Numerical Methods for Quantum Molecular Dynamics

KATHARINA KORMANN

UPPSALA UNIVERSITY
Department of Information Technology

UPPSALA UNIVERSITET

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KATHARINA KORMANN

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DIVISION OF SCIENTIFIC COMPUTING
DEPARTMENT OF INFORMATION TECHNOLOGY
UPPSALA UNIVERSITY
UPPSALA
SWEDEN

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Katharina Kormann

`katharina.kormann@it.uu.se`

Division of Scientific Computing
Department of Information Technology
Uppsala University
Box 337
SE-751 05 Uppsala
Sweden

`http://www.it.uu.se/`

Abstract

The time-dependent Schrödinger equation models the quantum nature of molecular processes. Numerical simulations of these models help in understanding and predicting the outcome of chemical reactions.

In this thesis, several numerical algorithms for evolving the Schrödinger equation with an explicitly time-dependent Hamiltonian are studied and their performance is compared for the example of a pump-probe and an interference experiment for the rubidium diatom. For the important application of interaction dynamics between a molecule and a time-dependent field, an efficient fourth order Magnus–Lanczos propagator is derived. Error growth in the equation is analyzed by means of a posteriori error estimation theory and the self-adjointness of the Hamiltonian is exploited to yield a low-cost global error estimate for numerical time evolution. Based on this theory, an h, p-adaptive Magnus–Lanczos propagator is developed that is capable to control the global error. Numerical experiments for various model systems (including a three dimensional model and a dissociative configuration) show that the error estimate is effective and the number of time steps needed to meet a certain accuracy is reduced due to adaptivity.

Moreover, the thesis proposes an efficient numerical optimization framework for the design of femtosecond laser pulses with the aim of manipulating chemical reactions. This task can be formulated as an optimal control problem with the electric field of the laser being the control variable. In the algorithm described here, the electric field is Fourier transformed and it is optimized over the Fourier coefficients. Then, the frequency band is narrowed which facilitates the application of a quasi-Newton method. Furthermore, the restrictions on the frequency band make sure that the optimized pulse can be realized by the experimental equipment. A numerical comparison shows that the new method can outperform the Krotov method, which is a standard scheme in this field.

List of Papers

This thesis is based on the following papers, which are referred to in the text by their Roman numerals.

I Kormann, K., Holmgren, S., Karlsson, H. O. (2008) Accurate time propagation for the Schrödinger equation with an explicitly time-dependent Hamiltonian. J. Chem. Phys. **128**:18410
   The author of this thesis implemented the methods and performed analysis as well as computations. She prepared a draft of the manuscript and finished it with the assistance from the co-authors. The ideas were developed in close cooperation with the co-authors.

II Kormann, K., Holmgren, S., Karlsson, H. O. (2009) Global Error Control of the Time-Propagation for the Schrödinger Equation with a Time-Dependent Hamiltonian. Technical Report 2009-021, Department of Information Technology, Uppsala University, 2009. Submitted to Journal of Scientific Computing.
   The author of this thesis implemented the methods and performed analysis as well as computations. She prepared a draft of the manuscript and finished it with the assistance from the co-authors. The ideas were developed in consultation with the co-authors.

III Kormann, K., Holmgren, S., Karlsson, H. O. (2009) A Fourier-Coefficient based Solution of an Optimal Control Problem in Quantum Chemistry. Technical Report 2009-022, Department of Information Technology, Uppsala University, 2009. Submitted to Journal of Optimization Theory and Applications.
   The author of this thesis implemented the methods and performed analysis as well as computations. She prepared a draft of the manuscript and finished it in consultation with the co-authors. The ideas were developed by the author in discussion with the co-authors.

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Contents

1. Introduction

Newtonian mechanics provides a model for processes that can be observed by the naked eye. Quantum mechanics, on the contrary, is a mathematical framework formulated to describe the probability distribution of particles, e.g., electrons and nuclei, which cannot be perceived directly with the human senses. The quantum nature of photons is demonstrated to students in school by the double-slit experiment; and physicists can measure scattering cross-sections or reaction rates in their laboratories. Solving the modeling equations for quantum mechanics reveals the dynamics of the particles, and thereby helps in understanding the observables in terms of the underlying molecular properties. Since it is generally impossible to find analytical solutions to these equations, computer simulations are inevitable.

Even though quantum processes are not directly observable, they govern chemical reactions and thereby become apparent. Hence, quantum dynamics is intrinsic to all kinds of natural occurrences. With the aim of controlling reactions, quantum chemists put efforts in probing and manipulating the dynamics of electrons and atomic nuclei. The upcoming of femtosecond lasers in the late 1980s made it possible to "watch" the motion of nuclei. The development of laser technologies has continued and around the turn of the millennium it even became possible to follow the motion of the electrons, now using attosecond pulses.

The possibility to control reactions on the molecular level opens new opportunities for chemical processes, for instance in the semiconductor or catalysis industries.[1] Furthermore, it has potential impact to electronics where scientists try to design miniaturized devices whose structures are made up of very few atoms only.[2] Quantum computing grounds on so-called qubits being a probabilistic superposition of two quantum states.[3]

In the next chapter, quantum dynamics models are introduced. Unfortunatelly, the number of degrees of freedoms within a molecule is often very large. For instance, in the full description of the quantum nature of just a single water molecule (H_2O), 39 spatial degrees of freedom are involved. More-

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[1] cf. the Science Blog of the Max–Planck–Gesellschaft on
http://www.scienceblog.com/community/older/1999/B/199901875.html.
[2] cf. the Imperial College Department of Physics on
http://www3.imperial.ac.uk/physics/admissions/pg/dtc/cqd.
[3] cf, the Standford Encyclopedia of Philosophy on
http://plato.stanford.edu/entries/qt-quantcomp.

over, the motion within a molecule ranges over scales of many orders of magnitude in both time and physical space. The so-called Born–Oppenheimer approximation is a useful simplification which allows for splitting electronic and nuclear motion. In this model, the 30 electronic and the nine nuclear degrees of freedom in the H_2O molecule model are separated. Still, the description for the dynamics of the nuclei remains high-dimensional, and the corresponding numerical simulation extremely challenging (see Chap. 3). This thesis concentrates on such nuclear Schrödinger equations. Chapts. 4 and 5 review time propagation and optimal control for the design of femtosecond laser pulses with the emphasis on the topics of Paper I-III. A focused summary of the content of the papers is provided in Chap. 6. The concluding Chapt. 7 collects both unresolved problems directly related to the research reported in Papers I-III and an outlook on interesting extensions of the presented work.

2. Time-dependent Quantum Dynamics

The Schrödinger equation was phrased for the first time by Erwin Schrödinger in a series of papers [76, 77, 78, 79]. His first article [77] considers the case of the hydrogen atom and the Schrödinger eigenvalue problem was devised starting from a classical Hamiltonian differential equation, taking into account several observations on the quantum nature of particles. Schrödinger's work is fundamental for today's quantum mechanics.

The general *time-dependent* form of the Schrödinger equation, which Schrödinger derived in his fourth article [78], reads

$$i\hbar \frac{\partial}{\partial t} \Psi(x, t) = \hat{H}\Psi(x, t), \qquad (2.1)$$

where $\hbar$ is Planck's constant divided by 2π and $\hat{H}$ is the (quantum) Hamiltonian operator containing the kinetic and the potential energies of the studied system. The wave function Ψ depends on spatial (x) and temporal (t) coordinates. Its significance is given by the square of its modulus, $\rho(x, t) = |\Psi(x, t)|^2$, which defines the so-called probability density, i.e., $\rho(x, t)$ gives the probability for the system to be in the configuration defined by x at time t. The partial differential equation (2.1) needs to be closed with an initial value, $\Psi(x, 0) = \Psi_0$, and boundary conditions.

2.1 Born–Oppenheimer Approximation

When describing the full dynamics of a molecule, the Hamiltonian is established by adding up the kinetic and the potential energies of each nuclei and each electron as well as the electron-nuclear potential energy. In this section, we will consider the time-independent Schrödinger equation (TISE),

$$\hat{H}\Psi(x) = \hat{E}\Psi(x).$$

Let us denote by R_i the coordinates of nucleus N_i, and by Z_i and M_i its charge and mass, respectively. For electron e_i, we denote its coordinates by r_i and by e and m we denote electronic charge and mass, respectively. With this nota-

tion, the full molecular Hamiltonian is given by (cf. Refs. [80, 92]),

$$
\begin{aligned}
\widehat{H} &= -\sum_i \frac{\hbar^2}{2M_i}\Delta_{\mathrm{N}_i} + \sum_{i>j}\frac{Z_i Z_j e^2}{|R_i - R_j|} - \sum_i \frac{\hbar^2}{2m}\Delta_{\mathrm{e}_i} + \sum_{i>j}\frac{e^2}{|r_i - r_j|} - \sum_{i>j}\frac{Z_j e^2}{|r_i - R_j|} \\
&= \widehat{T}_N + \widehat{V}_N + \widehat{T}_e + \widehat{V}_e + \widehat{V}_{eN},
\end{aligned}
$$

where Δ_* denotes the Laplacian with respect to the coordinates of particle (*). The number of degrees of freedom corresponds to $3n$ where n is the number of particles involved (x, y, and z coordinate for each one). The full system therefore rapidly becomes extremely high-dimensional, and also for small molecules it is necessary to separate electronic and nuclear coordinates as indicated in the introduction.

Since the mass of a nucleus is a factor 10^3 to 10^5 larger than the mass of an electron, the nuclei move much slower than the electrons. On the time-scale of the vibration of electrons, the positions of the nuclei are normally almost constant. In the Born–Openheimer approximation, it is assumed that the wave function $\Psi(r, R)$ can be split as

$$
\Psi(r, R) = \phi(r; R) \cdot \psi(R).
$$

Then the electronic Schrödinger equation is solved separately for fixed nuclear coordinates,

$$
\widehat{H}_e \phi(r; R) = \hat{E}^{\mathrm{el}}(R)\phi(r; R),
$$

with the electronic Hamiltonian being $\widehat{H}_e = \widehat{T}_e + \widehat{V}_e + \widehat{V}_{eN}$. With these assumptions, the full Hamiltonian reads

$$
\widehat{H}\big(\phi(r; R)\psi(R)\big) = -\sum_i \frac{\hbar^2}{2M_i}\big(\phi(r; R)\Delta_{\mathrm{N}_i}\psi(R) + 2\nabla_{N-i}\phi(r; R)\cdot\nabla_{\mathrm{N}_i}\psi(R) \\
+ \Delta_{\mathrm{N}_i}\phi(r; R)\psi(R)\big) + (\hat{E}^{\mathrm{el}}(R) + \hat{V}_N)\phi(r; R)\psi(R). \tag{2.2}
$$

The terms $2\nabla_{N-i}\phi(r; R)\cdot\nabla_{\mathrm{N}_i}\psi(R)$ and $\Delta_{\mathrm{N}_i}\phi(r; R)\psi(R)$ in (2.2) are difficult to handle. For most configurations, they are however of the same magnitude as the mass ratio between electrons and nuclei. Only at nuclear configurations where the molecule tends to change its electronic state, those terms become relevant. In order to simplify the nuclear TDSE, one therefore often applies a so-called *diabatic* transformation that models the kinetic couplings by potential coupling terms.

In computations for the nuclear wave packet, one usually includes a number of different electronic states and splits the wave packet into different parts for each state, $\psi(R) = (\psi_{\mathrm{state\,1}}(R),\dots,\psi_{\mathrm{state\,n}}(R))$. For a two-state system, for

instance, the Hamiltonian becomes a block matrix

$$\hat{H} = \begin{pmatrix} \hat{T} + \hat{V}_{\text{state 1}} & \hat{V}_c \\ \hat{V}_c^H & \hat{T} + \hat{V}_{\text{state 2}} \end{pmatrix},$$

where $\hat{V}_{1/2}$ is the potential energy surface (PES) of state 1 or 2, respectively, and $\hat{V}_c$ models the coupling of the two PES in the diabatic framework. By $(\cdot)^H$ we denote complex conjugation. A PES for a certain state is the sum of the internuclear repulsion and the eigenenergy.

A typical feature of an PES is that it goes to infinity as the internuclear distance approaches zero due to infinite nuclear-nuclear repulsion. Moreover, as the distance becomes large, the PES approach an asymptotic value, since the nuclei are too far apart from each other to interact. We can distinguish two classes of PES. The first type corresponds to a stable electronic state of the molecule, and the second one to unstable electronic states [92, Chap. 12.1]. For stable states there exist one or more vibrational eigenstates that are bounded, whereas the molecular bound eventually breaks once the system gets into an unstable state. The latter phenomenon is called dissociation.

2.2 Interactions with Time-dependent Fields

Given precomputed values for the electronic spectrum $\hat{E}^{\text{el}}(R)$ in the diabatic representation, we can form the molecular Hamiltonian describing the dynamics of the nuclei. As a second step, we do not only want to consider the dynamics of an isolated molecule but its interaction with a time-dependent field. Applications we have in mind are, for instance, multiple pulse optical spectroscopy or control of molecular dynamics by laser fields (cf. Ref. [92]). Optical spectroscopy can be applied to analyze the structure of complex molecules like biopolymers and the manipulation of molecular dynamics can initiate chemical reactions.

The vibrational period of motion of the nuclei in a molecule is on the time scale of tens or hundreds of femtoseconds. It was thus with the introduction of femtosecond lasers in the mid-1980s that it became experimentally possible to track and even manipulate the dynamics of molecular nuclei [60].[1] Zewail and his group probed various molecules with femtosecond pulse pairs [101], and later also demonstrated how molecular states can be controlled with the

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[1]Note that the recent development of attosecond lasers also facilitates physicists to probe the motion of electrons which takes place on the atto-scale, cf. Ref. [46].

help of time-delayed pulses [68].[2] Fleming and co-workers [74] used time-delayed pulses with controlled phase for manipulating molecules. The groups of Crim [85] and Zare [13] attempt to use tunable laser-pulses where the wavelength can be varied for steering chemical reactions. Advances in pulse shaping techniques based on grating and filtering by, amongst others, Weiner and co-workers [37, 95] spurred the development of femtosecond chemistry. The basic idea is to grate the incoming laser pulse to spatially disperse light of different frequencies which then can be delayed independently from each other through a spatial filter [96, 99]. This technique is also-called *Fourier transform femtosecond pulse shaping*.

To model interactions of a molecule with a femtosecond laser field, the molecular Hamiltonian (denoted $\hat{H}_0$ in the following) is augmented by an additional term representing the interaction with the electromagnetic field. For weak fields, this interaction can be modeled classically using a dipole approximation. Given the laser field $\varepsilon(t)$ and the transition dipole moment $\hat{\mu}$, the (nuclear) time-dependent Schrödinger equation (TDSE) reads,

$$i\hbar\frac{\partial}{\partial t}\psi(R,t) = \left(\hat{H}_0(R) + \hat{\mu}(R)\cdot\varepsilon(t)\right)\psi(R,t). \tag{2.3}$$

Fig. 2.1 shows a typical configuration where we have a molecule in its ground state and want to excite it to a target state with the help of a femtosecond pulse.

2.3   Physical and Mathematical Properties

In this section, we discuss some important properties of the physical model that also play an important role for the design of numerical methods. First of all, total probability in a closed quantum mechanical system is conserved. This means physically that no matter is destroyed or created. Probability conservation can be expressed as

$$\int |\psi(R,t)|^2 \, dx = 1 \text{ for all } t,$$

i.e., the L_2 norm of the wave function is conserved.

Another important property of the evolution of the TDSE is time-reversibility. No information is destroyed, as it would be if, e.g., diffusion was involved. Hence, if the Hamiltonian is known for the studied time interval, we can reconstruct the initial state from the final state.

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[2]A. H. Zewail was rewarded the 1999 Nobel price in Chemistry "for his pioneering investigations of chemical reactions on the time-scale they really occur." (quote from extended version of the press release of the Royal Swedish Academy of Sciences, see http://nobelprize.org/nobel_prizes/chemistry/laureates/1999/chemback99.pdf.
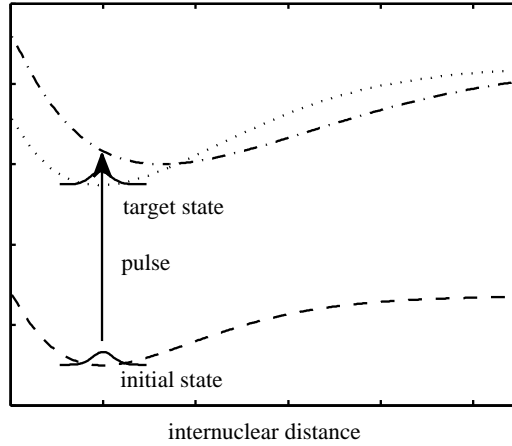
Figure 2.1: Schematic configuration of interaction of a molecule with a time-dependent field $\varepsilon(t)$. The ground state (dashed line) is coupled to an excited state with a laser field (dash-dot line). The second excited state (doted line) is coupled to the first excited state by a static crossing of the PES.

Another characteristic of the TDSE comes from the self-adjointness of the Hamiltonian which implies that the adjoint equation is exactly the same as the original TDSE. It is the self-adjointness — together with the imaginary unit i in the Schrödinger equation — that leads to both norm-conservation and time-reversibility.

Since classical Hamiltonian systems are well-studied, it is of interest that the TDSE can be rewritten as a classical system by defining the configuration variable $q(R, t) = \sqrt{2\hbar}\mathrm{Re}\left(\psi(R, t)\right)$ and the canonically conjugate momentum $p(R, t) = \sqrt{2\hbar}\mathrm{Im}\left(\psi(R, t)\right)$ (cf. Ref. [30]). An important conservation law for classical Hamiltonian systems is area conservation for the flow. Such a flow is called *symplectic*. This property in the classical version of the TDSE assures norm conservation of ψ (cf. Ref. [50]).

3. Numerical Challenges

The simulation of molecular processes based on the chemical model discussed in the previous chapter entails several challenges. Before discussing these difficulties, we review a standard discretization approach.

A common discretization technique for time-space dependent differential equations is to use the *method of lines*, i.e., one first discretizes the spatial variables yielding a system of ordinary differential equations (ODE). A standard method for spatial discretization in quantum chemistry is the pseudospectral method with a Fourier basis [23, 25]. An important reason for this is that the solutions are generally of class C^∞ and high accuracy methods are more efficient considering both computing time and memory requirements. Another reason for the popularity of the Fourier spectral method is that it can nicely be combined with the so-called split operator time-evolution method (see Sec. 4.1) yielding a full discretization which is easy to implement. Nevertheless, the pseudospectral method is not always flexible enough when boundary treatment for dissociative states, parallelization, or mesh adaptivity is needed. A study of these aspects is, however, not within the scope of this thesis and spatial discretization based on the Fourier spectral method is assumed throughout the text unless stated otherwise.

Once the spatial variables are discretized, we have to solve the following ODE system,

$$\frac{\mathrm{d}}{\mathrm{d}t} u(t) = -\frac{\mathrm{i}}{\hbar} H(t) u(t), \tag{3.1}$$

where H denotes a matrix that represents the Hamiltonian on the spatial grid and $u = (u_i)$ is the vector of the wave function values at the mesh points x_i, i.e., u_i approximates $\psi(x_i)$.

The first intricacy with such a discretization is the fact that the number of degrees of freedoms increases linearly with the number N of atoms in the system as indicated in Sec. 2.1. More precisely, the total number of degrees of freedom is $3N$ — three coordinates for each nucleus. Six degrees of freedoms are external (three translational and three rotational) giving $3N-6$ internal degrees of freedom [92, Chap. 12.4].[1] Only the internal degrees are of importance

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[1] Note that the number of internal degrees of freedom is $3N - 5$ for linear molecules where the rotation along the molecular axis is ill-defined.

for a quantum description of an isolated molecule. For a grid based model, the number of grid points grows exponentially with the dimensionality. Hence, only very small molecules can be handled using such numerical schemes. Adaptive mesh refinement [19], sparse grids [28], and parallelization [33, 75] are options to tackle slightly larger problems. However, further modeling is necessary to cope with molecules containing many atoms (cf. Ref. [16] for different strategies). A popular approach is to use the multi configuration time-dependent Hartree (MCTDH) method [58], and another, more recent ansatz is to approximate semiclassical models based on Hagedorn wave packets [21].

The wave function does not only depend on the spatial coordinates but also on time. Since multiple time scales are usually present in the model, a huge number of time steps is often necessary. High-frequency oscillations have to be resolved or modeled. High order and adaptive integrators or multi-scale algorithms can help in reducing the number of time steps. There are various sources for high-frequency oscillations depending on the particular type of application. For simulations of interaction with a time-dependent field, the oscillations of the laser field pose limitations to the step size. A simple multi-scale model, allowing for larger time steps, is the so-called rotating wave approximation (see Sec. 4.3). This is, however, limited to monochromatic pulses. A review of numerical integrators for highly oscillatory Hamiltonian systems is provided by Cohen et al. [18].

A third potential difficulty is the domain on which the Schrödinger equation is formulated, which is unbounded. For a wide class of problems the wave function stays within a certain domain, corresponding to that the molecule stays bounded. In such cases, the computational domain can be truncated and the PDE is usually closed by periodic or homogeneous Dirichlet boundary conditions. However, the modeling of dissociative processes poses difficulties on domain truncation. Standard methods to handle dissociative boundaries are complex absorbing potentials [56, 32] and perfectly matched layers [1, 62]. In both cases, artificial damping is introduced to the system and physical properties like norm-conservation and time-reversibility are no longer valid on the truncated domain. Therefore, numerical methods designed for bound states can be difficult to generalize to dissociative problems.

The challenges discussed so far concern solving one single TDSE problem. When this equation enters within an optimization loop, e.g., for finding the optimal shape of an interacting laser pulse, additional complexity is introduced. The Schrödinger equation has to be solved several times, and, moreover, an adjoint equation might have to be computed to calculate optimality conditions. This introduces extra demands on both computing power and memory size.

4. Time Propagation

As discussed in Chap. 3, the temporal dimension has to be treated with extra care since the number of time steps needed usually exceeds the number of grid points per dimension tremendously. Throughout this chapter, we consider the semi-discretized TDSE (3.1).

There is a large spectrum of methods designed for time-evolution of ODE systems. For our purpose, an explicit method[1] is preferable since solving a linear system can become very costly and memory consuming when high-order spatial methods in high dimension are involved. A suitable numerical integrator of the TDSE should attempt to preserve the essential physical properties of the model (discussed in Sec. 2.3). The monographs [34, 49, 72] present methods specially suited for Hamiltonian systems. There are two families of methods that are most often used for the TDSE, exponential integrators and partitioned Runge–Kutta (PRK) methods [51] which we both will discuss in more detail below.

Note that, in this thesis, we only consider the case where short time steps are required because we assume that the Hamiltonian is explicitly time-dependent. The situation with a time-independent Hamiltonian is relatively well-understood, see the study by Leforestier et al. [48].

4.1 Exponential Integrators

For a linear ODE with a time-independent right-hand-side, i.e., for the semi-discretized TDSE with time-independent Hamiltonian, the evolution operator (propagating the wave function from t_0 to t_f) is analytically given as the exponential of the Hamiltonian matrix times the time span. The situation becomes more complicated for time-dependent right-hand-sides but, for sufficiently small time intervals, the *Magnus expansion* [43, 55] provides an expression of the evolution operator $U(t + \Delta t, t)$ in the form of the exponential of a series expansion,

$$U(t + \Delta t, t) = \exp\left(\sum_{l \geq 0} \theta_l\right).$$

---

[1] A method that does not involve inversion of large matrices or iterative solvers.

Each term θ_l contains $l + 1$ integrals over l commutators of the Hamiltonian at different points in time. Since the lth ($l > 0$) term decays as $(\Delta t)^{l+2}$ for sufficiently small time steps, a truncated version of this expansion provides a natural starting point for numerical evolution methods.

One restriction is the condition given in Ref. [59] under which the series converges,

$$\int_t^{t+\Delta t} \left\| \frac{-\mathrm{i}}{\hbar} H(\tau) \right\| \, \mathrm{d}\tau < \pi. \tag{4.1}$$

This bound is problematic for the TDSE since the continuous Hamiltonian is an unbounded operator. The effect is that the estimate (4.1) becomes more and more restrictive the finer the spatial discretization of the TDSE. Nevertheless, the method gives good results in practice also for larger time steps which was explained by Hochbruck and Lubich [40] for a special form of the potential energy.

Once we have truncated the Magnus expansion, we have to compute the matrix exponential. The simplest approach is the Strang splitting method [88]. This propagator is known as split operator in the quantum chemistry community [22]. The method is second order accurate, so we simply evaluate the Hamiltonian at the mid-point to handle the time-dependence. Then, the Hamiltonian is split into its kinetic and potential energy part as follows

$$\exp\left(-\frac{\mathrm{i}}{\hbar} H\left(t + \frac{\Delta t}{2}\right)\Delta t\right) =$$
$$\exp\left(-\frac{\mathrm{i}}{\hbar} T \frac{\Delta t}{2}\right) \cdot \exp\left(-\frac{\mathrm{i}}{\hbar} V\left(t + \frac{\Delta t}{2}\right)\Delta t\right) \cdot \exp\left(-\frac{\mathrm{i}}{\hbar} T \frac{\Delta t}{2}\right).$$

Exploiting the first-same-as-last property, one can merge the last kinetic energy term with the first one of the next step. Since T is diagonal in Fourier space (assuming a spatial Fourier pseudospectral approximation) and V (almost) diagonal in real space [81], the essential cost for each time step is only one FFT/IFFT pair. Higher-order splitting methods are available and are related to PRK methods.

An alternative way of computing the matrix exponential is to use the *Lanczos algorithm* [71]. For this method, the error decays fast after a certain number of iterations [39]. One advantage compared to the splitting method is that the Lanczos scheme can handle more general Hamiltonians. A generalization is the so-called *Arnoldi algorithm* that can also tackle non-selfadjoint Hamiltonians. The error of the Lanczos algorithm after a certain number of iterations can be computed with little additional cost using an estimate analyzed in Ref. [41].

A truncation of the Magnus expansion after more than one term can be combined with the Lanczos algorithm to devise a higher order method. Evaluating higher Magnus terms is quite costly, though, since an increasing num-

ber of commutators has to be computed. Several attempts have been made to simplify the terms. Blanes et al. [6] rewrite the expansion reducing the total number of commutators for truncation up to a certain order and Blanes & Moan [8] split the matrix exponential to completely avoid commutators (at the price of several exponentials to be computed per time step). For the special case (2.3) with weak spatial dependence in the transition dipole moment, the second Magnus term is simplified by analytical manipulations to a block-diagonal matrix in Paper I. This yields a fourth order accurate propagator that is only marginally more computationally demanding than the second order scheme.

4.2 Partitioned Runge–Kutta Methods

Partitioned Runge–Kutta (PRK) methods are symplectic methods of Runge–Kutta type that are designed to mimic the conservation laws exhibited by classical Hamiltonian systems. As described in Sec. 2.3, the TDSE can be reformulated in such a system. However, most PRK methods are implicit. Explicit PRK methods are available for separable Hamiltonian functions where

$$H(p, q, t) = H(p) + H(q, t). \qquad (4.2)$$

If the Hamiltonian is explicitly time-dependent, this separation cannot be made. However, Gray and Verosky [30] exploit the Magnus expansion to be able to use explicit methods for time-dependent Hamiltonians as well. Sanz-Serna and Portillo [73] propose a more elegant procedure, where they introduce an additional conjugate pair of variables to represent the time dimension.

When the Hamiltonian is complex-valued, a separation as in (4.2) cannot be done either. This is, e.g., the case when modeling dissociation by adding complex terms to the potential or the kinetic energy.

By varying the number of stages it is possible to design optimal Runge–Kutta coefficients for special problems under certain accuracy and stability requirements. A lot of attempts have been made to devise efficient methods. Suzuki [89, 90, 91] and Yoshida [100] demonstrated how to construct high order symplectic methods. Later McLachlan [57] came up with the idea to construct methods with an optimal error constant for given order and Blanes & Moan [7] refined his ideas. Much effort has also been made to find PRK methods optimized for certain applications. The TDSE was considered, e.g., in Refs. [5] and [29], even though both articles only provide examples with time-independent Hamiltonians.

In Paper I, the numerical propagation for a model of the rubidium diatom (Rb_2) molecule is studied. In these calculations, the methods proposed in Ref. [7] proved to perform better than those tailored to the TDSE [5, 29].

4.3 Rotating Wave Approximation

For the simulation of molecule-laser-interaction, we have to resolve the oscillations of the laser pulse which requires small time steps. For computations with a low accuracy requirement, this shortage can be overcome with the help of the rotating wave approximation (RWA) [69]. Consider a two state system with Hamiltonian

$$\hat{H} = \begin{pmatrix} \hat{T} + \hat{V}_g(R) & f(t)\cos(\omega t) \\ f(t)\cos(\omega t) & \hat{T} + \hat{V}_e(R) \end{pmatrix},$$

where ω is the frequency of a (monochromatic) laser field and $f(\cdot)$ a slowly varying envelope function. Define the transformation

$$\hat{W} := \begin{pmatrix} I & 0 \\ 0 & e^{-i\omega t} \cdot I \end{pmatrix},$$

of the wave packet. Then, the TDSE for the transformed wave packet $\varphi := \hat{W}^{-1}\psi$ reads

$$i\hbar \frac{\partial \varphi}{\partial t} = \begin{pmatrix} \hat{T} + \hat{V}_g(R) & \frac{1}{2}f(t)\left(1 + e^{-i2\omega t}\right) \\ \frac{1}{2}f(t)\left(1 + e^{i2\omega t}\right) & \hat{T} + \hat{V}_e(R) - \hbar\omega \end{pmatrix}\varphi.$$

If the laser frequency is very high compared to the variations of the envelope, the time-averaged influence of the terms $e^{\pm i2\omega t}$ is insignificant. In the RWA this term is dismissed. In this way, no highly oscillatory term remains in the TDSE. However, only the average effect of the laser field is modeled. When propagating the solution of the RWA-TDSE, we do not have to resolve the oscillatory frequency of the laser field. This corresponds to a separation of scales where effects on the scale of π/ω and below are neglected. A detailed discussion of the modeling error introduced by the RWA can be found in Paper I.

A major shortcoming of the RWA multiscale ansatz is that it is designed for a pulse with one frequency and, therefore, not capable of tackling, e.g., a chirped pulse (where ω is time-dependent).

4.4 Error Control and Adaptivity

In order to design an algorithm that automates the choice of the time step and is capable of meeting a given error tolerance, adaptive step size control is desirable. A theoretical study of accuracy and convergence rates for several standard time-marching methods for the TDSE is provided by Lubich [52]. However, those estimates are not designed to be easily computable within a step size control algorithm.

Within the framework of Runge–Kutta methods, efficient techniques for local error control have been designed based on embedded methods of two consecutive orders. Admittedly, a straight-forward implementation for PRK methods suffers from the fact that symplecticity is lost (cf. Ref. [72]). Sophisticated techniques have been developed to circumvent this problem (cf., e.g., Ref. [4, 35]) which are, however, connected to specific applications.

For the Magnus expansion, on the other hand, an easy-to-compute error estimate based on extrapolation is available [6] and has been successfully applied to the TDSE (cf. Ref. [97] and Paper II). This can be combined with a Lanczos algorithm that chooses the size of the Krylov space to meet the same tolerance. The Lanczos error can be computed according to Ref. [41].

Those estimates only cover the local error. However, the main interest is to predict the global error. One way to connect local to global errors is to use *a posteriori* error control based on duality. These kinds of error estimates are widely used in the finite element community [3, 20] but are also available for ODE systems (cf. Ref. [17]). In Paper II, the ODE theory is applied to the semi-discrete TDSE (3.1). For a posteriori estimates, one considers the error in some functional of the solution at the final time,

$$e(t_f) = \langle \phi, u(t_f) - y(t_f) \rangle,$$

where ϕ is some state of interest, u is the solution to the semi-discrete TDSE (3.1), and y the numerically propagated result. In order to compute the a posteriori estimate, the *primal* problem (3.1) is considered together with the *dual* problem. The dual problem is solved backwards in time, starting from the functional ϕ and with the adjoint operator on the right-hand-side. In the TDSE, the Hamiltonian is self-adjoint, and the dual equation is the same as the primal. The dual problem is thus given by

$$\frac{\mathrm{d}}{\mathrm{d}t} v = -\frac{\mathrm{i}}{\hbar} H v, \qquad v(t_f) = \phi.$$

Knowing the solution to the dual problem, the error can be estimated using the formula

$$e(t_f) = \int_{t_0}^{t_f} \langle v(\tau), p(\tau) \rangle \, \mathrm{d}\tau,$$

where p is the perturbation of the ODE (3.1) induced by employing a numerical integrator.

Computing this error usually requires solving the dual problem. Since dual and primal equations are solved in different directions in time, it is reasonable in many situations to use the Cauchy–Schwarz inequality to split the inner product, yielding

$$|e(t_f)| \le \int_{t_0}^{t_f} \|v(\tau)\| \|p(\tau)\| \, \mathrm{d}\tau = \int_{t_0}^{t_f} \|p(\tau)\| \, \mathrm{d}\tau. \tag{4.3}$$

In the last step, the norm-conservation property is used to completely eliminate the influence of the dual problem. In this way, an easy-to-compute error estimate (that holds for any error functional) was derived in Paper II. Of course, when using the Cauchy–Schwarz inequality in estimate (4.3) some efficiency is lost, and it depends on the particular situation whether or not it pays off to eliminate the dual problem (see Paper II for further discussion).

4.5   Comparison of Various Methods

We conclude the chapter on time propagation by a comparative summary. Overall, the Magnus–Lanczos (or Arnoldi if necessary) combination could be considered to be the most versatile method since it can tackle complex impurities in the Hamiltonian as well as variable step sizes for error control. In the study reported in Paper I, it also proves to be very competitive in a comparison with Strang splitting and PRK methods for accurate simulations on an equidistant temporal grid. This study also shows that the Strang splitting method is very suitable for low-accuracy computations on simple configurations.

The Magnus–Lanczos method also has two drawbacks; firstly, the Lanczos algorithm is not time reversible, and, secondly, analytic manipulations of higher order Magnus terms for the specific configuration are necessary to optimize the performance (making other methods easier to implement). Note that the loss of time reversibility is often not that severe since the error in the Lanczos algorithm can be kept small compared to other errors for little extra cost. Nevertheless, it may cause difficulties, e.g., when formulating the discrete adjoint problem (cf. Sec. 5.2).

5. Quantum Optimal Control

In the laboratory, physicists use laser pulses to manipulate the energetic state of molecules and thereby initiate chemical reactions. They design the laser fields in a special way to get the desired outcome. This chapter is devoted to the question of how to use simulation and numerical optimization to find a suitably shaped laser field for a given purpose.

5.1   Optimal Control Formulation

Let us first express the optimization problem in mathematical terms. A generic objective would be to find a pulse ε that minimizes the function

$$\mathcal{J}_1(\varepsilon, \psi) = \frac{1}{t_f} \int_{t_0}^{t_f} \psi^*(R, t) \widehat{O} \psi(R, t) \, \mathrm{d}t, \tag{5.1}$$

where $\widehat{O} = \widehat{O}_1 \cdot \delta(t - t_f) + \widehat{O}_2(t)$ and ψ is the wave packet solving the TDSE (2.3) for the interaction with the laser field ε. The operator $\widehat{O}_1$ defines some target state at final time t_f and $\widehat{O}_2(t)$ allows us to include a time-dependent objective, such as the penalization of a special molecular state (that is undesired).

   In this form, the problem is ill-posed since there is no restriction on the strength of the pulse. A strategy to resolve this issue is to introduce a so-called Tikhonov regularization, i.e., to add the term

$$\mathcal{J}_2(\varepsilon) = \lambda \int_{t_0}^{t_f} \varepsilon^2(t) \, \mathrm{d}t, \qquad \lambda > 0,$$

to the objective function. The choice of the constant λ indirectly controls the total energy of the optimal pulse and has to be chosen in a way that the resulting pulse has a strength that can be achieved with the experimental equipment. The complete optimization problem now reads

$$\min_{\varepsilon \in L_2([t_0, t_f])} \quad \mathcal{J}(\varepsilon, \psi) = \mathcal{J}_1(\varepsilon, \psi) + \mathcal{J}_2(\varepsilon),$$

$$\text{subject to} \quad \mathrm{i}\hbar \frac{\partial}{\partial t} \psi = \left(\widehat{H}_0 + \mu \varepsilon(t) \right) \psi, \qquad \psi(R, t_0) = \psi_0. \tag{5.2}$$

It was shown by Peirce et al. [65] that (5.2) has a solution in the special case where

$$\mathscr{J}_1(\varepsilon,\psi) = \langle \psi(t_f) - \phi, \psi(t_f) - \phi \rangle.$$

The essential property of $\mathscr{J}_1$ in the proof is weak lower semi-continuity, and hence the reasoning in [65] can also be adopted to more general cases.

Problem (5.2) is an optimal control problem and the first step in solving it is to formulate the optimality system. The Lagrangian function corresponding to the system (5.2) is,

$$\mathscr{L}(\varepsilon,\psi,\chi) \;=\; \frac{1}{t_f} \int_{t_0}^{t_f} \langle \psi(\cdot,t)|\widehat{O}|\psi(\cdot,t)\rangle \,\mathrm{d}t + \lambda \int_{t_0}^{t_f} |\varepsilon(t)|^2 \,\mathrm{d}t$$
$$-2\int_{t_0}^{t_f} \mathrm{Re}\langle \chi | \left(\frac{\partial}{\partial t} + \frac{\mathrm{i}}{\hbar}\left(\hat{H}_0 + \hat{\mu}\varepsilon(t) \right) \right) |\psi\rangle \,\mathrm{d}t.$$

By differentiating with respect to the Lagrange multiplier, we arrive at the state equation

$$\mathrm{i}\hbar \frac{\partial}{\partial t} \psi = \left(\widehat{H}_0 + \lambda \varepsilon(t) \right) \psi, \qquad \psi(R,0) = \psi_0.$$

Differentiation with respect to the state variable gives the adjoint equation

$$\frac{\partial}{\partial t}\chi = -\frac{\mathrm{i}}{\hbar}\left(\hat{H}_0 + \hat{\mu}\varepsilon(t) \right)\chi - \frac{1}{t_f}\widehat{O}_1(t)\psi(r,t), \qquad \chi(x,t_f) = \widehat{O}_2\psi(r,t_f).$$

Finally, the first-order optimality condition $\nabla_\varepsilon \mathscr{L} = 0$ becomes

$$\frac{1}{\hbar}\mathrm{Im}\left(\langle \chi|\hat{\mu}|\psi\rangle \right) + \eta\varepsilon = 0. \tag{5.3}$$

5.2   Discretization

In order to be able to apply a numerical optimization algorithm to problem (5.2), the first step is to discretize the continuous problem. We limit our discussion to bound states and use the Fourier spectral method for spatial discretization. For time propagation, there are several arguments in favor of the Strang splitting method. Firstly, Strang splitting has proved to be very efficient for low accuracy computations. Since the TDSE may have to be solved hundreds of times, high accuracy is out of reach. Moreover, methods of order higher than two generally require evaluations of the pulse at points in-between the grid points where we usually do not have this information.[1] Last

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[1]When optimizing the Fourier coefficients as discussed below, the pulse can be evaluated at any point in time, though.

but not least the property of time-reversibility is important in connection with the (discrete) dual problem.

Denoting the discrete state variables by u_j, $j = 1, \ldots, N$, and the discrete control parameters by ϵ_j, and defining the evolution operator for time step j by

$$\mathcal{M}_j(\epsilon_j, \epsilon_{j+1}) := e^{-i\frac{\Delta t}{2}T} e^{-i\Delta t(V + \frac{1}{2}\mu(\epsilon_n + \epsilon_{n+1}))} e^{-i\frac{\Delta t}{2}T},$$

we can formulate the discrete state equation

$$u_0 = \mathcal{P}\psi_0,$$
$$u_{j+1} = \mathcal{M}_j(\epsilon_j, \epsilon_{j+1}) u_j, \qquad j = 0, \ldots, N-1,$$

where $\mathcal{P}$ denotes the projection of the wave packet to its discrete representation.

We now introduce Lagrangian multipliers v_j and formulate the discrete Lagrangian,

$$
\begin{aligned}
L(\epsilon_0, \ldots, \epsilon_N) \quad = \quad & \Delta x\, u_N^H O_2 u_N + \frac{\Delta x \cdot \Delta t}{t_f} \sum_{k=0}^{N-1} u_k^H O_1 u_k + \eta \cdot \Delta t \sum_{k=0}^{N} \epsilon_k^2 \\
& - 2 \cdot \Delta x \cdot \Delta t \operatorname{Re}\left(\sum_{k=0}^{N-1} v_{k+1}^H (\mathcal{M}_k(\epsilon_k, \epsilon_{k+1}) u_k - u_{k+1}) \right).
\end{aligned}
$$

From this, we can derive the discrete adjoint equation

$$v_N = -O_2 u_N \cdot \frac{1}{\Delta t},$$
$$v_j = \left(\mathcal{M}_j(\epsilon_j, \epsilon_{j+1}) \right)^H v_{j+1} - \frac{1}{T} O_1 u_j, \qquad j = N-1, \ldots, 1.$$

as well as the discrete first-order optimality condition, $j = 1, \ldots, N-1$,

$$\frac{\partial L}{\partial \epsilon_j} = 2 \cdot \Delta t \left(\lambda \cdot \epsilon_j - \operatorname{Re}\left(v_{j+1}^H \frac{\partial}{\partial \epsilon_j} \mathcal{M}_j u_j + v_j^H \frac{\partial}{\partial \epsilon_j} \mathcal{M}_{j-1} u_{j-1} \right) \cdot \Delta x \right) = 0.$$

For $j = 0$ and $j = N$, we will get the same expression but only with the first or second term of the real part, respectively. Note that we have first discretized and then differentiated to get the discrete optimality system (cf. Ref. [38, Chap. 3.2]).

5.3   Optimization Tools

Originally, quantum optimal control problems were studied that only included final time objectives. In the late 1980s, the pulse shaping problem was formulated as an optimal control problem and solved with the conjugate

gradient (CG) method [45, 65, 83]. The CG algorithm is a standard first order method which may suffer from slow convergence [26]. The efficiency of the numerical optimization was improved in a paper by Somlói and co-workers [87] who introduced the Krotov method [47] to quantum control. The Krotov iteration was refined by Zhu and co-workers [102, 103] and by Maday and Turinici [54]. The idea of this method is to solve the first-order optimality condition (5.3) for ε, yielding

$$\varepsilon(t) = -\frac{1}{\hbar\eta}\text{Im}\left(\langle\chi|\hat{\mu}|\psi\rangle\right).$$

Since χ and ψ depend on ε, a fixed point iteration is applied to find the optimal field.

In 2001, Ohtsuki et al. [63] showed how to include time-dependent targets of the general form (5.1) to the optimal control formulation. This time-dependent objective problem was also tackled with the Krotov method (cf. also the tutorial [98]).

All of these methods are based on the first order optimality condition. Usually, convergence can be improved using a quasi-Newton method that includes information of an approximate Hessian. Among those methods, the so-called Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm [14, 24, 27, 82] is the most successful one. The problem with the application of a quasi-Newton method to the quantum optimal control problem is the fact that the number of control parameters is the number of time steps, which is very large in general. Therefore, memory shortage will make it impossible to store the approximate Hessian.

In 1992, Judson and Rabitz [44], proposed an alternative way to design laser pulses: feedback control. For systems where the Hamiltonian is unknown or for molecules that are too large to be simulated on the computer, feedback control offers an alternative. The computer only successively generates pulses (usually based on some global optimization strategy) and then the fitness of the pulse is determined by an experiment. Assion et al. [2] point out that the experimental shaper manipulates the spectral phase which is why the optimization procedure should do the same. In Ref. [84], a special global optimization strategy is applied to find optimal Fourier coefficients with a computer simulation.

Using the Fourier coefficients as control variables like in feedback control algorithms, one can drastically reduce the dimensionality of the optimization problem as demonstrated in Paper III. In this way, it becomes feasible to use quasi-Newton methods even for long-time quantum optimal control problems. Moreover, one can make sure that the theoretically found pulses can be realized in practice.

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Note that the quasi-Newton method was also applied to quantum optimal control of Bose–Einstein condensate in the context of von Winckel and Borzì's study [94] on a suitable norm for minimization.

6. Summary of Papers

In this chapter, the content of the attached articles is briefly summarized. Paper I-II examine time propagation for the TDSE and Paper III deals with the quantum optimal control problem.

6.1 Paper I

Paper I contributes to the time evolution of the TDSE modeling the interaction of a molecule with a time-dependent field and has three main objectives. Firstly, the rotating wave approximation is analyzed and an expression for the error depending on the shape of the envelope function in relation to the fast oscillation of the laser field is devised. This shows that the results become more accurate when the RWA is applied in case the step size is larger than about the reciprocal of the oscillational period ω. On the other hand, the RWA introduces a systematic error on the time-scale of π/ω which is why reducing the step size further does not improve the quality of a simulation based on the RWA. A numerical study for Rb_2 also shows that the error introduced by the RWA has more influence on the phase information of the wave packet than on its absolute value.

The second goal of the article is to tailor the fourth order Magnus approximation for the specific problem of molecule-laser interaction. This is done by analytical simplifications based on the assumption that the transition dipole moment has a weak spatial dependence. The result is a highly efficient fourth order propagator. Finally, the paper provides a numerical comparison of different methods suitable for solving the TDSE modeling a relevant chemical problems. A pump-probe as well as an interference experiment for Rb_2 are considered.

6.2 Paper II

Paper II is concerned with error control and adaptivity. Starting from the theory in [17], we derive an a posteriori error estimate for the TDSE. Exploiting self-adjointness of the Hamiltonian, this estimate is simplified as discussed in Sec. 4.4. Nevertheless, the simplified estimate still holds for the case where self-adjointness is truncated due to an absorbing boundary layer. Based on

these ideas and the fourth order Magnus-Lanczos propagator devised in Paper I, a variable step-size implementation with global error bound is described. Especially, we discuss how to compute the perturbation in the Magnus expansion.

The efficiency of the estimate in various contexts is discussed and numerical examples are provided. In this study, we again examine the one-dimensional Rb_2 example. It is also shown that the method is applicable to larger molecules like chlorine dioxide (ClO_2) which is modeled as a three dimensional problem. Furthermore, the paper considers a configuration of the iodine bromide (IBr) molecule that includes a dissociative state.

6.3   Paper III

Paper III discusses the quantum optimal control problem (5.2) reformulated so that the laser field is optimized in Fourier space. The Fourier transform of the pulse facilitates a reduction of the dimensionality of the control variable, since the frequency band can be narrowed to a technically possible and physically relevant interval. With this reduced optimization space, it becomes feasible to apply a quasi-Newton method and exploit its favorable convergence properties. A comparison with the Krotov method (in its formulation given in Ref. [102]) for a configuration of the Rb_2 molecule suggests that the method indeed can outperform the Krotov method. We also test our algorithm for a Raman transition with a time-dependent objective. This optimization problem was considered by Palao et al. [64], where the Krotov method was used. For the Raman-transition example, we also perform an automatic choice of the included Fourier coefficients from a given interval. Furthermore, we discuss a memory efficient way to perform the gradient evaluations.

7. Outlook

This thesis describes efficient time propagation for the TDSE with an explicitly time-dependent Hamiltonian as well as a powerful way of finding optimal pulses. For the time-propagation, the Magnus expansion proved very practical in numerical simulations. However, Hochbruck and Lubich [40] point out stability issues and present an analysis for the TDSE with a specific form of the potential energy. Their assumptions are generally not valid for models of femtosecond pulse excitation experiments. Therefore, the stability of the Magnus approach needs to be studied further in order to theoretically verify the numerical stability observed in our experiments.

The results of Paper III show that the use of quasi-Newton methods for the quantum optimal control problem is very promising. However, in the solution process three parameters need to be chosen, namely the penalty parameter, the range of frequencies that is included for finding the appropriate pulse, and the initial value. In order to make the method easy to use, it would be worthwhile to automate the identification of these unknowns. Paper III proposes a first step towards an algorithm to identify the most important frequencies. Presumably, a study of the interaction between different frequencies helps to better understand this process. Since the choice of the initial value is very important for the convergence of the method and can even influence the solution produced by the optimization procedure, it might be beneficial to combine the local optimization strategy of Paper III with some global optimization strategy to find — possibly several — viable initial values.

This thesis only considers pseudospectral spatial discretizations with the Fourier basis. One direction of further research is how to combine the time-evolution method developed in Paper I-II with more flexible spatial discretizations. In order to be able to work on large molecules, efficient spatial methods which are implemented for massively parallel systems are necessary. Gustafsson [33] recently presented a parallel implementation based on high-order finite differences which could be used to apply the methods proposed in this thesis to larger quantum systems.

Other methods than Fourier-coefficient based schemes are also necessary when including dissociation. In [62], Nissen and Kreiss analyze the use of perfectly matched layers (within the finite difference framework) in order to handle dissociative states. It would be valuable to merge efficient time evolution, boundary treatment, and the massively parallel implementation to get a highly efficient and comprehensive solver for the TDSE.

One major problem when absorbing boundary conditions are involved is the fact that this modeling modifies the mathematical properties of the system that are exploited when constructing methods suitable for bounded systems. For instance, the gradient computation in the optimal control algorithm becomes much more complicated when time-reversibility of the equation can no longer be utilized. For this reason, it would be utile to consider pseudospectral methods based on polynomials specially suited for semi-infinite domains [11, 12] instead of domain truncation.

Also other classes of spatial discretizations are potentially interesting for the TDSE, such as finite elements where global error control based on an a posteriori error estimate can be derived for the spatial parts [19]. This would fit together with the time adaptivity presented in Paper II. Promising spatial discretization methods are also found among radial basis functions [15] which are especially adequate for high-dimensional problems as shown in Ref. [66] for the Black–Scholes equation. Radial basis functions were, for instance, applied to a 2D example TDSE in Ref. [42].

As mentioned in the chapter on numerical challenges, high-frequency oscillations put high demands on the numerical evolution algorithm. For this situation, laser chemists invented the RWA (cf. Sec. 4.3). Since the RWA is only applicable to monochromatic pulses, a more versatile modeling should be devised. Multiple time-scales also become apparent in quantum-classical dynamics where larger molecules are tackled by combining quantum models with Newtonian physics in order to reduce the dimensionality (cf., e.g., Refs. [70] and [61] for numerical evolution in quantum-classical systems).

Throughout this thesis, we were only concerned with the *linear* Schrödinger equation. However, there are phenomena that are described by a non-linear version of the Schrödinger equation. One such example is the *Gross–Pitaevskii* equation (GPE) [31, 67] which models the quantum nature of Bose–Einstein condensate [10]. In recent years, many attempts have been made to efficiently solve this equation. For example, Thalhammer et al. [93] compare different high order propagation methods for the GPE with time-independent potential. Also for other nonlinearities in the TDSE, time-splitting methods are considered; for example, Lubich [53] studies the Schrödinger–Poisson and the cubic nonlinear Schrödinger equation.

Like for the linear TDSE, state-to-state transition through manipulation by an external field is of interest for Bose–Einstein condensates (cf., e.g., [36]). Sklarz and Tannor [86] formulate the Krotov method for the arising optimal control problem, Borzì and Hohenester [9] use a multigrid optimization scheme, and von Winckel and Borzì [94] study the effect of different norms.

Many questions arise when considering a nonlinear TDSE. For example, it would be interesting to consider high-order methods also for equations with explicitly time-dependent Hamiltonian. Furthermore, the question arises

whether a quasi-Newton method can likewise be employed in a memory efficient way and improve the Krotov ansatz for the nonlinear TDSE.

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