle \Phi_\mu | \frac{\partial}{\partial q_a} \Phi_\mu \rangle &= 0. \end{aligned} \quad (2.116)$$

In the case that  $\mu$  is not equal to  $\nu$  the result is:

$$\frac{\partial}{\partial q_a} \langle \Phi_\mu | \Phi_\nu \rangle = \langle \Phi_\mu | \frac{\partial}{\partial q_a} \Phi_\nu \rangle + \langle \frac{\partial}{\partial q_a} \Phi_\mu | \Phi_\nu \rangle = \langle \Phi_\mu | \frac{\partial}{\partial q_a} \Phi_\nu \rangle + \langle \Phi_\nu | \frac{\partial}{\partial q_a} \Phi_\mu \rangle^* = 0 \quad (2.117)$$

Since the  $|\Phi_\nu\rangle$  are real,

$$\Rightarrow \langle \Phi_\mu | \frac{\partial}{\partial q_a} \Phi_\nu \rangle = -\langle \Phi_\nu | \frac{\partial}{\partial q_a} \Phi_\mu \rangle. \quad (2.118)$$

This means that the matrix  $\underline{\underline{T}}^{(1)}$  is antisymmetric with diagonal elements equal to zero. According to Baer [52],  $\underline{\underline{T}}^{(2)}$  can be written as

$$\underline{\underline{T}}^{(2)} = \underbrace{\frac{\partial}{\partial q_a} \underline{\underline{T}}^{(1)}}_{\text{anti-symmetric}} + \underbrace{\underline{\underline{T}}^{(1)} \cdot \underline{\underline{T}}^{(1)}}_{\text{symmetric}}. \quad (2.119)$$

This means that  $\underline{\underline{T}}^{(2)}$  is neither symmetric nor anti-symmetric. Equation (2.119) is derived in section 2.9.3.

## 2.9.2 Calculation of the kinetic coupling term $\mathbf{T}^{(1)}$ using a multiconfigurational wave function

The electronic multiconfigurational wave function  $|\Phi_\nu\rangle$  can be expressed as a linear combination of state configurations  $|D_j\rangle$

$$|\Phi_\nu(q_a)\rangle = \sum_j C_{\nu j}(q_a) |D_j(q_a)\rangle, \quad (2.120)$$

where the  $C_{\nu j}$  are the CI coefficients of the  $\nu$ -th electronic state.

Substituting equation (2.120) in equation (2.22) leads to [62]:

$$\begin{aligned} T_{\mu\nu}^{(1)}(q_a) &= \left\langle \sum_j C_{\mu j}(q_a) D_j(q_a) \left| \frac{\partial}{\partial q_a} \sum_k C_{\nu k}(q_a) D_k(q_a) \right. \right\rangle \\ &= \sum_j \sum_k C_{\mu j} \left( \frac{\partial}{\partial q_a} C_{\nu k} \right) \underbrace{\langle D_j(q_a) | D_k(q_a) \rangle}_{\delta_{jk}} + \sum_j \sum_k C_{\mu j}(q_a) C_{\nu k}(q_a) \langle D_j(q_a) | \frac{\partial}{\partial q_a} D_k(q_a) \rangle \\ &= \underbrace{\sum_j C_{\mu j} \left( \frac{\partial}{\partial q_a} C_{\nu j} \right)}_{A_{\mu\nu}^{(1)}} + \underbrace{\sum_j \sum_k C_{\mu j}(q_a) C_{\nu k}(q_a) \langle D_j(q_a) | \frac{\partial}{\partial q_a} D_k(q_a) \rangle}_{B_{\mu\nu}^{(1)}}. \quad (2.121) \end{aligned}$$

In the last expression  $A_{\mu\nu}^{(1)}$  is referred to as the CI term involving differentiation of the CI coefficients and the term  $B_{\mu\nu}^{(1)}$  contains derivatives of configurations or determinants [62]. As will we shown in section 3.6.1, the  $B_{\mu\nu}^{(1)}$  term ultimately leads to integrals of the form  $\langle \phi_l | \frac{\partial}{\partial q_a} | \phi_m \rangle$  where  $\phi_l$  and  $\phi_m$  are the orbitals by which the determinants  $D_j$  and  $D_k$  differ and is, therefore, referred to as the MO term. Matrix elements of determinants differing in more than two orbitals will vanish for the following reason: Since  $\frac{\partial}{\partial q_a}$  is a one-particle operator, according to the Condon-Slater rules [88], the matrix elements

$$\langle D_j(q_a) | \frac{\partial}{\partial q_a} D_k(q_a) \rangle$$

are non-zero only if the determinants  $D_j$  and  $D_k$  differ in less than two orbitals. Furthermore, the determinants  $D_j$  are assumed to be real and orthonormal:

$$\langle D_j | D_k \rangle = \delta_{jk}. \quad (2.122)$$

This leads to equations similar to the ones reported in (2.116) and (2.118) of the previous section:

$$\langle D_j | \frac{\partial}{\partial q_a} D_j \rangle = 0, \quad (2.123)$$

$$\langle D_j | \frac{\partial}{\partial q_a} D_k \rangle = -\langle D_k | \frac{\partial}{\partial q_a} D_j \rangle. \quad (2.124)$$

Whether the CI,  $A_{\mu\nu}^{(1)}$ , or the MO term,  $B_{\mu\nu}^{(1)}$ , is the dominant one is rather arbitrary. For instance, "diabatic" CASSCF orbitals [105, 106] change as little as possible as a function of geometry. Using the invariance of the CASSCF and MRCI energies with respect to unitary transformations, they are generated by maximizing the overlap of CASSCF orbitals at a displaced geometry with the orbitals at the reference geometry. Consequently, the relative contributions of the orbital and CI contributions to the matrix elements of  $T^{(1)}$  are modified: The orbital contribution is minimized, and to a very good approximation the matrix elements of  $T^{(1)}$  could be obtained from the CI-vectors alone. Therefore, given this smooth set of "CASSCF" orbitals, rapid variations of the total wave function are confined to the CI coefficients and can then be eliminated for instance by block-diagonalization yielding quasi-diabatic states and energies for CASSCF and MRCI wavefunctions. This "direct" diabatization scheme has been applied *e.g.* to the photodissociation of ozone [105, 106, 107] and  $H_2S$  [108].

### 2.9.3 Calculation of the kinetic coupling term $T^{(2)}$ using $T^{(1)}$

Substituting equation (2.120) in equation (2.23) yields

$$\begin{aligned} T_{\mu\nu}^{(2)}(q_a) &= \sum_j C_{\mu j} \left( \frac{\partial^2}{\partial q_a^2} C_{\nu j} \right) + \sum_j \sum_k C_{\mu j}(q_a) C_{\nu k}(q_a) \langle D_j(q_a) | \frac{\partial^2}{\partial q_a^2} D_k(q_a) \rangle \\ &+ 2 \cdot \sum_j \sum_k C_{\mu j}(q_a) \left( \frac{\partial}{\partial q_a} C_{\nu k}(q_a) \right) \langle D_j(q_a) | \frac{\partial}{\partial q_a} D_k(q_a) \rangle. \end{aligned} \quad (2.125)$$

Instead of evaluating the last equation the following expression taken from ref. [52] and derived below was used in this work to calculate  $\underline{\underline{T}}^{(2)}$  using  $\underline{\underline{T}}^{(1)}$ :

$$\underline{\underline{T}}^{(2)} = \frac{\partial}{\partial q_a} \underline{\underline{T}}^{(1)} + \underline{\underline{T}}^{(1)} \cdot \underline{\underline{T}}^{(1)}. \quad (2.126)$$

**Derivation of equation (2.126):**

Equation (2.126) can be proved by looking at a matrix element of  $\underline{T}^{(2)}$ :

$$\langle \Phi_\mu | \frac{\partial^2}{\partial q_a^2} \Phi_\nu \rangle \stackrel{?}{=} \frac{\partial}{\partial q_a} \langle \Phi_\mu | \frac{\partial}{\partial q_a} \Phi_\nu \rangle + \sum_\lambda \langle \Phi_\mu | \frac{\partial}{\partial q_a} \Phi_\lambda \rangle \langle \Phi_\lambda | \frac{\partial}{\partial q_a} \Phi_\nu \rangle. \quad (2.127)$$

From (2.118) follows

$$\langle \Phi_\mu | \frac{\partial}{\partial q_a} \Phi_\lambda \rangle = - \langle \frac{\partial}{\partial q_a} \Phi_\mu | \Phi_\lambda \rangle.$$

Inserting the last expression in (2.127) leads to

$$\begin{aligned} \langle \Phi_\mu | \frac{\partial^2}{\partial q_a^2} \Phi_\nu \rangle - \left( \langle \Phi_\mu | \frac{\partial^2}{\partial q_a^2} \Phi_\nu \rangle + \langle \frac{\partial}{\partial q_a} \Phi_\mu | \frac{\partial}{\partial q_a} \Phi_\nu \rangle \right) - \underbrace{\sum_\lambda - \langle \frac{\partial}{\partial q_a} \Phi_\mu | \Phi_\lambda \rangle \langle \Phi_\lambda | \frac{\partial}{\partial q_a} \Phi_\nu \rangle}_{\sum |\Phi_\lambda\rangle \langle \Phi_\lambda| = \underline{1}} \\ = \langle \Phi_\mu | \frac{\partial^2}{\partial q_a^2} \Phi_\nu \rangle - \langle \Phi_\mu | \frac{\partial^2}{\partial q_a^2} \Phi_\nu \rangle - \langle \frac{\partial}{\partial q_a} \Phi_\mu | \frac{\partial}{\partial q_a} \Phi_\nu \rangle + \langle \frac{\partial}{\partial q_a} \Phi_\mu | \frac{\partial}{\partial q_a} \Phi_\nu \rangle \stackrel{!}{=} 0 \quad \text{q. e. d.} \end{aligned}$$