Chapter 2

Theoretical concepts

2.1 Overview of the employed computational methods

All research carried out throughout this work is based on quantum mechanics and quantum dynamics. This chapter will introduce the reader to the most important theoretical concepts needed to understand how the results were obtained. Section 2.2 describes the theoretical background on which quantum chemical program packages as *Gaussian 98* [66] are based[1]. Such computational packages are used to calculate the potential energy surfaces and the (transition) dipole moments of a molecular model system. The section covers the so-called *ab initio* methods, based on the *Hartree-Fock* theory, as well as methods based on a functional of the charge density, i.e. the *density functional theory.* In section 2.3 the concepts of quantum dynamics are presented. In particular, the numerical methods needed for quantum dynamical simulations are introduced and discussed in some detail. The chapter finishes with an overview of several approaches to molecular control using laser fields.

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[1]More detailed discussions on this topic can be found in refs. [67, 68, 69, 70].

2.2 Quantum Chemistry

2.2.1 Born-Oppenheimer approximation

In order to perform quantum dynamical simulations an energetical description of the molecular system in terms of its eigenstates is needed. The solution of the *time independent Schrödinger equation* (TISE) gives the total energy E_{tot} of the molecule at a given time:

$$\hat{\mathsf{H}}_{mol} \left| \Psi \right\rangle = E_{tot} \left| \Psi \right\rangle . \tag{2.1}$$

Here the molecular Hamilton operator $\hat{\mathsf{H}}_{mol}$ describes all interactions among the electrons and nuclei of the system. For a molecule, however, there is no analytical solution of the TISE and different numerical approaches based on the so-called *Born-Oppenheimer approximation* [71] have been developed. The Born-Oppenheimer approximation, which allows to separate the motion of the heavy nuclei from that of the light electrons, is the first step to solve equation 2.1 and it will be explained in the following.

Consider a molecule composed of N_{nuc} nuclei with masses M_n, momenta $\vec{P}_n$ and nuclear charges Z_n at Cartesian coordinates $\vec{R}_n$ surrounded by N_{el} electrons with mass m_e, momenta $\vec{p}_j$ and charge e at coordinates $\vec{r}_j$. Then, the complete molecular Hamiltonian

$$\hat{\mathsf{H}}_{mol} = \hat{\mathsf{T}}_{el} + \hat{\mathsf{V}}_{el,nuc} + \hat{\mathsf{V}}_{el,el} + \hat{\mathsf{T}}_{nuc} + \hat{\mathsf{V}}_{nuc,nuc} \tag{2.2}$$

consists of terms for the kinetic energy of the electrons

$$\hat{\mathsf{T}}_{el} = \sum_{j=1}^{N_{el}} \frac{\vec{p}_j^{\,2}}{2m_e}, \tag{2.3}$$

for the kinetic energy of the nuclei

$$\hat{\mathsf{T}}_{nuc} = \sum_{n=1}^{N_{nuc}} \frac{\vec{P}_n^2}{2M_n}, \tag{2.4}$$

and of potential energy terms, including the Coulomb pair interaction between electrons

$$\hat{\mathsf{V}}_{el,el} = \sum_{i<j}^{N_{el}} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}, \tag{2.5}$$

between nuclei

$$\hat{\mathsf{V}}_{nuc,nuc} = \sum_{m<n}^{N_{nuc}} \frac{Z_m Z_n e^2}{|\vec{R}_m - \vec{R}_n|}, \tag{2.6}$$

and between electrons and nuclei

$$\hat{\mathbf{V}}_{el,nuc} = -\sum_{n=1}^{N_{nuc}} \sum_{j=1}^{N_{el}} \frac{Z_n e^2}{|\vec{r}_j - \vec{R}_n|}. \tag{2.7}$$

Since the mass of a nucleus is much larger than the mass of an electron, nuclear motion is usually much slower compared to the motion of the electrons. Thus, the electrons respond almost instantaneously to any change of the nuclear geometry. Based on this fact the Born-Oppenheimer approximation assumes that the electrons move in an electrostatic field generated by the "fixed" geometry of the nuclei. Therefore, it is possible to separate electronic and nuclear motions. This separation simplifies the TISE because the total wave function $|\Psi\rangle$ can be written as a product of a nuclear wave function $|\Psi_{nuc}\rangle$ and an electronic wave function $|\Psi_{el}\rangle$:

$$
\begin{aligned}
|\Psi\rangle &= \left|\Psi(\vec{R}_1, \vec{R}_2, ..., \vec{R}_{N_{nuc}}, \vec{r}_1, \vec{r}_2, ..., \vec{r}_{N_{el}})\right\rangle \\
&\approx \left|\Psi_{nuc}(\vec{R}_1, \vec{R}_2, ..., \vec{R}_{N_{nuc}})\right\rangle \times \left|\Psi_{el}(\vec{r}_1, \vec{r}_2, ..., \vec{r}_{N_{el}}; \{\vec{R}_1, \vec{R}_2, ..., \vec{R}_{N_{nuc}}\})\right\rangle.
\end{aligned} \tag{2.8}
$$

Here the nuclear wave function $|\Psi_{nuc}\rangle$ depends only on the nuclear coordinates $\vec{R}_n$; in contrast, the electronic wave function $|\Psi_{el}\rangle$ depends on the coordinates of the electrons $\vec{r}_j$ as well as *parametrically* on the nuclear coordinates $\vec{R}_n$. Since only those terms of the molecular Hamiltonian depending on the electronic coordinates act on the electronic wave function it is possible to write an electronic Schrödinger equation for a stationary molecular geometry:

$$\hat{\mathbf{H}}_{el} |\Psi_{el}\rangle = (\hat{\mathbf{T}}_{el} + \hat{\mathbf{V}}_{el,el} + \hat{\mathbf{V}}_{el,nuc}) |\Psi_{el}\rangle = E_{el} |\Psi_{el}\rangle \tag{2.9}$$

The solution of this equation provides the electronic energy E_{el} and wave function $|\Psi_{el}\rangle$ for a given nuclear geometry. The electronic energy together with the nuclear repulsion term $\hat{\mathbf{V}}_{nuc,nuc}$ forms the *potential energy hypersurface* (PES) of the molecule along the nuclear coordinates $\vec{R}_n$:

$$\hat{\mathbf{V}}^{PES}(\vec{R}_1, \vec{R}_2, ..., \vec{R}_{N_{nuc}}) = E_{el}(\vec{R}_1, \vec{R}_2, ..., \vec{R}_{N_{nuc}}) + \hat{\mathbf{V}}_{nuc,nuc}(\vec{R}_1, \vec{R}_2, ..., \vec{R}_{N_{nu}}). \tag{2.10}$$

Because of the separation ansatz (2.8) $\hat{\mathbf{V}}_{nuc,nuc}$ is constant with respect to the electronic coordinates.

The electron-nuclear interactions $\hat{\mathbf{V}}_{el,nuc}$ in the electronic Schrödinger equation (2.9) depend only parametrically on the nuclear coordinates $\vec{R}_n$, i.e. no transitions between different stationary electronic states occur. Therefore, potential energy surfaces of electronic states which are *energetically well separated* are well described within the Born-Oppenheimer approximation (eqn. (2.10)). In this work, only processes on these so-called

adiabatic PESs are considered, for each electronic state i a different $\hat{\mathbf{V}}_i^{PES}$ is used. Then, the nuclear Schrödinger equation

$$\hat{\mathbf{H}}_{nuc}\left|\Psi_{nuc}^i\right\rangle = (\hat{\mathbf{T}}_{nuc} + \hat{\mathbf{V}}_i^{PES})\left|\Psi_{nuc}^i\right\rangle = E_{nuc}^i\left|\Psi_{nuc}^i\right\rangle \tag{2.11}$$

describes the geometry of the nuclei in the average field generated by the fast moving electrons for a given electronic state i. Changes in the molecular geometry induced by laser fields are specified by the time-dependent nuclear Schrödinger equation which will be introduced in section 2.3. The solution of the time-independent nuclear Schrödinger equation (2.11) will be discussed in section 2.2.8.

2.2.2 Hartree-Fock method

Since the electronic Schrödinger equation (2.9) presents a multi-particle problem approximations have to be considered for its solution. In the *Hartree-Fock theory* [72] the N_{el} particle wave function $\left|\Psi_{el}\right\rangle$ is described as an anti-symmetric product of N_{el} single particle functions $\chi_i(\vec{x}_i)$, the so-called *Slater determinant*:

$$\left|\Psi_{el}\right\rangle = \frac{1}{\sqrt{N_{el}!}}\begin{vmatrix} \chi_1(\vec{x}_1) & \chi_2(\vec{x}_1) & \dots & \chi_{N_{el}}(\vec{x}_1) \\ \chi_1(\vec{x}_2) & \chi_2(\vec{x}_2) & \dots & \chi_{N_{el}}(\vec{x}_2) \\ \dots & \dots & \dots & \dots \\ \chi_1(\vec{x}_{N_{el}}) & \chi_2(\vec{x}_{N_{el}}) & \dots & \chi_{N_{el}}(\vec{x}_{N_{el}}) \end{vmatrix}. \tag{2.12}$$

Here each electron is described by a spin-orbital $\chi_i(\vec{x}_i)$ which is a product of a spatial orbital $\psi_i(\vec{r}_i)$ that depends on the position of the electron $\vec{r}_i$ and a spin orbital $\alpha(\omega)$ or $\beta(\omega)$ that depends only on its spin coordinate:

$$\chi_i(\vec{x}_i) = \chi_i(\vec{r}_i, \omega) = \psi_i(\vec{r}_i) \cdot \begin{cases} \alpha(\omega) \\ \beta(\omega) \end{cases} \tag{2.13}$$

Assuming the spin-orbitals $\chi_i(\vec{x}_i)$ form a complete orthonormal basis, they are determined by variational methods, i.e. the expectation value of the Slater determinant with the electronic Hamilton operator becomes a minimum:

$$\left\langle\Psi_{el}\right|\hat{\mathbf{H}}_{el}\left|\Psi_{el}\right\rangle = min. \tag{2.14}$$

This ansatz leads to the Hartree-Fock (HF) equations which give as solution the orbital eigenenergies ϵ_i and the spin-orbitals $\chi_i(\vec{x}_i)$ for each electron i:

$$\hat{\mathbf{F}}\chi_i(\vec{x}_i) = \epsilon_i\chi_i(\vec{x}_i), \qquad i = 1, ..., N_{el}. \tag{2.15}$$

The Fock operator $\hat{\mathbf{F}}$,

$$\hat{\mathbf{F}}(\vec{r_i}) = \hat{\mathbf{h}}(\vec{r_i}) + \hat{\mathbf{V}}^{HF} = \hat{\mathbf{h}}(\vec{r_i}) + \sum_{j=1}^{N_{el}} \left(\hat{\mathbf{J}}_j(\vec{r_i}) - \hat{\mathbf{K}}_j(\vec{r_i}) \right) \qquad (2.16)$$

consists of the single particle operator

$$\hat{\mathbf{h}}(\vec{r_i}) = \frac{\vec{p_i}^2}{2m_e} - \sum_{n=1}^{N_{nuc}} \frac{Z_n e}{|\vec{r_i} - \vec{R}_n|}, \qquad (2.17)$$

which describes the motion of a single electron in the field of the nuclear frame, and the Hartree-Fock potential $\hat{\mathbf{V}}^{HF}$ which describes the interaction of each electron with all the other electrons. In turn, $\hat{\mathbf{V}}^{HF}$ is composed of the Coulomb operator $\hat{\mathbf{J}}_j$

$$\hat{\mathbf{J}}_j \chi_i(\vec{x_i}) = \left[\int dx_j \chi_j^*(\vec{x_j}) \frac{1}{|\vec{r_i} - \vec{r_j}|} \chi_j(\vec{x_j}) \right] \chi_i(\vec{x_i}) \qquad (2.18)$$

and the exchange operator $\hat{\mathbf{K}}_j$

$$\hat{\mathbf{K}}_j \chi_i(\vec{x_i}) = \left[\int dx_j \chi_j^*(\vec{x_j}) \frac{1}{|\vec{r_i} - \vec{r_j}|} \chi_i(\vec{x_j}) \right] \chi_j(\vec{x_i}). \qquad (2.19)$$

The first term of $\hat{\mathbf{V}}^{HF}$ specifies an electron in the average field created by all other electrons. The second term arises from the anti-symmetric character of the Slater determinant (2.12) and has no classical analogy.

Since the Fock operator acting on the spin-orbitals $\chi_i(\vec{x_i})$ depends itself on these functions via the Hartree-Fock potential $\hat{\mathbf{V}}^{HF}$ an iterative method has to be used in order to solve the Hartree-Fock equations (2.15). First, an initial guess of the spin-orbitals χ_i is used to calculate $\hat{\mathbf{J}}$ and $\hat{\mathbf{K}}$ and, hence, the Fock operator $\hat{\mathbf{F}}$. Then, the Hartree-Fock equations are solved yielding new χ_i which are again used to calculate a new Fock operator. This procedure, known as the *self consistent field* method, is repeated until convergence is reached [68].

2.2.3   Basis sets

In practice the spatial part of the spin-orbitals ψ_i is unknown and it is expanded in a proper basis set $\phi_k(\vec{r})$. This is called the *linear combination of atomic orbitals* (LCAO) approximation:

$$\psi_i(\vec{r_i}) = \sum_{k=1}^{M} c_{ik} \phi_k(\vec{r}). \qquad (2.20)$$

The coefficients c_{ik} are derived variationally (discussed in the following section) until the lowest electronic energy is obtained (see eqn. 2.14).

The basis functions $\phi_k(\vec{r})$ are usually chosen as Cartesian Gaussian type orbitals (GTO), also called primitive Gauss-functions:

$$g(\vec{r}) = N \cdot x^{n_x} \cdot y^{n_y} \cdot z^{n_z} \cdot e^{-\alpha \vec{r}^2} \tag{2.21}$$

with normalization constant N and triple n_x, n_y, n_z set of integers; the sum $l = n_x + n_y + n_z$ is used to classify the primitive Gauss-functions as s-type ($l = 0$), p-type ($l = 1$), d-type ($l = 2$), f-type ($l = 3$) orbitals, etc. The factor α in the exponent determines the decline of the amplitude of the GTO with increasing radial distance. GTOs with large α are localized close to the nuclei, while GTOs with small α are rather diffuse.

The GTOs are usually optimized for isolated atoms and, therefore, often do not describe the nature of chemical bonds sufficiently enough. The best result would be obtained if each atomic orbital is described by an infinite number of GTOs and all coefficients could be optimized during a quantum chemical calculation. In practice, this is not possible because of the computational effort. Thus, linear combinations of primitive Gauss-functions $g(\vec{r})$, so called *contractions* $\phi(\vec{r})$, are used:

$$\phi(\vec{r}) = \sum_p d_p g_p(\vec{r}). \tag{2.22}$$

The coefficients d_p are chosen such that the contractions describe the electronic orbitals in the most realistic way.

If only the least number of contracted basis functions ϕ – constructed of an arbitrary number of primitive GTOs – per atom is used required to describe the occupied atomic orbitals of that atom, then a so-called *minimal basis set* is employed.[2] If more than one contraction is used the basis set is called *double zeta, triple-zeta*, etc. Their advantage compared to the minimal basis set is that they allow a better description of the anisotropy of the electron cloud around the atom by mixing e.g. localized functions with more diffuse functions. In case of *split valence* basis sets multiple contractions are only used for the valence electrons while the core electrons are described by a single contraction.

In order to describe polar bonds *polarization functions* are added to the basis set. These functions include higher l- and $m-$ quantum numbers than those used for the (valence) electrons in a minimal basis set to allow for better localization of the orbitals

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[2]This is not quite accurate, since usually five functions (1s,2s and 2p) are considered to constitute a minimal basis set for Li and Be, for example, even though the 2p orbital is not occupied in these atoms. The 2sp (2s and 2p), 3sp,4sp,3d,...,etc. shells are usually considered together.

along a chemical bond. In case of anions or Rydberg orbitals often *diffuse functions* are included in the basis set. A diffuse function is a GTO with a very small α-value. It allows a more realistic description of weakly bounded electrons with significant probability at relatively large distances from the nuclei.

In general, the quality of a basis set depends on the numbers of contractions used per energy level as well as on the number of primitive Gaussian type functions for each contraction. With increasing number of basis functions the computational effort grows bigger. Hence, a good choice of a basis set in terms of chemical accuracy and computational time is important. Usually geometrical optimizations are carried out using small basis sets, while electronic energies call for larger and more flexible basis sets. For an extensive overview of the commonly used basis sets in quantum chemistry the reader is referred to refs. [73, 74, 75, 76, 77, 78].

2.2.4   Roothaan-Hall equations

In order to solve the electronic Schrödinger equation (2.9) the basis set obtained from the LCAO ansatz (2.20) is inserted into the Hartree-Fock equations (2.15). Using the *Ritz variation method* for finding the optimal coefficient c_{ik} which minimizes the electronic energy (2.14), the *Roothaan-Hall* equations [79] are obtained:

$$\boldsymbol{F}\boldsymbol{C} = \boldsymbol{S}\boldsymbol{C}\boldsymbol{\epsilon} \tag{2.23}$$

with $\boldsymbol{F}$ being the Fock matrix with elements

$$\boldsymbol{F}_{ij} = \langle \phi_i(\vec{r})| \, \hat{\mathbf{F}}(\vec{r}) \, |\phi_j(\vec{r})\rangle \tag{2.24}$$

and $\boldsymbol{S}$ the overlap matrix with elements

$$\boldsymbol{S}_{ij} = \langle \phi_i(\vec{r})| \, \phi_j(\vec{r})\rangle \,. \tag{2.25}$$

The matrix $\boldsymbol{C}$ contains the coefficients c_{ik} of the basis functions $\phi_k(\vec{r})$. These equations must be solved iteratively, since the Fock-matrix depends on the coefficients c_{ik}. As described in section 2.2.2 an initial guess for $\boldsymbol{C}^0$ is needed in order to calculate the first Fock-matrix $\boldsymbol{F}^0$. Then, the eigenvalue problem is solved by diagonalization of $\boldsymbol{F}^0$.[3] As a

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[3]Equation (2.23) must be first orthogonalized using e.g. the transformation matrix $\boldsymbol{S}^{-1/2}$ to obtain the form of the usual matrix eigenvalue problem:

$$\boldsymbol{S}^{-\frac{1}{2}}\boldsymbol{F}\boldsymbol{S}^{-\frac{1}{2}}\boldsymbol{S}^{\frac{1}{2}}\boldsymbol{C} = \boldsymbol{F}'\boldsymbol{C}' = \boldsymbol{C}'\boldsymbol{\epsilon} = \boldsymbol{S}^{\frac{1}{2}}\boldsymbol{C}\boldsymbol{\epsilon}$$

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solution a new coefficient matrix $\boldsymbol{C}^1$ is obtained which is again used to construct a new
Fock matrix $\boldsymbol{F}^1$ to be again diagonalized. This procedure is repeated until a convergence
criterion is reached. Then, the coefficients c_{ik} of equation (2.20) provide for the given basis
set the optimal spin-orbitals $\chi_i(\vec{x})$ and their eigenenergies ϵ_i. The total electronic energy
E_{el} is the expectation value of the electronic Hamilton operator $\hat{\mathbf{H}}_{el}$ using the respective
Slater determinant $|\Psi_{el}\rangle$ constructed from the obtained spin-orbitals.

2.2.5   Electron correlation methods

Within the limits of the Hartree-Fock method the electron-electron interactions are ap-
proximated by an averaged potential. The difference between the total electronic Hartree-
Fock energy E_{HF} ($= E_{el}$) in the limit of a complete basis set and the exact non-relativistic
energy within the Born-Oppenheimer approximation is defined as the *correlation energy*
[80]:

$$E_{corr} = E_{exact} - E_{HF}. \tag{2.26}$$

Physically it corresponds to the motion of the electrons being correlated, on average they
are further apart than described by the HF wave function. Usually two types of correlation
effects are distinguished. The *dynamical* correlation found in all systems describes the
interaction between two adjacent electrons, e.g. two electrons belonging to the same
spatial MO. The *non-dynamical* or *static* correlation is caused by the inter-orbital pair
correlation where two MOs are spatially close. The negligence of the static correlation
can lead to a wrong ground state wave function, e.g. for the dissociation of a molecule.

In order to include correlation effects into the calculation "post" Hartree-Fock methods
are used. Besides methods based on perturbation theory (discussed in the following
section) there exist methods using more than one electronic configuration to solve the
electronic Schrödinger equation, like *configurational interaction* (CI) or *complete active
space self consistent field* (CASSCF) (especially used for electronic excited states).

In the CI method the wave function of the N_{el}-electron system is set up as a linear
combination of appropriate N_{el}-particle wave functions (Slater determinants); the coef-
ficients of this superposition are derived variationally. This superposition is constructed
using the Slater determinant for the electronic ground state (Hartree-Fock determinant)
plus determinants for a single excitation of an electron (CIS), determinants for a double
excitation of two electrons (CID), or both (CISD), and so on. If all excitations are in-
cluded the *full CI limit* is reached. If additionally an *infinite* number of basis functions is
included the exact non-relativistic solution of the electronic Schrödinger equation within
the Born-Oppenheimer approximation is obtained. In practice, a full CI is beyond cur-

rent computational power and even for a finite basis set CI based methods are usually truncated at 3rd or 4th order.

Often the determinants used for truncated CI do not describe properly the orbitals needed in the electronic excited states. A possible improvement relies on using multi-configurational methods, where not only the coefficients of the CI expansion but also the coefficients for constructing the MOs in the given basis are optimized simultaneously. In the multi-configurational method CASSCF the molecular orbitals are split in active and inactive orbitals. Within the active space a full CI is performed while the inactive space is left in a fixed configuration. A possible disadvantage of the CASSCF method is that it requires a good choice of the active space for which it is necessary to carry out several test calculations.

2.2.6 Møller-Plesset perturbation method

The standard way to include dynamical correlation effects is the *Møller-Plesset* (MP) method. This method is based on perturbation theory and, hence, the Hamilton operator is split into an unperturbed part $\hat{\mathbf{H}}^{(0)}$, whose solution is known, and a perturbation $\hat{\mathbf{V}}$:

$$\hat{\mathbf{H}} = \hat{\mathbf{H}}^{(0)} + \lambda\hat{\mathbf{V}}. \tag{2.27}$$

For small perturbations ($\lambda \ll 1$) the eigenfunctions and eigenenergies of the total Hamilton operator $\hat{\mathbf{H}}$ are expanded in a series:

$$E = E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \dots \tag{2.28}$$

$$|\Psi\rangle = |\Psi^{(0)}\rangle + \lambda|\Psi^{(1)}\rangle + \lambda^2|\Psi^{(2)}\rangle + \dots. \tag{2.29}$$

By inserting this ansatz into the Schrödinger equation, the following expressions for the energy corrections are obtained[4]:

$$E^{(1)} = \langle\Psi^{(0)}|\hat{\mathbf{V}}|\Psi^{(0)}\rangle \tag{2.30}$$

$$E^{(2)} = \langle\Psi^{(0)}|\hat{\mathbf{V}}|\Psi^{(1)}\rangle \tag{2.31}$$

$$\vdots \quad .$$

Using the Hartree-Fock method as a basis, the Fock operator $\hat{\mathbf{F}}$ is chosen as the unperturbed operator. Therefore, the perturbation is equal to the difference between the exact

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[4]Note that for the calculation of the nth-order energy the (n-1)th-order wave function is required. However, the knowledge of the nth-order wave function allows a calculation of the ($2n$+1)th-oder energy, see e.g. [81].

Hamiltonian and the Fock operator:

$$\hat{\mathbf{V}}(\vec{r}_i) = \hat{\mathbf{H}}(\vec{r}_i) - \hat{\mathbf{F}}(\vec{r}_i) = \sum_{i<j}^{N} \frac{1}{\hat{\mathbf{r}}_{ij}} - \sum_{i}^{N} \left(\hat{\mathbf{J}}_i - \hat{\mathbf{K}}_i \right). \tag{2.32}$$

Thus, the first correction term for the energy $E^{(1)}$ is already included in the Hartree-Fock energy E_{HF}. Often the expansion is stopped after the second order term, in the so-called *MP2*. Higher orders may further improve the total energy, but demand more computational time. It is important to note that the perturbation method may give energies which are below the exact non-relativistic energy, since it does not rely on the variational principle.

2.2.7   Time-dependent density functional theory

The *density functional theory* (DFT)[5] is based on a completely different approach compared to the so far discussed methods for calculating electronic energies. As found by Hohenberg and Kohn the charge density $\rho(r)$ provides enough information to calculate molecular energies [70]. The first Hohenberg-Kohn theorem (HK-I) states that the complete molecular potential V is a functional of the charge density $\rho(r)$ and since, in turn, the molecular potential is described completely by the Hamilton operator $\hat{\mathbf{H}}$, the full many particle ground state of the molecule Ψ is also a functional of $\rho(r)$ [84]:

$$\rho(r) \leftrightarrow V \leftrightarrow \Psi. \tag{2.33}$$

Therefore, it is possible to calculate the total electronic energy of the system E_{el} by minimizing the charge density functional

$$E_{el}[\rho_{el}] = \langle \Psi_{el}[\rho_{el}] | \, \hat{\mathbf{H}} \, | \Psi_{el}[\rho_{el}] \rangle = min, \tag{2.34}$$

which depends on the electron density

$$\rho_{el}(r) = \sum_{i}^{N_{el}} |\psi_i(r)|^2, \tag{2.35}$$

where ψ_i is the spatial part of the single particle functions for the electron i. In analogy to the HF equation (2.15), a set of single particle equations, the so-called *Kohn-Sham equations*, are solved iteratively. The Hartree-Fock potential $\hat{\mathbf{V}}^{HF}$ is replaced by the DFT potential defined as:

$$\hat{\mathbf{V}}^{DFT}(r) = \int \frac{\rho(r')}{|r - r'|} dr' + \hat{\mathbf{V}}_{XC}. \tag{2.36}$$

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[5]For a detailed discussion see refs. [82, 81, 83].

The first term describes the Coulomb electron-electron interaction similar to the exchange integral $\hat{\mathbf{J}}$ in HF theory. $\hat{\mathbf{V}}_{XC}$ is the potential due to the non-classical exchange-correlation energy E_{XC}. $\hat{\mathbf{V}}_{XC}$ is defined as:

$$\hat{\mathbf{V}}_{XC} = \frac{\delta E_{XC}}{\delta \rho}. \tag{2.37}$$

The energy for the non-classical electron correlation E_{XC} covers all kind of electronic interactions which cannot be described exactly. Only if the correlation energy E_{XC} were known exactly the solution of the Kohn-Sham equations would give the correct energy of the exact Hamiltonian of the electronic Schrödinger equation. Since this is not the case the energy obtained from a trial charge density ρ represents an upper limit to the exact ground state energy E_0^{exact}, provided that the exact functional is used:

$$E_{DFT}[\rho] \geq E_0^{exact}. \tag{2.38}$$

This is equivalent to the variational principle discussed in section 2.2.2 and it is known as the second Hohenberg-Kohn theorem (HK-II).

The energy calculated by DFT depending on the density ρ is a sum of energy functionals constructed from the kinetic energy of the non-interacting electrons $T[\rho]$, their interaction with the nuclei $V[\rho]$, the electron-electron repulsion $U[\rho]$ and the exchange correlation energy for the electron correlation E_{XC}:

$$E_{DFT}[\rho] = T[\rho] + V[\rho] + U[\rho] + E_{XC}[\rho]. \tag{2.39}$$

The quality of the DFT approach, therefore, depends on the functionals used for the exchange correlation energy. The Becke3LYP (B3LYP) hybrid functional which is a mixture of Hartree-Fock exchange with DFT exchange-correlation functional is commonly used. In particular the DFT exchange-correlation functional consists of the Becke's 1988 exchange functional (B88 or B) [85] and the Lee-Yang-Parr (LYP) correlation functional [86]. All functionals are combined by three parameters indicated by the number 3 in B3LYP. The parameters are derived by fitting the results of DFT calculations for test systems to experimental data.

It is obvious that the major disadvantage of the DFT method is the choice of the functionals for the exchange correlation energy since they will not give reliable results for all kind of molecular systems. The advantage of the DFT method is that the correlation energy is already included in the calculation. Methods based on HF theory require additional calculation for correlation energy via perturbation theory or variational methods. Thus, the computational effort for DFT calculations is usually smaller than for calculations based on HF.

For calculations of the electronic excited states the *time-dependent density functional theory* (TD-DFT) is applied [87]. If the molecular system is excited by a time-dependent

perturbation, e.g. a time-dependent electric field, then the polarizability shows discrete poles at the excitation energies of the unperturbed system [83]. The frequency dependent polarizability $\alpha(\omega)$ is related to the oscillator strength f_i and the electronic excitation energies $\omega_i = E_i - E_0$ by the following expression:

$$\alpha(\omega) = \sum_i \frac{f_i}{\omega_i^2 - \omega^2}. \tag{2.40}$$

For the electronic excitation energy $\omega = \omega_i$ the polarizability $\alpha(\omega)$ has poles. In the Kohn-Sham equations the orbital energies of the electronic ground state are shifted by a change in the perturbation frequency ω until a pole of the polarizability function, i.e. an exact excitation energy, is reached. Since the excitation energies in TD-DFT are derived in terms of the electronic ground state orbitals, sometimes they may not describe correctly the excited states of the molecule. In this case CASSCF or rather CASPT2 [6] are more reliable, but they also demand high computational effort.

2.2.8   Fourier-Grid-Hamiltonian method

Once the electronic Schrödinger equation is solved for different molecular geometries and, hence, the potential energy surfaces are obtained, the time independent nuclear Schrödinger equation (2.11) has to be solved for each electronic potential state i. In general, the nuclear Schrödinger equation describes all degrees of freedom of the molecule, as there are translations, rotations and vibrations. By changing the coordinate system from laboratory fixed coordinates to center of mass fixed coordinates the translational motion may be separated from the other degrees of freedom:

$$\left| \Psi_{nuc}^i \right\rangle = \left| \Psi_{trans}^i \right\rangle \times \left| \Phi_v^i \right\rangle. \tag{2.41}$$

Then, the solution of the nuclear Schrödinger equations in terms of internal coordinates[7]

$$\hat{\mathbf{H}} \left| \Phi_v^i \right\rangle = (\hat{\mathbf{T}} + \hat{\mathbf{V}}_i) \left| \Phi_v^i \right\rangle = E_v^i \left| \Phi_v^i \right\rangle \tag{2.42}$$

gives rotational-vibrational (rovibrational) eigenfunctions $\left| \Phi_v^i \right\rangle$ and eigenenergies E_v^i of the nuclear framework. A rovibrational eigenfunction of the molecular system can be used as an initial state for a quantum dynamical calculation solving the time-dependent nuclear Schrödinger equation (discussed in the following section).

In order to solve the Schrödinger equation of nuclear motion (2.42) a numerical method called *Fourier Grid Hamiltonian method* (FGH) [88, 89] has been applied throughout

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[6]CASPT2 also includes dynamical correlation via perturbation theory.
[7]For simplicity the indices *nuc* and *PES* of the operators are omitted, cf. eqn. (2.11).

this work. This method uses the fact that the kinetic energy operator $\hat{\mathbf{T}}$ is diagonal in momentum space while the potential energy operator $\hat{\mathbf{V}}$ is diagonal in position space. The *Fourier transformation* is used to transform the wave function from position space to momentum space and vice versa.

The method is explained in more detail using as an example the one-dimensional motion of a single particle. The Hamiltonian $\hat{\mathbf{H}}$ of a single particle of mass m and the momentum $\hat{\mathbf{p}}$ within a potential $V(\hat{\mathbf{x}})$ is given by:

$$\hat{\mathbf{H}} = \hat{\mathbf{T}} + V(\hat{\mathbf{x}}) = \frac{\hat{\mathbf{p}}^2}{2m} + V(\hat{\mathbf{x}}). \tag{2.43}$$

Two basis sets are chosen in which the Hamilton operator can be represented to span a subspace of the Hilbert space. In position space the basis vectors are the eigenvectors of the position operator $\hat{\mathbf{x}}$:

$$\hat{\mathbf{x}} \left| x \right\rangle = x \left| x \right\rangle. \tag{2.44}$$

Here, the eigenvectors form an orthonormal basis, i.e. they satisfy:

$$\left\langle x \mid x' \right\rangle = \delta(x - x'), \tag{2.45}$$

$$\hat{\mathbf{I}}_x = \int_{-\infty}^{\infty} dx \left| x \right\rangle \left\langle x \right|. \tag{2.46}$$

Therefore, the potential V is diagonal in position space:

$$\left\langle x' \right| V(\hat{\mathbf{x}}) \left| x \right\rangle = V(x)\delta(x - x'). \tag{2.47}$$

In momentum space the basis vectors are the eigenvectors of the momentum operator $\hat{\mathbf{p}}$,

$$\hat{\mathbf{p}} \left| k \right\rangle = k\hbar \left| k \right\rangle, \tag{2.48}$$

which also form a complete orthonormal basis set:

$$\left\langle k \mid k' \right\rangle = \delta(k - k'), \tag{2.49}$$

$$\hat{\mathbf{I}}_k = \int_{-\infty}^{\infty} dk \left| k \right\rangle \left\langle k \right|. \tag{2.50}$$

In momentum space the kinetic energy operator $\hat{\mathbf{T}}$ is diagonal:

$$\left\langle k' \right| \hat{\mathbf{T}} \left| k \right\rangle = T_k\delta(k - k') = \frac{\hbar^2 k^2}{2m}\delta(k - k'). \tag{2.51}$$

The basis vectors of position space and of momentum space are related to each other by the following expression:

$$\left\langle k \mid x \right\rangle = \frac{1}{\sqrt{2\pi}}e^{-ikx}. \tag{2.52}$$

Using this transformation and the completeness (2.50) of the basis vectors of the momentum space an expression for a matrix element of the Hamilton operator in position space is derived:

$$
\begin{aligned}
\langle x| \, \hat{\mathbf{H}} \, |x'\rangle &= \langle x| \, \hat{\mathbf{T}} \, |x'\rangle + V(x)\delta(x - x') \\
&= \langle x| \left\{ \int_{-\infty}^{\infty} |k'\rangle \langle k'| \, dk' \right\} \hat{\mathbf{T}} \left\{ \int_{-\infty}^{\infty} |k\rangle \langle k| \, dk \right\} |x'\rangle + V(x)\delta(x - x') \\
&= \int_{-\infty}^{\infty} \langle x| \, k\rangle \, T_k \, \langle k| \, x'\rangle \, dk + V(x)\delta(x - x') \\
&= \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{ik(x-x')} T_k dk + V(x)\delta(x - x').
\end{aligned}
\tag{2.53}
$$

Then, the continuous function x is replaced by a set of discrete grid points x_i. For a grid with N grid points, spaced by a fixed interval Δx, any grid point x_i is found by:

$$
x_i = i\Delta x, \qquad\qquad i = 1, ..., N.
\tag{2.54}
$$

The eigenvectors of the discrete basis satisfy

$$
\Delta x \, \langle x_i| \, x_j\rangle \;\; = \;\; \delta_{ij},
\tag{2.55}
$$

$$
\hat{\mathbf{I}}_x \;\; = \;\; \sum_{i=1}^{N} |x_i\rangle \, \Delta x \, \langle x_i| \, .
\tag{2.56}
$$

Using this discrete basis in position space the matrix elements $\langle x_i| \, \hat{\mathbf{H}} \, |x_j\rangle$ are given by:

$$
H_{ij} = \frac{1}{\Delta x} \left\{ \sum_{l=-N/2}^{N/2} \frac{e^{il2\pi(i-j)/N}}{N} \cdot T_l + V(x_i)\delta_{ij} \right\}
\tag{2.57}
$$

with

$$
T_l = \frac{\hbar^2}{2m} \cdot (l\Delta k)^2, \qquad \Delta k = \frac{2\pi}{N\Delta x}.
\tag{2.58}
$$

Any arbitray state function $|\Phi\rangle$ can be expressed as a linear combinations of the basis functions $|x_i\rangle$ which may loosely thought of as unit Dirac delta functions distributed on the grid points:

$$
|\Phi\rangle = \sum_{i} |x_i\rangle \, \Delta x \Phi(x_i) = \sum_{i} |x_i\rangle \, \Delta x \Phi_i,
\tag{2.59}
$$

with the Φ_i corresponding to the value of the wave function at the grid points. Then, the expectation value of the energy to the state function $|\Phi\rangle$ is

$$
E = \frac{\langle \Phi| \, \hat{\mathbf{H}} \, |\Phi\rangle}{\langle \Phi| \, \Phi\rangle} = \frac{\sum_{ij} \Phi_i^* \Delta x H_{ij} \Delta x \Phi_j}{\Delta x \sum_i |\Phi_i|^2}.
\tag{2.60}
$$

Minimizing this energy with respect to variation of the coefficients Φ_i yields the standard set of secular equations. Finding the roots of the secular determinant is a computationally inefficient procedure, but there exist numerous, efficient algorithms for diagonalizing Hermitian matrices. Diagonalization of the complete Hamiltonian matrix H_{ij} provides the eigenfunctions and eigenvalues of the Hamilton operator, i.e. $|\Phi_v^i\rangle$ and E_v^i in case of eqn. (2.42), on a given grid. The eigenfunctions obtained by this method are the exact solutions of the Hamilton operator $\hat{\mathsf{H}}$ for the given discrete subspace of the complete Hilbert space.

The major disadvantage of the method is its grid size dependency. The size of the grid representation of the Hamilton matrix which has to be diagonalized for a system with N grid points is N^2. For the one and two-dimensional problems discussed in this work up to about 4096 grid points were used, which is about the maximum standard computers can handle nowadays. If more grid points are needed for e.g. increasing the number of dimensions, the most important technical limitation is the amount of memory where the complete matrix has to be kept during the calculation. An advantage of the FGH method is that the discretisation used for position space is also used for the posterior quantum dynamical calculations (see section 2.3.1). Therefore, the numerical error caused by the transformation from one finite, reduced basis to another does not exist.

One possible solution to the problem of fast growing matrix sizes using the FGH method is to use an alternative technique, called *discrete variable representation* method (DVR) [90]. It uses, instead of a regular grid, a set of basis functions specially tailored to the problem. This usually reduces significantly the number of required grid points and, hence, the computational effort. Still, depending on the chosen basis functions, e.g. an irregular grid, the dynamical calculations may become more difficult if no basis transformation – which again may cause numerical errors – is performed.

Instead of diagonalizing the complete Hamilton matrix the method called *Chebychev relaxation* [91] can be used to obtain the rovibrational eigenfunctions and eigenenergies of a molecular system. Here a propagation in imaginary time is performed starting from a guessed initial wave function to relax the system to the energetically lowest eigenstate. The initial wave function must be chosen such that it is not orthogonal to the desired eigenfunction, for some systems this may lead to many trial runs. In order to get the next energetically higher eigenstates the calculated lower eigenfunctions must be projected out of the space of eigenfunctions in every time step of following relaxations. Since, due to this procedure the numerical error increases with the number of eigenstates, this method is restricted to problems where a rather small number of eigenstates and -energies is needed. In case of the symmetric double well potential, as used in this work, symmetric and anti-symmetric eigenfunctions have to be calculated separately since the initial guess must be of the proper symmetry. Still, the major advantage of this method compared to the FGH

method is the scaling of $N \cdot \log N$, making the Chebychev relaxation computationally more efficient.

2.3   Quantum dynamics

2.3.1   Time-dependent nuclear Schrödinger equation

The solution of the time-independent nuclear Schrödinger equation yields the rovibrational eigenstates and eigenenergies of the molecular system, as discussed in the previous section. In order to describe the time-dependent properties of the model system, e.g. its interaction with a time-dependent laser field, it is necessary to solve the time-dependent nuclear Schrödinger equation (TDSE). The resulting wave packet dynamics are obtained by solving the TDSE numerically as it will be discussed in the following sections. At first a general solution of TDSE using the time-dependent evolution operator is considered.

The dynamics of the nuclear frame of a molecule is described by the time-dependent nuclear Schrödinger equation:

$$i\hbar \frac{\partial}{\partial t} \left| \Psi(t) \right\rangle = \hat{\mathbf{H}}(t) \left| \Psi(t) \right\rangle , \tag{2.61}$$

with

$$\hat{\mathbf{H}}(t) = \hat{\mathbf{T}} + \hat{\mathbf{V}} + \hat{\mathbf{W}}(t). \tag{2.62}$$

The molecular Hamilton operator $\hat{\mathbf{H}}$ is given by the kinetic operator $\hat{\mathbf{T}}$ $(= \hat{\mathbf{T}}_{nuc})$, the potential $\hat{\mathbf{V}}$ $(= \hat{\mathbf{V}}^{PES})$ and a time-dependent interaction of the molecule with an electromagnetic field, e.g. a laser pulse, $\hat{\mathbf{W}}(t)$.

In case of more than one electronic state the wave function $\left| \Psi(t) \right\rangle$ can be written as a vector and the Hamilton operator as a matrix:

$$i\hbar \frac{\partial}{\partial t} \begin{pmatrix} \left| \Psi^0(t) \right\rangle \\ \vdots \\ \left| \Psi^n(t) \right\rangle \end{pmatrix} = \begin{pmatrix} \hat{\mathbf{H}}_{0,0} & \dots & \hat{\mathbf{H}}_{0,n} \\ \vdots & \ddots & \vdots \\ \hat{\mathbf{H}}_{n,0} & \dots & \hat{\mathbf{H}}_{n,n} \end{pmatrix} \begin{pmatrix} \left| \Psi^0(t) \right\rangle \\ \vdots \\ \left| \Psi^n(t) \right\rangle \end{pmatrix} \tag{2.63}$$

whereby the indexes $0, 1, \dots, n$ denote the electronic states. The time evolution of the i-th electronic states is described by the i-th time-dependent wave function $\left| \Psi^i(t) \right\rangle$. The

matrix elements of the Hamiltonian are then written as[8]:

$$\hat{\mathbf{H}}_{i,j}(t) = \hat{\mathbf{T}}_{i,j}\delta_{i,j} + \hat{\mathbf{V}}_{i,j}\delta_{i,j} + \hat{\mathbf{W}}_{i,j}(t). \tag{2.64}$$

The coupling between different electronic states results through the time-dependent electromagnetic field $\hat{\mathbf{W}}_{i,j}(t)$ which induces transitions from one electronic state to another. The diagonal elements of the matrix $\hat{\mathbf{W}}$ cause transitions within the electronic states, i.e. excitation from one rovibrational state to another.[9]

Irrespective of the number of implied electronic states the solution of equation (2.61) can be expressed in a general form using the time evolution operator $\hat{\mathbf{U}}$:

$$|\Psi(t)\rangle = \hat{\mathbf{U}}(t, t_0) |\Psi(t_0)\rangle. \tag{2.65}$$

Here the evolution operator $\hat{\mathbf{U}}(t, t_0)$ propagates the wave function $|\Psi\rangle$ from time t_0 to time t. Since the TDSE eqn. (2.61) must hold for any initial wave function $|\Psi(t_0)\rangle$ the evolution operator must satisfy the same equation. Hence, $\hat{\mathbf{U}}(t, t_0)$ can be rewritten in an integral form:

$$\hat{\mathbf{U}}(t, t_0) = \hat{\mathbf{1}} - \frac{i}{\hbar} \int_{t_0}^{t} \hat{\mathbf{H}}(t')\hat{\mathbf{U}}(t', t_0)dt'. \tag{2.66}$$

Equation (2.66) can be solved iteratively by plugging it into itself. Then the following expansion for the time evolution operator is derived[10]:

$$\hat{\mathbf{U}}(t, t_0) = \hat{\mathbf{1}} + \sum_{n=1}^{\infty}(-\frac{i}{\hbar})^n \int_{t_0}^{t} d\tau_n \int_{t_0}^{\tau_n} d\tau_{n-1} \dots \int_{t_0}^{\tau_2} d\tau_1 \hat{\mathbf{H}}(\tau_n)\hat{\mathbf{H}}(\tau_{n-1}) \dots \hat{\mathbf{H}}(\tau_1). \tag{2.67}$$

If the Hamilton operator is not explicitly a function of time the previous expression of the time evolution operator $\hat{\mathbf{U}}$ simplifies to:

$$\hat{\mathbf{U}}(t, t_0) = e^{-\frac{i}{\hbar}\hat{\mathbf{H}}(t-t_0)} \qquad \text{for} \qquad \hat{\mathbf{H}} \neq \hat{\mathbf{H}}(t). \tag{2.68}$$

In this case the system is *conservative*, i.e. the total energy of the molecule is constant.

---

[8]within the scope of the Born-Oppenheimer approximation, i.e. for adiabatic potentials, and without kinetic coupling.

[9]Spin-orbit coupling may cause transitions between electronic states of different spins. Since all simulations contemplated in this work have been applied only to singlet states these couplings are not included.

[10]A more detailed treatment of the time evolution operator can be found in ref. [92].

Time discretisation

The Hamilton operator is not explicitly time-independent since it includes a time-dependent perturbation $\hat{\mathbf{W}}(t)$ (see eqn. (2.62)) that covers all interactions of the molecule with electromagnetic radiation, e.g. laser pulses.

In practice, the time axis is discretised in adequately small segments Δt in which the Hamilton operator $\hat{\mathbf{H}}(t)$ can be considered to be time-independent. Therefore, the solution of TDSE (2.61) can be written as a product of partial evolution operators $\hat{\mathbf{U}}(t_i, t_{i-1})$, each of them propagating the wave function in very small time steps Δt.

$$|\Psi(t)\rangle = \hat{\mathbf{U}}(t, t_n)\hat{\mathbf{U}}(t_n, t_{n-1})\ldots\hat{\mathbf{U}}(t_1, t_0)\,|\Psi(t_0)\rangle \tag{2.69}$$

In accordance with eq. (2.68) each partial evolution operator is given as:

$$\hat{\mathbf{U}}(t_i, t_{i-1}) = e^{-\frac{i}{\hbar}\hat{\mathbf{H}}(t_i - t_{i-1})} = e^{-\frac{i}{\hbar}\hat{\mathbf{H}}(t_i)\Delta t} \tag{2.70}$$

with

$$t_i - t_{i-1} = \Delta t. \tag{2.71}$$

Space discretisation

For the solution of the time-dependent nuclear Schrödinger equation (2.61) numerical methods based on a grid representation [93, 94, 95] have been used throughout this work. As described in section 2.2.8 the position space is discretised by exchanging the continuous position variable r by a grid using N grid points r_i with constant spacing Δr:

$$|\Psi(r, t)\rangle \approx |\Psi(r_i, t)\rangle, \qquad r_i = i\Delta r, \qquad i = 1, ..., N. \tag{2.72}$$

Since in position space the operator of the potential energy $\hat{\mathbf{V}}$ is diagonal it is possible to calculate its effect simply by multiplication with the wave function:

$$\hat{\mathbf{V}}\,|\Psi(r_i, t)\rangle = V(r_i)\,|\Psi(r_i, t)\rangle, \qquad i = 1, ..., N. \tag{2.73}$$

The same is true for the interaction operator $\hat{\mathbf{W}}$ which is, as discussed in the previous section, time-independent within each time step Δt.

By Fourier transformation the wave function is converted from position to momentum space, in which the kinetic energy operator $\hat{\mathbf{T}}$ is diagonal. Then, the effect of $\hat{\mathbf{T}}$ is again just a multiplication:

$$\hat{\mathbf{T}}\,|\Psi(k_j, t)\rangle = \frac{\hbar^2 k_j^2}{2m}\,|\Psi(k_j, t)\rangle, \qquad j = -N/2, ..., N/2 \tag{2.74}$$

with

$$k_j = (j-1) \cdot \frac{2\pi}{N \cdot \Delta r}, \qquad j = 1, ..., N/2 \tag{2.75}$$

and

$$k_{j+N/2} = (j-1) \cdot \frac{2\pi}{N \cdot \Delta r} - k_{max}, \qquad j = 1, \ldots, N/2. \tag{2.76}$$

The maximal momentum k_{max} that can be represented on the grid is given by:

$$k_{max} = \frac{\pi}{\Delta r}. \tag{2.77}$$

2.3.2   Split operator

Because the total Hamilton operator is not diagonal in the grid representation, i.e. the kinetic energy operator $\hat{\mathbf{T}}$ does not commute with the potential energy operator $\hat{\mathbf{V}}$[11]:

$$[\hat{\mathbf{T}}, \hat{\mathbf{V}}] \neq 0. \tag{2.78}$$

the effect of the evolution operator cannot be directly calculated within this representation. Hence, the evolution operator $\hat{\mathbf{U}}$ cannot in general be split in the following way:

$$e^{-\frac{i}{\hbar}\hat{\mathbf{H}}\Delta t} = e^{-\frac{i}{\hbar}(\hat{\mathbf{T}}+\hat{\mathbf{V}})\Delta t} \neq e^{-\frac{i}{\hbar}\hat{\mathbf{T}}\Delta t} \cdot e^{-\frac{i}{\hbar}\hat{\mathbf{V}}\Delta t}. \tag{2.79}$$

However, for very small time steps Δt the following decomposition, in which the kinetic operator $\hat{\mathbf{T}}$ is split in two parts, is possible [96, 97, 98, 99]:

$$e^{-\frac{i}{\hbar}(\hat{\mathbf{T}}+\hat{\mathbf{V}})\Delta t} \approx e^{-\frac{i}{\hbar}\frac{\hat{\mathbf{T}}}{2}\Delta t} \cdot e^{-\frac{i}{\hbar}\hat{\mathbf{V}}\Delta t} \cdot e^{-\frac{i}{\hbar}\frac{\hat{\mathbf{T}}}{2}\Delta t} + \mathcal{O}(\Delta t)^3. \tag{2.80}$$

This decomposition of the Hamilton operator is called *split operator* and involves a numerical error of third order $\mathcal{O}(\Delta t)^3$. If the time intervals Δt are chosen sufficiently small the error of the calculation will be comparatively small. Small time steps also result in an approximately time-independent Hamilton operator because the time-dependent electromagnetic field $\hat{\mathbf{W}}$ changes very slowly within a single time interval. The Split operator is unitary and conserves the norm.

In practice, the time propagation of a wave function is done in several steps. First, the initial wave function on the grid at time t_0, e.g. an eigenfunction of the system, is transformed from position space to momentum space via Fourier transformation. Then, it is multiplied by $e^{-\frac{i}{\hbar}\frac{\hat{\mathbf{T}}}{2}\Delta t}$ and subsequently transformed back to position space. Next it is multiplied by $e^{-\frac{i}{\hbar}\hat{\mathbf{V}}\Delta t}$, transformed back to k-space and again multiplied by $e^{-\frac{i}{\hbar}\frac{\hat{\mathbf{T}}}{2}\Delta t}$. At the end, the wave function is transformed once again to position space and a wave function $|\Psi_k(t_0 + \Delta t)\rangle$ propagated by Δt is obtained. In this manner, the wave function is propagated step by step until a final time t_f.

---

[11]Here $\hat{\mathbf{V}}$ includes also the interaction with the laser field $\hat{\mathbf{W}}$.

2.3.3   Second Order Differencing

Another numerical method to solve the time-dependent Schrödinger equation is the so
called *n-th order differencing* (NOD) method. The time-dependent wave function $|\Psi(t)\rangle$
is expanded in the Taylor series [100, 101]:

$$|\Psi(t + \Delta t)\rangle = |\Psi(t)\rangle + \Delta t \cdot \frac{\partial}{\partial t} |\Psi(t)\rangle + \frac{\Delta t^2}{2!} \cdot \frac{\partial^2}{\partial t^2} |\Psi(t)\rangle + \frac{\Delta t^3}{3!} \cdot \frac{\partial^3}{\partial t^3} |\Psi(t)\rangle \ldots \quad (2.81)$$

and

$$|\Psi(t - \Delta t)\rangle = |\Psi(t)\rangle - \Delta t \cdot \frac{\partial}{\partial t} |\Psi(t)\rangle + \frac{\Delta t^2}{2!} \cdot \frac{\partial^2}{\partial t^2} |\Psi(t)\rangle - \frac{\Delta t^3}{3!} \cdot \frac{\partial^3}{\partial t^3} |\Psi(t)\rangle \ldots . \quad (2.82)$$

Substracting eqn. (2.82) from eqn. (2.81) results in

$$|\Psi(t + \Delta t)\rangle - |\Psi(t - \Delta t)\rangle = 2 \cdot \Delta t \cdot \frac{\partial}{\partial t} |\Psi(t)\rangle + 2 \cdot \frac{\Delta t^3}{3!} \cdot \frac{\partial^3}{\partial t^3} |\Psi(t)\rangle \ldots . \quad (2.83)$$

The expansion is truncated after the second term, for the so-called *second order differ-
encing* (SOD), yielding a formula to propagate the wave function from t to Δt:

$$|\Psi(t + \Delta t)\rangle = |\Psi(t - \Delta t)\rangle + 2 \cdot \Delta t \cdot \frac{\partial}{\partial t} |\Psi(t)\rangle + \mathcal{O}(\Delta t)^3, \quad (2.84)$$

with an error of third order. An initial wave function $|\Psi(t_0)\rangle$ as well as the wave function
at the first step $|\Psi(t_0 + \Delta t)\rangle$ are required. The initial function is chosen (just as in the
case of the method using the Split operator) defining an initial state of the system, e.g.
the lowest rovibrational eigenfunction of the electronic ground state. The wave function
after the first time step is derived from the *Runge-Kutta* method using the same accuracy
as in SOD:

$$|\Psi(t_0 + \Delta t)\rangle = |\Psi(t_0)\rangle + \Delta t \cdot \frac{\partial}{\partial t} |\Psi(t_0)\rangle + \frac{\Delta t}{2!} \cdot \frac{\partial^2}{\partial t^2} |\Psi(t_0)\rangle . \quad (2.85)$$

Note that the derivations of the wave functions can be expressed in terms of the TDSE
(2.61) as

$$\frac{\partial}{\partial t} |\Psi(t)\rangle = -\frac{i}{\hbar} \hat{\mathbf{H}}(t) |\Psi(t)\rangle \quad (2.86)$$

$$\frac{\partial^2}{\partial t^2} |\Psi(t)\rangle = -\frac{1}{\hbar^2} \hat{\mathbf{H}}(t) \hat{\mathbf{H}}(t) |\Psi(t)\rangle , \quad (2.87)$$

etc. for higher orders. As discussed in section 2.3.2 the Fourier transformation is used
to transform the wave function from position space to momentum space and *vice versa*.

Depending on the representation of the wave function the effect of the kinetic or poten-
tial operator, respectively, is calculated by multiplication with the wave function. More
Fourier transformations are needed if the potential and kinetic operator are coupled. The
advantage of the SOD scheme is that the Hamiltonian can include all kind of couplings.
Propagations using the Split operator do not allow to use a Hamilton operator which
includes coupling terms as $\hat{\mathbf{x}} \cdot \hat{\mathbf{p}}$ while in SOD there are no restrictions to the components
of the Hamilton operator.

A disadvantage of the SOD (or NOD in general) method is the need for very small
time steps to get reliable results. In accordance with the uncertainty principle, the time
step must not exceed a critical time step given by the maximum energy of the system:

$$
\begin{aligned}
\Delta t_{crit} &= \frac{\hbar}{E_{max}} \qquad \text{with} \\
E_{max} &= T_{max} + V_{max}.
\end{aligned}
\tag{2.88}
$$

The maximum potential energy V_{max} is given by the potential energy surface on the
respective grid. For the maximum kinetic energy on the same grid an expression derived
from eqn. (2.77) is used:

$$
T_{max} = \frac{\hbar^2 k_{max}^2}{2m}.
\tag{2.89}
$$

In practice, time steps for SOD are often much smaller than for the split operator method.
In addition, a time step at least five times smaller than the critical one is recommended
[93]. This fact makes SOD time consuming in terms of computational effort. It is also
important to notice that the SOD method is not conserving the norm, in contrast to the
split operator propagation scheme.

2.3.4   Time-dependent laser fields

The operator for the interaction of the molecule with the laser field $\hat{\mathbf{W}}$, as used in equa-
tion (2.64), is described by the semi-classical dipole approximation[12] in laboratory fixed
coordinates $\vec{R}$ as follows:

$$
\hat{\mathbf{W}}_{i,j}(t) = -\vec{\mu}^{ij} \cdot \vec{E}(\vec{R}, t),
\tag{2.90}
$$

with $\vec{\mu}^{ij}$ being the operator for the electric (transition) dipole moment between electronic
states i and j, and $\vec{E}$ the time-dependent electromagnetic laser field. The time-dependent

---

[12]The magnetic dipole and the electric quadrupole are neglected, because they are about two oders of
magnitude smaller than the electric dipole.

electromagnetic field $\vec{E}(\vec{R}, t)$ which is used to control intra-molecular motion is in general given by the following expression:

$$\vec{E}(\vec{R}, t) = \vec{\epsilon} \cdot E^0 \cdot s(t) \cdot \frac{e^{i(\vec{k}\vec{R} - \omega t)} + e^{-i(\vec{k}\vec{R} - \omega t)}}{2}, \tag{2.91}$$

where E^0 is the amplitude of the field with the carrier frequency ω, $\vec{\epsilon}$ the polarization vector, $\vec{k}$ the wave vector, and $s(t)$ the shape function which describes the envelope of the laser pulse. The term $e^{i\vec{k}\vec{R}}$ can be expanded in the Taylor series:

$$e^{i\vec{k}\vec{R}} \approx 1 + i\vec{k}\vec{R} + \dots. \tag{2.92}$$

Since all the molecules considered throughout this work are of dimensions no larger than 10 Å whereas the laser pulses cover a range of wavelengths starting from at least 100 Å, the Taylor series can be truncated after the first term. Then, an expression for a position-independent field is obtained:

$$\vec{E}(t) = \vec{\epsilon} \cdot E^0 \cdot s(t) \frac{e^{i\omega t} + e^{-i\omega t}}{2}. \tag{2.93}$$

Using the Euler formula and combining the polarization vector with the amplitude this equation simplifies to:

$$\vec{E}(t) = \vec{E^0} \cdot s(t) \cos(\omega t). \tag{2.94}$$

The shape function $s(t)$ used throughout this work is given by:

$$s(t) = \sin^2\left(\frac{\pi(t - t_d)}{t_p}\right) \qquad \text{for} \quad t_d \leq t \leq t_d + t_p, \tag{2.95}$$

with t_p being the pulse duration and t_d the starting time, also called delay time, of the current laser pulse in a laser pulse sequence.

In the following section the reader is introduced to the methods of laser pulse control applied throughout this work.

2.4 Laser pulse control

2.4.1 Analytical laser pulses

The control of a molecular system by means of an external laser field is one of the main goals in the field of quantum dynamics [50, 102, 103]. The objective is to drive the system

from a given initial state to a desired final state. In this section the different strategies are presented that have been applied in this work to design an appropriate laser pulse sequence which controls the model system in the desired way. The discussed strategies range from control methods based on manual optimization of the laser parameters (section 2.4.1 and 2.4.2) to methods based on algorithms acting as a "black-box" generating possible control pulses (section 2.4.3).

The conceptually easiest approach is to use analytical laser pulses. These are well defined laser fields with analytical shape functions such as (2.95) which are functioning as either a pump pulse to excite population from one energetically low lying state to another state higher in energy or as a dump pulse causing a stimulated emission back to an energetically lower state. Pump-dump schemes using analytical laser pulses developed by Paramonov and coworkers [104] and Tannor and Rice [50, 105] are a common approach to laser pulse control of a quantum dynamical system.

Before a suitable laser pulse sequence is constructed it is necessary to develop an efficient reaction mechanism that leads the system selectively from a initial state via one or more transition states to the final state. The laser pulses should be designed such that all transitions are selective, i.e. they only transfer population from the initial state to the desired state without exciting population to other states, and effective, in the sense that the desired amount of population is excited/deexcited.

An analytical laser pulse is usually of the form defined in eqn. (2.94). For a sequence of linearly polarized laser pulses with $\sin^2$-shape function the following expression is obtained:

$$E_i(t) = E_i^0 \cdot \sin^2\left(\frac{\pi(t - t_{d_i})}{t_{p_i}}\right) \cdot \cos(\omega_i(t - t_{d_i}) + \eta_i) \qquad \text{for} \quad t_{d_i} \leq t \leq t_{d_i} + t_{p_i}. \quad (2.96)$$

Here E_i^0 is the amplitude of the laser field, η_i the time-independent phase, t_{p_i} is the pulse duration, t_{d_i} the starting time and ω_i the frequency of the pulse i.[13]

For an initial guess of an appropriate laser pulse it is necessary to know the transition frequency ω_i, i.e. the energy gap between the affected states. Still, the optimal laser frequency is usually slightly detuned from the exact transition frequency. This is caused

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[13]For a chirped laser pulse the frequency ω becomes time-dependent:

$$\omega(t) = \omega_0 + \lambda\left(t - t_d - \frac{t_p}{2}\right), \qquad (2.97)$$

where the linear chirp rate λ causes a frequency sweep centered at the resonant frequency ω_0 of the desired transition.

by the interaction of the electric field with the diagonal elements of the transition dipole matrix $\mu_{vv'}$ $(= \langle v| \vec{\mu} |v'\rangle = \langle \Phi_v| \vec{\mu} |\Phi_{v'}\rangle)$. While the off-diagonal terms cause transitions between different states, the diagonal terms result in a shift of the energy of the levels. Since in general $\mu_{vv} \neq \mu_{v'v'}$ the energy levels will shift by a different amount causing a change in the energy difference of states compared with the system without laser field. Therefore, the optimal laser pulse frequency has to be found by detuning ω_i until a satisfactory result is obtained.

The choice of a suitable time duration of the laser pulse is rather affected by the uncertainty principle. If the laser pulse is on the one hand too short, then states different from the desired ones might also be affected. If the laser pulse is on the other hand relatively long, then competing effects like *intra-molecular vibrational redistribution* (IVR) may take place destroying the effectiveness of the laser control.

For a complete transition of the population in a two-level system from state $|1\rangle$ to state $|2\rangle$ (population inversion) a so-called π-*pulse* is most effective [106]. In terms of the *area theorem* (see e.g. ref. [107]) population inversion in a two-level system is obtained if the area A under the pulse envelope, multiplied by the transition dipole matrix element μ_{12}, and divided by Planck's constant, becomes equal to an odd multiple of π:

$$A = \int_0^{t_p} \Omega(t)dt = \frac{\mu_{12}}{\hbar} \int_0^{t_p} E^0 s(t) \, dt = (2N + 1) \cdot \pi \qquad \text{with} \quad N = 0, 1, \ldots, \qquad (2.98)$$

where $\Omega(t)$ is the so-called Rabi frequency. Then, the amplitude of the laser pulse E^0 depends on its duration and on the transition dipole matrix elements $\mu_{vv'}$. This is an approximation for a two-level system, but it can be extended to multi-level system using so-called *generalized π-pulses* [108]. However, even a simple π-pulse is very suitable for generating an initial guess for a laser pulse in a multi-level system. For $\sin^2$-shaped laser pulses their amplitude is then approximated by:

$$E_i^0 \approx \frac{2\pi \cdot \hbar}{\mu_{vv'} \cdot t_{p_i}} \qquad (2.99)$$

Eventually the laser pulse parameters must be optimized, manually or by using e.g. genetic algorithms.

A prerequisite for using analytical laser pulses is that a good insight into the quantum system is required. Transition dipole matrix elements μ_{mn} must be analysed to find the most effective transition and many different laser pulse parameters must be optimized. Often, it is a great challenge to design a suitable reaction mechanism that eventually yields full control over the molecular system. However, analysing the system and designing mechanisms for effective transitions give a very good understanding of how control is

achieved. The knowledge gained from these studies can be used by e.g. experimentalists to design a desired laser pulse sequence to reach an objective state.

2.4.2   STIRAP

There are cases where the intermediate state in a reaction mechanism should not be populated to prevent depopulation e.g. by spontaneous emission to states coupled to this intermediate state. If, in turn, no direct coupling between initial and target state exists, but only coupling between each of them and this intermediate state, a method called **sti**mulated **R**aman scattering involving **a**diabatic **p**assage (STIRAP) [109, 110] may be applied to the system. The method is based on a counter-intuitive sequence of two laser pulses. The pump pulse (P), which transfers population from the initial state to the intermediate level, follows the so-called *Stoke pulse* (S) (which is the dump pulse) that couples the intermediate state to the final state; both pulses overlap partially. The coupling scheme for a three-level system, called a Λ-type level-scheme[14], is shown in Figure 2.1. Coherent interaction of the states $|1\rangle$, $|2\rangle$ and $|3\rangle$ caused by the laser pulses leads to dressed eigenstates of the coupled system. One of those dressed states contains only components of the initial state $|1\rangle$ and final level $|3\rangle$, with no contribution of the radiatively decaying intermediate level $|2\rangle$. With the Stokes laser preceding the pump pulse, the system is prepared at the beginning of the interaction in this *trapped state*. Thus, no population is transferred through the intermediate "dark" state $|2\rangle$ and no losses due to radiative decay occur. The pump pulse transfers selectively all population from the initial $|1\rangle$ to the target state $|3\rangle$.

The radiative coupling of the states $|1\rangle$ and $|2\rangle$, as well as the states $|2\rangle$ and $|3\rangle$ is described in terms of their respective Rabi frequencies (cf. eqn. (2.98)):

$$\Omega_P(t) = \frac{\mu_{12} \cdot E_P(t)}{\hbar}, \tag{2.100}$$

$$\Omega_S(t) = \frac{\mu_{23} \cdot E_S(t)}{\hbar}, \tag{2.101}$$

where $E_P(t)$ and $E_S(t)$ are the linearly polarized laser fields of the pump and the Stokes pulse. Even though the coupling between the pairs of levels is strongest when the pulse frequencies are tuned to the respective resonance frequencies, it is not necessary for each transition to be induced resonantly. Only the combination of pump and Stokes frequencies should be resonant with the energy difference between initial and final state. The

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[14]because the transition path portrays the letter Λ

detunings of the pump and Stokes frequencies are defined as

$$\Delta_P = \omega_{12} - \omega_P, \tag{2.102}$$
$$\Delta_S = \omega_{23} - \omega_S, \tag{2.103}$$

where ω_{12} and ω_{23} are the resonant frequencies. The effective Rabi frequencies including the detuning are then written as

$$\Omega_P(\Delta) = \sqrt{\Omega_P^2(t) + \Delta_P^2}, \quad \text{and} \tag{2.104}$$
$$\Omega_S(\Delta) = \sqrt{\Omega_S^2(t) + \Delta_S^2}. \tag{2.105}$$

For $\Delta_P = \Delta_S = 0$ the STIRAP process becomes resonant.
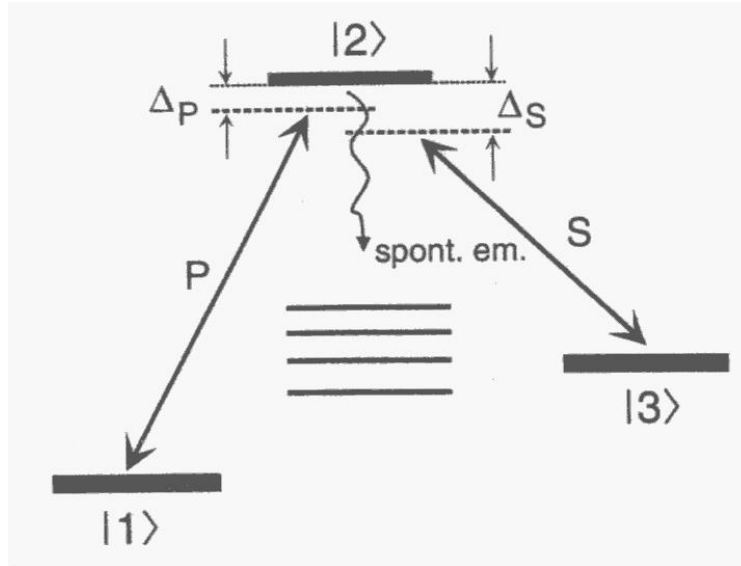

Figure 2.1: Three-level system for STIRAP excitation. The initial state $|1\rangle$ and the final state $|3\rangle$ are coupled by pump (P) and Stokes (S) lasers via the intermediate state $|2\rangle$. The state $|2\rangle$ may decay by spontaneous emission to other levels. The detuning of the pump and Stokes laser frequencies from the transition frequency to the intermediate state are Δ_P and Δ_S, respectively (adapted from ref. [110]).

STIRAP passages require usually longer laser pulses (up to ns) compared to simple pump-dump schemes. This can be a disadvantages if e.g. IVR is competing. The advantage is the possibility for population transfer between states that cannot be connected by a one-photon transition or only via radiatively decaying intermediate states using a pump-dump scheme.

2.4.3   Optimal Control theory

The main difference between optimal control and the methods described in the last sections is that in optimal control it is not necessary to predefine any sort of reaction mechanism for the system. Instead, only the initial state $|\psi_i(0)\rangle = |\Psi_i\rangle$ at time $t = 0$ and the final state $|\psi_f(T)\rangle = |\Psi_f\rangle$ at time $t = T$ are required for the computer algorithm of the method. The algorithm uses a variational scheme on an appropriate functional to generate a laser field which drives the quantum system from the given initial state to the desired final state. This method, developed by Rabitz and coworkers [111, 112], is based on the maximization of an *objective functional J* which consists of the total overlap of the initial wave function propagated to the final time T with the final state and the calculated optimal laser field $\vec{E}(t)$:

$$J(\Psi_i, \Psi_f, \vec{E}(t)) = |\langle \psi_i(T)| \Psi_f \rangle|^2 - \alpha \int_0^T |\vec{E}(t)|^2 dt. \qquad (2.106)$$

The parameter α is a penalty factor that controls the optimal laser field. This is done to avoid very high laser fields which could ionize the molecule. The penalty factor α may be chosen time-dependent:

$$\alpha = \alpha(t) = \frac{\alpha_0}{s(t)}. \qquad (2.107)$$

where α_0 is a time-independent parameter allowing to restrict the laser field according to a desired shape function $s(t)$. If the envelope of the laser pulse goes to zero, α reaches infinity and, therefore, it ensures that the allowed laser field also goes to zero [113]. Further, an additional term, which ensures that the Schrödinger equation is fulfilled for $|\psi_i(t)\rangle$ for all times t, is added to the functional:

$$J(\Psi_i, \Psi_f, \vec{E}(t)) =$$
$$|\langle \psi_i(T)| \Psi_f \rangle|^2 - \alpha \int_0^T |\vec{E}(t)|^2 dt$$
$$-2\Re\left\{ \langle \psi_i(T)| \Psi_f \rangle \int_0^T \langle \psi_f(t)| \frac{i}{\hbar}[\hat{\mathbf{H}}_0 - \vec{\mu}\vec{E}(t)] + \frac{\partial}{\partial t} |\psi_i(t)\rangle \, dt \right\}. \qquad (2.108)$$

The variation of this functional then gives a system of coupled equations for the control field [114]:

$$\vec{E}(t) = -\frac{s(t)}{\hbar\alpha_0} \cdot \Im\{\langle \psi_i(t)| \psi_f(t)\rangle \langle \psi_f(t)| \vec{\mu} |\psi_i(t)\rangle\} \qquad (2.109)$$

$$i\hbar\frac{\partial}{\partial t} |\psi_i(t)\rangle = [\hat{\mathbf{H}}_0 - \vec{\mu}\vec{E}(t)] |\psi_i(t)\rangle; \qquad |\psi_i(0)\rangle = |\Psi_i\rangle \qquad (2.110)$$

$$i\hbar\frac{\partial}{\partial t} |\psi_f(t)\rangle = [\hat{\mathbf{H}}_0 - \vec{\mu}\vec{E}(t)] |\psi_f(t)\rangle; \qquad |\psi_f(T)\rangle = |\Psi_f\rangle. \qquad (2.111)$$

Equation (2.110) describes the propagation of $|\Psi_i\rangle$ forward in time, whereas equation (2.111) describes the backward propagation of $|\Psi_f\rangle$. Both equations are coupled to the laser field which is calculated from $|\psi_i(t)\rangle$ and $|\psi_f(t)\rangle$ in equation (2.109) at every time step. This set of coupled equations is solved iteratively by a self consistent field method.

An advantage of the optimal control method is that no assumptions of the reaction mechanism are needed. The algorithm searches for any optimal reaction path that brings the system from its initial state to a desired final state. The disadvantage is that usually no general mechanism can be derived from the calculated optimal reaction path because the generated optimal laser field often gives very little information about the transitions taken place. Also, the computational effort may be very large since the method is not only iterative but also needs a forward and a backward time propagation for each time step.[15]

A modification of optimal control is called the *local control method* [115, 116, 117]. This method requires *a priori* knowledge of a path the system should follow from its initial state to the objective state. This path is specified as a time-dependent path of the expectation value $\left\langle \hat{W}(t) \right\rangle \equiv \langle \psi(t)| \hat{W} |\psi(t)\rangle$ of the target operator $\hat{W}$ that specifies the objective state of a molecule. The target operator is chosen such that its expectation value has a maximum value when the molecule reaches the objective state at the final controlling time t_f. Hence, the time-derivative of the expectation value of the target operator should have a positive value at any time to guarantee a monotonic increase and become maximal at final time. For this path a control field $E(t)$ is sought, which will exactly create the demanded dynamics of the chosen observable. According to the formulation (2.106) of the optimal control method the laser pulse leads to an extremal value of the objective functional $J[E(t)]$ defined by:

$$
\begin{aligned}
J[E(t)] \;&=\; \left\langle \hat{W}(t_f) \right\rangle - \int_{t_0}^{t_f} dt \frac{1}{\hbar A} [E(t)]^2 & (2.112)\\
&=\; \int_{t_0}^{t_f} dt \left[\frac{d}{dt} \left\langle \hat{W}(t) \right\rangle - \frac{1}{\hbar A} [E(t)]^2 \right] + \left\langle \hat{W}(t_0) \right\rangle, & (2.113)
\end{aligned}
$$

where the second term of eqn. (2.112), controlled parametrically by A, presents the penalty due to the laser energy. The integrand of eqn. (2.113) is considered a known function of time

$$
\frac{d}{dt} \left\langle \hat{W}(t) \right\rangle - \frac{1}{\hbar A} [E(t)]^2 = g(t) \qquad (2.114)
$$

which determines one of the possible paths in the functional space of the objective functional. By differentiating $\left\langle \hat{W}(t) \right\rangle$ with respect to t obeying the TDSE with $\hat{\mathsf{H}} =$

---

[15]The backward time propagation is also a problem for non time-reversible systems, e.g. dissipative systems.

$\hat{\mathbf{H}}_0 - \hat{\mu}E(t)$ one derives[16]:

$$
\frac{d}{dt}\left\langle \hat{W}(t) \right\rangle = \frac{d}{dt}(\langle \psi(t)| \hat{W} |\psi(t)\rangle) \tag{2.115}
$$

$$
= -\frac{i}{\hbar} \langle \psi(t)| [\hat{W}, \hat{\mathbf{H}}_0] |\psi(t)\rangle + \frac{i}{\hbar} \langle \psi(t)| [\hat{W}, \hat{\mu}] |\psi(t)\rangle E(t) \tag{2.116}
$$

For the special case where the function $g(t)$ is chosen to be zero ($g(t) = 0$) the value of $\left\langle \hat{W}(t) \right\rangle$ increases in proportion to the pulse energy, cf. eqn. (2.114). Since the objective state gives the maximum value to $\left\langle \hat{W}(t) \right\rangle$, the local control pulse always brings the molecule towards the objective state. The quality of the control pulse depends on the choice of the target operator $\hat{W}$; this makes the problem local at any time t. If $[\hat{W}, \hat{\mathbf{H}}_0] = 0$ is required then the expression for the local control pulse is obtained as:

$$
E(t) = -2A \cdot \Im\{\langle \psi(t)| \hat{W}\hat{\mu} |\psi(t)\rangle\}. \tag{2.117}
$$

As example the population inversion in a three-level system is considered. Then, the target operator reads [117]:

$$
\hat{W} = |1\rangle w_1 \langle 1| + |2\rangle w_2 \langle 2| + |3\rangle w_3 \langle 3| , \tag{2.118}
$$

where w_1 to w_3 are the weights of the respective states, e.g. $|1\rangle$ being the initial, $|2\rangle$ the intermediate, and $|3\rangle$ the target. The choice of these weights determines the reaction mechanism which the algorithm assumes for calculating an optimal pulse sequence, e.g. $w_1 = 0$, $w_2 = 1$ and $w_3 = 2$. The transition moment operator $\hat{\mu}$ coupling all states included in the reaction mechanism is assumed to have a form of:

$$
\hat{\mu} = |3\rangle \mu_{32} \langle 2| + |2\rangle \mu_{21} \langle 1| + h.c. \tag{2.119}
$$

In order to solve the coupled equations of the local control pulse (2.117) and the TDSE (2.110) no iteration is required. First the control pulse is calculated at t with $\psi(t)$, then $E(t)$ is substituted into the TDSE and propagated to $t + \Delta t$. This procedure is repeated until the target state is reached.

The major advantage of the local control algorithm is that only a single forward propagation[17] is performed for each time step. This makes the algorithm computationally less expensive than the optimal control algorithm. The disadvantage is the need of a rough idea of a reaction mechanism to set up a proper target operator.

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[16]The target operator $\hat{W}$ is considered time-independent.

[17]In case of an target state $\hat{W}$ that does not commute with the molecular Hamilton operator ($[\hat{W}, \hat{\mathbf{H}}] \neq 0$) a backward propagation scheme using the initial state, e.g. a pure state, as the target state has to be used. In turn, combining an appropriate choice of the target operator and backwards time-propagation technique allows to apply the local control method to wave packet shaping [117].