Dissertation

submitted to the

Combined Faculties for the Natural Sciences and for Mathematics

of the Ruperto-Carola University of Heidelberg, Germany

for the degree of

Doctor of Natural Sciences

Put forward by

Mag. rer. nat. Michael Ruggenthaler

born in Kitzbühel, Austria

Oral examination: 27.05.2009

Time-Dependent Density Functional Theory for Intense Laser-Matter Interaction

Zusammenfassung

Die Dynamik von Vielteilchensystemen in starken, zeitabhängigen Feldern erfordert eine nicht-perturbative Behandlung aller Konstituenten und ihrer Korrelationen. Eine direkte numerische Lösung der zeitabhängigen Schrödinger-Gleichung ist jedoch lediglich für sehr einfache Systeme zielführend. Daher benötigt man zur Beschreibung von Mehrelektronensystemen in intensiven Laserfeldern praktikable Methoden, um das quantenmechanische Vielteilchen-Problem näherungsweise zu lösen. Eine prinzipiell exakte Herangehensweise stellt die zeitabhängige Dichtefunktionaltheorie dar. In dieser Arbeit wird eine mathematisch rigorose Formulierung der Grundlagen dieser Theorie präsentiert. Desweiteren wird die zeitliche Nichtlokalität der Austausch-Korrelations-Funktionale untersucht und eine formale Definition des Begriffes "quantum memory" gegeben. Der fundamentale Prozess der Rabi-Oszillation wird aus Sicht der zeitabhängigen Dichtefunktionaltheorie betrachtet, und die Inkompatibilität mit Näherungen basierend auf endlich vielen Niveaus wird gezeigt. Schlußendlich wird diese Theorie verwendet, um die Elektronendynamik von C_{60} in einem intensiven Laserpuls zu berechnen. Obwohl der Laser die kollektiven Moden des C_{60} nicht direkt anregen kann, wird das Harmonischenspektrum stark von der Vielteilchendynamik beeinflußt. Die Effizienz dieses Vielteilchen-Rekollisionsprozesses im Vergleich zur üblichen Einteilchennäherung für die Erzeugung hoher Harmonischer wird zusätzlich durch zwei analytische Modelle abgeschätzt.

Abstract

In order to properly describe the dynamics of a many-particle system in strong, time-dependent fields, a nonperturbative treatment of all constituents and of their correlation is needed. An ab initio solution of the time-dependent many-body Schrödinger equation is only feasible for simple systems. Hence, for many-electron systems in intense laser fields practicable methods for solving the quantum-mechanical many-body problem are required. An formally exact approach is the time-dependent density functional theory. In this work a mathematically rigorous formulation of the foundations of this theory is given. Further the non-locality in time of the exchange-correlation functionals is examined, and we formally define the notion of "quantum memory". We investigate the fundamental process of Rabi oscillations from a density-functional point of view and find the few-level approximation to be in conflict with the basis of time-dependent density functional theory. Finally, we apply the theory to calculate the electron dynamics of C_{60} in intense laser pulses. Although the laser light is far off-resonant with respect to the collective modes of the C_{60} the multi-electron dynamics strongly influences the harmonic spectra. The efficiency of this multi-particle recollision process with respect to the usual single active electron approximation of high-order harmonic generation is estimated by two analytical models.

The following peer reviewed articles were published in connection with this thesis work:

- *Recollision-Induced Plasmon Excitation in Strong Laser Fields,*
  M. Ruggenthaler, S.V. Popruzhenko and D. Bauer, Phys. Rev. A **78**, 033413 (2008).

Articles submitted to peer reviewed journals:

- *Rabi Oscillations and Few-Level Approximations in Time-Dependent Density Functional Theory,*
  M. Ruggenthaler and D. Bauer, submitted to Phys. Rev. Lett.

Articles in preparation for peer reviewed journals:

- *On the Mathematical Foundation of Time-Dependent Density Functional Theory ,*
  M. Ruggenthaler and D. Bauer

Articles in proceedings:

- *Many-Electron Effects in Laser-Induced Recollions,*
  M. Ruggenthaler, S.V. Popruzhenko, P. Koval, F. Wilken, D. Bauer and C.H. Keitel,
  MPI für Kernphysik Progress Report 2007-2008, 173 (2008)

The following talks were presented in connection with this thesis work:

- *Time-dependent density functional theory: Causality and other problems,*
  M. Ruggenthaler and D. Bauer,
  Spring Meeting of the German Physical Society, 19. - 23. March 2007, Düsseldorf, Germany

- *Recollision-induced excitation of plasmons,*
  D. Bauer, S.V. Popruzhenko, and M. Ruggenthaler,
  Heraeus Seminar "Novel Light Sources and Applications", February 3-9, 2008, Obergurgl, Austria

- *Extended strong-field approximation including collectivity,*
  M. Ruggenthaler and D. Bauer,
  Spring Meeting of the German Physical Society, 10. - 14. March 2008, Darmstadt, Germany

- *C60 in strong laser fields: collective and geometry effects,*
  D. Bauer, S.V. Popruzhenko, and M. Ruggenthaler,
  LPHYS08, June 30 - July 4, 2008, Trondheim, Norway

- *Resonant dynamics in time-dependent density functional theory?,*
  M. Ruggenthaler and D. Bauer,
  Spring Meeting of the German Physical Society, 2. - 6. March 2009, Hamburg, Germany

Contents

Introduction

Assume we are asked to calculate the dynamics of a microscopic system, such as an atom or a molecule, subject to some time-dependent perturbation. Of course we know that quantum theory provides all necessary instruments. Usually, by assuming relativistic effects to be negligible, one would start from the Schrödinger equation. It is straightforward to write down this fundmental equation for a specific system. However, the solution to the many-body Schrödinger equation, even for time-independent systems, is, in general, not known. The calculation of the eigenstates is a very demanding task. An ab initio numerical calculation within a reasonable amount of time is only possible for quite simple systems [1]. Nevertheless, we ignore this first severe problem and assume the initial state to be given.

Now let us turn our attention to the dynamics of this quantum system. Even more than in the time-independent case an ab initio solution of the time-dependent many-body Schrödinger equation is extremely involved. One is therefore in need of efficient methods or approximate theories to handle this problem. For very constrictive assumptions the actual evolution of the system can be approximated by, e.g., the ubiquitous two-level approximation of quantum optics [2], which describes the dynamics of a resonantly driven system. Note, however, that one does need further information about the system to set up such a few-level scheme. For very weak time-dependent fields, perturbation theories may describe the dynamics of the system quite well [3]. For stronger driving fields, however, perturbation theory is not applicable anymore. This strong field domain has become more and more important since the advances in laser technology have led to the possibility of monitoring real-time dynamics of electrons, and unexpected strong field phenomena were observed [3]. For this high intensity regime other feasible approaches to quantum dynamics different from perturbation theory in the driving fields have to be used.

A very successful description of atoms or molecules in intense laser fields is the so-called strong field approximation [4–7]. In this approximation only one electron is assumed to interact with the field, while the rest of the system is an inert background for the actual dynamics. An extension of this strong field approximation to multi-particle systems can be formulated. However, this intense-field many-body S-matrix theory [8] becomes very involved if more than only a few particles are considered and knowledge of the electronic structure of the target is required as an input.

On the computational side we know that the challenges posed by many-body systems arise due to the interaction of all their constituents: Every particle "feels" all other particles. A noninteracting system, on the other hand, can be treated computationally much

faster [1, 3]. Hence, an accurate mean-field approach, where each particle feels an effective field, could describe many-body quantum dynamics very efficiently. Any mean-field theory will, however, a only lead to an approximate description and may not be able to reproduce important physical properties of the system. At least, this is the case if we consider the deduced wavefunction of the noninteracting system to be the fundamental variable. However, if we reformulate quantum mechanics in terms of another variable, this fundamental problem may be overcome. This is exactly the idea behind density functional theory [9] and its time-dependent formulation [10]. Under certain restrictions the one-body probability density is uniquely determined by the external field applied to the many-body system, and every observable is, in principle, determined by the density alone. The Schrödinger equation and the corresponding wavefunction in this approach may be seen as a tool to generate the fundamental variable, i.e., the exact density of the system. One may introduce an auxiliary system of noninteracting particles, which does not necessarily have physical significance, but which leads to the exact one-particle density of the physical system. In consequence this noninteracting many-body Schrödinger-like equation decouples into a set of single-particle equations, the so-called Kohn-Sham equations [11]. The solution of the nonlinear Kohn-Sham equations is computationally inexpensive in comparison to the corresponding solution of the interacting Schrödinger equation [1, 3] unless the calculation of the mean-field potential is too involved. The applicability of the Kohn-Sham approach, if certain mathematical restrictions are respected, is not limited to a specific intensity regime or system. From a physical point of view one may term the time-dependent density functional theory and the Kohn-Sham scheme to be a universal reformulation of quantum mechanics.

Unfortunately, the problem is not yet solved. Even if we know that there is an effective potential, which will generate the physical (interacting) density in a noninteracting system, its exact form is usually not known. Again we have to make approximations to actually predict the dynamics of the microscopic system. Nevertheless, a detailed inspection of the foundations of time-dependent density functional theory and of exactly solvable examples provide routes to successively improve this approach to many-body quantum dynamics.

The formal foundations of time-dependent density functional theory were established in the famous Runge-Gross paper [10] back in 1984. From that time on the interest in and the application of time-dependent density functional theory have constantly grown throughout physics and chemistry [11]. Many people have contributed, but beside review articles [see, e.g., reference [12]] and a recent collection of work [11], an ab initio approach to the foundations of the theory is, to the best of our knowledge, missing. Also a mathematically rigorous formulation [26, 30], which exists for ground-state density functional theory, has, to the best of our knowledge, never been pursued. Although initially the main focus of applied time-dependent density functional theory was on the linear response of complex quantum systems, nonperturbative quantum dynamics now enjoys more and more attraction. While in linear response calculations only the functional derivatives of the effective potentials in the vicinity of the ground-state are of importance, in the nonperturbative regime one requires the full time-dependent effective potential. Already in the early years of time-dependent density functional theory major differences to the ground-state density functional theory were recognized. For instance, the effective potential at

time t depends on the initial state and also on previous densities at times $t' < t$, i.e., it has "memory" [13]. Simple approximations for the effective potential as, e.g., the local density approximation, are adequate for some problems, but may lead to wrong predictions for others [11]. More elaborate approximations, of course, improve the reliability of the Kohn-Sham approach to quantum dynamics. The study of simple nonperturbative problems from a time-dependent density functional theory point of view [14,15] as well as fundamental considerations [13] led to further insight into the structure of effective potentials [11]. Still, essential problems remain, such as resonant dynamics in time-dependent density functional theory.

This work presents an unified ab initio approach to time-dependent density functional theory. The formal theory is redefined to the extent that we can state a mathematically rigorous formulation. For certain restrictions on the spatial behavior of the initial configurations as well as for the Hamiltonians the existence of the effective potential can be proven. This gives new insight into the foundations and highlights open problems of time-dependent density functional theory. A formal definition of "quantum memory" is given. The question of functional differentiability of the effective potentials is shown to be linked to the properties of the set of possible density variations. The possibility of an ab initio time-local approximation for the effective potentials is discussed. Further the connection of "quantum memory" and wavefunction-dependence of effective potentials is presented. We find that whenever the wavefunction is expressible by the instantaneous density, "quantum memory" and initial state-dependence vanish. Resonant dynamics are analyzed from a density functional perspective using a one-dimensional helium model system. It is shown that a simple adiabatic approximation exhibits resonant behavior without population transfer. This feature is found to be essentially of classical origin. The incompatibility of few-level approximations with time-dependent density functional theory is discussed. Finally we consider the radiation of a C_{60} fullerene subject to an intense laser pulse. Here we identify the novel strong field phenomenon of recollision-induced plasmon excitation and develop two analytical models for this process in the spirit of the strong field approximation.

This thesis is divided into three main parts: In **chapter one** general many-body theory for nonrelativistic systems in second quantization is reviewed. The basic theorem of time-dependent density functional theory is deduced, and a proper mathematical formulation of the theory is given. The nonlocality in time of the effective potential is investigated. Finally, approximations for the effective potential are presented and recently published criticism on the foundations of the theory is addressed. In **chapter two** the Hamiltonian of an arbitrary system in a general multiphoton field is introduced and the usual approximations leading to a semi-classical description are surveyed. The strong field approximation and its extension to multi-particle phenomena are deduced. In **chapter three** resonant interactions in time-dependent density functional theory are investigated. Further, the radiation of a C_{60} fullerene subject to an intense laser pulse is considered, with the emphasis on the role of radiation owing to collective effects. Finally, a conclusion and an outlook on future work is given.

3

Chapter 1

Many-Body Quantum Theory

Quantum theory has been established about a century ago and led to deep insights into nature. Starting with a nonrelativistic theory of matter, i.e., the Schrödinger equation, the next step was to incorporate special relativity into quantum theory via the Klein-Gordon and Dirac equation. Further development led to quantum field theories such as quantum electrodynamics, which describes the interaction of electrically charged particles via photons, or quantum chromodynamics, the theory of the strong force (colour force). From a fundamental point of view one could be tempted to believe that in order to understand nature we only have to find the most fundamental laws governing its smallest constituents and that complex systems are nothing but the sum of their parts. This reductionist's point of view naturally leads to the conclusion that after we have extensively studied the quantum mechanics of simple systems no new phenomena will emerge when studying large systems. So why bother about an old theory which has been replaced by more accurate theories on the smallest scales?

Many-particle physics tells us that a complex system may be more than the sum of the properties of the system's parts. The interplay of the constituents of a system leads to new and unexpected phenomena such as superconductivity, superfluidity or the quantum hall effect [16]. Also in the dynamics of quite simple atomic or molecular systems new phenomena emerge due to correlation and collectivity of the electrons. Most famous in the field of strong laser-matter interaction is the nonsequentiel double ionization [17] which could only be explained by including correlation between the electrons involved. Hopefully, the development of methods to compute the dynamics of complex many-particle systems yields novel physical insights. One such approach is time-dependent density functional theory.

We will review briefly the second quantized description of a general many-body quantum system and then reformulate the problem to be solved in terms of quantum fluid dynamics. Though this is not the usual way to consider the many-body problem in quantum mechanics, this approach will naturally lead to the Runge-Gross theorem which forms the basis of time-dependent density functional theory and will further give some guidance how to systematically improve the approximations in this theory. Also nonequilibrium Green's functions and the Keldysh formalism are closely interlinked with time-dependent

density functional theory. We will introduce a proper action functional defined on the Keldysh time contour. Further some approximations of the effective potentials are discussed and we will also consider recent criticism on the fundaments of time-dependent density functional theory.

Of special interest are the formal theory and the foundations of time-dependent density functional theory as well as a consistent derivation of the theory. Time-independent density functional theory will only be shortly reviewed with the focus on the fundamental ideas and problems to become aware of the similarities as well as the differences between density functional theory and its time-dependent formulation. The mathematically rigorous formulation of density functional theory will be used as a guiding line for our formulation of time-dependent density functional theory. We give strict conditions under which the formally exact theory becomes mathematically rigorous. Further we give a formal definition of the term "quantum memory" via functional derivatives. We point out that functional differentiability is connected to the properties of the set of possible density variations. The possibility of an ab initio time-local approximation to the exchange-correlation potential is discussed. Furthermore, the wavefunction-dependence of the potentials is explored and we evidence that "quantum memory" and initial state dependence disappear whenever the wavefunction is locally representable by the density.

1.1 Second Quantization

In order to describe a general many-body quantum system it is convenient to reformulate the problem field-theoretically. The Schrödinger equation then is rewritten with creation and annihilation operators, which simplifies the notation and encodes the fundamental statistics (fermionic or bosonic) in the (anti)commutation-relations of these operators. In what follows we adopt the derivation in reference [18].

We have a division of the N-particle Hilbertspace $\mathcal{H}_N := \bigotimes_{i=1}^N \mathcal{H}_1^i$ into a totally symmetric $\mathcal{H}_N^{(+)} := \mathbb{S}_{i=1}^N \mathcal{H}_1^i$ and antisymmetric subspace $\mathcal{H}_N^{(-)} := \bigwedge_{i=1}^N \mathcal{H}_1^i$,

$$\mathcal{H}_N = \mathcal{H}_N^{(+)} \oplus \mathcal{H}_N^{(-)}. \tag{1.1}$$

Either the possible states of a system are in the symmetric subspace $\mathcal{H}_N^{(+)}$, i.e., the system is bosonic, or all possible states are in the antisymmetric subspace $\mathcal{H}_N^{(-)}$, i.e., the system is fermionic. Due to the spin-statistic theorem bosons have integer spin and fermions have spin $1/2, 3/2, \dots$. Thus the corresponding wavefunctions have to be (anti)symmetrized. The eigenstates $|\varphi_\alpha\rangle$ of a single-particle observable $\widehat{\varphi}$, with α being a complete set of quantum numbers, are assumed to form a complete and orthonormalized basis for $\mathcal{H}_1$. Hence, one can construct a basis for $\mathcal{H}_N^{(\pm)}$ with these single-particle eigenstates. We will distinguish between the spectrum of $\widehat{\varphi}$ to be continuous or discrete.

1.1.1 Observable with Continuous Spectrum

For a continuous spectrum of $\widehat{\varphi}$ we have:

$$
\begin{aligned}
\widehat{\varphi}|\varphi_\alpha\rangle &= \varphi_\alpha|\varphi_\alpha\rangle, & (1.2) \\
\langle\varphi_\alpha|\varphi_\beta\rangle &= \delta(\varphi_\alpha - \varphi_\beta) \equiv \delta(\alpha - \beta), & (1.3) \\
\int d\alpha|\varphi_\alpha\rangle\langle\varphi_\alpha| &= \mathbb{1}_1. & (1.4)
\end{aligned}
$$

Note here that we have an orthonormalization condition (1.3) in terms of a Dirac delta function $\delta(\alpha - \beta)$. This is the cause for the main difference between the continuous and the discrete case. The (anti)symmetrized N-particle state reads

$$
|\varphi_{\alpha_1}...\varphi_{\alpha_N}\rangle^\epsilon = \frac{1}{N!}\sum_{\mathcal{P}} \epsilon^p \mathcal{P}|\varphi_{\alpha_1}...\varphi_{\alpha_N}\rangle, \tag{1.5}
$$

with $\mathcal{P}$ the permutation operator, $\epsilon = \pm$ indicating bosonic $(+)$ or fermionic $(-)$ systems, and p the number of transpositions of $\mathcal{P}$. The generalized orthonormalization condition is

$$
\begin{aligned}
{}^\epsilon\langle\varphi_{\beta_1}...\varphi_{\beta_N}|\varphi_{\alpha_1}...\varphi_{\alpha_N}\rangle^\epsilon &= \frac{1}{N!}\sum_{\mathcal{P}_\alpha} \epsilon^{p_\alpha} \mathcal{P}_\alpha \left\{ \langle\varphi_{\beta_1}^1|\varphi_{\alpha_1}^1\rangle...\langle\varphi_{\beta_N}^N|\varphi_{\alpha_N}^N\rangle \right\} & (1.6) \\
&= \frac{1}{N!}\sum_{\mathcal{P}_\alpha} \epsilon^{p_\alpha} \mathcal{P}_\alpha \left[\delta(\beta_1 - \alpha_1)...\delta(\beta_N - \alpha_N) \right].
\end{aligned}
$$

The subindex α for $\mathcal{P}_\alpha$ indicates that the operator only acts on the single particle wavefunctions with the same subindex. The corresponding completeness relation for the N-particle case is then found by

$$
\int ... \int d\beta_1...d\beta_N |\varphi_{\beta_1}...\varphi_{\beta_N}\rangle^\epsilon \, {}^\epsilon\langle\varphi_{\beta_1}...\varphi_{\beta_N}| = \mathbb{1}_N^\epsilon \tag{1.7}
$$

with $\mathbb{1}_N^\epsilon$ the identity operator in $\mathcal{H}_N^\epsilon$.

Now we will circumvent the cumbersome task of (anti)symmetrizing the wavefunctions by introducing creation and annihilation operators and the vacuum state. The **creation operator** $a_{\varphi_\alpha}^\dagger \equiv a_\alpha^\dagger$ is defined as

$$
\begin{aligned}
a_\alpha^\dagger : \mathcal{H}_N^\epsilon &\rightarrow \mathcal{H}_{N+1}^\epsilon & (1.8) \\
|\varphi_{\beta_1}...\varphi_{\beta_N}\rangle^\epsilon &\mapsto a_\alpha^\dagger|\varphi_{\beta_1}...\varphi_{\beta_N}\rangle^\epsilon = \sqrt{N+1}|\varphi_\alpha\varphi_{\beta_1}...\varphi_{\beta_N}\rangle^\epsilon,
\end{aligned}
$$

connecting the different many-particle Hilbertspaces. The order of the creation operators is of importance as we find

$$
\left[a_{\alpha_1}^\dagger, a_{\alpha_2}^\dagger \right]_{-\epsilon} := a_{\alpha_1}^\dagger a_{\alpha_2}^\dagger - \epsilon a_{\alpha_2}^\dagger a_{\alpha_1}^\dagger = 0. \tag{1.9}
$$

The creation operators commute in the bosonic and anticommute in the fermionic case. Thus, strictly speaking, we have two different creation operators. However, we will treat

them here in a general manner. What kind of creation operator is chosen depends on the particle described.

The adjoint operator $\left(a_\alpha^\dagger\right)^\dagger = a_\alpha$ is defined via

$$a_\alpha : \mathcal{H}_N^\epsilon \quad \to \quad \mathcal{H}_{N-1}^\epsilon \tag{1.10}$$

$$|\varphi_{\beta_1}\varphi_{\beta_2}...\varphi_{\beta_N}\rangle^\epsilon \quad \mapsto \quad a_\alpha|\varphi_{\beta_1}\varphi_{\beta_2}...\varphi_{\beta_N}\rangle^\epsilon = \frac{1}{\sqrt{N}}\left\{\delta(\alpha-\beta_1)|\varphi_{\beta_2}...\varphi_{\beta_N}\rangle^\epsilon\right.$$
$$+\epsilon\delta(\alpha-\beta_2)|\varphi_{\beta_1}\varphi_{\beta_3}...\varphi_{\beta_N}\rangle^\epsilon +$$
$$+...+$$
$$\left.+\epsilon^{N-1}\delta(\alpha-\beta_N)|\varphi_{\beta_1}\varphi_{\beta_3}...\varphi_{\beta_{N-1}}\rangle^\epsilon\right\}.$$

The **annihilation operator** a_α destroys an orbital $|\varphi_\alpha\rangle$ and generates a multi-particle state with $N-1$ particles. This behavior can already be seen by the definition (1.8)

$$^\epsilon\langle\varphi_{\beta_1}...\varphi_{\beta_N}|a_\alpha = \sqrt{N+1}\,^\epsilon\langle\varphi_\alpha\varphi_{\beta_1}...\varphi_{\beta_N}|. \tag{1.11}$$

The annihilation operators obey

$$[a_{\alpha_1}, a_{\alpha_2}]_{-\epsilon} = 0. \tag{1.12}$$

We now introduce the **vacuum state** via the relation

$$a_\alpha|0\rangle := 0. \tag{1.13}$$

With this a general multi-particle state is generated as

$$|\varphi_{\alpha_1}...\varphi_{\alpha_N}\rangle^\epsilon = \frac{1}{\sqrt{N!}}a_{\alpha_1}^\dagger...a_{\alpha_N}^\dagger|0\rangle \tag{1.14}$$

and the adjoint thereof is

$$^\epsilon\langle\varphi_{\alpha_1}...\varphi_{\alpha_N}| = \frac{1}{\sqrt{N!}}\langle 0|a_{\alpha_N}...a_{\alpha_1}. \tag{1.15}$$

The (anti)commutation relations for the creation and annihilation operators are

$$\left[a_{\alpha_1}, a_{\alpha_2}^\dagger\right]_{-\epsilon} = \delta(\alpha_1-\alpha_2). \tag{1.16}$$

A general N-particle observable $\widehat{A}$ usually consists of one- and two-particle contributions

$$\widehat{A} = \sum_{i=1}^N \widehat{A}_1^{(i)} + \frac{1}{2}\sum_{i,j}^{i\neq j}\widehat{A}_2^{(i,j)}. \tag{1.17}$$

We may express the operator $\widehat{A}$ in terms of the operators a_α and $a_\alpha^\dagger$. By using the completeness relation (1.7) one finds for the one-particle contribution

$$\sum_{i=1}^N \widehat{A}_1^{(i)} = \int...\int d\alpha_1...d\alpha_N d\beta_1...d\beta_N |\varphi_{\alpha_1}...\rangle^\epsilon\,^\epsilon\langle\varphi_{\alpha_1}...|\sum_{i=1}^N \widehat{A}_1^{(i)}|\varphi_{\beta_1}...\rangle^\epsilon\,^\epsilon\langle\varphi_{\beta_1}...|$$

$$= \int\int d\alpha d\beta\langle\varphi_\alpha|\widehat{A}_1|\varphi_\beta\rangle a_\alpha^\dagger \mathbb{1}_{N-1}^\epsilon a_\beta$$

$$\equiv \int\int d\alpha d\beta\langle\varphi_\alpha|\widehat{A}_1|\varphi_\beta\rangle a_\alpha^\dagger a_\beta, \tag{1.18}$$

with $\mathbb{1}_{N-1}^\epsilon$ the identity of $\mathcal{H}_{N-1}^\epsilon$. In an analogous manner one finds

$$
\begin{aligned}
\frac{1}{2} \sum_{i,j}^{i \neq j} \widehat{A}_2^{(i,j)} &= \frac{1}{2} \int ... \int d\alpha d\beta d\gamma d\delta \langle \varphi_\alpha^{(1)} \varphi_\beta^{(2)} | \widehat{A}_2 | \varphi_\gamma^{(1)} \varphi_\delta^{(2)} \rangle a_\alpha^\dagger a_\beta^\dagger \mathbb{1}_{(N-2)}^\epsilon a_\gamma a_\delta \\
&\equiv \frac{1}{2} \int ... \int d\alpha d\beta d\gamma d\delta \langle \varphi_\alpha^{(1)} \varphi_\beta^{(2)} | \widehat{A}_2 | \varphi_\gamma^{(1)} \varphi_\delta^{(2)} \rangle a_\alpha^\dagger a_\beta^\dagger a_\gamma a_\delta. \qquad (1.19)
\end{aligned}
$$

The matrix element may also be calculated with (anti)symmetrized two-particle states without any change, in contrast to the discrete case later on.

Two important operators of special interest are the **occupation density operator**

$$
\widehat{n}_\alpha = a_\alpha^\dagger a_\alpha, \qquad (1.20)
$$

with $\widehat{n}_\alpha | \varphi_{\beta_1} ... \varphi_{\beta_2} \rangle^\epsilon = \left\{ \sum_{i=1}^N \delta(\alpha - \beta_i) \right\} | \varphi_{\beta_1} ... \varphi_{\beta_2} \rangle^\epsilon$, leading to the microscopic occupation density and

$$
\widehat{N} = \int d\alpha \, \widehat{n}_\alpha \qquad (1.21)
$$

the **particle number operator**.

A very important one-particle observable with continuous spectrum from which to construct creation and annihilation operators is the position space operator

$$
\widehat{\boldsymbol{r}}. \qquad (1.22)
$$

The corresponding operators are called the **field operators**

$$
\widehat{\psi}(\boldsymbol{r}), \widehat{\psi}^\dagger(\boldsymbol{r}), \qquad (1.23)
$$

obeying the previously calculated (anti)commutation relations

$$
\begin{aligned}
\left[\widehat{\psi}(\boldsymbol{r})^\dagger, \widehat{\psi}(\boldsymbol{r}')^\dagger \right]_{-\epsilon} &= \left[\widehat{\psi}(\boldsymbol{r}), \widehat{\psi}(\boldsymbol{r}') \right]_{-\epsilon} = 0, \qquad (1.24) \\
\left[\widehat{\psi}(\boldsymbol{r}), \widehat{\psi}(\boldsymbol{r}')^\dagger \right]_{-\epsilon} &= \delta(\boldsymbol{r} - \boldsymbol{r}').
\end{aligned}
$$

The associated eigenstates are created again by successive application of the creation operator

$$
| \boldsymbol{r}_1 \boldsymbol{r}_2 ... \boldsymbol{r}_N \rangle^{(\epsilon)} = \frac{1}{\sqrt{N!}} \widehat{\psi}^\dagger(\boldsymbol{r}_1) ... \widehat{\psi}^\dagger(\boldsymbol{r}_N) | 0 \rangle. \qquad (1.25)
$$

Via the completeness relation one may rewrite the field operators in terms of general construction operators $a_\alpha^\dagger$, a_α,

$$
\begin{aligned}
| \boldsymbol{r} \rangle &= \psi^\dagger(\boldsymbol{r}) | 0 \rangle = \int d\alpha \, | \varphi_\alpha \rangle \langle \varphi_\alpha | \boldsymbol{r} \rangle = \int d\alpha \, \varphi_\alpha^*(\boldsymbol{r}) | \varphi_\alpha \rangle \\
&= \int d\alpha \, \varphi_\alpha^*(\boldsymbol{r}) a_\alpha^\dagger | 0 \rangle \\
\Rightarrow \widehat{\psi}^\dagger(\boldsymbol{r}) &= \int d\alpha \, \varphi_\alpha^*(\boldsymbol{r}) a_\alpha^\dagger, \; \widehat{\psi}(\boldsymbol{r}) = \int d\alpha \, \varphi_\alpha(\boldsymbol{r}) a_\alpha. \qquad (1.26)
\end{aligned}
$$

1.1.2 Observable with Discrete Spectrum

For a discrete spectrum of $\widehat{\varphi}$ we have:

$$\widehat{\varphi}|\varphi_\alpha\rangle = \varphi_\alpha|\varphi_\alpha\rangle, \tag{1.27}$$

$$\langle\varphi_\alpha|\varphi_\beta\rangle = \delta_{\alpha\beta}, \tag{1.28}$$

$$\sum_\alpha |\varphi_\alpha\rangle\langle\varphi_\alpha| = \mathbb{1}_1. \tag{1.29}$$

Analogously to the continuous case the (anti)symmetrized N-particle state is found by

$$|\varphi_{\alpha_1}...\varphi_{\alpha_N}\rangle^\epsilon = C_\epsilon \sum_\mathcal{P} \epsilon^p \mathcal{P} |\varphi_{\alpha_1}...\varphi_{\alpha_N}\rangle, \tag{1.30}$$

which is formally different to equation (1.5) due to the normalization constant C_ϵ. Because in the discrete case we have the orthonormalization condition (1.28) we find the normalization constant by

$$1 \stackrel{!}{=} {}^\epsilon\langle\varphi_{\alpha_1}...\varphi_{\alpha_N}|\varphi_{\alpha_1}...\varphi_{\alpha_N}\rangle^\epsilon. \tag{1.31}$$

With the definition of the **occupation number** n_i, which tells us how often a one-particle state $|\varphi_{\alpha_i}\rangle$ is found in the N-particle state $|\varphi_{\alpha_1}...\varphi_{\alpha_N}\rangle^\epsilon$, we find

$$C_\epsilon \equiv C = \left(N! \prod_i n_i! \right)^{-1/2}. \tag{1.32}$$

Note that the occupation numbers n_i for the different statistics fulfill:

$$\begin{aligned} \sum_i n_i &= N, \\ n_i &= 0,1 \quad \text{fermions} \\ n_i &= 0,1,2,... \quad \text{bosons.} \end{aligned} \tag{1.33}$$

We call

$$|\varphi_{\alpha_1}...\varphi_{\alpha_N}\rangle^\epsilon \equiv |N; n_1 n_2 ... n_i ...\rangle^\epsilon \tag{1.34}$$

the occupation number representation and its states the **Fock states**. With these states we find the generalized orthonormalization condition

$$^\epsilon\langle N; ...n_i...|\overline{N}; ...\overline{n}_i...\rangle^\epsilon = \delta_{N\overline{N}} \prod_i \delta_{n_i \overline{n}_i} \tag{1.35}$$

and the completeness relation

$$\sum_{n_1} ... \sum_{n_i} ...|N; ...n_i...\rangle^{\epsilon\,\epsilon}\langle N; ...n_i...| = \mathbb{1}_N^\epsilon. \tag{1.36}$$

Again we define the **creation operator** $a_{\alpha_r}^\dagger \equiv a_r^\dagger$ by

$$
\begin{aligned}
a_r^\dagger : \mathcal{H}_N^\epsilon &\rightarrow \mathcal{H}_{N+1}^\epsilon \\
|N; ...n_r...\rangle^\epsilon &\mapsto a_r^\dagger|N; ...n_r...\rangle^\epsilon = \sqrt{n_r + 1}|\varphi_{\alpha_r}\underbrace{\varphi_{\alpha_1}\varphi_{\alpha_1}...}_{n_1}...\underbrace{\varphi_{\alpha_r}\varphi_{\alpha_r}...}_{n_r}...\rangle^\epsilon \\
&= \epsilon^{N_r}\sqrt{n_r + 1}|\underbrace{\varphi_{\alpha_1}\varphi_{\alpha_1}...}_{n_1}...\underbrace{\varphi_{\alpha_r}\varphi_{\alpha_r}...}_{n_r+1}...\rangle^\epsilon .
\end{aligned}
\tag{1.37}
$$

Here we have

$$
N_r = \sum_{i=1}^{r-1} n_i \tag{1.38}
$$

the number of occupied states before the created state α_r. Accordingly the creation operators act in the bosonic case as

$$
a_r^\dagger|N; ...n_r...\rangle^{(+)} = \sqrt{n_r + 1}|N + 1; ...n_r + 1...\rangle^{(+)}, \tag{1.39}
$$

and in the fermionic case as

$$
a_r^\dagger|N; ...n_r...\rangle^{(-)} = (-1)^{N_r}\delta_{n_r,0}|N + 1; ...n_r + 1...\rangle^{(-)}. \tag{1.40}
$$

A general N-particle Fock state can be created by

$$
|N; n_1...n_i...\rangle^\epsilon = \prod_{p=1...} \frac{(a_p^\dagger)^{n_p}}{\sqrt{n_p!}} \epsilon^{N_p}|0\rangle. \tag{1.41}
$$

Accordingly we define the **annihilation operator** $a_r \equiv (a_r^\dagger)^\dagger$ as

$$
\begin{aligned}
a_r : \mathcal{H}_N^\epsilon &\rightarrow \mathcal{H}_{N-1}^\epsilon \\
|N; ...n_r...\rangle^\epsilon &\mapsto a_r|N; ...n_r...\rangle^\epsilon = \epsilon^{N_r}\sqrt{n_r}|N - 1; ...n_r - 1...\rangle^\epsilon .
\end{aligned}
\tag{1.42}
$$

The annihilation operator thus leads to:

$$
\begin{aligned}
a_r|N; ...n_r...\rangle^{(+)} &= \sqrt{n_r}|N - 1; ...n_r - 1...\rangle^{(+)} \quad \text{bosonic} \\
a_r|N; ...n_r...\rangle^{(-)} &= (-1)^{N_r}\delta_{n_r,1}|N - 1; ...n_r - 1...\rangle^{(-)} \quad \text{fermionic}.
\end{aligned}
\tag{1.43}
$$

The associated (anti)commutation relations are

$$
[a_r, a_s]_{-\epsilon} = \left[a_r^\dagger, a_s^\dagger\right]_{-\epsilon} = 0, \tag{1.44}
$$

$$
\left[a_r, a_s^\dagger\right]_{-\epsilon} = \delta_{rs}. \tag{1.45}
$$

A general N-particle operator $\widehat{A}$ (1.17) can be rewritten in terms of the discrete construction operators as

$$
\widehat{A} = \sum_{p,r}\langle\varphi_p|\widehat{A}_1|\varphi_r\rangle a_p^\dagger a_r + \frac{1}{2}\sum_{p,r,s,t}\langle\varphi_p^{(1)}\varphi_r^{(2)}|\widehat{A}_2|\varphi_t^{(1)}\varphi_s^{(2)}\rangle a_p^\dagger a_r^\dagger a_s a_t. \tag{1.46}
$$

The only difference to the continuous case is that one has to use the unsymmetrized two-particle states. This occurs due to the different normalizations. We define the **occupation number operator** by

$$\widehat{n}_r = a_r^\dagger a_r, \tag{1.47}$$

leading to $\widehat{n}_r|N; ...n_r...\rangle^\epsilon = n_r|N; ...n_r...\rangle^\epsilon$, and the **particle number operator**

$$\widehat{N} = \sum_r \widehat{n}_r. \tag{1.48}$$

We can rewrite the previously introduced field operators via the completeness relation of the creation and annihilation operators in accordance with the continuous case. Therefore any general multi-particle wavefunction $|\Psi\rangle$ in terms of the basis induced by $\{|\varphi_\alpha\rangle\}$ can be constructed as [19]

$$
\begin{aligned}
|\Psi\rangle &= \sum_{\alpha_1,...,\alpha_N} c_{\alpha_1,...,\alpha_N} a_{\alpha_1}^\dagger ... a_{\alpha_N}^\dagger |0\rangle \\
&= \int d^3r_1...d^3r_N \left(\sum_{\alpha_1,...,\alpha_N} c_{\alpha_1,...,\alpha_N} \varphi_{\alpha_1}(\boldsymbol{r}_1)...\varphi_{\alpha_N}(\boldsymbol{r}_N) \right) \widehat{\psi}^\dagger(\boldsymbol{r}_1)...\widehat{\psi}^\dagger(\boldsymbol{r}_N)|0\rangle \\
&= \int d^3r_1...d^3r_N \, \psi(\boldsymbol{r}_1, ..., \boldsymbol{r}_N) \, \widehat{\psi}^\dagger(\boldsymbol{r}_1)...\widehat{\psi}^\dagger(\boldsymbol{r}_N)|0\rangle.
\end{aligned}
\tag{1.49}
$$

Here $\psi(\boldsymbol{r}_1, ..., \boldsymbol{r}_N)$ is the wavefunction in position space. This construction immediately takes care of the right symmetrization as only the (anti)symmetrized part of the wavefunction survives. This can be seen directly if one interchanges two coordinates, say $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$. Due to the (anti)commutation relations of the field operators one gains a factor ϵ in the integral. For the wavefunction not to be zero, i.e., $|\Psi\rangle \neq -|\Psi\rangle$, the change of the coordinates in the position space-wavefunction have to generate a further ϵ.

1.1.3 Hamiltonian in Second Quantized Notation

In order to formulate the Schrödinger equation in second quantized description we introduce the **spin-valued field operators** in the **Schrödinger picture** [18]

$$\widehat{\psi}_\sigma(\boldsymbol{r}), \widehat{\psi}_\sigma^\dagger(\boldsymbol{r}), \tag{1.50}$$

which annihilate or create a particle with spin σ and which are subject to the associated (anti)commutation relations

$$\left[\widehat{\psi}_\sigma(\boldsymbol{r}), \widehat{\psi}_{\sigma'}^\dagger(\boldsymbol{r}')\right]_{-\epsilon} = \delta(\boldsymbol{r} - \boldsymbol{r}')\delta_{\sigma\sigma'}. \tag{1.51}$$

The Hamiltonian in the Schrödinger picture reads

$$\widehat{H}(t) = \widehat{T} + \widehat{V}_{\text{int}} + \widehat{V}(t). \tag{1.52}$$

Here the operator $\widehat{T} = \sum_{i=1}^{N} \frac{1}{2}k_i^2$ is the kinetic energy operator, $\widehat{V}_{\text{int}} = \frac{1}{2}\sum_{i,j=1}^{i\neq j} v_{\text{int}}(|\boldsymbol{r}_i - \boldsymbol{r}_j|)$ the particle-particle interaction and $\widehat{V}(t) = \sum_{i=1}^{N} v(\boldsymbol{r}_i, t)$ the external potential operator. We use **atomic units** throughout this chapter, i.e., $m = |e| = \hbar = 1$. The kinetic energy operator and the external potential are one-particle operators, while the interaction operator $\widehat{V}_{\text{int}}$ is a two-particle operator. From equation (1.18) we know how to express $\widehat{T}$ in terms of the spin-valued field operators,

$$
\begin{aligned}
\widehat{T} &= \sum_{\sigma,\sigma'} \int\int d^3r d^3r' \langle \boldsymbol{r}\sigma|\widehat{T}_1|\boldsymbol{r}'\sigma'\rangle \widehat{\psi}_\sigma^\dagger(\boldsymbol{r})\widehat{\psi}_{\sigma'}(\boldsymbol{r}') \\
&= \sum_{\sigma,\sigma'} \int\int d^3r d^3r' \left(\sum_{\tilde{\sigma}}\int d^3k \langle \boldsymbol{r}\sigma|\boldsymbol{k}\tilde{\sigma}\rangle\langle \boldsymbol{k}\tilde{\sigma}|\widehat{T}_1|\boldsymbol{r}'\sigma'\rangle\right)\widehat{\psi}_\sigma^\dagger(\boldsymbol{r})\widehat{\psi}_{\sigma'}(\boldsymbol{r}') \\
&= \sum_{\sigma,\sigma'} \int\int d^3r d^3r' \left(-\frac{1}{2}\boldsymbol{\nabla}_{\boldsymbol{r}'}^2\delta(\boldsymbol{r}-\boldsymbol{r}')\delta_{\sigma,\sigma'}\right)\widehat{\psi}_\sigma^\dagger(\boldsymbol{r})\widehat{\psi}_{\sigma'}(\boldsymbol{r}') \\
&= \sum_{\sigma} \int d^3r \widehat{\psi}_\sigma^\dagger(\boldsymbol{r})\left(-\frac{1}{2}\boldsymbol{\nabla}_{\boldsymbol{r}}^2\right)\widehat{\psi}_\sigma(\boldsymbol{r}).
\end{aligned}
\tag{1.53}
$$

Note that via the relation (1.26) the kinetic energy operator may be reexpressed in terms of the continuous $\boldsymbol{k}$-representation which is induced by the wave-vector operator $\widehat{\boldsymbol{k}}$. One then finds in terms of the construction operators $a_{\boldsymbol{k},\sigma}$ and $a_{\boldsymbol{k},\sigma}^\dagger$

$$
\widehat{T} = \sum_{\sigma} \int d^3k \frac{k^2}{2} a_{\boldsymbol{k},\sigma}^\dagger a_{\boldsymbol{k},\sigma}.
\tag{1.54}
$$

For the other operators the reformulation in Fourier-space works analogously.
The particle-particle interaction operator is expressed via the spin-valued field operators following equation (1.19) as

$$
\widehat{V}_{\text{int}} = \frac{1}{2}\sum_{\sigma,\sigma'} \int\int d^3r d^3r' v_{\text{int}}(|\boldsymbol{r}-\boldsymbol{r}'|)\widehat{\psi}_\sigma^\dagger(\boldsymbol{r})\widehat{\psi}_{\sigma'}^\dagger(\boldsymbol{r}')\widehat{\psi}_{\sigma'}(\boldsymbol{r}')\widehat{\psi}_\sigma(\boldsymbol{r}).
\tag{1.55}
$$

Here we have used the fact that the interaction between the particles is spin-independent. For the external potential this does not hold in general. But we will assume throughout this work, that the **external potential operator is spin-independent**. We then find

$$
\widehat{V}(t) = \sum_{\sigma} \int d^3r\, v(\boldsymbol{r},t)\, \widehat{\psi}_\sigma^\dagger(\boldsymbol{r})\widehat{\psi}_\sigma(\boldsymbol{r}).
\tag{1.56}
$$

Thus, with the definition of the density operator

$$
\widehat{n}(\boldsymbol{r}) := \sum_{\sigma} \widehat{\psi}_\sigma^\dagger(\boldsymbol{r})\widehat{\psi}_\sigma(\boldsymbol{r})
\tag{1.57}
$$

and the two-particle density operator

$$
\widehat{\varrho}(\boldsymbol{r},\boldsymbol{r}') := \sum_{\sigma,\sigma'} \widehat{\psi}_\sigma^\dagger(\boldsymbol{r})\widehat{\psi}_{\sigma'}^\dagger(\boldsymbol{r}')\widehat{\psi}_{\sigma'}(\boldsymbol{r}')\widehat{\psi}_\sigma(\boldsymbol{r}),
\tag{1.58}
$$

the Hamiltonian in second quantized notation reads

$$
\begin{aligned}
\widehat{H}(t) &= \sum_\sigma \int d^3 r \widehat{\psi}_\sigma^\dagger(\boldsymbol{r}) \left(-\frac{1}{2}\boldsymbol{\nabla}_{\boldsymbol{r}}^2\right) \widehat{\psi}_\sigma(\boldsymbol{r}) + \int d^3 r \, v(\boldsymbol{r}, t)\, \widehat{n}(\boldsymbol{r}) \\
&+ \frac{1}{2} \int \int d^3 r d^3 r' \, v_{\text{int}}(|\boldsymbol{r} - \boldsymbol{r}'|) \, \widehat{\varrho}(\boldsymbol{r}, \boldsymbol{r}').
\end{aligned} \tag{1.59}
$$

The first quantized-notation for a general many-body Hamiltonian can be restored if we apply the second-quantized Hamiltonian (1.59) to the general expression for a wavefunction (1.49), where $\Psi(\boldsymbol{r}_1\sigma_1, ..., \boldsymbol{r}_N\sigma_N)$ is the associated wavefunction in configuration space [19].

1.2 Quantum Fluid Dynamics

For a strongly perturbed complex system common many-body techniques based on diagrammatic approaches [18] are demanding and not very useful [11, 20, 21]. Even in the linear response regime such calculations are very cumbersome.

Another way to look at many-body dynamics would be to reformulate the problem in terms of collective variables, such as the density or current-density of the system. This leads to quantum fluid dynamics, i.e., we study the time-evolution of the density and the current. To reformulate the problem at hand in such a manner we will need a deep understanding of how the density and the current-density are determined by the system and vice versa. Such considerations naturally lead to an extended Runge-Gross theorem [23] and the formulation of time-dependent density functional theory [10]. It will be shown that the continuity equation (1.71) and the local force balance equation (1.83) are a formally closed set of equations uniquely defining the time-dependent density. An exact quantum fluid dynamical reformulation is possible [20, 21].

First we will derive the equation of motion for the field operators in the Heisenberg picture. Further the continuity and the local force-balance equation are derived for the general case of a mixed state. Then we present the extended Runge-Gross proof and show the formal exactness of the quantum fluid dynamical reformulation of quantum mechanics.

1.2.1 Conservation Laws in the Laboratory Reference Frame

We begin by deducing the Heisenberg equation of motion for the spin-valued field operators. Let $\widehat{A}(t)$ be a general operator in the Schrödinger picture. Then this operator in the **Heisenberg picture** reads $\widehat{A}_{\text{H}}(t) := \widehat{U}^{-1}(t, t_0)\widehat{A}(t)\,\widehat{U}(t, t_0)$, with $\widehat{U}(t, t_0)$ the unitary time-evolution operator of the system starting at $t = t_0$. For the Hamiltonian $\widehat{H}_{\text{H}}(t)$ in the Heisenberg picture we have [18]

$$
\mathrm{i}\frac{d\widehat{A}_{\text{H}}(t)}{dt} = \left[\widehat{A}_{\text{H}}(t), \widehat{H}_{\text{H}}(t)\right]_{-} + \mathrm{i}\frac{\partial \widehat{A}_{\text{H}}(t)}{\partial t}, \tag{1.60}
$$

independent of the spin-statistics. Here we define

$$\frac{\partial \widehat{A}_{\mathrm{H}}(t)}{\partial t} := \widehat{U}^{-1}(t, t_0) \frac{\partial \widehat{A}(t)}{\partial t} \widehat{U}(t, t_0). \tag{1.61}$$

If we now look at the Heisenberg representation of the field operators we have

$$\mathrm{i}\frac{d\widehat{\psi}_{\sigma,\mathrm{H}}(\boldsymbol{r}, t)}{dt} = \left[\widehat{\psi}_{\sigma,\mathrm{H}}(\boldsymbol{r}, t), \widehat{H}_{\mathrm{H}}(t)\right]_{-} + \mathrm{i}\underbrace{\frac{\partial \widehat{\psi}_{\sigma,\mathrm{H}}(\boldsymbol{r}, t)}{\partial t}}_{=0}. \tag{1.62}$$

One may now calculate the above commutator (for fermions as well as bosons) of the Hamiltonian in the Heisenberg picture either in terms of the Heisenberg field operators $\widehat{\psi}_{\sigma,\mathrm{H}}(\boldsymbol{r}, t)$ or with the field operators $\widehat{\psi}_{\sigma}(\boldsymbol{r})$, which are the Schrödinger picture field operators [18]. For the kinetic energy operator $\widehat{T}_{\mathrm{H}}(t)$ we find in accordance with (1.53)

$$\left[\widehat{\psi}_{\sigma,\mathrm{H}}(\boldsymbol{r}, t), \widehat{T}_{\mathrm{H}}(t)\right]_{-} = \left[\widehat{\psi}_{\sigma,\mathrm{H}}(\boldsymbol{r}, t), \sum_{\sigma'} \int d^3 r' \widehat{\psi}_{\sigma',\mathrm{H}}^{\dagger}(\boldsymbol{r}', t) \left(-\frac{1}{2}\boldsymbol{\nabla}_{r'}^2\right) \widehat{\psi}_{\sigma',\mathrm{H}}(\boldsymbol{r}', t)\right]_{-}$$

$$= \left(-\frac{1}{2}\boldsymbol{\nabla}_r^2\right) \widehat{\psi}_{\sigma,\mathrm{H}}(\boldsymbol{r}, t). \tag{1.63}$$

The above result may also be derived by

$$\left[\widehat{\psi}_{\sigma,\mathrm{H}}(\boldsymbol{r}, t), \widehat{T}_{\mathrm{H}}(t)\right]_{-} = \widehat{U}^{-1}(t, t_0) \left[\widehat{\psi}_{\sigma}(\boldsymbol{r}), \widehat{T}\right]_{-} \widehat{U}(t, t_0). \tag{1.64}$$

Accordingly we can calculate the other parts of the commutator (1.62) and end up with [20, 22]

$$\mathrm{i}\frac{d}{dt}\widehat{\psi}_{\sigma,\mathrm{H}}(\boldsymbol{r}, t) = \left(-\frac{1}{2}\boldsymbol{\nabla}_{\boldsymbol{r}}^2\right) \widehat{\psi}_{\sigma,\mathrm{H}}(\boldsymbol{r}, t) + v(\boldsymbol{r}, t)\widehat{\psi}_{\sigma,\mathrm{H}}(\boldsymbol{r}, t) \tag{1.65}$$

$$+ \sum_{\sigma'} \int d^3 r' v_{\mathrm{int}}(|\boldsymbol{r} - \boldsymbol{r}'|)\widehat{\psi}_{\sigma',\mathrm{H}}^{\dagger}(\boldsymbol{r}', t)\widehat{\psi}_{\sigma',\mathrm{H}}(\boldsymbol{r}', t)\widehat{\psi}_{\sigma,\mathrm{H}}(\boldsymbol{r}, t).$$

For the Heisenberg density operator $\widehat{n}_{\mathrm{H}}(\boldsymbol{r}, t)$ we define the time-dependent density by averaging with the usual density matrix $\widehat{\rho}_0 = \sum_m p_m |\Psi_m\rangle\langle\Psi_m|$ as

$$n(\boldsymbol{r}, t) = \langle\widehat{n}_{\mathrm{H}}(\boldsymbol{r}, t)\rangle_0 = \mathrm{tr}\left(\widehat{\rho}_0 \, \widehat{n}_{\mathrm{H}}(\boldsymbol{r}, t)\right). \tag{1.66}$$

The angle brackets denote averaging over the density matrix. Note that we can change from the Heisenberg to the Schrödinger picture by taking the operators time-independent and the density matrix time-dependent. This can be done because the trace is invariant under cyclic permutations of operators. Note further that the density matrix obeys the von Neumann equation for its time evolution and is a constant of motion for the Heisenberg equation. Hence,

$$n(\boldsymbol{r}, t) = \langle\widehat{n}(\boldsymbol{r})\rangle_t = \mathrm{tr}\left(\widehat{\rho}(t) \, \widehat{n}(\boldsymbol{r})\right). \tag{1.67}$$

15

The current-density operator (in the Schrödinger picture) is defined via

$$\widehat{\boldsymbol{j}}(\boldsymbol{r}) := \frac{1}{2\mathrm{i}} \sum_\sigma \left\{ \widehat{\psi}_\sigma^\dagger(\boldsymbol{r}) \boldsymbol{\nabla}_{\boldsymbol{r}} \widehat{\psi}_\sigma(\boldsymbol{r}) - \left[\boldsymbol{\nabla}_{\boldsymbol{r}} \widehat{\psi}_\sigma^\dagger(\boldsymbol{r}) \right] \widehat{\psi}_\sigma(\boldsymbol{r}) \right\} \tag{1.68}$$

and the expectation value thereof reads

$$\boldsymbol{j}(\boldsymbol{r}, t) = \left\langle \widehat{\boldsymbol{j}}(\boldsymbol{r}) \right\rangle_t. \tag{1.69}$$

We find with

$$\begin{aligned}
\frac{\partial n(\boldsymbol{r}, t)}{\partial t} &= \left\langle \frac{\partial}{\partial t} \sum_\sigma \widehat{\psi}_{\sigma,\mathrm{H}}^\dagger(\boldsymbol{r}, t) \widehat{\psi}_{\sigma,\mathrm{H}}(\boldsymbol{r}, t) \right\rangle_0 = -\mathrm{i} \left\langle [\widehat{n}_\mathrm{H}(\boldsymbol{r}, t), \widehat{H}_\mathrm{H}(t)]_- \right\rangle_0 \\
&= -\mathrm{i} \left\langle [\widehat{n}(\boldsymbol{r}), \widehat{H}(t)]_- \right\rangle_t,
\end{aligned} \tag{1.70}$$

the **continuity equation** [11, 18]

$$\boxed{\frac{\partial}{\partial t} n(\boldsymbol{r}, t) + \boldsymbol{\nabla}_{\boldsymbol{r}} \boldsymbol{j}(\boldsymbol{r}, t) = 0.} \tag{1.71}$$

This is the **local balance equation for the number of particles**. By Gauss' law the continuity equation expresses the change of the number of particles in a certain volume by the flux of the current through the surface of the volume.

In order to calculate the time derivative of $\boldsymbol{j}(\boldsymbol{r}, t)$ we will calculate the commutator of the operator $\widehat{\boldsymbol{j}}(\boldsymbol{r})$ with $\widehat{H}(t)$ averaged over the time-dependent density matrix.
In a first step we calculate the commutator with the external potential operator $\widehat{V}(t)$,

$$\begin{aligned}
\left[\widehat{\boldsymbol{j}}(\boldsymbol{r}), \widehat{V}(t) \right]_- &= \int d^3 r' v(\boldsymbol{r}', t) \left[\widehat{\boldsymbol{j}}(\boldsymbol{r}), \widehat{n}(\boldsymbol{r}') \right]_- \\
&= -\mathrm{i} \left(\boldsymbol{\nabla}_{\boldsymbol{r}} v(\boldsymbol{r}, t) \right) \widehat{n}(\boldsymbol{r}).
\end{aligned} \tag{1.72}$$

The other commutators are

$$\begin{aligned}
\left[\widehat{\boldsymbol{j}}(\boldsymbol{r}), \widehat{V}_\mathrm{int} \right]_- &= \frac{1}{2} \int d^3 r' d^3 r'' v_\mathrm{int}(|\boldsymbol{r}' - \tilde{\boldsymbol{r}}|) \left[\widehat{\boldsymbol{j}}(\boldsymbol{r}), \widehat{\varrho}(\boldsymbol{r}', \boldsymbol{r}'') \right]_- \\
&= -\mathrm{i} \int d^3 r' \left(\boldsymbol{\nabla}_{\boldsymbol{r}} v_\mathrm{int}(|\boldsymbol{r} - \boldsymbol{r}'|) \right) \widehat{\varrho}(\boldsymbol{r}, \boldsymbol{r}'),
\end{aligned} \tag{1.73}$$

and

$$\begin{aligned}
\left[\widehat{j}_\nu(\boldsymbol{r}), \widehat{T} \right]_- &= -\frac{1}{2} \sum_{\sigma'} \int d^3 r' \left[\widehat{j}_\nu(\boldsymbol{r}), \widehat{\psi}_{\sigma'}^\dagger(\boldsymbol{r}') \boldsymbol{\nabla}_{\boldsymbol{r}'}^2 \widehat{\psi}_{\sigma'}(\boldsymbol{r}') \right]_- \\
&= -\frac{\mathrm{i}}{4} \sum_\sigma \left\{ \widehat{\psi}_\sigma^\dagger(\boldsymbol{r}) \left(\frac{\partial}{\partial r^\nu} \boldsymbol{\nabla}_{\boldsymbol{r}}^2 \widehat{\psi}_\sigma(\boldsymbol{r}) \right) - \left(\frac{\partial}{\partial r^\nu} \widehat{\psi}_\sigma^\dagger(\boldsymbol{r}) \right) \left(\boldsymbol{\nabla}_{\boldsymbol{r}}^2 \widehat{\psi}_\sigma(\boldsymbol{r}) \right) \right. \\
&\quad \left. - \left(\boldsymbol{\nabla}_{\boldsymbol{r}}^2 \widehat{\psi}_\sigma^\dagger(\boldsymbol{r}) \right) \left(\frac{\partial}{\partial r^\nu} \widehat{\psi}_\sigma(\boldsymbol{r}) \right) + \left(\frac{\partial}{\partial r^\nu} \boldsymbol{\nabla}_{\boldsymbol{r}}^2 \widehat{\psi}_\sigma^\dagger(\boldsymbol{r}) \right) \widehat{\psi}_\sigma(\boldsymbol{r}) \right\}.
\end{aligned} \tag{1.74}$$

With the help of the **momentum-stress-tensor**

$$
\widehat{T}_{\mu\nu}(\boldsymbol{r}) \;:=\; \frac{1}{2} \sum_\sigma \left\{ \left(\frac{\partial}{\partial r^\mu} \widehat{\psi}_\sigma^\dagger(\boldsymbol{r}) \right) \frac{\partial}{\partial r^\nu} \widehat{\psi}_\sigma(\boldsymbol{r}) + \left(\frac{\partial}{\partial r^\nu} \widehat{\psi}_\sigma^\dagger(\boldsymbol{r}) \right) \frac{\partial}{\partial r^\mu} \widehat{\psi}_\sigma(\boldsymbol{r}) \right.
$$
$$
\left. - \frac{1}{2} \frac{\partial^2}{\partial r^\mu \partial r^\nu} \left(\widehat{\psi}_\sigma^\dagger(\boldsymbol{r}) \widehat{\psi}_\sigma(\boldsymbol{r}) \right) \right\}, \tag{1.75}
$$

which is a symmetric second rank tensor, we may rewrite the last commutator:

$$
\left[\widehat{j}_\nu(\boldsymbol{r}), \widehat{T} \right]_- = -\mathrm{i} \sum_\mu \frac{\partial}{\partial r^\mu} \widehat{T}_{\mu\nu}(\boldsymbol{r}) = -\mathrm{i} \partial_\mu \widehat{T}_{\mu\nu}(\boldsymbol{r}). \tag{1.76}
$$

Here we have introduced the abbreviation $\frac{\partial}{\partial r^\mu} \equiv \partial_\mu$ and the Einstein-convention, i.e., we sum over multiple indices. The interaction expression is accordingly

$$
\left[\widehat{j}_\nu(\boldsymbol{r}), \widehat{V}_{\mathrm{int}} \right]_- = \int d^3 r' \; (\partial_\nu v_{\mathrm{int}}(|\boldsymbol{r} - \boldsymbol{r}'|)) \, \widehat{\varrho}(\boldsymbol{r}, \boldsymbol{r}') =: \widehat{V}_{\mathrm{int}\,\nu}(\boldsymbol{r}). \tag{1.77}
$$

One may rewrite the above expression as the divergence of a symmetric second rank tensor. This form has the advantage to immediately reveal the quantum version of Newton's third law, as will be shown below. The derivation of the divergence form makes use of the symmetry of $\widehat{\varrho}(\boldsymbol{r}, \boldsymbol{r}')$:

$$
\begin{aligned}
\left[\widehat{j}_\nu(\boldsymbol{r}), \widehat{V}_{\mathrm{int}} \right]_- &= -\mathrm{i} \int d^3 r' \, (\partial_\nu v_{\mathrm{int}}(|\boldsymbol{r} - \boldsymbol{r}'|)) \, \widehat{\varrho}(\boldsymbol{r}, \boldsymbol{r}') \tag{1.78} \\[4pt]
&= -\frac{\mathrm{i}}{2} \int d^3 r' \, (\partial'_\nu v_{\mathrm{int}}(|\boldsymbol{r}'|)) \left[\widehat{\varrho}(\boldsymbol{r} - \boldsymbol{r}', \boldsymbol{r}) + \widehat{\varrho}(\boldsymbol{r}, \boldsymbol{r} - \boldsymbol{r}') \right] \\[4pt]
&= \frac{\mathrm{i}}{2} \int d^3 r' \, (\partial'_\nu v_{\mathrm{int}}(|\boldsymbol{r}'|)) \left[\widehat{\varrho}(\boldsymbol{r} + \boldsymbol{r}', \boldsymbol{r}) - \widehat{\varrho}(\boldsymbol{r}, \boldsymbol{r} - \boldsymbol{r}') \right].
\end{aligned}
$$

In deriving the third line, we employed a change of integration-variable $\boldsymbol{r}' \to -\boldsymbol{r}'$ for $\widehat{\varrho}(\boldsymbol{r} - \boldsymbol{r}', \boldsymbol{r})$. With the translation operator,

$$
e^{r'^\mu \partial_\mu} \widehat{\varrho}(\boldsymbol{r}, \boldsymbol{r} - \boldsymbol{r}') = \widehat{\varrho}(\boldsymbol{r} + \boldsymbol{r}', \boldsymbol{r}), \tag{1.79}
$$

and the operator identity

$$
e^{r'^\mu \partial_\mu} - 1 = \int_0^1 d\lambda \, r'^\mu \partial_\mu e^{\lambda r'^\mu \partial_\mu}, \tag{1.80}
$$

we may rewrite

$$
\begin{aligned}
\left[\widehat{j}_\nu(\boldsymbol{r}), \widehat{V}_{\mathrm{int}} \right]_- &= \frac{\mathrm{i}}{2} \int d^3 r' \left(e^{r'^\mu \partial_\mu} - 1 \right) (\partial'_\nu v_{\mathrm{int}}(|\boldsymbol{r}'|)) \, \widehat{\varrho}(\boldsymbol{r}, \boldsymbol{r} - \boldsymbol{r}') \\[4pt]
&= \frac{\mathrm{i}}{2} \int d^3 r' \, r'^\mu \partial_\mu \, (\partial'_\nu v_{\mathrm{int}}(|\boldsymbol{r}'|)) \int_0^1 d\lambda \, \widehat{\varrho}(\boldsymbol{r} + \lambda \boldsymbol{r}', \boldsymbol{r} - (1 - \lambda)\boldsymbol{r}') \\[4pt]
&= -\mathrm{i} \partial_\mu \widehat{W}_{\mu\nu}(\boldsymbol{r}) \tag{1.81}
\end{aligned}
$$

with the **interaction-stress-tensor** [20]

$$\widehat{W}_{\mu\nu}(\boldsymbol{r}) := -\frac{1}{2} \int d^3r' \frac{r'^{\nu}r'^{\mu}}{|\boldsymbol{r'}|} \frac{\partial v_{\text{int}}(|\boldsymbol{r'}|)}{\partial |\boldsymbol{r'}|} \int_0^1 d\lambda\, \widehat{\varrho}(\boldsymbol{r} + \lambda\boldsymbol{r'}, \boldsymbol{r} - (1-\lambda)\boldsymbol{r'}). \qquad (1.82)$$

The parameter λ is the natural parameter of the geodesic that connects two interacting particles [20]. In the laboratory (Eulerian) reference frame, i.e., the frame is fixed while the system is moving, the geodesics are simply straight lines. Later on we will change to a moving reference frame in which the geodesics will not be straight lines anymore.

The expectation value taken with the density matrix $\widehat{\rho}(t)$ then leads to [11, 18]

$$\boxed{\frac{\partial}{\partial t} j_\nu(\boldsymbol{r}, t) = -n(\boldsymbol{r}, t)\partial_\nu v(\boldsymbol{r}, t) - \partial_\mu \underbrace{\left\langle \widehat{T}_{\mu\nu}(\boldsymbol{r}) \right\rangle_t}_{=:T_{\mu\nu}(\boldsymbol{r}, t)} - \partial_\mu \underbrace{\left\langle \widehat{W}_{\mu\nu}(\boldsymbol{r}) \right\rangle_t}_{=:W_{\mu\nu}(\boldsymbol{r}, t)}.} \qquad (1.83)$$

This is a **local force balance equation**, a local quantum version of Newton's third law. The internal integral forces, the kinetic force $\partial_\mu T_{\mu\nu}(\boldsymbol{r}, t)$ and the interaction force $\partial_\mu W_{\mu\nu}(\boldsymbol{r}, t)$, due to their form as divergences obey

$$\int d^3r\, \partial_\mu \underbrace{(T_{\mu\nu}(\boldsymbol{r}, t) + W_{\mu\nu}(\boldsymbol{r}, t))}_{=:\Pi_{\mu\nu}(\boldsymbol{r}, t)} = 0. \qquad (1.84)$$

Thus the integral kinetic and integral interaction forces become zero. The symmetric second rank tensor $\Pi_{\mu\nu}(\boldsymbol{r}, t)$ represents the local internal stress in the quantum fluid.

The local balance equation for the number of particles (1.71), i.e., the continuity equation and the local force balance equation (1.83) form the basis of the **fluid dynamical description of the quantum many-body problem** [10]. We will show, by fixing the initial state, the boundary condition of the external potentials and by assuming a density Taylor-expandable at $t = t_0$, equations (1.71) and (1.83) determine the current and the density uniquely. The tensor of internal stress $\Pi_{\mu\nu}(\boldsymbol{r}, t)$ is shown to be an operator of the density as well as the current. Thus equations (1.71) and (1.83) can be seen as a formally closed system of equations fixing the dynamics of the collective variables $n(\boldsymbol{r}, t)$ and $\boldsymbol{j}(\boldsymbol{r}, t)$. The velocity $\boldsymbol{v}(\boldsymbol{r}, t) := \boldsymbol{j}(\boldsymbol{r}, t)/n(\boldsymbol{r}, t)$ may be used as collective variable too.

Before we turn to the derivation of the extendend Runge-Gross proof, which will also form the basis of our time-dependent density functional theory formulation, we rewrite the fundamental equations of the fluid dynamical description [20, 21]. We separate the contribution of the convective motion of the particles to the tensor $\Pi_{\mu\nu}(\boldsymbol{r}, t)$, i.e.,

$$C_{\mu\nu}(\boldsymbol{r}, t) := n(\boldsymbol{r}, t)v_\mu(\boldsymbol{r}, t)v_\nu(\boldsymbol{r}, t). \qquad (1.85)$$

This is the **macroscopic momentum-flow tensor**, where $v_\mu(\boldsymbol{r}, t) = j_\mu(\boldsymbol{r}, t)/n(\boldsymbol{r}, t)$. If we further define the convective derivative

$$D_t := \frac{\partial}{\partial t} + \boldsymbol{v}(\boldsymbol{r}, t) \cdot \boldsymbol{\nabla}_{\boldsymbol{r}} \qquad (1.86)$$

we can rewrite the **continuity equation**,

$$\boxed{D_t n + n\partial_\mu v_\mu = 0}\,, \tag{1.87}$$

and the **local force balance equation**,

$$\boxed{n D_t v_\nu + \partial_\mu P_{\mu\nu} + n\partial_\nu v_{\text{ext}} = 0}\,. \tag{1.88}$$

Note that we introduced the subindex 'ext' to the external potential to distinguish between the velocity vector field $\boldsymbol{v}$ and the external potential. The exact **stress tensor** is defined by

$$P_{\mu\nu}(\boldsymbol{r}, t) = \breve{T}_{\mu\nu}(\boldsymbol{r}, t) + W_{\mu\nu}(\boldsymbol{r}, t) \tag{1.89}$$

with the kinetic part as

$$\breve{T}_{\mu\nu}(\boldsymbol{r}, t) = \frac{1}{2}\sum_\sigma \left\langle (q_\mu\widehat{\psi}_\sigma)^\dagger q_\nu\widehat{\psi}_\sigma + (q_\nu\widehat{\psi}_\sigma)^\dagger q_\mu\widehat{\psi}_\sigma - \frac{1}{2}\partial_\mu\partial_\nu(\widehat{\psi}_\sigma^\dagger\widehat{\psi}_\sigma) \right\rangle_t \tag{1.90}$$

and $q_\mu = -\mathrm{i}\partial_\mu - v_\mu$, which accounts for the separation of the macroscopic convective motion. Since the convective motion has been split from $\Pi_{\mu\nu}(\boldsymbol{r}, t) = P_{\mu\nu}(\boldsymbol{r}, t) + C_{\mu\nu}(\boldsymbol{r}, t)$ only the relative motion of the particles contribute to $P_{\mu\nu}(\boldsymbol{r}, t)$. This form will later on be used to rewrite the problem in a Lagrangian noninertial reference frame from which one can deduce approximations of interest.

1.2.2 Extendend Runge-Gross Theorem

After having formulated the continuity equation (1.71) and the local force balance equation (1.83) we turn to the famous **Runge-Gross (Runge-Gross) theorem** [10]. However, we will adopt an extendend version thereof introduced by van Leeuwen in [23]. Extensive use will be made of the second quantization, introduced in section 1.1. Note that in the original Runge-Gross proof no restriction to analytic densities in time was made. We will examine the question how the density and the current-density of a general many-body system are connected to the interaction potential $v_{\text{int}}(|\boldsymbol{r} - \boldsymbol{r}'|)$ and the external potential $v(\boldsymbol{r}, t)$. In particular one may ask if there is only one external potential generating a given time-dependent density for a chosen interaction potential and initial state. Is it possible to generate a physical (interacting) time-dependent density via some special external potential acting on an auxiliary (noninteracting) system?

Proof. In a first step we will take the divergence of (1.83) and use the continuity equation to find

$$\frac{\partial^2}{\partial t^2} n(\boldsymbol{r}, t) = \boldsymbol{\nabla}_{\boldsymbol{r}} \cdot [n(\boldsymbol{r}, t)\boldsymbol{\nabla}_{\boldsymbol{r}} v(\boldsymbol{r}, t)] + \underbrace{\partial_\nu\partial_\mu\Pi_{\mu\nu}(\boldsymbol{r}, t)}_{=:q(\boldsymbol{r}, t)}. \tag{1.91}$$

This will be our basic equation. We will only consider finite systems with external potentials bounded at infinity. $q(\boldsymbol{r}, t)$ decays exponentially at infinity if the density does. Assume now we have solved the many-body problem for the Hamiltonian

$$\widehat{H}(t) = \widehat{T} + \widehat{V}_{\text{int}} + \widehat{V}(t) \tag{1.92}$$

and the initial density matrix $\widehat{\rho}_0$ at time $t = t_0$. We have found the time-dependent density matrix $\widehat{\rho}(t)$ and the density $n(\boldsymbol{r}, t)$. For a second system with the Hamiltonian

$$\widehat{H}'(t) = \widehat{T} + \widehat{V}'_{\text{int}} + \widehat{V}'(t), \tag{1.93}$$

having a different external potential and interaction operator, we assume the solution for an initial density matrix ρ'_0 at $t = t_0$ being $\rho'(t)$. The interaction operator $\widehat{V}'_{\text{int}}$ is chosen such that its expectation value and its derivatives are finite. For both systems equation (1.91) is fulfilled. For the second system we thus find

$$\frac{\partial^2}{\partial t^2} n'(\boldsymbol{r}, t) = \boldsymbol{\nabla}_{\boldsymbol{r}} \cdot [n'(\boldsymbol{r}, t) \boldsymbol{\nabla}_{\boldsymbol{r}} v'(\boldsymbol{r}, t)] + \underbrace{\partial_\nu \partial_\mu \Pi'_{\mu\nu}(\boldsymbol{r}, t)}_{=:q'(\boldsymbol{r}, t)}, \tag{1.94}$$

with the local internal stress tensor $\widehat{\Pi}'_{\mu\nu}(\boldsymbol{r})$ redefined accordingly.

Now we will ask the question:

> Can we find an external potential $v'(\boldsymbol{r}, t)$ for a given interaction potential $v'_{\text{int}}(|\boldsymbol{r} - \boldsymbol{r}'|)$ which will lead to the same time-dependent density $n(\boldsymbol{r}, t)$ as the initial system Hamiltonian $\widehat{H}(t)$?

We require

$$n(\boldsymbol{r}, t_0) = \text{tr}\,(\widehat{\rho}_0\,\widehat{n}(\boldsymbol{r})) \overset{!}{=} \text{tr}\,(\widehat{\rho}'_0\,\widehat{n}(\boldsymbol{r})) = n'(\boldsymbol{r}, t_0). \tag{1.95}$$

Both initial configurations should lead to the same initial density. We use equation (1.94) to relate the different systems. This equation is a second order partial differential equation in time. Therefore a second initial condition has to be posed:

$$\left.\frac{\partial}{\partial t} n(\boldsymbol{r}, t)\right|_{t=t_0} = \text{tr}\left(\widehat{\rho}_0\,\boldsymbol{\nabla}_{\boldsymbol{r}} \cdot \widehat{\boldsymbol{j}}(\boldsymbol{r})\right) \overset{!}{=} \text{tr}\left(\widehat{\rho}'_0\,\boldsymbol{\nabla}_{\boldsymbol{r}} \cdot \widehat{\boldsymbol{j}}(\boldsymbol{r})\right) = \left.\frac{\partial}{\partial t} n'(\boldsymbol{r}, t)\right|_{t=t_0}. \tag{1.96}$$

Furthermore we will use the abbreviation

$$f^{(k)}(\boldsymbol{r}) = \left.\frac{\partial^k}{\partial t^k} f(\boldsymbol{r}, t)\right|_{t=t_0} \tag{1.97}$$

for the k-th time derivative of some function $f(\boldsymbol{r}, t)$ at time $t = t_0$. As an important restriction we assume the **reference density** $n(\boldsymbol{r}, t)$ **to be analytic at** $t = t_0$, i.e., within a nonzero radius of convergence the density is exactly defined via its Taylor series

$$n(\boldsymbol{r}, t) = \sum_{k=0}^{\infty} \frac{1}{k!}\, n^{(k)}(\boldsymbol{r})(t - t_0)^k. \tag{1.98}$$

We will now choose an external potential $v'(\boldsymbol{r}, t)$ such that

$$n'^{(k)}(\boldsymbol{r}) = n^{(k)}(\boldsymbol{r}) \tag{1.99}$$

holds for all $k > 1$. This can be done using equation (1.94). In a first step we have for the local force balance equation at $t = t_0$

$$n'^{(2)}(\boldsymbol{r}) = \boldsymbol{\nabla}_{\boldsymbol{r}} \cdot \left[n'^{(0)}(\boldsymbol{r}) \boldsymbol{\nabla}_{\boldsymbol{r}} v'^{(0)}(\boldsymbol{r}) \right] + q'^{(0)}(\boldsymbol{r}). \tag{1.100}$$

Here we have the initial condition $n'^{(0)}(\boldsymbol{r}) = n^{(0)}(\boldsymbol{r})$ and

$$q'^{(0)}(\boldsymbol{r}) = \mathrm{tr} \left(\widehat{\rho}'_0 \, \left(\partial_\nu \partial_\mu \widehat{\Pi}'_{\mu\nu}(\boldsymbol{r}) \right) \right) \tag{1.101}$$

with the initial density matrix $\widehat{\rho}'_0$. If we demand

$$n'^{(2)}(\boldsymbol{r}) \overset{!}{=} n^{(2)}(\boldsymbol{r}) \tag{1.102}$$

the above equation defines $v'^{(0)}(\boldsymbol{r})$ via

$$\boldsymbol{\nabla}_{\boldsymbol{r}} \cdot \left[n^{(0)}(\boldsymbol{r}) \boldsymbol{\nabla}_{\boldsymbol{r}} v'^{(0)}(\boldsymbol{r}) \right] = n^{(2)}(\boldsymbol{r}) - q'^{(0)}(\boldsymbol{r}). \tag{1.103}$$

This equation is of Sturm-Liouville type. For a given boundary condition it has a unique solution if a solution exists. We will choose $v'^{(0)}(\boldsymbol{r}) \to 0$ for $|\boldsymbol{r}| \to \infty$. Thus also the gauge is fixed. Otherwise we have a solution modulo a constant c. With this choice of the initial potential we have guaranteed by construction that $n'^{(2)}(\boldsymbol{r}) = n^{(2)}(\boldsymbol{r})$, which we will also need later on. To construct $v'^{(1)}(\boldsymbol{r})$ we differentiate equation (1.94) at $t = t_0$ leading to

$$
\begin{aligned}
\boldsymbol{\nabla}_{\boldsymbol{r}} \cdot \left[n'^{(0)}(\boldsymbol{r}) \boldsymbol{\nabla}_{\boldsymbol{r}} v'^{(1)}(\boldsymbol{r}) \right] &= n'^{(3)}(\boldsymbol{r}) - q'^{(1)}(\boldsymbol{r}) \\
&\quad - \boldsymbol{\nabla}_{\boldsymbol{r}} \cdot \left[n'^{(1)}(\boldsymbol{r}) \boldsymbol{\nabla}_{\boldsymbol{r}} v'^{(0)}(\boldsymbol{r}) \right],
\end{aligned}
\tag{1.104}
$$

with

$$q'^{(1)}(\boldsymbol{r}) = \frac{\partial}{\partial t} q'(\boldsymbol{r}, t) \Big|_{t=t_0} = -\mathrm{i}\, \mathrm{tr} \left(\widehat{\rho}'_0 \, \left[\partial_\nu \partial_\mu \widehat{\Pi}'_{\mu\nu}(\boldsymbol{r}), \widehat{H}'_0 \right]_{-} \right), \tag{1.105}$$

and $H'_0 := \widehat{T} + \widehat{V}'_{\mathrm{int}} + \widehat{V}'(t) \Big|_{t=t_0}$ in accordance with equation (1.59). With the initial conditions (1.95) and (1.96) and the requirement

$$n'^{(3)}(\boldsymbol{r}) \overset{!}{=} n^{(3)}(\boldsymbol{r}), \tag{1.106}$$

the right hand side of equation (1.104) is known, and by imposing the same boundary condition as before we fix $v'^{(1)}(\boldsymbol{r})$ uniquely. In the next step we differentiate equation (1.94) two times. Here we will find a term of the form $\boldsymbol{\nabla}_{\boldsymbol{r}} \cdot \left[n'^{(2)}(\boldsymbol{r}) \boldsymbol{\nabla}_{\boldsymbol{r}} v'^{(0)}(\boldsymbol{r}) \right]$. However, via the first step of our construction we guarantee that $n'^{(2)}(\boldsymbol{r}) = n^{(2)}(\boldsymbol{r})$ holds, leading again to the same kind of differential equation and to a uniquely defined $v'^{(2)}(\boldsymbol{r})$. For the k-th derivative of equation (1.94) we thus find

$$n'^{(k+2)}(\boldsymbol{r}) = q'^{(k)}(\boldsymbol{r}) + \sum_{l=0}^{k} \binom{k}{l} \boldsymbol{\nabla}_{\boldsymbol{r}} \cdot \left[n'^{(k-l)}(\boldsymbol{r}) \boldsymbol{\nabla}_{\boldsymbol{r}} v'^{(l)}(\boldsymbol{r}) \right]. \tag{1.107}$$

By imposing the condition

$$n'^{(k+2)}(\boldsymbol{r}) \overset{!}{=} n^{(k+2)}(\boldsymbol{r}) \tag{1.108}$$

we end up with

$$
\begin{aligned}
\boldsymbol{\nabla}_{\boldsymbol{r}} \cdot \left[n'^{(0)}(\boldsymbol{r}) \boldsymbol{\nabla}_{\boldsymbol{r}} v'^{(k)}(\boldsymbol{r}) \right] &= n^{(k+2)}(\boldsymbol{r}) - q'^{(k)}(\boldsymbol{r}) \\
&\quad - \sum_{l=0}^{k-1} \binom{k}{l} \boldsymbol{\nabla}_{\boldsymbol{r}} \cdot \left[n'^{(k-l)}(\boldsymbol{r}) \boldsymbol{\nabla}_{\boldsymbol{r}} v'^{(l)}(\boldsymbol{r}) \right].
\end{aligned}
\tag{1.109}
$$

The right hand side of equation (1.109) is fixed. The terms $v'^{(l)}(\boldsymbol{r})$ for $l < k$ were previously defined and $q'^{(k)}(\boldsymbol{r})$ can be computed by multiple commutators of $\partial_\nu \partial_\mu \widehat{\Pi}'_{\mu\nu}(\boldsymbol{r})$ with the time derivatives of the Hamiltonian $\widehat{H}(t)$ at time $t = t_0$ up to order $k - 1$, i.e., successive application of the Heisenberg equation. With the chosen boundary conditions $v'^{(k)}(\boldsymbol{r})$ is uniquely determined. Finally we have generated the formal Taylor expansion of the exact external potential

$$v'(\boldsymbol{r}, t) = \sum_{k=0}^{\infty} \frac{1}{k!} \, v'^{(k)}(\boldsymbol{r})(t - t_0)^k \tag{1.110}$$

which determines the potential within its radius of convergence. As we have assumed a reference density $n(\boldsymbol{r}, t)$ analytic at $t = t_0$ and hence we can disregard a possible zero convergence radius. For a finite convergence radius we may propagate $\widehat{\rho}'_0$ until some time t_1 within the region of convergence, ending up with $\widehat{\rho}'(t_1)$. This density matrix may now be used as a new initial configuration and the above procedure can be repeated. This amounts to an analytic continuation along the real time-axis. $\square$

Theorem 1.2.1 (Extended Runge-Gross Uniqueness Theorem) *Let $n(\boldsymbol{r}, t)$, the density of a general many-body system with Hamiltonian $\widehat{H}(t) = \widehat{T} + \widehat{V}_{\mathrm{int}} + \widehat{V}(t)$ and initial configuration $\widehat{\rho}_0$, be analytic at $t = t_0$. For a system with interaction $\widehat{V}'_{\mathrm{int}}$ and the initial configuration $\widehat{\rho}'_0$ subject to the constraints*

$$
\begin{aligned}
n(\boldsymbol{r}, t_0) &= n'(\boldsymbol{r}, t_0), \\
\mathrm{tr}\left(\widehat{\rho}_0 \, \boldsymbol{\nabla}_{\boldsymbol{r}} \cdot \widehat{\boldsymbol{j}}(\boldsymbol{r}) \right) &= \mathrm{tr}\left(\widehat{\rho}'_0 \, \boldsymbol{\nabla}_{\boldsymbol{r}} \cdot \widehat{\boldsymbol{j}}(\boldsymbol{r}) \right),
\end{aligned}
$$

the external potential $v'(\boldsymbol{r}, t)$ and Hamiltonian $\widehat{H}'(t)$ leading to the same density is uniquely defined.

What are the consequences? If we have two systems with different particle-particle interactions and we find an initial configuration for each of those systems fulfilling the above requirements we know that there are uniquely defined external potentials leading to the same density in both systems at later times. Especially if we assume the second system to be noninteracting, i.e., $\widehat{V}'_{\mathrm{int}} \equiv 0$, we are formally able to exactly reproduce the density of an interacting system provided we find an appropriate initial configuration for the noninteracting system. Now suppose we have two different initial configurations, both leading

to the same initial density and the first time derivative thereof. Further, both are subject to the same interaction, i.e., $\widehat{V}_{\text{int}} = \widehat{V}'_{\text{int}}$. Then we realize, if we propagate the two different initial configurations with the same (analytic) external potential, that both systems will have the same (analytic) density, although their time-dependent density matrices will not be the same.

Now we can proof the possibility of a formally closed **quantum fluid dynamical description**:

Proof. From the continuity (1.71) and the local force balance equation (1.83) we deduced the fundamental relation (1.91) used to proof the Runge-Gross theorem. An analytic density determines uniquely the corresponding external potential and vice versa if the initial configuration is fixed, leading to an invertible mapping [10]

$$v_{\widehat{\rho}_0} : n(\boldsymbol{r}, t) \mapsto v(\boldsymbol{r}, t). \tag{1.111}$$

One could reformulate this statement in terms of the current-density as well. Thus both collective variables are equivalent as well as combinations thereof like the velocity. From the solution of the von Neumann equation we have a mapping

$$\widetilde{\rho}_{\widehat{\rho}_0} : v(\boldsymbol{r}, t) \mapsto \widehat{\rho}(t) \tag{1.112}$$

(in the original Runge-Gross paper the mappings were denoted as $v_{\widehat{\rho}_0} = G^{-1}$ and $\widetilde{\rho} = F$). If no special gauge was chosen we would have a mapping onto a class of density matrices

$$[\widehat{\rho}(t)] := \{\rho'(t) = \exp[-\mathrm{i}\,\alpha(t)]\widehat{\rho}(t)|\ \alpha(t) \text{ purely time-dependent function}\}$$

corresponding to the definition of a class of external potentials

$$[v] := \{v' = v + c(t)|c(t) \text{ purely time-dependent function}\},$$

with $\partial_t \alpha(t) = c(t)$. A composition of both mappings then leads to

$$\widetilde{\rho}_{\widehat{\rho}_0} \circ v_{\widehat{\rho}_0} : n(\boldsymbol{r}, t) \mapsto \widehat{\rho}_{\widehat{\rho}_0}(t). \tag{1.113}$$

Therefore the density (with the initial configuration and the choice of gauge) determines the associated density matrix. We may consider the density matrix $\widehat{\rho}_{\widehat{\rho}_0}([n]; t)$ to be an operator of the density or another collective variable. Hence every expectation value of an observable may also be considered an operator of the density, especially, the local internal stress

$$\Pi_{\mu\nu}([n]; \boldsymbol{r}, t) = \mathrm{tr}\left(\widehat{\rho}_{\widehat{\rho}_0}([n]; t)\widehat{\Pi}_{\mu\nu}(\boldsymbol{r})\right) \tag{1.114}$$

is defined by the density $n(\boldsymbol{r}, t)$. Therefore we have a formally closed set of quantum fluid dynamical equations, i.e., the continuity equation (1.71) and the local force balance equation (1.83), as long as we consider densities which are analytic at $t = t_0$ and fix the initial condition as well as the gauge. $\square$

The deduced Runge-Gross theorem forms the basis of time-dependent density functional

theory. It is obvious that the density functional description is intimately related to a fluid dynamical description. This was already noted in the second Runge-Gross theorem [10]. In fact, the quantum fluid dynamical reformulation is part of the density functional formalism of time-dependent problems. The time-independent density functional theory may be interpreted as exact quantum hydrostatics [20, 21].

1.3 Time-Dependent Density Functional Theory

Time-dependent density functional theory is a formally exact way to treat the quantum many-body problem. Instead of the wavefunction on the configuration space $\mathbb{R}^{3N}$ one deals with the one-particle density on $\mathbb{R}^3$, independent of the number of particles (N) involved. This offers a computationally more favorable way to handle strongly perturbed complex systems as the effort for a wavefunction-based ab initio solution of the multi-particle problem grows exponentially [1] with the number of particles. The usual way to do time-dependent density functional theory calculations is by adopting the time-dependent Kohn-Sham scheme. The Runge-Gross theorem does prove that under certain conditions there is a one-to-one correspondence between the density and the external potential, and that one is in principle able to model a physical (interacting) many-body system by a non-interacting system. This noninteracting problem describing a physical system then can be solved via a set of nonlinear, selfconsistent differential equations, called the Kohn-Sham equations. The effort for the solution of the Kohn-Sham equations only scales linearly with the number of particles [1]. However, the main problem of time-dependent density functional theory in practice lies in the formulation of the Kohn-Sham equations and the approximations, which ultimately have to be made.

We will begin by introducing the derivatives of nonlinear mappings and their mathematical implications. Then a short introduction into ground-state density functional theory will be given with emphasis on fundamental issues. The problem of v-representability and related questions will be posed, which are of interest for time-dependent density functional theory. The mathematically sound derivation of ground-state density functional theory will be used as a guiding line for a proper formulation of time-dependent density functional theory. The problems associated with an action functional are considered and some approximations for the exchange-correlation potential are discussed. Further we consider the nonlocality in time of the potentials expressed via the density, which is usually termed "quantum memory". Finally also recently published criticism of the fundaments on the theory is addressed.

1.3.1 Differentiation of Nonlinear Mappings

We will now introduce the derivatives of (nonlinear) mappings between real Banach spaces. They are of fundamental importance in density functional theory as well as time-dependent density functional theory.

Let $\mathcal{B}_a$ and $\mathcal{B}_b$ be two real Banach spaces with norm $\|.\|_a$ and $\|.\|_b$, respectively. Note that most of the following theorems and lemmas are true also for normed vector spaces without completeness [24]. Let further denote with $\mathcal{L}(\mathcal{B}_a, \mathcal{B}_b)$ the space of all linear mappings between $\mathcal{B}_a$ and $\mathcal{B}_b$, which itself is a real Banach space.

Definition 1.3.1 *Let $\mathcal{U} \subset \mathcal{B}_a$ be nonempty and open, $f : \mathcal{U} \to \mathcal{B}_b$.*

1. *f is called **Gâteaux differentiable** at $x_0 \in \mathcal{U}$ if there exists a continuous linear operator $T \in \mathcal{L}(\mathcal{B}_a, \mathcal{B}_b)$ which satisfies*

$$\lim_{\epsilon \to 0} \frac{f[x_0 + \epsilon h] - f[x_0]}{\epsilon} = T[h] \tag{1.115}$$

*for all $h \in \mathcal{B}_a$. The operator T is called the **Gâteaux derivative** of the operator f at x_0. We denote*

$$df[x_0; .] := T[.]. \tag{1.116}$$

2. *f is called **Fréchet differentiable** at $x_0 \in \mathcal{U}$ if the convergence in (1.115) is uniform with respect to $h \in \{\widetilde{h} \in \mathcal{B}_a | \|\widetilde{h}\|_a \leq 1\}$. The operator T is then called the **Fréchet derivative** of the operator f at x_0. We denote*

$$Df[x_0; .] := T[.]. \tag{1.117}$$

Some definitions of the Gâteaux derivative do not pose the condition of linearity. However, there are sufficient conditions for the linearity of this derivative known [25]. Note that the derivative of f at some position is a linear operator, mapping the initial Banach space onto a second one. The Gâteaux (Fréchet) derivative $d(D)f : \mathcal{U} \to \mathcal{L}(\mathcal{B}_a, \mathcal{B}_b)$, however, is an operator-valued mapping. df is the functional analogon to the partial derivative of ordinary analysis. $df[x_0; h]$ is the Gâteaux differential at x_0 in direction h. The Fréchet derivative Df is the generalization of the total derivative. It reflects the idea of linear approximation of an operator. The Fréchet derivative is continuous in x_0 whereas for a Gâteaux derivative this is not guaranteed. Further it is obvious that if the Fréchet derivative exists the Gâteaux derivative exists as well and $Df = df$. The converse is not true in general.

The functional derivatives are linear operators between spaces of functions. Under certain conditions these linear operators can be represented in terms of an integral operator

$$df([x_0; h]; r) = \int_{\Omega'} d\mu'(r') \left. \frac{\delta f([x]; r)}{\delta x(r')} \right|_{x=x_0} h(r') \tag{1.118}$$

where we have assumed $r' \in \Omega'$ of $\mathcal{B}_a = \mathcal{B}_a(\Omega')$, $r \in \Omega$ of $\mathcal{B}_b = \mathcal{B}_b(\Omega)$ and an associated integral measure $d\mu'$. In physics the kernel of the integral operator

$$\left. \frac{\delta f([x]; r)}{\delta x(r')} \right|_{x=x_0} \tag{1.119}$$

is often referred to as the derivative of the operator f. In general it is assumed that if a mapping is differentiable it can be represented by the kernel of an integral operator.

The following lemma is also frequently found to be used as definition for the Fréchet derivative [25, 26].

Lemma 1.3.1 *Let $\mathcal{U} \subset \mathcal{B}_a$ be nonempty, open and $f : \mathcal{U} \to \mathcal{B}_b$ a mapping. Then f is* **Fréchet differentiable** *at $x_0 \in \mathcal{U}$ if and only if there exists a continuous linear operator $T \in \mathcal{L}(\mathcal{B}_a, \mathcal{B}_b)$ which satisfies*

$$f[x_0 + h] = f[x_0] + T[h] + R[x_0; h], \tag{1.120}$$

with

$$\lim_{\|h\|_a \to 0} \frac{R[x_0; h]}{\|h\|_a} = 0. \tag{1.121}$$
$$(\forall \epsilon > 0 \ \exists \delta > 0 : \|h\|_a \le \delta \Rightarrow \|R[x_0; h]\|_b \le \epsilon \|h\|_a)$$

The operator $R[x_0; .]$ is called the remainder of the derivative at x_0 and $T[.] = Df[x_0; .]$.

The proof for this lemma is on page 113 of [24].

A simple example for a Fréchet differentiable mapping is the following. Let $\mathcal{B}_a$ be some real Hilbert space with inner product $\langle .|. \rangle$ and $\mathcal{B}_b = \mathbb{R}$. For a linear continuous operator $\widehat{O} : \mathcal{B}_a \to \mathcal{B}_a$ we define the (bilinear) functional

$$
\begin{aligned}
f : \mathcal{B}_a &\to \mathbb{R} \\
x &\mapsto \langle x | \widehat{O} x \rangle.
\end{aligned}
\tag{1.122}
$$

We find $f[x + h] = f[x] + \langle \widehat{O}^* x + \widehat{O} x | h \rangle + f[h]$. The mapping $h \mapsto \langle \widehat{O}^* x + \widehat{O} x | h \rangle$ is a linear and continuous functional, and $f[h]$ is of second order in h. With the help of lemma (1.3.1) we find f to be Fréchet differentiable with

$$Df[x_0; h] = \langle \widehat{O}^* x_0 + \widehat{O} x_0 | h \rangle \tag{1.123}$$

for all $h \in \mathcal{B}_a$.

Theorem 1.3.1 *Let $\mathcal{B}_a, \mathcal{B}_b, \mathcal{B}_c$ be real Banach spaces and $\mathcal{U} \subset \mathcal{B}_a$ as well as $\mathcal{V} \subset \mathcal{B}_b$ be open.*

1. *If we have $f, g : \mathcal{U} \to \mathcal{V}$ Gâteaux differentiable at $x_0 \in \mathcal{U}$ then also $f + g$ and λf $(\lambda \in \mathbb{R})$ are differentiable with derivatives*

$$
\begin{aligned}
d(f + g)[x_0; .] &= df[x_0; .] + dg[x_0; .], \\
d(\lambda f)[x_0; .] &= \lambda df[x_0; .].
\end{aligned}
\tag{1.124}
$$

2. *(Mean value theorem) Let $f : \mathcal{U} \to \mathcal{V}$ be Gâteaux differentiable and let the "interval" $I = \{x_0 + \lambda h : 0 \le \lambda \le 1\}$ be part of $\mathcal{U}$. Then we find*

$$\|f[x_0 + h] - f[x_0]\|_b \le \sup_{\xi \in I} \|df[\xi; .]\| \|h\|_a, \tag{1.125}$$

   with $\|df[\xi; .]\| = \sup_{\|x\|_a \le 1} \|df[\xi; x]\|_b$ the associated operator norm.

3. *If $f : \mathcal{U} \to \mathcal{V}$ is Gâteaux differentiable and $df : \mathcal{U} \to \mathcal{L}(\mathcal{B}_a, \mathcal{B}_b)$ is continuous, then f is Fréchet differentiable and $df = Df$. We say f is continuously differentiable, $f \in C^1(\mathcal{U}, \mathcal{V})$.*

4. *(Chain rule) Let $f : \mathcal{U} \to \mathcal{V}$ and $g : \mathcal{V} \to \mathcal{B}_c$ with $f[\mathcal{U}] \subset \mathcal{V}$ be Gâteaux differentiable at $x_0 \in \mathcal{U}$ and $f[x_0] \in \mathcal{V}$. Then $g \circ f$ is Gâteaux differentiable at $x_0 \in \mathcal{U}$ with derivative*

$$d(g \circ f)[x_0; .] = dg[f[x_0]; .] \circ df[x_0; .] = dg[f[x_0]; df[x_0; .]]. \tag{1.126}$$

The proofs for the theorem are on page 121 of [24] and on page 398 of [26]. Of course the same properties also hold for Fréchet derivatives.

If we now introduce the concept of higher derivatives we will find a functional analogon to the theorem of Taylor.

If the Fréchet derivative $Df : \mathcal{U} \to \mathcal{L}(\mathcal{B}_a, \mathcal{B}_b)$ itself is Fréchet differentiable, we say f is twice Fréchet differentiable, i.e., $f \in C^2(\mathcal{U}, \mathcal{B}_b)$,

$$D^2 f : \mathcal{U} \to \mathcal{L}(\mathcal{B}_a, \mathcal{L}(\mathcal{B}_a, \mathcal{B}_b)). \tag{1.127}$$

It can be shown [24, 26] that there exists an isomorphism

$$\mathcal{L}(\mathcal{B}_a, \mathcal{L}(\mathcal{B}_a, \mathcal{B}_b)) \cong \mathcal{L}^{(2)}(\mathcal{B}_a, \mathcal{B}_b). \tag{1.128}$$

$\mathcal{L}^{(2)}(\mathcal{B}_a, \mathcal{B}_b)$ is the space of continuous mappings $\mathcal{B}_a \times \mathcal{B}_a$ onto $\mathcal{B}_b$. Thus we can associate the second Fréchet derivative with

$$D^2 f : \mathcal{U} \to \mathcal{L}^{(2)}(\mathcal{B}_a, \mathcal{B}_b), \tag{1.129}$$

and $D^2 f[x_0 : ., .]$ a continuous bilinear map. Higher derivatives are further defined as

$$D^n f : \mathcal{U} \to \mathcal{L}^{(n)}(\mathcal{B}_a, \mathcal{B}_b) \cong \mathcal{L}(\mathcal{B}_a, \mathcal{L}^{(n-1)}(\mathcal{B}_a, \mathcal{B}_b)), \tag{1.130}$$

with $D^{(n)} f[x_0; ., ..., .]$ a continuous n-times multilinear mapping.

Theorem 1.3.2 (Theorem of Taylor) *Let $f : \mathcal{U} \to \mathbb{R}$ be $(n+1)$-times Fréchet differentiable and $\{x_0 + \lambda h : 0 \leq \lambda \leq 1\} \subset \mathcal{U}$. Then there exists a $\vartheta \in]0, 1[$ with*

$$
\begin{aligned}
f[x_0 + h] &= f[x_0] + Df[x_0; h] + \frac{1}{2} D^2 f[x_0; h, h] + ... \\
&+ \frac{1}{n!} D^n f[x_0; h, ..., h] + \frac{1}{(n+1)!} D^{n+1} f[x_0 + \vartheta h; h, ..., h, h].
\end{aligned}
\tag{1.131}
$$

The proof is to be found on page 122 in [24].

As can be seen from the above theorems, many of the properties of ordinary analysis can be extended to the functional case. (Local) Extrema can be associated with zeros of the first functional derivative $df[x_0] = 0$ [24–26] and a fundamental theorem of calculus connecting functional derivatives and integration of functions with values in a Banach space can be found [26].

If a functional attains a local extremum on the boundary of the region of definition one can no longer use the afore defined functional derivatives. There the concept of variation is of interest.

Definition 1.3.2 *Let $\mathcal{M} \subset \mathcal{B}_a$ be a nonempty subset, $x_0 \in \mathcal{M}$ and $f : \mathcal{M} \to \mathbb{R}$. For $h \in \mathcal{B}_a$ suppose that there is an $r > 0$ such that $x_0 + \lambda h \in \mathcal{M}$ for all $0 \leq \lambda < r$. Then the n-th* **variation** *of f in the direction h is defined as*

$$\Delta^n f[x_0; h] = \frac{d^n}{d\lambda^n} f[x_0 + \lambda h]|_{\lambda=0} \tag{1.132}$$

if these derivatives exist.

It can then be shown [26] that if $x_0 \in \mathcal{M}$ is an interior point of $\mathcal{M}$ the Gâteaux derivative df exists if and only if the first variation $\Delta f[x_0; h]$ exists for all $h \in \mathcal{M}$ and

$$\Delta f[x_0; .] = df[x_0; .]. \tag{1.133}$$

For Fréchet differentiable functionals $f : \mathcal{U} \to \mathbb{R}$ one may formulate a constrained variational problem. If one has a constraint $g[x] = y_0$ with $g : \mathcal{U} \to \mathcal{B}_b$ and $y_0 \in \mathcal{B}_b$, one may look for extremal points of the functional $f|_{\mathcal{M}} : \mathcal{M} \to \mathbb{R}$ where $\mathcal{M} = \{x \in \mathcal{U} | g[x] = y_0\}$ is the level surface of g through the point y_0. This leads to tangent spaces of level surfaces and Lagrangian multipliers [26]. The example of interest will be the quantum mechanical energy functional $E_v[n]$, assumed to be differentiable under the constraint $\int n(x)dx = N$, i.e., conservation of the particle number.

1.3.2 Density Functional Theory

Ground-state density functional theory is a well established theory for calculating densities of atomic, molecular and solid state systems. The success of this theory, for which Walter Kohn was awarded the Nobel price in chemistry [1], is due to its rigorous foundation as well its applicability to all sorts of different physical problems. Even quantum electrodynamics may be reformulated in terms of a four-current density functional theory [9].

Hohenberg-Kohn Theory

The main idea of density functional theory is to find the (exact) ground-state density by minimization of the energy of the system. This idea is indeed much older than actual density functional theory and goes back to Thomas [27] and Fermi [28]. However, while those first attempts were of semi-empirical nature, Hohenberg and Kohn [29] were able to formulate a rigorous density functional approach to the many-body problem in quantum mechanics.

In this subsection, we will concentrate on time-independent Hamiltonians of the form (1.52), i.e., $\widehat{V} = \sum_i^N v(\boldsymbol{r}_i)$, with Coulombic interaction for a N-particle system. We will suppress the spin-degrees of freedom in what follows in order to keep the notation as simple as possible. Following reference [26] we assume the real-valued one-particle operator $v(\boldsymbol{r}) \in X = L^2(\mathbb{R}^3) + L^\infty(\mathbb{R}^3)$. This is a Banach space with norm

$$\|v\| = \inf\{\|v_1\|_2 + \|v_2\|_\infty | v_1 \in L^2(\mathbb{R}^3), v_2 \in L^\infty(\mathbb{R}^3), v = v_1 + v_2\} \tag{1.134}$$

and assures that $\widehat{H}$ is self-adjoint on the domain of the kinetic energy operator $\mathrm{dom}(\widehat{T}) = \{\Psi \in L^2(\mathbb{R}^{3N})|\widehat{T}\Psi < \infty\}$ in accordance to the Kato-Rellich theorem [26]. A Kato-perturbation $\widehat{B}$ is a densely defined linear operator $\widehat{B}$ with $\mathrm{dom}(\widehat{T}) \subset \mathrm{dom}(\widehat{B})$ obeying $\|\widehat{B}x\| \leq a\|\widehat{T}x\| + b\|x\|$ with $0 \leq a < 1$ and some b for all $x \in \mathrm{dom}(\widehat{T})$. The Kato-Rellich theorem then proves that the sum of $\widehat{B}$ with the kinetic energy operator, i.e., $\widehat{T} + \widehat{B}$, is self-adjoint. The Coulomb-interaction $\widehat{V}_{\mathrm{int}}$, for instance, is a Kato-perturbation [26]. Hence, $\widehat{H}_0 = \widehat{T} + \widehat{V}_{\mathrm{int}}$ is self-adjoint, and Kato-perturbations thereof, i.e., $\widehat{H}_0 + \widehat{V}$, are again hermitian. Note that in [30] the space under consideration is the dual of $L^1(\mathbb{R}^3) \cap L^3(\mathbb{R}^3)$, i.e., $L^{3/2}(\mathbb{R}^3) + L^\infty(\mathbb{R}^3)$. Via the solution of the N-particle Schrödinger equation we have a mapping $F : v \mapsto \Psi$ (due to consistency we denote the mappings in accordance to reference [10]). With $D : \Psi \mapsto n(\boldsymbol{r}) = \langle\Psi|\widehat{n}(\boldsymbol{r})|\Psi\rangle$ we thus can define a mapping between the external one-particle potentials and the one-particle densities

$$
\begin{aligned}
G : X \cap Y &\rightarrow \{n \in L^1(\mathbb{R}^3)|0 \leq n\} =: L^1_+(\mathbb{R}^3) \\
v(\boldsymbol{r}) &\mapsto n([v], \boldsymbol{r})
\end{aligned}
\tag{1.135}
$$

where Y is the set of all potentials for which the Hamiltonian $\widehat{H}$ has a (unique) ground-state $\Psi \in \mathrm{dom}(\widehat{T})$. Now we want to know if this mapping has an inverse, i.e., if G is one-to-one for its range. To determine this property we need to know under which conditions imposed upon n there is a potential $v \in X \cap Y$ such that the Hamiltonian $\widehat{H} = \widehat{H}[v]$ has a ground-state Ψ which defines $n = n[\Psi]$. It can be shown [26] that the range of the mapping G obeys

$$
\mathrm{ran}\, G \subset \{n \in L^1(\mathbb{R}^3) \cap L^3(\mathbb{R}^3)|0 \leq n, n^{1/2} \in H^1(\mathbb{R}^3)\} \equiv \mathbb{D}(\mathbb{R}^3)
\tag{1.136}
$$

with $H^1(\mathbb{R}^3) = \{n|n \in L^2(\mathbb{R}^3), \boldsymbol{\nabla}n \in L^2(\mathbb{R}^3)\}$. And for all $n \in \mathbb{D}(\mathbb{R}^3)$ there is a state $\Psi \in \mathrm{dom}(\widehat{T})$ such that $n = n[\Psi]$. However, this does only give an estimation of the range of G. Especially as we need to have a Ψ being the ground-state of the associated Hamiltonian.

If we turn away from the problem of not knowing either the exact domain $X \cap Y$ and the exact range $\mathrm{ran}\, G$ of the mapping G, we may consider our initial idea of minimization of the ground-state energy of some system. If we define the ground-state energy functional

$$
E[v] = \inf_{\Psi \in \mathrm{dom}(\widehat{T})/\{0\}} \frac{\langle\Psi|\widehat{H}[v]|\Psi\rangle}{\langle\Psi|\Psi\rangle}
\tag{1.137}
$$

we find the following theorem.

Theorem 1.3.3 *The ground-state energy functional $E[v]$ has the following properties*

1. *$E[v]$ is concave for all $v \in X$, i.e., for all $v_1, v_2 \in X$ and all $0 \leq t \leq 1$ one has $E[tv_1 + (1-t)v_2] \geq tE[v_1] + (1-t)E[v_2]$.*

2. *$E[v]$ is monotonously increasing, i.e., if $v_1, v_2 \in X$ and $v_1(x) \leq v_2(x)$ for all $x \in \mathbb{R}^3$, then $E[v_1] \leq E[v_2]$.*

3. *$E[v]$ is continuous with respect to the norm of X and is locally Lipschitz.*

The proof is to be found in [26] on page 435.

The main result of density functional theory is the Hohenberg-Kohn theorem which proves the injectivity of the mapping $G : X \cap Y \to \text{ran } G$. Therefore one is able to construct a bijective mapping G from some unknown set of potentials to the corresponding set of densities, which is invertible.

Theorem 1.3.4 (Hohenberg-Kohn Theorem) *Suppose $v_1, v_2 \in X$ are potentials for which the Hamiltonian $H[v_1]$ and $H[v_2]$, respectively, have different ground-states Ψ_1, Ψ_2. Then the densities $n[\Psi_1] \neq n[\Psi_2]$ for all points $\boldsymbol{r}$ in a set of positive Lebesgue measure.*

Proof. The proof is given in accordance to [26] and holds only for nondegenerate ground-states. A generalization of the proof is given in [9].

Let $\widehat{H} = \widehat{H}_0 + \int d^3r \, v(\boldsymbol{r}) \, \widehat{n}(\boldsymbol{r})$. Then we know $E[v_i] = \langle \Psi_i | \widehat{H}[v_i] | \Psi_i \rangle$ for $\Psi_i \in \text{dom}(\widehat{T})$ and $\|\Psi_i\| = 1$. Further it holds that $E[v_i] \leq \langle \Psi | \widehat{H}[v_i] | \Psi \rangle$ for all $\Psi \in \text{dom}(\widehat{T})$ and $\|\Psi\| = 1$. Especially if we impose the restriction $\Psi_i \neq \Psi$ we find with the afore mentioned conditions $E[v_i] < \langle \Psi | \widehat{H}[v_i] | \Psi \rangle$. Therefore we find, if we assume $n[\Psi_1] = n[\Psi_2]$,

$$
\begin{aligned}
E[v_1] &= \langle \Psi_1 | \widehat{H}_0 | \Psi_1 \rangle + \int d^3r \, v_2(\boldsymbol{r}) \, n([\Psi_1]; \boldsymbol{r}) + \int d^3r \, [v_1(\boldsymbol{r}) - v_2(\boldsymbol{r})] \, n([\Psi_1]; \boldsymbol{r}) \\
&> E[v_2] + \int d^3r \, [v_1(\boldsymbol{r}) - v_2(\boldsymbol{r})] \, n([\Psi_1]; \boldsymbol{r}).
\end{aligned}
$$

Similarly we find

$$
E[v_2] > E[v_1] + \int d^3r \, [v_2(\boldsymbol{r}) - v_1(\boldsymbol{r})] \, n([\Psi_2]; \boldsymbol{r}).
$$

Adding both inequalities leads to

$$
E[v_1] + E[v_2] > E[v_1] + E[v_2],
$$

which is a contradiction. $\square$

Note here that the assumption $\widehat{H}[v_1]$ and $\widehat{H}[v_2]$ have different ground-states exclude the possibility that $v_1 = v_2 + c$, with c a constant.

The Hohenberg-Kohn theorem establishes an invertible mapping between an unknown set of densities and the corresponding external potentials (up to some constant). Originally Hohenberg and Kohn [29] assumed that every well-behaved density n would be defined in terms of some (possibly degenerate [9]) ground-state Ψ associated with some potential v, i.e., that the densities are **pure-state-v-representable**. Accordingly they introduced the set of pure-state-v-representable densities

$$
\begin{aligned}
A = \quad & \{ n \in L^1 \cap L^3(\mathbb{R}^3) | 0 \leq n, \sqrt{n} \in H^1(\mathbb{R}^3), \quad (1.138) \\
& \exists \, \text{ground-state } \Psi : \Psi \mapsto n, \|\Psi\|_2 = 1 \}
\end{aligned}
$$

on which they defined the Hohenberg-Kohn functional

$$
\begin{aligned}
F_{\text{HK}}[n] &:= E[v] - \int d^3r \, v(\boldsymbol{r}) \, n(\boldsymbol{r}) && (1.139) \\
&= \langle \Psi[n] | \widehat{T} + \widehat{V}_{\text{int}} | \Psi[n] \rangle && (1.140)
\end{aligned}
$$

which is well defined because of the Hohenberg-Kohn theorem. The mapping $G = D \circ F$ is invertible (up to a constant). Therefore, also F and D are invertible, provided we have the mapping $D^{-1} : n \mapsto \Psi[n]$ [9]. Note that $F_{\mathrm{HK}}[n]$ is universal in the sense that it does not depend on the chosen potential v. With this functional the Hohenberg-Kohn variational principle reads:

Theorem 1.3.5 (Hohenberg-Kohn variational Principle) *For every $v \in X \cap Y$ the ground-state energy is*

$$E[v] = \min_{n \in A} E_v[n] = \min_{n \in A} \left[F_{\mathrm{HK}}[n] + \int d^3r \, v(\boldsymbol{r}) \, n(\boldsymbol{r}) \right]. \qquad (1.141)$$

The proof is to be found in [26] on page 436.

As the variational principle (so far nothing was said about functional differentiability) is only defined for pure-state-v-representable densities we meet three major drawbacks: We do not know the sets Y and A as well as the form of F_{HK}. The Hohenberg-Kohn theorem only provides us the existence of a mapping G. If we want to formulate the variational principle in terms of a functional derivative

$$DE_v[n; .] = 0 \quad \Leftrightarrow \quad \frac{\delta E_v[n]}{\delta n(\boldsymbol{r})} = 0 \qquad (1.142)$$

we need to show norm convergence in the domain of definition, or at least in the vicinity of the supposed minimal point. To do this we need to know which densities are pure-state-v-representable. Although Hohenberg and Kohn [29] hoped that all reasonably well-behaved nonnegative functions would be pure-state-v-representable, this is not true. Two different types of extensions of the pure-state-v-representable functions have been found:

Ensemble-v-representable functions which can be easily incorporated into the Hohenberg-Kohn theory by extending the domain of the Hohenberg-Kohn functional to density matrices $\rho[n]$ [9],

$$F_{\mathrm{EHK}}[n] := \mathrm{tr} \left(\rho[n](\widehat{T} + \widehat{V}_{\mathrm{int}}) \right). \qquad (1.143)$$

Note that also the pure-state-v-representable functions are covered by the ensemble-v-representable ones.

However, there are still non-ensemble-v-representable functions. And again an extension of the Hohenberg-Kohn functional to the domain of the so called N-**representable** functions can be constructed. One such extension is the Lieb functional [9]

$$F_{\mathrm{L}}[n] := \inf_{\rho \to n} \mathrm{tr} \left(\rho(\widehat{T} + \widehat{V}_{\mathrm{int}}) \right), \qquad (1.144)$$

where the search is over all density matrices of N-particle wavefunctions constituting an orthonormal basis in the Hilbert space considered. Clearly all integrable nonnegative functions are N-representable. Those extensions come under the heading of constraint search [9]. Note that $F_{\mathrm{L}}[n]$ is the Legendre transform of $E[v]$ [30]. It has been proven [31] that $F_{\mathrm{L}}[n]$ is differentiable for ensemble-v-representable densities but nowhere else. This

enables us to formulate the variational principle in terms of a functional derivative.

A further problem is the extension of the Hohenberg-Kohn theory to arbitrary values of $N = \int n(\boldsymbol{r}) d^3r$ (not necessarily integer) [9] leading to F_{frac} from which one can formulate the search for a stationary point of

$$\frac{\delta}{\delta n(\boldsymbol{r})} \left(E_v[n] - \mu \left(\int d^3r \, n(\boldsymbol{r}) - N \right) \right) = 0. \tag{1.145}$$

This leads to the Euler-Lagrange equation

$$\frac{\delta E_v[n]}{\delta n(\boldsymbol{r})} = \frac{\delta F_{\text{frac}}[n]}{\delta n(\boldsymbol{r})} + v(\boldsymbol{r}) = \mu \tag{1.146}$$

with μ the Lagrangian multiplier, which physically is the chemical potential.

Associated with the extension of the Hohenberg-Kohn functional to fractional particle number is the derivative discontinuity [9] at integer particle numbers. This behavior of the ground-state energy is the key to understand the minimization of energy of two separated neutral atoms with regard to the numbers of particles at each atom [9].

The Kohn-Sham Equations

The HK theorem states that all ground-state properties of the many-body system are determined by its ground-state density. However, beside solving the many-particle Schrödinger equation, we do not know how to calculate this density in general. Another possible route offers the so called Kohn-Sham scheme. One self-consistently solves nonlinear single-particle equations, the so-called Kohn-Sham equations, instead of the full Schrödinger equation, such that both ground-state densities are equal. Computationally the Kohn-Sham scheme is much more favorable as its calculation time scales almost linearly with the number of particles involved, whereas the Schrödinger equation scales exponentially [1].

Although we have specified the interaction of the particles to be Coulombic we could state the Hohenberg-Kohn theorem also for other interactions or no interaction at all. This leads for a general noninteracting Hamiltonian

$$\widehat{H}_{\text{KS}} = \widehat{T} + \widehat{V}_{\text{KS}} \tag{1.147}$$

to the energy functional

$$E_{\text{KS}}[n] = T_{\text{KS}}[n] + \int d^3r \, v_{\text{KS}}(\boldsymbol{r}) \, n(\boldsymbol{r}), \tag{1.148}$$

which yields the exact ground-state density via minimization of $E_{\text{KS}}[n]$. The solutions of the multi-particle Kohn-Sham equation will be determinants, where every single orbital is a solution of the corresponding single-particle Kohn-Sham equation. With the assumption that for every interacting-v-representable density there exists a local effective potential generating the same density in a noninteracting system, we can use this noninteracting auxiliary system to compute the density. Again we meet the problem of extending the

domain of the noninteracting Hohenberg-Kohn functional, i.e., the Kohn-Sham functional, to all possible densities. This can indeed be done, and functional differentiability as well as the existence of the assumed local effective potentials can be proven [9]:

Theorem 1.3.6 (Kohn-Sham Theorem) *The exact ground-state density n of an arbitrary interacting system can be obtained by a self-consistent solution of the following set of equations:*

$$\left(-\frac{1}{2}\boldsymbol{\nabla}^2 + v(\boldsymbol{r}) + \int d^3r'\, v_{\text{int}}(|\boldsymbol{r} - \boldsymbol{r}'|)\, n(\boldsymbol{r}') + v_{\text{xc}}([n];\boldsymbol{r})\right)\phi_k(\boldsymbol{r}) = \epsilon_k\phi_k(\boldsymbol{r})$$

with $\epsilon_1 \leq \epsilon_2 \leq ...$, $n(\boldsymbol{r}) = \sum_{k=1}^{\infty} \gamma_k|\phi_k(\boldsymbol{r})|^2$ and occupation numbers γ_k satisfying

$$\begin{aligned}
\gamma_k = 1 &: \quad \epsilon_k < \mu \\
0 \leq \gamma_k \leq 1 &: \quad \epsilon_k = \mu \\
\gamma_k = 0 &: \quad \epsilon_k > \mu
\end{aligned} \tag{1.149}$$

as well as $\sum_{k=1}^{\infty} \gamma_k = N$. The exchange-correlation potential is defined as

$$\begin{aligned}
v_{\text{xc}}([n];\boldsymbol{r}) &= \frac{\delta E_{\text{xc}}[n]}{\delta n(\boldsymbol{r})} \tag{1.150} \\
&= \frac{\delta}{\delta n(\boldsymbol{r})}\left(F_{\text{L}}[n] - \frac{1}{2}\int\int d^3r\,d^3r'\,n(\boldsymbol{r})v_{\text{int}}(|\boldsymbol{r} - \boldsymbol{r}'|)n(\boldsymbol{r}') - T_{\text{L}}[n]\right),
\end{aligned}$$

with

$$T_{\text{L}}[n] = \inf_{\rho \to n} \text{tr}\left(\rho\,\widehat{T}\right), \tag{1.151}$$

$\rho = \sum_m p_m|\Psi_m\rangle\langle\Psi_m|$ *and $\{|\Psi_m\rangle\}$ a complete set of antisymmetric orthonormal N-particle wavefunctions.*

Here one introduced the **exchange-correlation energy functional $E_{\text{xc}}[n]$**. This functional and its derived exchange-correlation potential are the crucial definitions for a non-interacting description of the interacting system. The exchange-correlation energy functional relates the auxiliary system of noninteracting particles to the physical one. Again we merely have a proof of existence. We do not know the exact form of $E_{\text{xc}}[n]$, from which it would be very simple to construct everything else. Therefore we need reasonable approximations for the exchange-correlation energy and the exchange-correlation potential. Another problem is known under the heading of **noninteracting-v-representability**. Though the above theorem proves that for every interacting-v-representable density there exists some corresponding single-particle potential generating the density, it is not known if all interacting v-representable densities are noninteracting-v-representable by a single determinant. In the above theorem there is no restriction to single determinantal states. To proof noninteracting-v-representability by a single determinant we would need a proof of the functional differentiability of [9]

$$T_{\text{det}}[n] = \inf_{\Phi \to n} \langle\Phi|\widehat{T}|\Phi\rangle \tag{1.152}$$

where $\Phi = \frac{1}{\sqrt{N!}}\det\{\phi_k(\boldsymbol{r}_i)\}$.

We have seen that one can find the ground-state properties of a many-body system by considering the density alone. An energy-minimizing density is unique and it can even be found within a noninteracting theory. The whole theory can be extended to spin-polarized systems, finite temperature ensembles, excited states and many more applications [9]. Though density functional theory is rigorous with respect to its foundations there are various problems unresolved, i.e., v-representability, construction of the different exact functionals, knowledge of the sets Y and A and so forth [9]. However, the successes of density functional theory are manifold, and the theory is widely used throughout physics and chemistry.

1.3.3 Time-Dependent Density Functional Theory

Now we turn to density functional theory for time-dependent systems of the form (1.52) governed by the von Neumann equation

$$\mathrm{i}\frac{\partial\widehat{\rho}(t)}{\partial t} = \left[\widehat{H}(t),\widehat{\rho}(t)\right]_{-} \tag{1.153}$$

and a given initial condition $\widehat{\rho}_0 = \widehat{\rho}(t_0)$ at time t_0. The initial states will in general not be restricted to ground-states. With the time-evolution operator

$$\widehat{U}(t,t_0) = \mathcal{T}_{\mathrm{D}}\left\{\exp\left(-\mathrm{i}\int_{t_0}^{t}dt'\widehat{H}(t')\right)\right\}, \tag{1.154}$$

where $\mathcal{T}_{\mathrm{D}}$ is the Dyson time-ordering operator, one finds that for every t and $\widehat{\rho}(t) = \widehat{U}(t,t_0)\widehat{\rho}_0\widehat{U}^{\dagger}(t,t_0)$

$$n(\boldsymbol{r},t) = \mathrm{tr}\left(\widehat{\rho}(t)\,\widehat{n}(\boldsymbol{r})\right) \in L_+^1(\mathbb{R}^3). \tag{1.155}$$

As for the time-independent density functional theory we examine the spaces in which we are operating.

In order to define the domain and the image of the Runge-Gross mapping we will turn to equation (1.107), i.e.,

$$n^{(k+2)}(\boldsymbol{r}) = q^{(k)}(\boldsymbol{r}) + \sum_{l=0}^{k}\binom{k}{l}\boldsymbol{\nabla}_{\boldsymbol{r}}\cdot\left[n^{(k-l)}(\boldsymbol{r})\boldsymbol{\nabla}_{\boldsymbol{r}}v^{(l)}(\boldsymbol{r})\right].$$

This is the fundamental defining equation between the set of external potentials $v(\boldsymbol{r},t)$, the initial configuration $\widehat{\rho}_0$, the interaction $\widehat{V}_{\mathrm{int}}$ and densities $n(\boldsymbol{r},t)$. In order to associate a density uniquely with the external potential all orders of equation (1.107) have to exist. It seems clear that equation (1.107) is well-defined as long as we assume $\widehat{\rho}_0$ such that all its wavefunctions are $\mathcal{C}^{\infty}(\mathbb{R}^{3N})$ and $v^{(k)}(\boldsymbol{r}) \in \mathcal{C}^{\infty}(\mathbb{R}^3)$ for all k, where $\mathcal{C}^i(\mathbb{R}^3)$ is the space of i-times continuously differentiable functions on $\mathbb{R}^3$. We further have to assume that the

interaction $\widehat{V}_{\text{int}}$ does not introduce problems with respect to the multiple commutators in the definition of $q^{(k)}$. However, even if those rigorous conditions are not met, all orders of equation (1.107), i.e., the Taylor expansion of the density, may exist if the external potential is itself analytic at $t = t_0$.

The other fundamental equation can be constructed if the local force balance equations of two systems leading to the same density defined in section 1.2.2 are set equal [35]

$$\boldsymbol{\nabla}_{\boldsymbol{r}} \cdot \left[n^{(0)}(\boldsymbol{r}) \boldsymbol{\nabla}_{\boldsymbol{r}} v_{\text{Hxc}}^{(k)}(\boldsymbol{r}) \right] = \tag{1.156}$$

$$q^{(k)}(\boldsymbol{r}) - (q')^{(k)}(\boldsymbol{r}) - \sum_{l=0}^{k-1} \binom{k}{l} \boldsymbol{\nabla}_{\boldsymbol{r}} \cdot \left[n'^{(k-l)}(\boldsymbol{r}) \boldsymbol{\nabla}_{\boldsymbol{r}} v_{\text{Hxc}}^{(l)}(\boldsymbol{r}) \right].$$

This equation links two different system and will lead to the Kohn-Sham scheme. Equation (1.156) is a Sturm-Liouville equation. Also the afore-mentioned equation (1.107) amounts to a Sturm-Liouville problem if we want the potentials being defined via the densities.

Let us consider a general differential equation of the form

$$\partial_\mu \left(p(\boldsymbol{r}) \partial_\mu u(\boldsymbol{r}) \right) + \left(\lambda k(\boldsymbol{r}) - q(\boldsymbol{r}) \right) u(\boldsymbol{r}) = 0 \tag{1.157}$$

with the conditions

1. $p(\boldsymbol{r}), q(\boldsymbol{r}), k(\boldsymbol{r}) \in \mathbb{R}$

2. $p(\boldsymbol{r}) \in \mathcal{C}^3(\bar{\Omega});\ q(\boldsymbol{r}), k(\boldsymbol{r}) \in \mathcal{C}^1(\bar{\Omega})$

3. $p(\boldsymbol{r}) > 0, k(\boldsymbol{r}) > 0$ in $\bar{\Omega}$

4. $\lambda \in \mathbb{C}$

where Ω is an open, simply connected and bounded set of $\mathbb{R}^n$ for which the divergence theorem is applicable, $\partial\Omega$ is its boundary with $\bar{\Omega} = \Omega \cup \partial\Omega$, and $\mathcal{C}^i(\bar{\Omega})$ is the space of i-times continuously differentiable functions on $\bar{\Omega}$. We define the Hilbert space for the operator

$$\widehat{A}u(\boldsymbol{r}) = \frac{1}{k(\boldsymbol{r})} \left\{ -\partial_\mu \left[p(\boldsymbol{r}) \partial_\mu \right] + q(\boldsymbol{r}) \right\} u(\boldsymbol{r}) \tag{1.158}$$

to be linear as [32]

$$\mathcal{H}_k := \left\{ u(\boldsymbol{r}) \,\middle|\, \int_\Omega |u(\boldsymbol{r})|^2 k(\boldsymbol{r}) d^n r < \infty \right\}. \tag{1.159}$$

The domain of the operator is

$$\text{dom}(\widehat{A}) = \left\{ u(\boldsymbol{r}) \,\middle|\, u \in \mathcal{C}^1(\bar{\Omega}),\ u \in \mathcal{C}^2(\Omega),\ \widehat{A}u \in \mathcal{H}_k;\ u = 0 \text{ on } \partial\Omega \right\}. \tag{1.160}$$

The reciprocal of $\widehat{A}$, i.e., $\widehat{A}^{-1}$, exists if and only if $\lambda = 0$ is not an eigenvalue of the boundary value problem. As shown in section 2.3 of [32] this is true for $q(\boldsymbol{r}) \geq 0$. What is the range of the operator $\widehat{A}$ on its domain , i.e., how does

$$\text{ran}(\widehat{A}) = \left\{ f \,\Big|\, \widehat{A}u = f \;\forall u \in \text{dom}(\widehat{A}) \right\} \tag{1.161}$$

look like? If we specialize on $q \equiv 0$ we find that for

$$f \in \mathbb{B}(\bar{\Omega}) := \left\{ f \,\big|\, f \in \mathcal{C}^1(\bar{\Omega}) \text{ or } f \text{ Hoelder continuous in } \bar{\Omega} \right\}, \tag{1.162}$$

i.e., $|f(\boldsymbol{r}) - f(\boldsymbol{r}')| \leq H|\boldsymbol{r} - \boldsymbol{r}'|^{\alpha}$ for all $\boldsymbol{r}$, $\boldsymbol{r}' \in \bar{\Omega}$ with H and $0 < \alpha < 1$ independent of $\boldsymbol{r}$, $\boldsymbol{r}'$, there exists a Green's function $g(\boldsymbol{r}, \boldsymbol{r}')$ leading to

$$u(\boldsymbol{r}) = \int_{\Omega} g(\boldsymbol{r}, \boldsymbol{r}') f(\boldsymbol{r}') k(\boldsymbol{r}') d^n r. \tag{1.163}$$

Thus we know that

$$\mathbb{B}(\bar{\Omega}) \subseteq \text{ran}(\widehat{A}). \tag{1.164}$$

Note here that if we consider one-dimensional problems one has less restrictions [32].

We turn again to the problem of the Runge-Gross mapping, however, restricted to an appropriate (finite) region $\bar{\Omega} \subset \mathbb{R}^3$. Because of Hölder's inequality [24] we have

$$L^q(\bar{\Omega}) \subset L^p(\bar{\Omega}) \text{ for } 1 \leq p < q \leq \infty. \tag{1.165}$$

Further we assume every $v^{(k)}(\boldsymbol{r}) \in \text{dom}(\widehat{A})$ and find

$$v(\boldsymbol{r}, t) \in \text{dom}(\widehat{A}) \subset L^2(\bar{\Omega}) + L^{\infty}(\bar{\Omega}) \tag{1.166}$$

for every $t \in [t_0, t_1]$, where $t_1 > t_0$ in accordance to Kato-perturbations of the free Hamiltonian [26]. We define the **set of potentials** at consideration as

$$\mathcal{V}(\widehat{\rho}_0, \widehat{V}_{\text{int}}) := \quad \Big\{ v | v \text{ analytic at } t = t_0, \; v(t) \in \text{dom}(\widehat{A}), \tag{1.167}$$
$$v \in \mathbb{R}, \; n[v] \text{ analytic at } t = t_0 \Big\}.$$

For the space of time-dependent densities we first note that via equation (1.107), i.e., $n^{(k+2)}[v]$, it is obvious that an external potential $v \in \mathcal{V}(\widehat{\rho}_0, \widehat{V}_{\text{int}})$ will define $n^{(k)}(\boldsymbol{r})$ for $k > 1$ and hence will not influence the initial conditions. Thus for a chosen initial condition we have

$$n(\boldsymbol{r}, t) = n_0(\boldsymbol{r}) + \underbrace{\text{tr}\left(\widehat{\rho}_0 \boldsymbol{\nabla}_{\boldsymbol{r}} \cdot \widehat{\boldsymbol{j}}(\boldsymbol{r}) \right) (t - t_0)}_{= n^{(1)}(\boldsymbol{r}, t)} + \sum_{k=2}^{\infty} \frac{1}{k!} n^{(k)}(\boldsymbol{r}) (t - t_0)^k. \tag{1.168}$$

We will introduce the **set of densities** as an affine set of variations δn via

$$\delta \mathcal{N}(\widehat{\rho}_0, \widehat{V}_{\text{int}}) := \left\{ \delta n \, \middle| \, \delta n = \sum_{k=2}^{\infty} \frac{1}{k!} \, n^{(k)}([v]; \boldsymbol{r}) \, (t - t_0)^k, \right. \tag{1.169}$$
$$\left. v \in \mathcal{V}(\widehat{\rho}_0, \widehat{V}_{\text{int}}), \, \widehat{\rho}_0 \right\}.$$

Accordingly, as $n(\boldsymbol{r}, t) = n_0(\boldsymbol{r}) + n^{(1)}(\boldsymbol{r}, t) + \delta n(\boldsymbol{r}, t)$ we define

$$\mathcal{N}(\widehat{\rho}_0, \widehat{V}_{\text{int}}) := \left\{ n \, \middle| \, n = n_0 + n^{(1)} + \delta n, \text{with } \delta n \in \delta \mathcal{N}(\widehat{\rho}_0, \widehat{V}_{\text{int}}) \right\}$$
$$= n_0(\boldsymbol{r}) + n^{(1)}(\boldsymbol{r}, t) + \delta \mathcal{N}(\widehat{\rho}_0, \widehat{V}_{\text{int}}). \tag{1.170}$$

In the following we may use the set $\mathcal{N}(\widehat{\rho}_0, \widehat{V}_{\text{int}})$ synonymously with $\delta \mathcal{N}(\widehat{\rho}_0, \widehat{V}_{\text{int}})$. However, it is usually more intuitive if we use $\mathcal{N}(\widehat{\rho}_0, \widehat{V}_{\text{int}})$. With the triangle inequality on $L^1(\Omega)$ we have for $\delta n_1, \delta n_2 \in \delta \mathcal{N}(\widehat{\rho}_0, \widehat{V}_{\text{int}})$

$$\|\delta n_1 + \delta n_2\|_1 \leq \|\delta n_1\|_1 + \|\delta n_2\|_1 = 0. \tag{1.171}$$

Hence, all combinations of variations $\delta n \in \delta \mathcal{N}(\widehat{\rho}_0, \widehat{V}_{\text{int}})$ will again lead to some variation with respect to $\|.\|_1$. However, it is not clear that all combinations of variations $\delta n \in \delta \mathcal{N}(\widehat{\rho}_0, \widehat{V}_{\text{int}})$ will again be part of the set $\delta \mathcal{N}(\widehat{\rho}_0, \widehat{V}_{\text{int}})$. Further, the set of potentials as well as the set of densities may be the empty set if the initial configuration or the interaction is not well chosen.

Lemma 1.3.2 *Let $\widehat{\rho}_0$ be some density matrix and $\widehat{V}_{\text{int}}$ some specified interaction, then the initial state dependent mapping*

$$v_{\widehat{\rho}_0} : \mathcal{N}(\widehat{\rho}_0, \widehat{V}_{\text{int}}) \rightarrow \mathcal{V}(\widehat{\rho}_0, \widehat{V}_{\text{int}}) \tag{1.172}$$
$$n(\boldsymbol{r}, t) \mapsto v_{\widehat{\rho}_0}([n]; \boldsymbol{r}, t)$$

is bijective (invertible).

Proof. The extended Runge-Gross proof (1.2.1) shows that there is a uniquely defined (with chosen boundary conditions) external potential $v(\boldsymbol{r}, t) \in \mathcal{V}(\widehat{\rho}_0, \widehat{V}_{\text{int}})$, Taylor-expandable about $t = t_0$, which is associated with the density $n(\boldsymbol{r}, t) \in \mathcal{N}(\widehat{\rho}_0, \widehat{V}_{\text{int}})$. $\square$

The **initial state dependence** has a severe consequence. If we constructed the exact mapping $v_{\widehat{\rho}_0}$ it would be different for every initial state. However, we can circumvent this problem by a restriction that is almost always made. If we assume the initial density being a ground-state density then, by virtue of the Hohenberg-Kohn theorem, the initial state is uniquely defined by its density and thus we do not have any initial state dependence. A different way to handle initial state dependence is to use prehistories [13, 34]. This scheme makes use of the fact that initial state dependence and history dependence can be reexpressed in terms of one another.

The inverse mapping $v_{\widehat{\rho}_0}^{-1}$ will be denoted by $n_{\widehat{\rho}_0}$ and amounts to solve the von Neumann equation and calculate the time-dependent density. With the mapping [see the definition (1.112)]

$$
\begin{aligned}
\widetilde{\rho}_{\widehat{\rho}_0} : \mathcal{V}(\widehat{\rho}_0, \widehat{V}_{\text{int}}) &\rightarrow \mathcal{R}(\widehat{\rho}_0, \widehat{V}_{\text{int}}) \subset \mathcal{L}_t \left[L^2(\mathbb{R}^{3N}), L^2(\mathbb{R}^{3N}) \right] \\
v(\boldsymbol{r}, t) &\mapsto \widetilde{\rho}_{\widehat{\rho}_0}([v]; t)
\end{aligned}
\tag{1.173}
$$

which is defined via the solution of the von Neumann equation, we can formulate

Lemma 1.3.3 *For a chosen initial configuration $\widehat{\rho}_0$ and interaction $\widehat{V}_{\text{int}}$ the time-dependent density matrix associated with the Hamiltonian $\widehat{H}(t) = \widehat{H}([v]; t)$ with $v \in \mathcal{V}(\widehat{\rho}_0, \widehat{V}_{\text{int}})$ is uniquely defined by the density, i.e.,*

$$
\widehat{\rho}_{\widehat{\rho}_0} : \mathcal{N}(\widehat{\rho}_0, \widehat{V}_{\text{int}}) \rightarrow \mathcal{R}(\widehat{\rho}_0, \widehat{V}_{\text{int}})
\tag{1.174}
$$

is invertible. Therefore also the expectation value of some operator $\widehat{O}(t)$, i.e., $O([n]; t) = \text{tr}(\widehat{\rho}_{\widehat{\rho}_0}([n]; t) \, \widehat{O}(t))$, is defined by the density alone.

Proof. With the mapping $v_{\widehat{\rho}_0} : \mathcal{N}(\widehat{\rho}_0, \widehat{V}_{\text{int}}) \rightarrow \mathcal{V}(\widehat{\rho}_0, \widehat{V}_{\text{int}})$ we have

$$
\rho_{\widehat{\rho}_0} = \widetilde{\rho}_{\widehat{\rho}_0} \circ v_{\widehat{\rho}_0} : \mathcal{N}(\widehat{\rho}_0, \widehat{V}_{\text{int}}) \rightarrow \mathcal{R}(\widehat{\rho}_0, \widehat{V}_{\text{int}}).
\tag{1.175}
$$

The inverse mapping from $\mathcal{R}(\widehat{\rho}_0, \widehat{V}_{\text{int}})$ to $\mathcal{N}(\widehat{\rho}_0, \widehat{V}_{\text{int}})$ is defined by

$$
\widehat{\rho}(t) \mapsto \text{tr}\left(\widehat{\rho}(t) \, \widehat{n}(\boldsymbol{r}) \right) = n(\boldsymbol{r}, t).
\tag{1.176}
$$

$\square$

This conclusion is the same as in section 1.2.2 where we showed the formal exactness of the quantum fluid dynamical reformulation of the many-body problem. All observables are defined by the density alone. This is an important building block of time-dependend density functional theory as we only need the time-dependend density to find all physical entities, at least in principle.

Until now we have merely shown that one may switch from density matrices to densities or currents. So far, the only route to determine the dynamical properties of the system is by solving the initial problem, i.e., the many-body Schrödinger equation. The extended Runge-Gross proof states that the density of an interacting system can formally be calculated by solving a corresponding equation of noninteracting particles in an effective potential. Such an approach would be computationally favorable. The corresponding effective potential was found to be uniquely defined by the density and the initial state. Strictly speaking, however, the proof in section 1.2.2 did only state that the Sturm-Liouville equations (1.109) have *unique solutions*. When do we know that such a solution exists? First we restate the extended Runge-Gross uniqueness theorem.

Theorem 1.3.7 (Extended Runge-Gross Uniqueness Theorem) *Let* $n(\boldsymbol{r}, t) \in \mathcal{N}(\widehat{\rho_0}, \widehat{V}_{\mathrm{int}})$ *and* $v_{\widehat{\rho_0}}([n]; \boldsymbol{r}, t) = v(\boldsymbol{r}, t)$ *the associated external potential. For a system with interaction* $\widehat{V}'_{\mathrm{int}}$ *and the initial configuration* $\widehat{\rho}'_0$ *subject to the constraints*

$$
\begin{aligned}
n(\boldsymbol{r}, t_0) &= n'(\boldsymbol{r}, t_0), \\
\mathrm{tr}\left(\widehat{\rho}_0 \, \boldsymbol{\nabla}_{\boldsymbol{r}} \cdot \widehat{\boldsymbol{j}}(\boldsymbol{r})\right) &= \mathrm{tr}\left(\widehat{\rho}'_0 \, \boldsymbol{\nabla}_{\boldsymbol{r}} \cdot \widehat{\boldsymbol{j}}(\boldsymbol{r})\right),
\end{aligned}
$$

the external potential $v'(\boldsymbol{r}, t) \in \mathcal{V}(\widehat{\rho}'_0, \widehat{V}'_{\mathrm{int}})$ *leading to the same density is uniquely defined.*

However, it is not clear that

$$
n \in \mathcal{N}(\widehat{\rho}_0, \widehat{V}_{\mathrm{int}}) \text{ and } n \in \mathcal{N}(\widehat{\rho}'_0, \widehat{V}'_{\mathrm{int}}), \tag{1.177}
$$

or reformulated, that all equations (1.109), which are **Sturm-Liouville boundary value problems**, have **existing solutions**. Now let us come back to the general considerations at the beginning of this section. In our case we have

1. $q(\boldsymbol{r}) \equiv 0$

2. $k(\boldsymbol{r}) \equiv 1$.

The condition $n(\boldsymbol{r}, t_0) > 0$ could be removed. If the initial density has points equal to zero we could use a later density as new initial density $n(\boldsymbol{r}, t'_0)$ and find via forward and backward propagation and the associated local force balance equations the external potential on the whole time interval $[t_0, t_1]$. Only if there were no $t \in [t_0, t_1]$ for which $n(\boldsymbol{r}, t) > 0$ the above considerations would not work. Thus we find the following corollary

Corollary 1.3.1 *For* $n_0(\boldsymbol{r}) > 0$ *and* $n_0(\boldsymbol{r}) \in \mathcal{C}^3(\bar{\Omega})$ *the* k-*th term* $v'^{(k)}(\boldsymbol{r})$ *of the Taylor expansion of* $v'(\boldsymbol{r}, t)$ *exists if* $f^{(k)}$ *is Hölder continuous on* $\bar{\Omega}$ *or element of* $\mathcal{C}^1(\bar{\Omega})$ *for*

$$
\boldsymbol{\nabla}_{\boldsymbol{r}} \cdot [n_0(\boldsymbol{r}) \boldsymbol{\nabla}_{\boldsymbol{r}} v'^{(k)}(\boldsymbol{r})] = f^{(k)}(\boldsymbol{r}). \tag{1.178}
$$

For usual physical situations where the system under study is confined to some small region in space, the condition of Hölder continuity seems perfectly valid. The right hand side $f^{(k)}(\boldsymbol{r})$ comes from the divergence of the local forces and can be assumed finite. Therefore we may assume the existence for a large class of physical problems. This is in correspondence to [12] where similar arguments with respect to $f^{(k)}(\boldsymbol{r})$ are pursued.

In a next step we will now look for a way to describe the dynamics of the system without solving the Schödinger equation. In analogy to the time-independent theory we will establish an auxiliary noninteracting system which gives the same density as the physical one. This is the well known Kohn-Sham scheme. Note, however, that in the above derivation we constructed the external potential via knowledge of the density. The interacting density as input would not lead to some predictive theory. Therefore, like in time-independent density functional theory, one introduces the **exchange-correlation potential**, linking the interacting (physical) system to the auxiliary system. The exchange-correlation potential accounts for all internal forces.

Theorem 1.3.8 (Time-Dependent Kohn-Sham Uniqueness Theorem) *Let*
$n(\boldsymbol{r}, t) \in \mathcal{N}(\widehat{\rho}_0, \widehat{V}_{\text{int}})$ *and* $v(\boldsymbol{r}, t) \equiv v_{\widehat{\rho}_0}([n]; \boldsymbol{r}, t)$ *the associated external potential. If we have an initial noninteracting configuration* $\widehat{\rho}'_0$ *subject to the constraints*

$$
\begin{aligned}
n(\boldsymbol{r}, t_0) &= n'(\boldsymbol{r}, t_0), \\
\operatorname{tr}\left(\widehat{\rho}_0 \, \boldsymbol{\nabla}_{\boldsymbol{r}} \cdot \widehat{\boldsymbol{j}}(\boldsymbol{r})\right) &= \operatorname{tr}\left(\widehat{\rho}'_0 \, \boldsymbol{\nabla}_{\boldsymbol{r}} \cdot \widehat{\boldsymbol{j}}(\boldsymbol{r})\right),
\end{aligned}
$$

then we have an uniquely defined one-particle potential $v_{\text{KS}}([n]; \boldsymbol{r}, t) \equiv v'_{\widehat{\rho}'_0}([n]; \boldsymbol{r}, t) \in \mathcal{V}(\widehat{\rho}'_0)$ *leading to the Kohn-Sham Hamiltonian*

$$
\widehat{H}_{\text{KS}}(t) = \widehat{T} + \widehat{V}_{\text{KS}}(t) \tag{1.179}
$$

generating the physical density. The (orbital) Kohn-Sham equations then read as

$$
i\partial_t \phi_k(\boldsymbol{r}, t) = \left(-\frac{1}{2}\boldsymbol{\nabla}^2 + v(\boldsymbol{r}, t) + v_{\text{H}}([n]; \boldsymbol{r}, t) + v_{\text{xc}}([n]; \boldsymbol{r}, t) \right) \phi_k(\boldsymbol{r}, t).
$$

The exchange-correlation potential is defined via

$$
v_{\text{xc}}([n]; \boldsymbol{r}, t) \equiv v_{\widehat{\rho}_0, \widehat{\rho}'_0}^{\text{xc}}([n]; \boldsymbol{r}, t) := v'_{\widehat{\rho}'_0}([n]; \boldsymbol{r}, t) - v_{\widehat{\rho}_0}([n]; \boldsymbol{r}, t) - v_{\text{H}}([n]; \boldsymbol{r}, t) \tag{1.180}
$$

with $v_{\text{H}}([n]; \boldsymbol{r}, t) = \int d^3 r' v_{\text{int}}(|\boldsymbol{r} - \boldsymbol{r}'|) n(\boldsymbol{r}, t)$ *the Hartree potential.*

Proof. One can use the extended Runge-Gross uniqueness theorem with the specialization on the noninteracting case. Analogously we can set both local force balance equations defined in section 1.2.2 equal and find equation (1.156)

$$
\begin{aligned}
\boldsymbol{\nabla}_{\boldsymbol{r}} \cdot &\left[n^{(0)}(\boldsymbol{r}) \boldsymbol{\nabla}_{\boldsymbol{r}} v_{\text{Hxc}}^{(k)}([n]; \boldsymbol{r}) \right] = \\
&q^{(k)}(\boldsymbol{r}) - (q')^{(k)}(\boldsymbol{r}) - \sum_{l=0}^{k-1} \binom{k}{l} \boldsymbol{\nabla}_{\boldsymbol{r}} \cdot \left[n'^{(k-l)}(\boldsymbol{r}) \boldsymbol{\nabla}_{\boldsymbol{r}} v_{\text{Hxc}}^{(l)}([n]; \boldsymbol{r}) \right],
\end{aligned}
$$

where $v_{\text{Hxc}}([n]; \boldsymbol{r}, t) \equiv v_{\widehat{\rho}_0, \widehat{\rho}'_0}^{\text{Hxc}}([n]; \boldsymbol{r}, t) := v'_{\widehat{\rho}'_0}([n]; \boldsymbol{r}, t) - v_{\widehat{\rho}_0}([n]; \boldsymbol{r}, t)$. This is again a Sturm-Liouville problem, and the solution, if existing, is unique if the boundary values are chosen. Note that $\mathcal{V}(\widehat{\rho}_0) \equiv \mathcal{V}(\widehat{\rho}_0, \widehat{V}_{\text{int}} \equiv 0)$. $\square$

Again the existence is guaranteed if the right hand side of equation (1.156) is Hölder continuous due to corollary 1.3.1. Note that we may now construct everything of interest if we calculate $v_{\text{Hxc}}^{(k)}([n]; \boldsymbol{r})$ in the above proposed way. Further we can calculate the next term of the density Taylor expansion via equation (1.107), which then can be used to calculate the next order of the Hartree-exchange-correlation potential and so forth. Beside the obvious implication of being able to reproduce an interacting time-dependent density via some noninteracting system, the time-dependent Kohn-Sham theorem also includes information about the **noninteracting-v-representability question for time-dependent systems**. If we have found some initial configuration subject to the above restrictions, the density is noninteracting-v-representable. The form

of the initial state defines whether a density is noninteracting-pure-state-v-representable or noninteracting-ensemble-v-representable. For switch-on processes where the system is time independent up to some time $t = t_0$ and afterwards an external perturbation is switched on, one can always find an appropriate noninteracting initial state via the so-called Harriman construction [33]. The question if we can find a noninteracting initial state being the ground-state of some noninteracting system leads to the noninteracting-v-representability for stationary systems as considered in section 1.3.2.

An important feature of time-dependent density functional theory is the nonlocality of the mappings in space as well as in time. The nonlocality in space is already met in the static density functional theory. However, in the time-dependent formulation one in general finds that the Kohn-Sham potential $v_{\widehat{\rho}_0'}([n]; \boldsymbol{r}, t)$ does not only depend on the density at the time of consideration but also on previous times, i.e., it depends on the entire history of the density [11]. The **nonlocality in time** will be extensively considered later on.

Rigorous Formulation

Until now we tried to give quite general conclusions at the expense of not knowing the exact set of densities and potentials, and at the expense of not having a general proof of existence of the uniquely defined external potential for the extended Runge-Gross theorem. We will now leave this route and will give a combined existence and uniqueness theorem for restrictive conditions. However, the set of densities and external potentials will again be unknown. Nevertheless we proof that the set of all densities is the same for any smooth interaction as long as one finds smooth initial configurations subject to the same initial conditions. Obviously, the Kohn-Sham construction is guaranteed as $v_{\text{int}} \equiv 0$ is trivially infinitely differentiable. Though this seems quite academic, a mathematically rigorous formulation can be seen as a proof of principle for the physically more attractive cases, which in general will not obey the assumed restrictions. Further, the main assumption, i.e., smooth functions, leaves us with the possibility to approximate any none-smooth function arbitrarily well.

Let Ω and $\partial\Omega$ be defined as before. Then the following lemma holds.

Lemma 1.3.4 *Let $\widehat{\rho}_0$ be such that all its wavefunctions are in $\mathcal{C}^\infty(\bar{\Omega}^N)$, v analytic in $t = t_0$, $v^{(k)} \in \mathcal{C}^\infty(\bar{\Omega}) \ \forall \ k$, and $v_{\text{int}}(|\boldsymbol{r} - \boldsymbol{r}'|)$ infinitely differentiable. Then*

$$n^{(k+2)}(\boldsymbol{r}) = q^{(k)}(\boldsymbol{r}) + \sum_{l=0}^{k} \left(\begin{array}{c} k \\ l \end{array} \right) \boldsymbol{\nabla}_{\boldsymbol{r}} \cdot \left[n^{(k-l)}(\boldsymbol{r}) \boldsymbol{\nabla}_{\boldsymbol{r}} v^{(l)}(\boldsymbol{r}) \right] \tag{1.181}$$

is well-defined and $n^{(k+2)}(\boldsymbol{r}) \in \mathcal{C}^\infty(\bar{\Omega})$ exists for all k.

Proof. Obviously we have $n_0(\boldsymbol{r})$ and $n^{(1)}(\boldsymbol{r})$ in $\mathcal{C}^\infty(\bar{\Omega})$. Thus $n^{(2)}(\boldsymbol{r})$ is in $\mathcal{C}^\infty(\bar{\Omega})$ if $q^{(0)}(\boldsymbol{r})$ is infinitely differentiable, where

$$q^{(0)}(\boldsymbol{r}) = \text{tr} \left[\widehat{\rho}_0 \ \left(\partial_\nu \partial_\mu \widehat{\Pi}_{\mu\nu}(\boldsymbol{r}) \right) \right]. \tag{1.182}$$

$\widehat{\Pi}_{\mu\nu}(\boldsymbol{r})$ consists of partial derivatives with respect to $\boldsymbol{r}$ and of derivatives of $v_{\text{int}}(|\boldsymbol{r} - \boldsymbol{r}'|)$. We have assumed $v_{\text{int}}(|\boldsymbol{r} - \boldsymbol{r}'|)$ infinitely differentiable. Hence we have $q^{(0)}(\boldsymbol{r}) \in \mathcal{C}^{\infty}(\bar{\Omega})$. For $n^{(3)}(\boldsymbol{r})$ we need to know $q^{(1)}(\boldsymbol{r})$. This is the commutator of $\partial_{\nu}\partial_{\mu}\widehat{\Pi}_{\mu\nu}(\boldsymbol{r})$ with $\widehat{H}(t)$ at $t = t_0$. All functions in $\widehat{H}(t)$ are infinitely differentiable. Again the above reasoning applies, and we find $q^{(1)}(\boldsymbol{r}) \in \mathcal{C}^{\infty}(\bar{\Omega})$. All higher terms are to be found via successive application of the Heisenberg equation for $\partial_{\nu}\partial_{\mu}\widehat{\Pi}_{\mu\nu}(\boldsymbol{r})$ with $\widehat{H}(t)$ at $t = t_0$. The only difference to the above reasoning is the appearance of $v^{(k)}(\boldsymbol{r})$-terms, which are again infinitely differentiable. Therefore one can successively construct all $n^{(k)}(\boldsymbol{r}) \in \mathcal{C}^{\infty}(\bar{\Omega})$. $\square$

Note that a restriction on $v_{\text{int}}(|\boldsymbol{r} - \boldsymbol{r}'|)$ being infinitely differentiable in $\boldsymbol{r}$ for almost all $\boldsymbol{r}'$ with respect to the Lebesgue measure on $\bar{\Omega}$, i.e., the set of exceptional points $\boldsymbol{r}'$ has zero measure, may also be possible. The Lebesgue integral in turn does not depend on a set of finite measure. Therefore any function defined via a Lebesgue integral with respect to $\boldsymbol{r}'$ over $v_{\text{int}}(|\boldsymbol{r} - \boldsymbol{r}'|)$ and some other infinitely differentiable function is infinitely differentiable with respect to $\boldsymbol{r}$. Hence we have $q^{(0)}(\boldsymbol{r}) \in \mathcal{C}^{\infty}(\bar{\Omega})$. For higher orders of $q^{(k)}$ this reasoning may also work. However, as one also introduces delta-distributions and derivatives thereof due to the the (anti)commutation relations, it is not clear if the evaluation of the distributions at nondifferentiable points of $v_{\text{int}}(|\boldsymbol{r} - \boldsymbol{r}'|)$ is well-defined.

Now, let $\widehat{V}_{\text{int}}$ and $\widehat{V}'_{\text{int}}$ be chosen such that they have finite expectation values and $v_{\text{int}}(|\boldsymbol{r} - \boldsymbol{r}'|)$ and $v'_{\text{int}}(|\boldsymbol{r} - \boldsymbol{r}'|)$ are infinitely differentiable. Further we assume $\widehat{\rho}_0$ consisting of $\mathcal{C}^{\infty}$ wavefunctions. We then define

$$\mathcal{V}^*(\widehat{\rho}_0, \widehat{V}_{\text{int}}) := \quad \{v \,|\, v \text{ analytic in } t = t_0, \; v^{(k)} \in \mathcal{C}^{\infty}(\bar{\Omega}) \; \forall \, k, \qquad (1.183)$$
$$v^{(k)} = 0 \text{ on } \partial\Omega \; \forall \, k, \; n[v] \text{ analytic in } t = t_0\}$$

the **set of all smooth external potentials**.

In accordance to definition (1.170) we define

$$\mathcal{N}^*(\widehat{\rho}_0, \widehat{V}_{\text{int}}) := \left\{ n \,\middle|\, n = \sum_{k=0}^{\infty} \frac{1}{k!} \, n^{(k)}([v]; \boldsymbol{r}) \, (t - t_0)^k, \; v \in \mathcal{V}^*(\widehat{\rho}_0, \widehat{V}_{\text{int}}), \widehat{\rho}_0 \right\} \quad (1.184)$$

the **set of all smooth time-dependent densities**. We could have also defined the set of corresponding variations δn. Obviously there is a one-to-one correspondence between $v \in \mathcal{V}^*(\widehat{\rho}_0, \widehat{V}_{\text{int}})$ and $n \in \mathcal{N}^*(\widehat{\rho}_0, \widehat{V}_{\text{int}})$ in accordance to lemma 1.3.2, the Runge-Gross mapping.
With this we can reformulate the extended Runge-Gross theorem as follows

Theorem 1.3.9 *Let* $n(\boldsymbol{r}, t) \in \mathcal{N}^*(\widehat{\rho}_0, \widehat{V}_{\text{int}})$ *and* $v_{\widehat{\rho}_0}([n]; \boldsymbol{r}, t) = v(\boldsymbol{r}, t) \in \mathcal{V}^*(\widehat{\rho}_0, \widehat{V}_{\text{int}})$ *the associated external potential. For a system with interaction* $v'_{\text{int}} \in \mathcal{C}^{\infty}(\bar{\Omega}^2)$ *and the initial configuration* $\widehat{\rho}'_0$ *consisting of infinitely differentiable functions subject to the constraint*

$$n(\boldsymbol{r}, t_0) = n'(\boldsymbol{r}, t_0) > 0,$$
$$\text{tr}\left(\widehat{\rho}_0 \, \boldsymbol{\nabla}_{\boldsymbol{r}} \cdot \widehat{\boldsymbol{j}}(\boldsymbol{r})\right) = \text{tr}\left(\widehat{\rho}'_0 \, \boldsymbol{\nabla}_{\boldsymbol{r}} \cdot \widehat{\boldsymbol{j}}(\boldsymbol{r})\right),$$

there exists a unique effective potential

$$v_{\widehat{\rho}_0,\widehat{\rho}'_0}([n];\boldsymbol{r},t) = \sum_{k=0}^{\infty} \frac{1}{k!} \, (v')^{(k)}(\boldsymbol{r}) \, (t-t_0)^k,$$

where $(v')^{(k)}(\boldsymbol{r})$ is defined via

$$\boldsymbol{\nabla}_{\boldsymbol{r}} \cdot \left[n^{(0)}(\boldsymbol{r}) \boldsymbol{\nabla}_{\boldsymbol{r}} (v')^{(k)}(\boldsymbol{r}) \right] =$$
$$q^{(k)}(\boldsymbol{r}) - (q')^{(k)}(\boldsymbol{r}) - \sum_{l=0}^{k-1} \binom{k}{l} \boldsymbol{\nabla}_{\boldsymbol{r}} \cdot \left[n'^{(k-l)}(\boldsymbol{r}) \boldsymbol{\nabla}_{\boldsymbol{r}} (v')^{(k)}(\boldsymbol{r}) \right],$$

with $\left(v + v_{\widehat{\rho}_0,\widehat{\rho}'_0} \right) \in \mathcal{V}^*(\widehat{\rho}'_0, \widehat{V}'_{\mathrm{int}})$ generating the same density. It holds that

$$\mathcal{N}^*(\widehat{\rho}_0, \widehat{V}_{\mathrm{int}}) = \mathcal{N}^*(\widehat{\rho}'_0, \widehat{V}'_{\mathrm{int}}).$$

Proof. From the proof of lemma 1.3.4 we know that all $q^{(k)}$ and $(q')^{(k)}$ are infinitely differentiable. As we have assumed $n_0(\boldsymbol{r}) > 0$ we can apply corollary 1.3.1 from which it is clear that

$$\boldsymbol{\nabla}_{\boldsymbol{r}} \cdot \left[n^{(0)}(\boldsymbol{r}) \boldsymbol{\nabla}_{\boldsymbol{r}} (v')^{(k)}(\boldsymbol{r}) \right] =$$
$$q^{(k)}(\boldsymbol{r}) - (q')^{(k)}(\boldsymbol{r}) - \sum_{l=0}^{k-1} \binom{k}{l} \boldsymbol{\nabla}_{\boldsymbol{r}} \cdot \left[n'^{(k-l)}(\boldsymbol{r}) \boldsymbol{\nabla}_{\boldsymbol{r}} (v')^{(k)}(\boldsymbol{r}) \right]$$

has an existing solution if the right hand side is $\mathcal{C}^1(\bar{\Omega})$. Obviously $(v')^{(0)}(\boldsymbol{r})$ exists due to corollary 1.3.1 and is infinitely differentiable. In the next step we can use $(v')^{(0)}(\boldsymbol{r})$ in the Sturm-Liouville equation defining $(v')^{(1)}(\boldsymbol{r})$. Again existence is guaranteed and we have $(v')^{(1)}(\boldsymbol{r}) \in \mathcal{C}^\infty(\bar{\Omega})$. One can now successively construct $v_{\widehat{\rho}_0,\widehat{\rho}'_0}$. Then $(v + v_{\widehat{\rho}_0,\widehat{\rho}'_0})$ is given via its Taylor series within its radius of convergence. The case of zero convergence radius can be disregarded because then also the density n would be nonanalytic. This construction holds for every $n \in \mathcal{N}^*(\widehat{\rho}_0, \widehat{V}_{\mathrm{int}})$, and we have $n \in \mathcal{N}^*(\widehat{\rho}'_0, \widehat{V}'_{\mathrm{int}})$ as well. $\square$

The special case of a rigorous Kohn-Sham theorem is straightforward as $v_{\mathrm{int}} \equiv 0$ is of course infinitely differentiable. Only a noninteracting initial configuration is needed. We point out that we actually find

$$\mathcal{N}^*(\widehat{\rho}_0, \widehat{V}_{\mathrm{int}}) \equiv \mathcal{N}^*(n_0, n^{(1)}), \tag{1.185}$$

the **set of all analytic and smooth time-dependent densities does not depend on the interaction**. Only the initial density n_0 and the first time derivative of the density $n^{(1)}$ are important.

Action Functional and Symmetry-Causality Paradox

So far time-dependent density functional theory did not use any minimization principle like in the time-independent formulation. In density functional theory the exchange-correlation potential is the functional derivative of $E_{\mathrm{xc}}[n]$ (theorem 1.3.6), whereas in time-dependent density functional theory we have introduced $v_{\widehat{\rho}_0,\widehat{\rho}_0}^{\mathrm{xc}}([n];\boldsymbol{r},t)$ via the differences

of the initial state dependend mappings of the interacting and the noninteracting case. In time-dependent density functional theory we could use an action principle instead of the minimization of the energy. It will be shown, however, that there are a lot of problems connected with this idea.

Let us look at the usual action principle in quantum mechanics which requires the action functional [12]

$$\widetilde{A}[\psi] = \int_{t_0}^{t_1} dt \, \langle \Psi(t)|\mathrm{i}\partial_t - \widehat{H}(t)|\Psi(t)\rangle \tag{1.186}$$

to be stationary under variations $|\delta\Psi(t)\rangle$ satisfying $|\delta\Psi(t_0)\rangle = |\delta\Psi(t_1)\rangle = 0$. This and the fact that the real and imaginary part of $|\delta\Psi(t)\rangle$ can be varied independently leads after partial integration of the variation

$$\begin{aligned}
\delta\widetilde{A}[\Psi] &= \int_{t_0}^{t_1} dt \, \langle \delta\Psi(t)|\mathrm{i}\partial_t - \widehat{H}(t)|\Psi(t)\rangle + \int_{t_0}^{t_1} dt \, \langle (\mathrm{i}\partial_t - \widehat{H}(t))\Psi(t)|\delta\Psi(t)\rangle \\
&+ \mathrm{i}\langle \psi(t)|\delta\psi(t)\rangle|_{t=t_0}^{t=t_1} = 0
\end{aligned} \tag{1.187}$$

to the Schrödinger equation

$$\left(\mathrm{i}\partial_t - \widehat{H}(t)\right)|\Psi(t)\rangle = 0. \tag{1.188}$$

However, if one tries to formulate this action principle accordingly within a density functional approach the supposed obvious way to use [10]

$$\widetilde{A}_{\Psi_0}[n] = \int_{t_0}^{t_1} dt \, \langle \Psi[n](t)|\mathrm{i}\partial_t - \widehat{H}(t)|\Psi[n](t)\rangle \tag{1.189}$$

will fail. A first problem is to fix some gauge. The density only fixes the wavefunction up to a time-dependent phase. The time-derivative in the definition of the Runge-Gross action functional now leads to different functionals depending on the gauge chosen. We could circumvent this problem by using variations of

$$A_{\Psi_0}[v] = \int_{t_0}^{t_1} dt \, \langle \Psi[v](t)|\mathrm{i}\partial_t - \widehat{H}(t)|\Psi[v](t)\rangle. \tag{1.190}$$

Here the phase is determined by the external potential chosen to propagate the initial state $|\Psi(t_0)\rangle$. By the virtue of the Runge-Gross theorem we can vary the external potential instead of the density as both uniquely define each other. Note that we use v as a parameter to vary the v-representable wavefunctions and let $\widehat{H}(t)$ being fixed. Variations of v uniquely define the variations of the wavefunction. In fact, as the Schrödinger equation is first order in time we are no longer allowed to pose a second boundary condition, i.e., the boundary condition $|\delta\Psi(t_0)\rangle = 0$ defines the later variations $|\delta\Psi(t)\rangle$ uniquely for some chosen external potential variation. Further we are not allowed to consider the real and imaginary part of $|\delta\Psi\rangle$ to be independent as both are determined via the potential variation δv. All these problems induced by the restriction of the variational freedom to v-representable wavefunctions accumulated [12] in the so called **symmetry-causality**

paradox.

We will make a short detour back to density functional theory. We had found at the end of the Hohenberg-Kohn theory section 1.3.2

$$F_{\mathrm{L}}[n] = E[v] - \int d^3r \; n(\boldsymbol{r}) \; v(\boldsymbol{r}), \tag{1.191}$$

the Legendre transform of $E[v]$, to be Fréchet differentiable. Further it holds by a generalization of the Hellman-Feynman theorem [12] that

$$\frac{\delta E[v]}{\delta v(\boldsymbol{r})} = n(\boldsymbol{r}), \qquad \frac{\delta F_{\mathrm{L}}[n]}{\delta n(\boldsymbol{r})} = -v(\boldsymbol{r}). \tag{1.192}$$

For the time-dependent case it would seem natural that such relations should also be found for our action functional. In the original Runge-Gross paper [10] the functional (1.190) was assumed to obey

$$\frac{\delta \widetilde{A}_{\Psi_0}[n]}{\delta n(\boldsymbol{r}, t)} = 0 \tag{1.193}$$

at the exact density by construction. However, the restriction of the wavefunctions to v-representable ones poses, as indicated above, severe problems for such a variational approach. Nevertheless we will assume equation (1.193) to be valid. Then we have via

$$\widetilde{A}_{\Psi_0}[n] = A_{\Psi_0}[n] - \int dt \; d^3r \; n(\boldsymbol{r}, t) \; v(\boldsymbol{r}, t) \tag{1.194}$$

with $A_{\Psi_0}[n] = \int_{t_0}^{t_1} dt \; \langle \Psi[n](t) | \mathrm{i}\partial_t - \widehat{T} - \widehat{V}_{\mathrm{int}} | \Psi[n](t) \rangle$ an universal functional of the density, the equation

$$\frac{\delta A_{\Psi_0}[n]}{\delta n(\boldsymbol{r}, t)} = v_{\Psi_0}([n]; \boldsymbol{r}, t). \tag{1.195}$$

Accordingly, we have via the Legendre transformation

$$\widetilde{A}_{\Psi_0}[v] = -A_{\Psi_0}[n] + \int dt \; d^3r \; v(\boldsymbol{r}, t) \; n(\boldsymbol{r}, t) \tag{1.196}$$

the relation

$$\frac{\delta \widetilde{A}_{\Psi_0}[v]}{\delta v(\boldsymbol{r}, t)} = n_{\Psi_0}([v]; \boldsymbol{r}, t). \tag{1.197}$$

Here we have introduced a relative minus in comparison to (1.192). Accordingly we could now define the exchange-correlation potential via the kernel of the functional derivative of the exchange-correlation functional

$$
\begin{aligned}
A^{\mathrm{xc}}_{\psi_0, \Phi_0}[n] = {} & A_{\Phi_0}[n] \\
& - \frac{1}{2} \int dt d^3r d^3r' n(\boldsymbol{r}, t) v_{\mathrm{int}}(|\boldsymbol{r} - \boldsymbol{r}'|) n(\boldsymbol{r}', t) - A_{\psi_0}[n]
\end{aligned}
\tag{1.198}
$$

where $A_{\Phi_0}[n]$ is the analogous functional for the noninteracting (Kohn-Sham) system with the initial noninteracting state $|\Phi_0\rangle$. However, if we now look at the kernel of the second functional derivative of $\widetilde{A}_{\Psi_0}[v]$

$$\frac{\delta^2 \widetilde{A}_{\Psi_0}[v]}{\delta v(\boldsymbol{r},t)\delta v(\boldsymbol{r}',t')} = \frac{\delta n_{\Psi_0}([v];\boldsymbol{r},t)}{\delta v(\boldsymbol{r}',t')} \tag{1.199}$$

which is just the usual linear response kernel

$$\chi_{\psi_0}([v];\boldsymbol{r},t,\boldsymbol{r}',t') = \frac{\delta n_{\Psi_0}([v];\boldsymbol{r},t)}{\delta v(\boldsymbol{r}',t')} \tag{1.200}$$

we meet a contradiction between causality and symmetry. While $\frac{\delta^2 \widetilde{A}_{\Psi_0}[v]}{\delta v(\boldsymbol{r},t)\delta v(\boldsymbol{r}',t')}$ is symmetric in its arguments $v(\boldsymbol{r},t)$ and $v(\boldsymbol{r}',t')$, $\chi([v];\boldsymbol{r},t,\boldsymbol{r}',t')$ is a causal kernel [11, 12]. Therefore the original Runge-Gross action functional $\widetilde{A}_{\Psi_0}[n]$ is wrong under the assumption of the above variational principle.

This finding can be formally generalized, leading to the following theorem.

Theorem 1.3.10 *Let $\widehat{\rho}_0$ be any initial configuration and $\widehat{V}_{\text{int}}$ some chosen interaction. Then there exist no twice differentiable functionals $\widetilde{A}_{\widehat{\rho}_0} : \mathcal{V}(\widehat{\rho}_0, \widehat{V}_{\text{int}}) \to \mathbb{R}$ and $A_{\widehat{\rho}_0} : \mathcal{N}(\widehat{\rho}_0, \widehat{V}_{\text{int}}) \to \mathbb{R}$ with the kernels*

$$\frac{\delta \widetilde{A}_{\widehat{\rho}_0}[v]}{\delta v(\boldsymbol{r},t)} = n_{\widehat{\rho}_0}([v];\boldsymbol{r},t) \quad , \quad \frac{\delta A_{\widehat{\rho}_0}[n]}{\delta n(\boldsymbol{r},t)} = v_{\widehat{\rho}_0}([n];\boldsymbol{r},t). \tag{1.201}$$

Proof. Assume we had some differentiable functional $\widetilde{A}_{\widehat{\rho}_0}[v]$ fulfilling the above condition. Then the symmetry and causality requirement (1.199) leads to a contradiction. If we had a functional $A_{\widehat{\rho}_0}[n]$ fulfilling the above requirement then we could by the Legendre transformation (1.196) construct a differentiable functional $\widetilde{A}_{\widehat{\rho}_0}[v]$, leading to a contradiction. $\square$

Although this theorem seems to be devastating for the attempt to derive the Kohn-Sham formalism based on an action principle there are ways to do so. The problems obviously arise through the usual quantum mechanical variational principle and the connected v-representability problem. One is not free to force the initial and final variation to be zero within a density functional approach. One possible route around this problem was introduced by van Leeuwen in [35] where he uses a Keldysh contour for time-dependent density functional theory, which only needs to take into account the initial boundary condition. Another way is found by introducing superoperators and Liouville space [11]. Only recently Vignale in [37] redefined the variational principle for time-dependent density functional theory as

$$\delta \widetilde{A}_{\psi_0}[n] = \mathrm{i}\langle \psi[n](t)|\delta\psi[n](t)\rangle, \tag{1.202}$$

solving the symmetry-causality paradox via a correction term not expressible as a functional derivative. The correction term would be zero if one enforced the final boundary condition of the usual variational principle.

Keldysh Formalism

Green's function methods are a primary tool to treat the quantum many-body problem [18]. However, the calculation of Green's functions for interacting systems is a very demanding task. Usually one uses perturbation theories to find approximations to the interacting Green's function. We distinguish three major branches: equilibrium zero temperature, equilibrium finite temperature and nonequilibrium Green's functions. All of those rely on the Gell-Mann-Low and on Wick's theorem [18] to derive a perturbation theory in terms of noninteracting Green's functions, which give rise to Feynman diagrams. In the first case one has a time-independent Hamiltonian and only looks at the ground-state. In the interaction picture one then singles out the free (noninteracting) part of the Hamiltonian and looks at the interaction as a perturbation, which is adiabatically switched on until t_0 and afterwards adiabatically switched off. The Gell-Mann-Low theorem guarantees that this procedure leads to the interacting ground-state at t_0 in the interaction picture. Because we only consider the ground-state (of a fermionic system), Wick's theorem is easily applied via normal ordering, finally leading to a diagrammatic perturbation theory in terms of two-point functions, i.e., Green's functions. However, if we look at an equilibrium finite temperature problem we do not only have the ground-state but a statistical mixture, the grand canonical ensemble, to calculate the expectation value. This poses a problem for the application of Wick's theorem, as the normal ordering does not lead to vanishing expressions like in the zero temperature case. Here one makes use of the Matsubara method [11, 18], which introduces complex times and the so-called Matsubara (Green's) functions to derive a generalized Wick's theorem. For the case of a nonequilibrium finite temperature problem a further generalization has to be done. Beside the particle-particle interaction one does also have a time-dependent one particle interaction which has to be considered. For the derivation of a diagrammatic perturbation theory one therefore introduces the so-called Keldysh time contour and nonequilibrium Green's functions [11,12].

We will use this formalism to introduce an action functional into time-dependent density functional theory following van Leeuwen [12,35].

Assume we have a system which is isolated until $t < t_0$ such that we have for the initial Hamiltonian $\widehat{H}_0$ the system in its thermal equilibrium

$$\widehat{\rho}_0 = \frac{\exp[-\beta(\widehat{H}_0 - \mu\widehat{N})]}{\mathrm{tr}\{\exp[-\beta(\widehat{H}_0 - \mu\widehat{N})]\}}, \tag{1.203}$$

with the inverse temperature $\beta = 1/k_\mathrm{B}T$, the chemical potential μ and the number operator $\widehat{N}$. If now $\widehat{H}_0$ and $\widehat{N}$ commute we can rewrite the initial density matrix with the evolution operator using a complex time argument as $\widehat{\rho}_0 = \exp[\beta\mu\widehat{N}]\widehat{U}(t_0 - \mathrm{i}\beta, t_0)/\mathrm{tr}\{\exp[\beta\mu\widehat{N}]\widehat{U}(t_0 - \mathrm{i}\beta, t_0)\}$. Thus a general observable may be expressed as

$$O(t) = \frac{\mathrm{tr}\left\{\exp(\beta\mu\widehat{N})\widehat{U}(t_0 - \mathrm{i}\beta, t_0)\widehat{U}(t_0, t)\widehat{O}\widehat{U}(t, t_0)\right\}}{\mathrm{tr}\left\{\exp(\beta\mu\widehat{N})\widehat{U}(t_0 - \mathrm{i}\beta, t_0)\right\}}. \tag{1.204}$$

47

Reading the numerator from right to left a further reformulation is possible as we can construct a time contour γ from t_0 to t, then back to t_0 and finally along the imaginary axis from t_0 to $t_0 - i\beta$. Because of the group property one may extend this contour up to $t \to \infty$. This time contour is called the **Keldysh contour** [11] leading to

$$O(z) = \frac{\operatorname{tr}\left\{\exp(\beta\mu\widehat{N})\mathcal{T}_\mathcal{C}\left[\exp(-i\int_\gamma dz'\widehat{H}(z'))\widehat{O}(z)\right]\right\}}{\operatorname{tr}\left\{\exp(\beta\mu\widehat{N})\mathcal{T}_\mathcal{C}\left[\exp(-i\int_\gamma dz'\widehat{H}(z'))\right]\right\}} \qquad (1.205)$$

where z and z' are the corresponding time variables and $\mathcal{T}_\mathcal{C}$ is the contour time ordering operator rearranging the times later on the contour to the left. The contour time argument in $\widehat{O}(z)$ indicates the position in the ordering. Points on the real axis (physical time) can either be on the forward branch (t_-) or on the backward branch (t_+) leading to cases where a later point on the contour may be earlier in real time. Keldysh functions $f(z)$ may be different for the same real-time argument t, depending on which branch they are , i.e., $f(t_-) \neq f(t_+)$. Keldysh functions with the property $f(t_-) = f(t_+)$ will be called physical.

The complex branch from t_0 to $t_0 - i\beta$ is analogous to the Matsubara method, which is used to rewrite the interacting many-body problem in terms of the noninteracting one leading to a generalized form of Wick's theorem [18]. For our purposes, depending on the initial configuration chosen, we may neglect the complex branch [11,12,35] later on.

We define the Keldysh space consisting of two point functions of the form [11]

$$k(z, z') = \delta(z, z')k^\delta(z) + \theta(z, z')k^>(z, z') + \theta(z', z)k^<(z, z') \qquad (1.206)$$

with $\theta(z, z')$ is equal to 1 for z later on the contour than z', 0 otherwise, and $\delta(z, z') = d\theta(z, z')/dz$. The Keldysh Green's functions are part of this space. For $k(z, z')$ we further define the greater and lesser functions

$$k^>(t, t') \equiv k(t_+, t'_-), \quad k^<(t, t') \equiv k(t_-, t'_+) \qquad (1.207)$$

and the retarded and advanced functions

$$k^R(t, t') = \delta(t, t')k^\delta(t) + \theta(t - t')\left[k^>(t, t') - k^<(t, t')\right], \qquad (1.208)$$
$$k^A(t, t') = \delta(t, t')k^\delta(t) - \theta(t' - t)\left[k^>(t, t') - k^<(t, t')\right] \qquad (1.209)$$

on the physical time axis. The retarded function $k^R(t, t')$ is zero for $t < t'$ and analogously $k^A(t, t')$ is zero for $t' < t$.

With t_{0-} the earlist time on the contour and $\widehat{U}(z, z') = \mathcal{T}_\mathcal{C}\{\exp[-i\int_{z'}^z d\bar{z}\widehat{H}(\bar{z})]\}$ we will now introduce the action functional

$$\widetilde{A}[v] = i\ln\operatorname{tr}\left\{\exp(\beta\mu\widehat{N})\widehat{U}(t_0 - i\beta, t_{0-})\right\}, \qquad (1.210)$$

which is merely a tool for generating equations of motion. Note that for a physical potential we have $\widehat{U}(t_0 - i\beta, t_{0-}) = \widehat{U}(t_0 - i\beta, t_0)$ and that the thermal density matrix $\widehat{\rho}_0$ is itself a functional of the density [36]. From

$$i\partial_z\widehat{U}(z, z') = \widehat{H}(z)\widehat{U}(z, z'), \quad i\partial_{z'}\widehat{U}(z, z') = -\widehat{U}(z, z')\widehat{H}(z') \qquad (1.211)$$

we find for some variation $\delta\widehat{V}(z)$

$$
\begin{aligned}
\mathrm{i}\partial_z\delta\widehat{U}(z,z') &= \delta\widehat{V}(z)\widehat{U}(z,z') + \widehat{H}(z)\delta\widehat{U}(z,z') && (1.212) \\
\mathrm{i}\partial_{z'}\delta\widehat{U}(z,z') &= -\delta\widehat{U}(z,z')\widehat{H}(z') - \widehat{U}(z,z')\delta\widehat{V}(z'). && (1.213)
\end{aligned}
$$

With $\widehat{U}(z,z) = 1$ and $\delta\widehat{U}(z,z) = 0$

$$
\delta\widehat{U}(z,z') = -\mathrm{i}\int_{z'}^{z} d\bar{z}\,\widehat{U}(z,\bar{z})\delta\widehat{V}(\bar{z})\widehat{U}(\bar{z},z') \tag{1.214}
$$

along the Keldysh contour going from t_{0-} to $t_0 - \mathrm{i}\beta$. Note that the variations on the forward direction $\delta\widehat{V}(t_-)$ are independent of the variations on the backward branch $\delta\widehat{V}(t_+)$. If we assume a variation of the form

$$
\delta\widehat{V}(z) = \int d^3r\,\delta v(\boldsymbol{r},z)\widehat{n}(\boldsymbol{r}) \tag{1.215}
$$

and functional differentiability we end up with

$$
\begin{aligned}
\frac{\delta\widetilde{A}[v]}{\delta v(\boldsymbol{r},z)} &= \frac{\mathrm{tr}\left\{\exp(\beta\mu\widehat{N})\mathcal{T}_\mathcal{C}\left[\exp(-\mathrm{i}\int_\gamma dz'\widehat{H}(z'))\widehat{n}(\boldsymbol{r},z)\right]\right\}}{\mathrm{tr}\left\{\exp(\beta\mu\widehat{N})\mathcal{T}_\mathcal{C}\left[\exp(-\mathrm{i}\int_\gamma dz'\widehat{H}(z'))\right]\right\}} \\
&= n([v];\boldsymbol{r},z).
\end{aligned} \tag{1.216}
$$

We are of course interested in physical potentials, i.e., $v(\boldsymbol{r},t_-) = v(\boldsymbol{r},t_+)$ as well as physical densities, i.e., $n(\boldsymbol{r},t_-) = n(\boldsymbol{r},t_+)$. If we now look at the density-response function, i.e., the linear response kernel, we find in Keldysh space

$$
\begin{aligned}
\chi([v];\boldsymbol{r},z,\boldsymbol{r}',z') &= \frac{\delta n([v];\boldsymbol{r},z)}{\delta v(\boldsymbol{r}',z')} && (1.217) \\
&= \frac{\delta\widetilde{A}[v]}{\delta v(\boldsymbol{r},z)\delta v(\boldsymbol{r}',z')} = \chi([n];\boldsymbol{r}',z',\boldsymbol{r},z).
\end{aligned}
$$

In Keldysh space the response function, which is a second functional derivative, is symmetric in its space-time arguments. However, if we calculate the actual physical response for a physical variation $\delta v(\boldsymbol{r}',t'_\pm) = \delta v(\boldsymbol{r}',t')$

$$
\begin{aligned}
\delta n([v;\delta v];\boldsymbol{r},t) &= \delta n([v;\delta v];\boldsymbol{r},t_\pm) && (1.218) \\
&= \int_\gamma dz' \int d^3r'\,\chi([v];\boldsymbol{r},t_\pm,\boldsymbol{r}',z')\delta v(\boldsymbol{r}',z')
\end{aligned}
$$

we find, as noted before, that the complex branch integration does not contribute as $\delta v(\boldsymbol{r}',t) \neq 0$ only for $t > t_0$. Further, with $\chi = \chi^>$ on the forward branch and $\chi = \chi^<$ on the backward branch, we end up with a retarded, i.e., causal, kernel

$$
\begin{aligned}
\delta n([v;\delta v];\boldsymbol{r},t) &= \int_{t_0}^{t} dt' \int d^3r'\,[\chi^>([v];\boldsymbol{r},t,\boldsymbol{r}',t') - \chi^<([v];\boldsymbol{r},t,\boldsymbol{r}',t')]\delta v(\boldsymbol{r}',t') \\
&= \int_{t_0}^{\infty} dt' \int d^3r'\,\chi^{\mathrm{R}}([v];\boldsymbol{r},t,\boldsymbol{r}',t')\delta v(\boldsymbol{r}',t').
\end{aligned} \tag{1.219}
$$

Therefore the second functional derivative, if expressed in physical time, is causal, whereas it is symmetric on the Keldysh contour.

For general initial configuration $\widehat{\rho}_0$ we thus define the **action functional in Keldysh space** as

$$\widetilde{A}_{\widehat{\rho}_0}[v] = \mathrm{i} \ln \mathrm{tr} \left\{ \widehat{\rho}_0 \exp(\beta \widehat{H}_0) \widehat{U}(t_0 - \mathrm{i}\beta, t_{0-}) \right\}. \qquad (1.220)$$

As is usually done one could ignore the complex branch [12, 35]. It is straightforward to redefine the contour $\bar{\gamma}$ going from t_0 to t and back to t_0 and use a properly redefined functional

$$\bar{A}_{\widehat{\rho}_0}[v] := \mathrm{i} \ln \mathrm{tr} \left\{ \widehat{\rho}_0 \widehat{U}(t_0, t_{0-}) \right\} \qquad (1.221)$$

with $\widehat{U}(t_0, t_{0-})$ the time-evolution operator on the new contour $\bar{\gamma}$. This solves the symmetry-causality paradox in time-dependent density functional theory.

Accordingly one can then define via a Legendre transformation, assuming a one-to-one relation between $n(\boldsymbol{r}, z)$ and $v(\boldsymbol{r}, z)$ on the Keldysh contour,

$$A_{\widehat{\rho}_0}[n] = -\widetilde{A}_{\widehat{\rho}_0}[v] + \int_\gamma dz \int d^3 r \, v(\boldsymbol{r}, z) \, n(\boldsymbol{r}, z) \qquad (1.222)$$

which has the property $\delta A_{\widehat{\rho}_0}[n]/\delta n(\boldsymbol{r}, z) = v_{\widehat{\rho}_0}([n]; \boldsymbol{r}, z)$. The functional

$$\widetilde{A}_{\widehat{\rho}_0}[n] = A_{\widehat{\rho}_0}[n] - \int_\gamma dz \int d^3 r \, v(\boldsymbol{r}, z) \, n(\boldsymbol{r}, z), \qquad (1.223)$$

where $v(\boldsymbol{r}, z)$ is some fixed potential, can be used as a basis for a variational principle in time-dependent density functional theory, leading to

$$\frac{\delta \widetilde{A}_{\widehat{\rho}_0}[n]}{\delta n(\boldsymbol{r}, z)} = v_{\widehat{\rho}_0}([n]; \boldsymbol{r}, z) - v(\boldsymbol{r}, z) = 0 \qquad (1.224)$$

whenever $v_{\widehat{\rho}_0}([n]; \boldsymbol{r}, z) = v(\boldsymbol{r}, z)$, i.e., the right density is chosen.

The whole procedure can be repeated for a noninteracting system. For an initial noninteracting configuration $\widehat{\rho}_0'$ we then may define the exchange-correlation action functional

$$A^{\mathrm{xc}}_{\widehat{\rho}_0, \widehat{\rho}_0'}[n] = A_{\widehat{\rho}_0'}[n] - A_{\widehat{\rho}_0}[n] - \frac{1}{2} \int dz d^3 r \int dz' d^3 r' \frac{n(\boldsymbol{r}, z) n(\boldsymbol{r}', z')}{|\boldsymbol{r} - \boldsymbol{r}'|} \qquad (1.225)$$

which leads via a functional derivative to

$$\frac{\delta A^{\mathrm{xc}}_{\widehat{\rho}_0, \widehat{\rho}_0'}[n]}{\delta n(\boldsymbol{r}, z)} = v^{\mathrm{xc}}_{\widehat{\rho}_0, \widehat{\rho}_0'}([n]; \boldsymbol{r}, z). \qquad (1.226)$$

Approximations for the Exchange-Correlation Potential

The exchange-correlation potential is the crucial point in the usual way to use density functional theories, i.e., the Kohn-Sham construction. All of the complex inner forces are hidden within the Hartree-exchange-correlation potential, and one usually assumes that the exchange-correlation part is small compared to the Hartree-term. Further, one employs approximations for the exchange-correlation part coming from known solutions of particular systems, e.g., the homogeneous electron gas. However, for the case of time-dependent density functional theory another point comes into play. The exact exchange-correlation potentials are nonlocal in time, i.e., they have memory. This point will be thoroughly discussed later on. Until now most approximations adopt an adiabatic point of view. These adiabatic approximations only depend on the instantaneous density. Further, there are known **exact conditions** which should, in principle, be satisfied by the exact exchange-correlation potential [11]. Though most approximations seem to be very crude, one often finds good agreement with experiment [11].

The most common approximation is the **adiabatic local density approximation** [9,11]

$$v_{\mathrm{xc}}^{\mathrm{ALDA}}([n]; \boldsymbol{r}, t) = \left. \frac{\delta E_{\mathrm{xc}}[n]}{\delta n} \right|_{n=n(\boldsymbol{r},t)}, \tag{1.227}$$

where $E_{\mathrm{xc}}[n]$ is the exchange-correlation energy of the corresponding time-independent system. One usually assumes the equilibrium system to be nearly homogeneous such that every small volume element can be considered independent of the other volume elements. Each element then is regarded to be a homogeneous many-body system of the local density with the exchange-correlation energy of the homogeneous electron gas $E_{\mathrm{xc}}^{\mathrm{heg}}[n]$. This energy functional can be decomposed $E_{\mathrm{xc}}^{\mathrm{heg}}[n] = E_{\mathrm{x}}^{\mathrm{heg}}[n] + E_{\mathrm{c}}^{\mathrm{heg}}[n]$ into an exchange energy term analytically known

$$E_{\mathrm{x}}^{\mathrm{heg}}[n] = -\frac{3}{4} \left(\frac{3}{\pi} \right)^{1/3} \int d^3r \, n^{4/3}(\boldsymbol{r}) \tag{1.228}$$

and a correlation term $E_{\mathrm{c}}^{\mathrm{heg}}[n]$ for which several approximations exist [9]. A possible derivation which is closely connected to the time-dependent case is based upon the many-body equation of motion [21]. The many-body equation of a homogeneous equilibrium system is

$$i\partial_t \widehat{\psi}_{\sigma,\mathrm{H}} = -\frac{1}{2} \boldsymbol{\nabla}^2 \widehat{\psi}_{\sigma,\mathrm{H}} + \int d^3r' v_{\mathrm{int}}(|\boldsymbol{r} - \boldsymbol{r}'|) \widehat{n}_{\mathrm{H}}(\boldsymbol{r}, t) \widehat{\psi}_{\sigma,\mathrm{H}}. \tag{1.229}$$

The associated stress tensor, i.e., equation (1.89), then reads

$$P_{\mu\nu}[n] = \delta_{\mu\nu} \left(\frac{2}{3} E_{\mathrm{kin}} - \frac{1}{6} \int d^3r \, r^\mu \frac{\partial v_{\mathrm{int}}(|\boldsymbol{r}|)}{\partial r^\mu} \varrho^{\mathrm{heg}}(|\boldsymbol{r}|) \right) \tag{1.230}$$

with E_{kin} the kinetic energy per volume and ϱ^{heg} the two-particle density of the homogeneous electron gas. We can separate the Hartree contribution to the stress tensor by using

the pair correlation function defined in general as $G_2(\boldsymbol{r}, \boldsymbol{r}') = \langle \sum_\sigma \widehat{\psi}_\sigma^\dagger(\boldsymbol{r}) \widehat{n}(\boldsymbol{r}') \widehat{\psi}_\sigma(\boldsymbol{r}) \rangle - n(\boldsymbol{r}) n(\boldsymbol{r}')$ instead of the full two-particle density, i.e.,

$$P'_{\mu\nu}[n] = \delta_{\mu\nu} \left(\frac{2}{3} E_{\text{kin}} - \frac{1}{6} \int d^3 r \; r^\mu \frac{\partial v_{\text{int}}(|\boldsymbol{r}|)}{\partial r^\mu} G_2^{\text{heg}}(|\boldsymbol{r}|) \right). \tag{1.231}$$

The noninteracting term, i.e., equation (1.90), is

$$\breve{T}_{\mu\nu}[n] = \delta_{\mu\nu} \left(\frac{2}{3} E_{\text{kin}}^{\text{iF}} \right) \tag{1.232}$$

with $E_{\text{kin}}^{\text{iF}}$ the energy per volume of the ideal Fermi gas. The exchange-correlation potential can thus be found via

$$\partial_\mu v_{\text{xc}}([n]; \boldsymbol{r}) = \frac{1}{n} \partial_\nu \left(P'_{\mu\nu} - \breve{T}_{\mu\nu} \right). \tag{1.233}$$

This equation can be brought into the more familiar form of the Poisson equation

$$\boldsymbol{\nabla}_{\boldsymbol{r}}^2 v_{\text{xc}}([n]; \boldsymbol{r}) = 4\pi \rho_{\text{xc}}(\boldsymbol{r}) \tag{1.234}$$

with

$$\rho_{\text{xc}} = \frac{1}{4\pi} \partial_\mu \left(\frac{\partial_\nu (P'_{\mu\nu} - \breve{T}_{\mu\nu})}{n} \right) \tag{1.235}$$

the exchange-correlation "charge-density". Of course, this approximate treatment is to be expected to fail if the density is far from homogeneous or if the density inserted into this approximation is rapidly changing. Nevertheless, even for such cases, the adiabatic local density approximation works surprisingly well for many applications [11].

The exact Hartree-exchange-correlation potential should in principle contain memory effects, i.e., it should dependend on previous densities. Hence a further important step in the approximations of the potential is to go beyond adiabatic approaches. It is expected, that memory is very important to describe, for instance, resonant dynamics [13]. In order to derive a **nonadiabatic local density approximation** one may argue as follows: Assume one considers the time-dependent problem not in the laboratory reference frame but in a noninertial reference frame which moves with an infinitesimal fluid element. This amounts to a transformation from an Eulerian to a Lagrangian reference frame. In a comoving Lagrangian frame $(\boldsymbol{\xi}, t)$ the density $n(\boldsymbol{r}, t)$ and the current density $\boldsymbol{j}(\boldsymbol{r}, t)$ become exact integrals of motion [20], i.e.,

$$\widetilde{n}(\boldsymbol{\xi}, t) = n_0(\boldsymbol{\xi}), \quad \widetilde{\boldsymbol{j}}(\boldsymbol{\xi}, t) = 0. \tag{1.236}$$

In such a reformulation one can in principle deduce nonadiabatic local density approximations in a similar way as adiabatic local density approximations in the time-independent case. Assume, the time-independent density of the Lagrangian reference frame to be nearly homogeneous. Then every small volume element can be considered as an homogeneous system of the local density, independent of the other elements. In addition, we

we have to pose the restriction that the deformation of the initial system is homogeneous too. This idea was pursued by Tokatly in [20, 21].

The transformation from an Euclidean coordinate system $(x^1, ..., x^n)$ to a general reference frame $(z^1, ..., z^n)$ at some point $P = (x_0^1, ..., x_0^n)$ with

$$
\begin{aligned}
x^\mu &= x^\mu(z^1, ..., z^n) \\
z^\mu &= z^\mu(x^1, ..., x^n)
\end{aligned}
\tag{1.237}
$$

and the help of the inverse function theorem [38]

$$
\frac{\partial z^\mu}{\partial x^\alpha} \frac{\partial x^\alpha}{\partial z^\nu} = \delta^\mu_\nu
\tag{1.238}
$$

is for a **vector** $\boldsymbol{r} = (r^1, ..., r^n)$ relative to $(x^1, ..., x^n)$

$$
\xi^\nu = \left. \frac{\partial z^\nu}{\partial x^\mu} \right|_P r^\mu,
\tag{1.239}
$$

for a **covector** $\mathbf{r} = (r_1, ..., r_n)$ relative to $(x^1, ..., x^n)$

$$
\xi_\mu = \left. \frac{\partial x^\nu}{\partial z^\mu} \right|_P r_\nu
\tag{1.240}
$$

and a **quadratic form** (on vectors) $\widetilde{g}_{\mu\nu}$ relative to $(x^1, ..., x^n)$

$$
g_{\mu\nu} = \left. \frac{\partial x^\alpha}{\partial z^\mu} \right|_P \widetilde{g}_{\alpha\beta} \left. \frac{\partial x^\beta}{\partial z^\nu} \right|_P.
\tag{1.241}
$$

The covariant derivative of a zero rank tensor f can be written as

$$
\nabla_\mu f = \frac{\partial f}{\partial z^\mu}.
\tag{1.242}
$$

The (covariant) divergence of a vector field (T^μ) in terms of the Christoffel symbols (connexion) $\Gamma^\mu_{\nu\alpha}$ compatible with the **pseudo Riemannian metric**

$$
g_{\mu\nu} = \frac{\partial x^\alpha}{\partial z^\mu} \frac{\partial x^\alpha}{\partial z^\nu}
\tag{1.243}
$$

reads as

$$
\mathrm{div}T = \nabla_\mu T^\mu = T^\mu_{;\mu} = \frac{\partial T^\mu}{\partial z^\mu} + \Gamma^\mu_{\alpha\mu} T^\alpha,
\tag{1.244}
$$

with $\Gamma^\alpha_{\mu\nu} = (1/2) g^{\alpha\beta}(\partial g_{\beta\nu}/\partial z^\mu + \partial g_{\mu\beta}/\partial z^\nu - \partial g_{\mu\nu}/\partial z^\beta)$. This can be further simplified if we assume $g_{\mu\nu} = g_{\nu\mu}$

$$
\Gamma^\mu_{\alpha\mu} = \frac{1}{2} g^{\mu\beta} \frac{\partial g_{\mu\beta}}{\partial z^\alpha} = \frac{1}{2g} \frac{\partial g}{\partial z^\alpha} = \frac{\partial}{\partial z^\alpha} \ln(\sqrt{|g|}),
\tag{1.245}
$$

where $g = \det(g_{\mu\nu})$, and we used $\partial \det(A)/\partial A_{\mu\nu} = \det(A)(A^{-1})_{\nu\mu}$ to rewrite

$$\frac{\partial g}{\partial z^\alpha} = \frac{\partial g_{\mu\nu}}{\partial z^\alpha}\frac{\partial g}{\partial g_{\mu\nu}} = \frac{\partial g_{\mu\nu}}{\partial z^\alpha}gg^{\nu\mu} = g^{\mu\nu}\frac{\partial g_{\mu\nu}}{\partial z^\alpha}g, \tag{1.246}$$

with $g^{\mu\alpha}g_{\alpha\nu} = \delta_\mu^\nu$. The covariant divergence can thus be written as

$$\nabla_\mu T^\mu = \frac{1}{\sqrt{|g|}}\frac{\partial}{\partial z^\mu}\left(\sqrt{|g|}T^\mu\right). \tag{1.247}$$

Therefore the covariant Laplacian reads as

$$\Delta = \nabla_\mu\nabla^\mu = \nabla_\mu g^{\mu\alpha}\nabla_\alpha = \nabla_\mu g^{\mu\alpha}\frac{\partial}{\partial z^\alpha} = \frac{1}{\sqrt{|g|}}\frac{\partial}{\partial z^\mu}\sqrt{|g|}g^{\mu\alpha}\frac{\partial}{\partial z^\alpha}. \tag{1.248}$$

With this knowledge we can deduce the quantum equations of motion for the Lagrangian reference frame. The transformation is defined via

$$\frac{\partial \boldsymbol{r}(\boldsymbol{\xi},t)}{\partial t} = \boldsymbol{v}(\boldsymbol{r}(\boldsymbol{\xi},t),t) = \frac{\boldsymbol{j}(\boldsymbol{r}(\boldsymbol{\xi},t),t)}{n(\boldsymbol{r}(\boldsymbol{\xi},t),t)}, \quad \boldsymbol{r}(\boldsymbol{\xi},0) = \boldsymbol{\xi}, \tag{1.249}$$

where the propability density and probability current are defined by equation (1.66) and (1.69). The function $\boldsymbol{r}(\boldsymbol{\xi},t)$ corresponds to the trajectory of an infinitesimally small fluid element. Every fluid element is uniquely labeled by its initial position, i.e., its Lagrangian coordinate $\boldsymbol{\xi}$. The corresponding time-dependent metric is $g_{\mu\nu} = g_{\mu\nu}(\boldsymbol{\xi},t)$, which is also denoted the **deformation tensor**. With the transformation [20] of

$$|\boldsymbol{r} - \boldsymbol{r}'| = \int_0^1 \sqrt{g_{\mu\nu}(\partial x^\mu/\partial\lambda)(\partial x^\nu/\partial\lambda)}d\lambda := l_{\boldsymbol{\xi},\boldsymbol{\xi}'}, \tag{1.250}$$

where $\partial x^\mu/\partial\lambda := (\partial\xi^\mu/\partial r^\alpha(\lambda))(\partial r^\alpha(\lambda)/\partial\lambda)$ and $\boldsymbol{r}(\lambda) = \boldsymbol{r}' + (\boldsymbol{r}-\boldsymbol{r}')\lambda$, we have

$$v_{\text{int}}(|\boldsymbol{r}-\boldsymbol{r}'|) = v_{\text{int}}(l_{\boldsymbol{\xi},\boldsymbol{\xi}'}). \tag{1.251}$$

Further one finds for the equal time (anti)commutation relations with g being the square of the Jacobian and therefore positive

$$\left[\widehat{\psi}_{\sigma,\text{H}}(\boldsymbol{\xi},t), \widehat{\psi}^\dagger_{\sigma',\text{H}}(\boldsymbol{\xi}',t)\right]_{-\epsilon} = \frac{1}{\sqrt{g}}\delta^3(\boldsymbol{\xi}-\boldsymbol{\xi}')\delta_{\sigma,\sigma'}. \tag{1.252}$$

If we renormalize the creation and annihilation operators

$$\widetilde{\widehat{\psi}}^\dagger_{\sigma,\text{H}}(\boldsymbol{\xi},t) = g^{1/4}\widehat{\psi}^\dagger_{\sigma,\text{H}}(\boldsymbol{\xi},t), \quad \widetilde{\widehat{\psi}}_{\sigma,\text{H}}(\boldsymbol{\xi},t) = g^{1/4}\widehat{\psi}_{\sigma,\text{H}}(\boldsymbol{\xi},t) \tag{1.253}$$

we automatically take the change of unit volume in the deformed reference frame into account. Therefore also the definition of the density changes to $\widetilde{\widehat{n}}_\text{H}(\boldsymbol{\xi}',t) = \sum_\sigma \widetilde{\widehat{\psi}}^\dagger_{\sigma,\text{H}}(\boldsymbol{\xi},t)\widetilde{\widehat{\psi}}_{\sigma,\text{H}}(\boldsymbol{\xi},t)$. Hence one finds with the kinetic momentum

$$\widehat{K}_\mu = -\mathrm{i}\frac{\partial}{\partial\xi^\mu} - \widetilde{v}_\mu \tag{1.254}$$

$\widetilde{v}_\mu = g_{\mu\nu}(\partial\xi^\nu/\partial x^\alpha)v^\alpha$ the **quantum equation of motion in the comoving Lagrangian reference frame**

$$i\frac{\partial\widehat{\widetilde{\psi}}_{\sigma,\mathrm{H}}(\boldsymbol{\xi},t)}{\partial t} = \left(g^{-\frac{1}{4}}\frac{\widehat{K}_\mu\sqrt{g}\widehat{K}^\mu}{2}g^{-\frac{1}{4}} + v_{\mathrm{ext}}(\boldsymbol{\xi},t) - \frac{\widetilde{v}_\mu\widetilde{v}^\mu}{2}\right)\widehat{\widetilde{\psi}}_{\sigma,\mathrm{H}}(\boldsymbol{\xi},t)$$
$$+ \int d^3\xi' v_{\mathrm{int}}(l_{\boldsymbol{\xi},\boldsymbol{\xi}'})\widehat{\widetilde{n}}_{\mathrm{H}}(\boldsymbol{\xi}',t)\widehat{\widetilde{\psi}}_{\sigma,\mathrm{H}}(\boldsymbol{\xi},t). \tag{1.255}$$

The quantum equation of motion in the laboratory reference frame is given by equation (1.65). Here we gave the external potential the subindex 'ext' to be distinguishable from the velocity vector field $\boldsymbol{v}$. Note that the interaction depends on the length of the geodesic $v_{\mathrm{int}}(l_{\boldsymbol{\xi},\boldsymbol{\xi}'})$ on the space with the time dependent metric $g_{\mu\nu}(\boldsymbol{\xi},t)$. One can show the validity of (1.236) using

$$\widehat{\widetilde{j}}_{\mathrm{H}}^\mu = g^{\mu\nu}\left[-\frac{i}{2}\sum_\sigma\left(\widehat{\widetilde{\psi}}_{\sigma,\mathrm{H}}^\dagger\partial_\nu\widehat{\widetilde{\psi}}_{\sigma,\mathrm{H}} - (\partial_\nu\widehat{\widetilde{\psi}}_{\sigma,\mathrm{H}}^\dagger)\widehat{\widetilde{\psi}}_{\sigma,\mathrm{H}}\right) - \widetilde{v}_\nu\widehat{\widetilde{n}}_{\mathrm{H}}\right] \tag{1.256}$$

where $\partial/\partial\xi^\mu \equiv \partial_\mu$. Note that the density in the laboratory reference frame is recovered via $n(\boldsymbol{r},t) = \widetilde{n}(\boldsymbol{\xi}(\boldsymbol{r},t),t)/\sqrt{g(\boldsymbol{\xi}(\boldsymbol{r},t),t)}$. Finally one arrives at the **local force balance equation in the Lagrangian frame**

$$\widetilde{n}\left[\partial_t\widetilde{v}_\mu + \partial_\mu\left(v_{\mathrm{ext}} - \frac{\widetilde{v}_\nu\widetilde{v}^\nu}{2}\right)\right] + \sqrt{g}\widetilde{P}_{\mu;\nu}^\nu = 0 \tag{1.257}$$

with $\widetilde{P}_{\mu\nu} = (\partial x^\alpha/\partial\xi^\mu)(\partial x^\beta/\partial\xi^\nu)P_{\alpha\beta}$, $P_{\alpha\beta}$ defined via equation (1.89), and the covariant derivative is

$$\widetilde{P}_{\mu;\nu}^\nu = \frac{1}{\sqrt{g}}\partial_\nu\left(\sqrt{g}\widetilde{P}_\mu^\nu\right) - \frac{1}{2}\frac{\partial g_{\alpha\beta}}{\partial\xi^\mu}\widetilde{P}^{\alpha\beta}. \tag{1.258}$$

The first term is a linear acceleration force, the second term is proportional to the moving frame independent of the particle momentum, and the third term describes the forces of internal stress. Equations (1.255) and (1.257) constitute the full set of equations of the quantum many-body problem in the Lagrangian frame [21]. Like in the laboratory reference frame one may now define a system of noninteracting particles in an effective external potential. The Kohn-Sham equations of motion thus read

$$i\frac{\partial\widehat{\widetilde{\psi}}_{\sigma,\mathrm{H}}(\boldsymbol{\xi},t)}{\partial t} = \left(g^{-\frac{1}{4}}\frac{\widehat{K}_\mu\sqrt{g}\widehat{K}^\mu}{2}g^{-\frac{1}{4}} + v_{\mathrm{ext}}(\boldsymbol{\xi},t) + v_{\widehat{\rho}_0,\widehat{\rho}_0'}^{\mathrm{Hxc}}([\widetilde{\boldsymbol{v}}];\boldsymbol{\xi},t)\right.$$
$$\left. - \frac{\widetilde{v}_\mu\widetilde{v}^\mu}{2}\right)\widehat{\widetilde{\psi}}_{\sigma,\mathrm{H}}(\boldsymbol{\xi},t) \tag{1.259}$$

and

$$\partial_\mu v_{\widehat{\rho}_0,\widehat{\rho}_0'}^{\mathrm{Hxc}}([\widetilde{\boldsymbol{v}}];\boldsymbol{\xi},t) = \frac{\sqrt{g}}{n_0}\left(\widetilde{P}_{\mu;\nu}^\nu[\widehat{\rho}_0,\widetilde{\boldsymbol{v}}] - \widetilde{T}_{\mu;\nu}^\nu[\widehat{\rho}_0',\widetilde{\boldsymbol{v}}]\right). \tag{1.260}$$

Here $\widetilde{P}^{\nu}_{\mu;\nu}[\widehat{\rho}_0, \widetilde{\boldsymbol{v}}]$ are the internal stress forces of the interacting problem and $\widetilde{\widetilde{T}}^{\nu}_{\mu;\nu}[\widehat{\rho}'_0, \widetilde{\boldsymbol{v}}]$ its noninteracting counterpart just like in the laboratory reference frame. Note that one may rewrite the dependence of the internal stress forces on the velocity into a dependence on the time-dependent metric $g_{\mu\nu}$ and an effective magnetic field $\widetilde{F}_{\mu\nu}$ [21]. In this geometric reformulation of time-dependent density functional theory one encounters naturally a vector field as the fundamental collective variable and no longer just a scalar one. This reformulation has strong resemblances to current density functional theory [11] and leads to similar results for a nonadiabatic local density approximation.

For the nonadiabatic local density approximation we follow the same route as in the static case (1.229). We assume the initial density to be almost homogeneous. However, we further pose the restriction that the inhomogeneity of the deformation is negligible, i.e., $g_{\mu\nu} \simeq g_{\mu\nu}(t)$, leading to [21]

$$i\partial_t \widehat{\widetilde{\psi}}_{\sigma,\mathrm{H}} = -\frac{g_{\mu\nu}(t)}{2}\partial_\mu\partial_\nu\widehat{\widetilde{\psi}}_{\sigma,\mathrm{H}} + \int d^3\xi' v_{\mathrm{int}}(l_{\boldsymbol{\xi},\boldsymbol{\xi}'})\widehat{\widetilde{n}}_{\mathrm{H}}(\boldsymbol{\xi}', t)\widehat{\widetilde{\psi}}_{\sigma,\mathrm{H}}. \tag{1.261}$$

Due to the density being stationary in the Lagrangian reference frame one can then handle the nearly homogeneous many-body system as in the equilibrium case. With an elastic approximation for Coulombic systems [21] and the transformation back into the laboratory reference frame one finds the Hartree-exchange-correlation potential by use of the Poisson equation where the first term generates the Hartree-term,

$$\boldsymbol{\nabla}^2 v_{\mathrm{Hxc}}^{\mathrm{TDLDA}}([n, g_{\mu\nu}]; \boldsymbol{r}, t) = 4\pi\left(n + \rho_{\mathrm{xc}}[n, g_{\mu\nu}]\right), \tag{1.262}$$

$$\rho_{\mathrm{xc}} = \frac{1}{4\pi}\frac{\partial}{\partial r^\mu}\left[\frac{1}{n}\frac{\partial}{\partial r^\nu}P_{\mu\nu}^{xc}[n, g_{\mu\nu}]\right] \tag{1.263}$$

and

$$P_{\mu\nu}^{\mathrm{xc}} = \frac{2}{3}g_{\mu\nu}\sqrt{g}E_{\mathrm{xc}}^{\mathrm{kin}}\left[\frac{n}{\sqrt{g}}\right] + L_{\mu\nu}[g_{\alpha\beta}]E_{\mathrm{xc}}^{\mathrm{pot}}\left[\frac{n}{\sqrt{g}}\right]. \tag{1.264}$$

With the initial condition $g_{\mu\nu}(\boldsymbol{r}, 0) = \delta_{\mu\nu}$ we further have

$$\partial_t g_{\mu\nu} = -v^\alpha\partial_\alpha g_{\mu\nu} - (\partial_\mu v^\alpha)g_{\alpha\nu} - (\partial_\nu v^\alpha)g_{\alpha\mu}, \tag{1.265}$$

$L_{\mu\nu}[g_{\alpha\beta}]$ some purely geometric factor, $E_{\mathrm{xc}}^{\mathrm{kin}}$ the kinetic and $E_{\mathrm{xc}}^{\mathrm{pot}}$ the potential energy of the homogeneous electron gas. Thus for every time-step one has to solve equation (1.265) and apply the deduced time-dependent metric to calculate $P_{\mu\nu}^{\mathrm{xc}}$ and ρ_{xc}. Via solution of the Poisson equation (1.262) one finds the nonadiabatic local density approximation, which then can be used to propagate the Kohn-Sham-equation [39].

Another important approximation is the so-called (adiabatic) **exact exchange approximation**. There one usually uses the same energy functional as in the Hartree-Fock approach which cancels all unphysical self-interactions of the Kohn-Sham orbitals. This is of special importance for our further considerations and can be applied in general via optimized effective potentials to find the corresponding local potentials [40].

However, even more involved nonadiabatic as well as adiabatic exact exchange methods are available [11]. We will derive the exact exchange method for a simple but instructive case, namely a spin singlet system. In Hartree-Fock approximation the many-body wavefunction is expressed as a Slater determinant of spin-orbitals,

$$\psi_i(\boldsymbol{r})|\sigma\rangle_i \in L^2(\mathbb{R}^3) \otimes \mathbb{C}^2, \tag{1.266}$$

where the subindex i contains all quantum numbers including the spin index. The two-particle Slater determinant reads

$$|\Psi\rangle = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_{(1)}(\boldsymbol{r}_1)|\sigma_1\rangle_{(1)} & \psi_{(1)}(\boldsymbol{r}_2)|\sigma_2\rangle_{(1)} \\ \psi_{(2)}(\boldsymbol{r}_1)|\sigma_1\rangle_{(2)} & \psi_{(2)}(\boldsymbol{r}_2)|\sigma_2\rangle_{(2)} \end{vmatrix}. \tag{1.267}$$

The basis set for the two-particle wavefunctions contains all possible combinations of spin projections and orthonormal spatial wavefunctions. With the Schrödinger Hamiltonian $\widehat{H}$ we find the energy for a general N-body Slater determinant to be

$$\begin{aligned} E[\{\psi_i|\sigma\rangle_i\}] &= \sum_{i=1}^{N} \langle \psi_i|\widehat{T} + \widehat{V}|\psi_i\rangle \\ &+ \frac{1}{2} \sum_{i \neq j} \int d^3r\, d^3r'\, \big[|\psi_j(\boldsymbol{r}')|^2 |\psi_i(\boldsymbol{r})|^2 v_{\text{int}}(|\boldsymbol{r} - \boldsymbol{r}'|) \\ &- \psi_i^*(\boldsymbol{r}')\psi_j^*(\boldsymbol{r}) v_{\text{int}}(|\boldsymbol{r} - \boldsymbol{r}'|)\psi_i(\boldsymbol{r})\psi_j(\boldsymbol{r}')\delta_{\sigma_i\sigma_j} \big]. \end{aligned} \tag{1.268}$$

By variation with respect to the orbitals the ground-state energy is found. Via Lagrangian multipliers the condition that all orbitals should be normalized is incorporated, leading to the **Hartree-Fock equation**

$$\left[\widehat{T} + \widehat{V} + \sum_{i=1}^{N} \int d^3r' |\psi_i(\boldsymbol{r}')|^2 v_{\text{int}}(|\boldsymbol{r} - \boldsymbol{r}'|) \right] \psi_j(\boldsymbol{r}) \tag{1.269}$$

$$- \left[\sum_{i=1}^{N} \int d^3r' \psi_i^*(\boldsymbol{r}') v_{\text{int}}(|\boldsymbol{r} - \boldsymbol{r}'|)\psi_j(\boldsymbol{r}') \right] \psi_i(\boldsymbol{r})\delta_{\sigma_i\sigma_j} = \epsilon_j \psi_j(\boldsymbol{r}).$$

The third term is called the direct term and the fourth term is the **nonlocal exchange term**. The nonlocality is the main difference to density functional theory, where one uses local potentials to account for exchange and also correlation. The Hartree-Fock approximation does not account for any correlation. However, the so-called multi-configurational Hartree-Fock approach, which assumes the wavefunction to consist of a linear combination of Slater determinants, overcomes this restriction.

It can be shown that also for Hartree-Fock theory one can find an appropriate density functional reformulation [41] which gives rise to local exact exchange potentials. For the special case of a spin singlet

$$|\Psi\rangle_{\text{S}} := \frac{1}{\sqrt{2}} \left(|\psi\rangle|\psi\rangle \right) \left(|\uparrow\rangle|\downarrow\rangle - |\downarrow\rangle|\uparrow\rangle \right) \tag{1.270}$$

Hartree-Fock and exchange-only density functional theory coincide due to $n(\boldsymbol{r}) = 2|\psi(\boldsymbol{r})|^2$, and the Kohn-Sham equation reads

$$\epsilon\,\psi(\boldsymbol{r}) = \left[-\frac{1}{2}\boldsymbol{\nabla}^2 + v(\boldsymbol{r}) + \int d^3r'|\psi(\boldsymbol{r}')|^2 v_{\text{int}}(|\boldsymbol{r}-\boldsymbol{r}'|) \right]\psi(\boldsymbol{r}). \qquad (1.271)$$

We therefore find the (adiabatic) exact Hartree-exchange potential for the spin-singlet case

$$v_{\text{Hx}}([n];\boldsymbol{r},t) := \frac{1}{2}\int d^3r' n(\boldsymbol{r},t) v_{\text{int}}(|\boldsymbol{r}-\boldsymbol{r}'|). \qquad (1.272)$$

Beside adiabatic and nonadiabatic local density approximation as well as the exact exchange approximation many others, e.g., hybrid functionals, are known and were successfully applied to physical problems [9, 11].

1.3.4 Quantum Memory

As already pointed out, exchange-correlation potentials in time-dependent density functional theory are more complex than ground-state density functionals as one has to deal with, e.g., initial configuration dependence [11]. However, the problem of initial state dependence is mostly avoided by choosing the ground-state as the initial state. The second main difference is not that obvious, although it is strongly interlinked with initial state dependence [13, 34], namely "quantum memory", i.e., the potential does somehow depend on previous densities. The elusive term "quantum memory" has never been rigorously defined and a proper investigation is of importance for the development of approximations for the exchange-correlation potential.

To see how memory appears in time-dependent density functional theory we follow the arguments of van Leeuwen [42] and assume an initial configuration and interaction chosen. If the interval at consideration is $[t_0, T]$ with $T > t_0$ and $n(\boldsymbol{r}, t)$ is only given within this interval, one cannot construct the associated potential for some time $T' > T$. There are different systems with the same density until time T which may differ afterwards. Therefore the potential does only depend on the density in the same time interval $[t_0, T]$. Also if one only has the density in some time interval $[T'', T]$ with $t_0 < T'' < T$, then one does not have enough information to construct the associated potential on the time interval $[t_0, T]$. There may be more than one or no possible potential generating the density on the subinterval for an initial configuration. However, if the configuration at T'' were known one could of course construct a potential at least in the interval $[T'', T]$. Nevertheless this would amount to propagate the known initial state at t_0 with some unknown potential.

We can conclude: In general we need the density $n(\boldsymbol{r}, t)$ on the whole time interval $[t_0, T]$ in order to construct the potential $v(\boldsymbol{r}, T)$. One cannot construct the

potential by only knowing the density at the same time. Therefore $v[n]$ has to have "memory" of the density at earlier times. One can replace "memory" by "initial state dependence" and vice versa.

Functional Derivative and Formal Definition of Memory

This subsection is dedicated to the definition of the term "memory". Although it is known that the exchange-correlation potential in general depends on previous densities, to the best of our knowledge, a proper definition of what is meant by the notion of "memory" has never been given. One usually connects nonadiabaticity with frequency-dependence of the exchange-correlation kernel [11]. Following this idea, a formal definition of "memory" in terms of the functional derivative of a general nonlinear mapping is proposed. It is highlighted that the functional differentiability of the Runge-Gross mapping $v_{\widehat{\rho}_0}$ depends on the properties of the set of density and potential variations.

From a formal viewpoint one could argue that due to the analytic continuation procedure in the extended Runge-Gross proof one does need knowledge of $v_{\widehat{\rho}_0}([n]; \boldsymbol{r}, t)$ and hence $n(\boldsymbol{r}, t)$ in previous intervals of convergence to uniquely define the potential at some later time. Only knowing the density at some point later then t_0 does not define the associated potential at that time. If we have the initial configuration and the density or potential as a Taylor series about t_0 everything else is uniquely defined for later times. Any small variation of the density leads to a different density and potential on the whole time axis and manifests itself in a different Taylor series representation about t_0. For $n \in \mathcal{N}(\widehat{\rho}_0, \widehat{V}_{\text{int}})$ and $v \in \mathcal{V}(\widehat{\rho}_0, \widehat{V}_{\text{int}})$ no time-local variation is possible. Only variations Δn are allowed which will lead to $n + \Delta n \in \mathcal{N}(\widehat{\rho}_0, \widehat{V}_{\text{int}})$ and $v + \Delta v \in \mathcal{V}(\widehat{\rho}_0, \widehat{V}_{\text{int}})$. We will call such variations v-**representable variations**. To determine the potential due to some altered density at time $t > t_0$ one needs the previous altered densities. This amounts to a modified Taylor expansion about t_0, which leads to the potential at time t. Otherwise there may be different $v_{\rho_0}([n + \Delta n]; \boldsymbol{r}, t)$ which are the same at t but different elsewhere.

Assume now Gâteaux differentiability of the mapping

$$v_{\widehat{\rho}_0} : \delta\mathcal{N}(\widehat{\rho}_0, \widehat{V}_{\text{int}}) \subseteq \mathcal{B}_n(\bar{\Omega}) \to \mathcal{V}(\widehat{\rho}_0, \widehat{V}_{\text{int}}) \subseteq \mathcal{B}_v(\bar{\Omega}), \tag{1.273}$$

i.e., $dv_{\widehat{\rho}_0} : \delta\mathcal{N}(\widehat{\rho}_0, \widehat{V}_{\text{int}}) \to \mathcal{L}(\mathcal{B}_n(\bar{\Omega}), \mathcal{B}_v(\bar{\Omega}))$ exists with $\mathcal{B}_n(\bar{\Omega})$ and $\mathcal{B}_v(\bar{\Omega})$ the corresponding Banach spaces. Hence for every $\delta n \in \delta\mathcal{N}(\widehat{\rho}_0, \widehat{V}_{\text{int}})$, i.e., the space of allowed density variations (1.169), and $h \in \mathcal{B}_n(\bar{\Omega})$ we have with $n = n_0 + n^{(1)} + \delta n$

$$\lim_{\epsilon \to 0} \frac{v_{\widehat{\rho}_0}([n + \epsilon h]; \boldsymbol{r}, t) - v_{\widehat{\rho}_0}([n]; \boldsymbol{r}, t)}{\epsilon} = dv_{\widehat{\rho}_0}([n, h]; \boldsymbol{r}, t). \tag{1.274}$$

The choice of $\delta\mathcal{N}(\widehat{\rho}_0, \widehat{V}_{\text{int}})$ instead of the usual $\mathcal{N}(\widehat{\rho}_0, \widehat{V}_{\text{int}})$ guarantees that $n + \epsilon h$ will respect the initial conditions and norm conservation at least for $h \in \delta\mathcal{N}(\widehat{\rho}_0, \widehat{V}_{\text{int}})$. The assumption of functional differentiability may not be well chosen. However, one may at least assume v-**representable differentiability**. This means, we assume in accordance

to definition 1.3.2 that for some $n \in \mathcal{N}(\widehat{\rho}_0, \widehat{V}_{\mathrm{int}})$ and $h \in \mathcal{B}_n(\bar{\Omega})$ there is an $\epsilon > 0$ for which all $n + \lambda h$ with $0 \leq \lambda < \epsilon$ are v-representable, and the variation

$$\Delta v_{\widehat{\rho}_0}([n, h]; \boldsymbol{r}, t) = \frac{d}{d\lambda} v_{\widehat{\rho}_0}([n + \lambda h]; \boldsymbol{r}, t) \bigg|_{\lambda=0} \tag{1.275}$$

exists. If these infinitesimal v-representable variations exist for all $h \in \mathcal{B}_n(\bar{\Omega})$ they are just the usual Gâteaux derivatives [26]. Thus the question of **Gâteaux differentiability** is strongly interlinked with the question whether the **set of density variations** $\delta\mathcal{N}(\widehat{\rho}_0, \widehat{V}_{\mathrm{int}})$ **forms a Banach space**.

An indication for functional v-representable differentiability can be found in [11] on page 23 where the invertibility of the linear response functions is shown if one starts from a ground-state.

Due to Gâteaux differentiability and analyticity of the corresponding functions we assume the functional differential to be analytic itself, i.e.,

$$dv_{\widehat{\rho}_0}([n, h]; \boldsymbol{r}, t) = \sum_{k=0}^{\infty} \frac{1}{k!} \, dv_{\widehat{\rho}_0}^{(k)}([n, h]; \boldsymbol{r}) \, (t - t_0)^k \tag{1.276}$$

with

$$dv_{\widehat{\rho}_0}^{(k)}([n, h]; \boldsymbol{r}) = \lim_{\epsilon \to 0} \frac{v_\epsilon'^{(k)}(\boldsymbol{r}) - v^{(k)}(\boldsymbol{r})}{\epsilon}, \tag{1.277}$$

$v_{\widehat{\rho}_0}([n + \epsilon h]; \boldsymbol{r}, t) \equiv v_\epsilon'(\boldsymbol{r}, t)$ and $v_{\widehat{\rho}_0}([n]; \boldsymbol{r}, t) \equiv v(\boldsymbol{r}, t)$ both analytically continued along the real time axis. Correspondingly, in order to find the first Gâteaux derivative at n in direction h we need to know the density n and the variation h on the whole interval $[t_0, t]$, i.e., from the initial time t_0 until the time t we are interested in.

Usually one further assumes the Gâteaux differential to be representable by an integral operator of the form

$$dv_{\widehat{\rho}_0}([n, h]; \boldsymbol{r}, t) = \int_{t_0}^{t} dt' \int_{\Omega} d^3 r' \, \frac{\delta v_{\widehat{\rho}_0}([n']; \boldsymbol{r}, t)}{\delta n'(\boldsymbol{r}', t')} \bigg|_{n'=n} h(\boldsymbol{r}', t') \tag{1.278}$$

with the integral kernel $\frac{\delta v_{\widehat{\rho}_0}([n']; \boldsymbol{r}, t)}{\delta n'(\boldsymbol{r}', t')} \bigg|_{n'=n} \equiv \chi^{-1}([n]; \boldsymbol{r}, t; \boldsymbol{r}', t')$ the inverse linear response kernel.

We will call a differentiable operator $O([n]; \boldsymbol{r}, t)$ nonlocal in time if the integral kernel

$$\frac{\delta O([n']; \boldsymbol{r}, t)}{\delta n'(\boldsymbol{r}', t')} \bigg|_{n'=n} \neq \delta(t - t') f([n]; \boldsymbol{r}, \boldsymbol{r}', t'), \tag{1.279}$$

i.e., it cannot be written as a delta-like operator in time. Physically this means that there is at least one time $t' < t$ for which the variation influences the later response at time t. Note that f may contain derivatives in time. Due to $h \in \mathcal{C}^{\infty}([t_0, t])$ any number of derivatives in time are allowed. Therefore we may rewrite

$$f([n]; \boldsymbol{r}, \boldsymbol{r}', t') = \sum_{k=0}^{\infty} g_k([n]; \boldsymbol{r}, \boldsymbol{r}', t') \, \partial_{t'}^k. \tag{1.280}$$

If all derivatives of the analytic function $h(\boldsymbol{r}, t)$ at time t are known one also knows the variations for previous times. Therefore we also have to exclude such cases because we would have implicit dependence on previous times. Hence we state the following formal definition:

A Gâteaux differentiable operator $O([n]; \boldsymbol{r}, t)$ is **nonlocal in time**, i.e., has **memory**, if its kernel obeys

$$\left. \frac{\delta O([n']; \boldsymbol{r}, t)}{\delta n'(\boldsymbol{r}', t')} \right|_{n'=n} \neq \delta(t - t') f([n]; \boldsymbol{r}, \boldsymbol{r}', t'), \quad (1.281)$$

for any operator $f([n]; \boldsymbol{r}, \boldsymbol{r}', t')$, which does not consist of an infinite number of time derivatives.

Of course, even a finite number of time derivatives of h may be seen as a weaker kind of nonlocality. Nevertheless we will use the terms **nonlocality**, **history dependence**, and **memory** according to the above definition. However, a kernel which involves a time derivative will still be called nonadiabatic although one does in principle only need the density variation at that time t. This is done to agree with the literature [11] and with the usual notion of adiabaticity, which does imply that the inverse linear response kernel of the ground-state density is frequency independent.

The Runge-Gross Mapping

The potential mapping $v_{\widehat{\rho}_0}$ has memory in the above sense. Nonlocality in time has important physical implications for $v_{\widehat{\rho}_0}$. For the ground-state inverse linear response kernel $\chi^{-1}([n_{\mathrm{GS}}]; \boldsymbol{r}, t; \boldsymbol{r}', t')$ we have [11]

$$\chi^{-1}([n_{\mathrm{GS}}]; \boldsymbol{r}, t; \boldsymbol{r}', t') \equiv \chi^{-1}([n_{\mathrm{GS}}]; \boldsymbol{r}, \boldsymbol{r}', t - t'). \quad (1.282)$$

If we Fourier-transform with respect to $t - t'$ we obtain a frequency dependend inverse linear response kernel

$$\chi^{-1}([n_{\mathrm{GS}}]; \boldsymbol{r}, \boldsymbol{r}', \omega). \quad (1.283)$$

Nonlocality in time for $v_{\widehat{\rho}_0}$ amounts to a general ω-dependence. If we had locality in time in the above sense only a "special" ω-dependence would be present as a derivative in time corresponds to multiplication with ω after Fourier transformation. However, due to combinations of time derivatives also this "special ω-dependence" may be quite general. Hence, even if memory exists, some local, however, nonadiabatic approximation may cover the most important characteristics of $\chi^{-1}([n_{\mathrm{GS}}]; \boldsymbol{r}, \boldsymbol{r}', \omega)$.

For the Kohn-Sham scheme we have to consider the exchange-correlation potential mapping

$$v_{\widehat{\rho}_0, \widehat{\rho}_0'}^{\mathrm{xc}} : \delta\mathcal{N}(\widehat{\rho}_0, \widehat{V}_{\mathrm{int}}) \cap \delta\mathcal{N}(\widehat{\rho}_0') \subseteq \mathcal{B}_n^{\mathrm{xc}}(\bar{\Omega}) \to \mathcal{V}(\widehat{\rho}_0, \widehat{V}_{\mathrm{int}}) \cap \mathcal{V}(\widehat{\rho}_0'). \quad (1.284)$$

Again we assume differentiability. The differentiability is guaranteed if $v_{\widehat{\rho}_0}$ and $v_{\widetilde{\rho}_0'}$ are differentiable at δn for all $h \in \mathcal{B}_n^{\mathrm{xc}}(\bar{\Omega})$. Following the above reasoning we assume with $v_{\widehat{\rho}_0,\widetilde{\rho}_0'}^{\mathrm{xc}} = v_{\widetilde{\rho}_0'} - v_{\widehat{\rho}_0} - v_{\mathrm{H}}$, where the differentiability of v_{H} is trivial, that

$$dv_{\widehat{\rho}_0,\widetilde{\rho}_0'}^{\mathrm{xc}}([n,h];\boldsymbol{r},t) = \int_{t_0}^t dt' \int_\Omega d^3r' \left.\frac{\delta v_{\widehat{\rho}_0,\widetilde{\rho}_0'}^{\mathrm{xc}}([n'];\boldsymbol{r},t)}{\delta n'(\boldsymbol{r}',t')}\right|_{n'=n} h(\boldsymbol{r}',t') \tag{1.285}$$

and

$$\frac{\delta v_{\widehat{\rho}_0,\widetilde{\rho}_0'}^{\mathrm{xc}}([n'];\boldsymbol{r},t)}{\delta n'(\boldsymbol{r}',t')} = \frac{\delta v_{\widetilde{\rho}_0'}([n'];\boldsymbol{r},t)}{\delta n'(\boldsymbol{r}',t')} - \frac{\delta v_{\widehat{\rho}_0}([n'];\boldsymbol{r},t)}{\delta n'(\boldsymbol{r}',t')} - \frac{\delta(t-t')}{|\boldsymbol{r}-\boldsymbol{r}'|}. \tag{1.286}$$

Here the memory arises due to the difference of two time-nonlocal terms, i.e., the non-locality in the auxiliary noninteracting potential $v_{\widetilde{\rho}_0'}$ and the memory in the interacting potential $v_{\widehat{\rho}_0}$. Further one usually defines [11]

$$\left.\frac{\delta v_{\widehat{\rho}_0,\widetilde{\rho}_0'}^{\mathrm{xc}}([n'];\boldsymbol{r},t)}{\delta n'(\boldsymbol{r}',t')}\right|_{n'=n_{\mathrm{GS}}} =: f_{\mathrm{xc}}([n_{\mathrm{GS}}];\boldsymbol{r},\boldsymbol{r}',t-t') \tag{1.287}$$

as the so-called **exchange-correlation kernel**, which is the central object of interest in linear response time-dependent density functional theory. Again a local approximation may capture the most important characteristics of the exchange-correlation kernel. Thinking about an **ab initio time-local approximation** (via time derivatives) of the exchange-correlation kernel has also pragmatic and computational implications and is not mere nitpicking. From the approximation of the exchange-correlation kernel one could construct a local approximation of the exchange-correlation potential. While effective potentials involving derivatives of the density or the current density are quite harmless, memory potentials (involving time integrals over previous times) could seriously spoil the computational efficiency of the time-dependent Kohn-Sham scheme.

Complex Functional Derivative and Wavefunction Dependence

The Runge-Gross mapping and the exchange-correlation potential are both nonlocal in time with respect to the density. It seems that memory is the price we pay if we leave the complex configuration space of the usual many-body quantum theory and replace its fundamental variable, i.e., the wavefunction, by a quite simple variable, the one-particle density. If we express the Runge-Gross mapping in terms of the configuration, i.e, wave-functions, and define nonlocality in time with respect to this new variable, do we still find "memory"? Via the bijective mapping

$$\begin{aligned}\widehat{\rho}_{\rho_0} : \mathcal{N}(\widehat{\rho}_0,\widehat{V}_{\mathrm{int}}) &\to \mathcal{R}(\widehat{\rho}_0,\widehat{V}_{\mathrm{int}})\\ n(\boldsymbol{r},t) &\mapsto \widehat{\rho}_{\rho_0}([n];t)\end{aligned}$$

one can find the mapping of interest:

$$\widetilde{v}_{\widehat{\rho}_0} = v_{\widehat{\rho}_0} \circ \widehat{\rho}_{\rho_0}^{-1} : \mathcal{R}(\widehat{\rho}_0,\widehat{V}_{\mathrm{int}}) \to \mathcal{V}(\widehat{\rho}_0,\widehat{V}_{\mathrm{int}}). \tag{1.288}$$

We now meet problems if we want to look at the functional derivatives of $\widetilde{v}_{\widehat{\rho}_0}$. First of all, $\mathcal{R}(\widehat{\rho}_0, \widehat{V}_{\text{int}})$ is a subset of the space of linear operators between two complex Banach spaces. This space itself is a complex Banach space. The functional derivatives, however, were introduced only on real Banach spaces. Further we note that the derivative is now with respect to a (linear) operator. This fact does not introduce serious mathematical problems, as the space for those operators is still a Banach space. Nevertheless, if we want to express the Gâteaux differential via an integral operator this fact will introduce formal problems we want to avoid. Therefore we will restrict our considerations to pure states $\widehat{\rho}_0 = |\Psi_0\rangle\langle\Psi_0|$.

With equation (1.83), i.e.,

$$\frac{\partial}{\partial t} j_\nu(\boldsymbol{r}, t) = -n(\boldsymbol{r}, t)\partial_\nu v(\boldsymbol{r}, t) - \partial_\mu\langle\Psi(t)|\widehat{T}_{\mu\nu}(\boldsymbol{r})|\Psi(t)\rangle - \partial_\mu\langle\Psi(t)|\widehat{W}_{\mu\nu}(\boldsymbol{r})|\Psi(t)\rangle,$$

we formally find

$$\partial_\nu\widetilde{v}_{\Psi_0}([\Psi]; \boldsymbol{r}, t) = \tag{1.289}$$
$$-\frac{\partial_t j_\nu(\boldsymbol{r}, t) - \partial_\mu\langle\Psi(t)|\widehat{T}_{\mu\nu}(\boldsymbol{r})|\Psi(t)\rangle - \partial_\mu\langle\Psi(t)|\widehat{W}_{\mu\nu}(\boldsymbol{r})|\Psi(t)\rangle}{n(\boldsymbol{r}, t)}.$$

One already sees that $\widetilde{v}_{\Psi_0}$ does not depend on previous wavefunctions. Equation (1.289) merely defines $\widetilde{v}_{\Psi_0}$ and cannot be used for propagation to obtain the wavefunction itself [42]. Otherwise we could predict the (input) wavefunction by only knowing the definition of the mapping [see the discussion of dependence on future densities in subsection 1.3.5]. If a proper extension of the functional derivative to complex Banach spaces is found, we can state analogously to the formal definition of nonlocality in time (1.281) that $\widetilde{v}_{\Psi_0}$ **does not have memory**. Note further that also the **initial state dependence of the mapping is lost** as we only need the wavefunction and a time derivative of the wavefunction at time t. Only the set of allowed v-representable wavefunctions $|\Psi\rangle \in \mathcal{R}(\Psi_0, \widehat{V}_{\text{int}})$ still depends on the initial state.

A straightforward extension of functional derivatives to complex Banach spaces is analogous to the usual variational calculus where one does use $|\Psi\rangle \to |\Psi\rangle + |\delta\Psi\rangle$ and neglects all terms of order $(|\delta\Psi\rangle)^2$ and higher. This is in accordance with the so-called $\mathbb{C}\mathbb{R}$-calculus [43] extended to general nonlinear mappings.

First we examine complex derivatives for functions which do not obey the Cauchy-Riemann conditions. This leads to the so-called $\mathbb{C}\mathbb{R}$-**calculus (Wirtinger-calculus)**. For a (nonholomorphic) function $f(z) = f(z, z^*)$ and $z = x + iy$ we introduce the **Wirtinger derivatives**, which are formally (varying z without z^* is not possible) defined as

$$\left.\frac{\partial f(z, z^*)}{\partial z}\right|_{z^*=\text{const}} \qquad \text{the } \mathbb{R}\text{-derivative}, \tag{1.290}$$

$$\left.\frac{\partial f(z, z^*)}{\partial z^*}\right|_{z=\text{const}} \qquad \text{the conjugate } \mathbb{R}\text{-derivative}. \tag{1.291}$$

These formal partial derivatives exist if the mapping interpreted as $f : \mathbb{R}^2 \to \mathbb{R}^2$ is real ($\mathbb{R}$) differentiable. Equivalently one may rewrite

$$\frac{\partial f}{\partial z} = \frac{1}{2}\left(\frac{\partial f}{\partial x} - i\frac{\partial f}{\partial y}\right), \quad \frac{\partial f}{\partial z^*} = \frac{1}{2}\left(\frac{\partial f}{\partial x} + i\frac{\partial f}{\partial y}\right), \tag{1.292}$$

which leads trivially to the fact that f is holomorphic in z (z^*) if and only if $\partial f/\partial z^* = 0$ $(\partial f/\partial z = 0)$. The complex-derivative identities are

$$\frac{\partial f^*}{\partial z^*} = \left(\frac{\partial f}{\partial z}\right)^*, \quad \frac{\partial f^*}{\partial z} = \left(\frac{\partial f}{\partial z^*}\right)^*, \tag{1.293}$$

$$df = \frac{\partial f}{\partial z}dz + \frac{\partial f}{\partial z^*}dz^*, \tag{1.294}$$

$$\frac{\partial h(g)}{\partial z} = \frac{\partial h}{\partial g}\frac{\partial g}{\partial z} + \frac{\partial h}{\partial g^*}\frac{\partial g^*}{\partial z}, \quad \frac{\partial h(g)}{\partial z^*} = \frac{\partial h}{\partial g}\frac{\partial g}{\partial z^*} + \frac{\partial h}{\partial g^*}\frac{\partial g^*}{\partial z^*}. \tag{1.295}$$

For the multivariate case, i.e., $\boldsymbol{z} = (z_1, ..., z_n)^T \in \mathbb{C}^n$, we define the pair of conjugate coordinate vectors $(\boldsymbol{z}, \boldsymbol{z}^*)$ by

$$\boldsymbol{c} = \begin{pmatrix} \boldsymbol{z} \\ \boldsymbol{z}^* \end{pmatrix} \in \mathbb{C}^{2n}$$

and will further use the equivalent notation for $\boldsymbol{f} : \mathbb{C}^n \to \mathbb{C}^m$

$$\boldsymbol{f}(\boldsymbol{c}) = \boldsymbol{f}(\boldsymbol{z}, \boldsymbol{z}^*) = \boldsymbol{f}(\boldsymbol{z}) \in \mathbb{C}^m.$$

Then the **cogradient operator** is defined as

$$\frac{\partial}{\partial \boldsymbol{z}} = \left(\frac{\partial}{\partial z_1} ... \frac{\partial}{\partial z_n}\right) \tag{1.296}$$

and the **conjugate cogradient operator** is

$$\frac{\partial}{\partial \boldsymbol{z}^*} = \left(\frac{\partial}{\partial z_1^*} ... \frac{\partial}{\partial z_n^*}\right). \tag{1.297}$$

Therefore we find the **differential rule**

$$d\boldsymbol{f}(\boldsymbol{c}) = \frac{\partial \boldsymbol{f}(\boldsymbol{c})}{\partial \boldsymbol{c}}d\boldsymbol{c} = \frac{\partial \boldsymbol{f}(\boldsymbol{c})}{\partial \boldsymbol{z}}d\boldsymbol{z} + \frac{\partial \boldsymbol{f}(\boldsymbol{c})}{\partial \boldsymbol{z}^*}d\boldsymbol{z}^* \tag{1.298}$$

with the **Jacobian**

$$J_{\boldsymbol{f}}(\boldsymbol{c}) = \frac{\partial \boldsymbol{f}(\boldsymbol{c})}{\partial \boldsymbol{z}} = \begin{pmatrix} \frac{\partial f_1}{\partial z_1} & \cdots & \frac{\partial f_1}{\partial z_n} \\ \cdot & & \\ \cdot & & \\ \cdot & & \\ \frac{\partial f_m}{\partial z_1} & \cdots & \frac{\partial f_m}{\partial z_n} \end{pmatrix} \tag{1.299}$$

and the **conjugate Jacobian**

$$J_{\boldsymbol{f}}^c(\boldsymbol{c}) = \frac{\partial \boldsymbol{f}(\boldsymbol{c})}{\partial \boldsymbol{z}^*} = \begin{pmatrix} \frac{\partial f_1}{\partial z_1^*} & \cdots & \frac{\partial f_1}{\partial z_n^*} \\ \cdot & & \\ \cdot & & \\ \cdot & & \\ \frac{\partial f_m}{\partial z_1^*} & \cdots & \frac{\partial f_m}{\partial z_n^*} \end{pmatrix}. \tag{1.300}$$

Applying (1.293) we have in general

$$J_{\boldsymbol{f}}^*(\boldsymbol{c}) \neq J_{\boldsymbol{f}}^c(\boldsymbol{c}). \tag{1.301}$$

However, for $\boldsymbol{f}(\boldsymbol{c}) \in \mathbb{R}^m$ we have $J_{\boldsymbol{f}}^*(\boldsymbol{c}) = J_{\boldsymbol{f}}^c(\boldsymbol{c})$. For two mappings $\boldsymbol{h} : \mathbb{C}^m \to \mathbb{C}^r$ and $\boldsymbol{g} : \mathbb{C}^n \to \mathbb{C}^m$ and its composition $\boldsymbol{h} \circ \boldsymbol{g} = \boldsymbol{h}(\boldsymbol{g})$ the chain rule reads

$$\frac{\partial \boldsymbol{h}(\boldsymbol{g})}{\partial \boldsymbol{z}} = \frac{\partial \boldsymbol{h}}{\partial \boldsymbol{g}}\frac{\partial \boldsymbol{g}}{\partial \boldsymbol{z}} + \frac{\partial \boldsymbol{h}}{\partial \boldsymbol{g}^*}\frac{\partial \boldsymbol{g}}{\partial \boldsymbol{z}} = J_{\boldsymbol{h}}J_{\boldsymbol{g}} + J_{\boldsymbol{h}}^c J_{\boldsymbol{g}}^{c^*} = J_{\boldsymbol{h} \circ \boldsymbol{g}} \tag{1.302}$$

and

$$\frac{\partial \boldsymbol{h}(\boldsymbol{g})}{\partial \boldsymbol{z}^*} = \frac{\partial \boldsymbol{h}}{\partial \boldsymbol{g}}\frac{\partial \boldsymbol{g}}{\partial \boldsymbol{z}^*} + \frac{\partial \boldsymbol{h}}{\partial \boldsymbol{g}^*}\frac{\partial \boldsymbol{g}}{\partial \boldsymbol{z}^*} = J_{\boldsymbol{h}}J_{\boldsymbol{g}}^c + J_{\boldsymbol{h}}^c J_{\boldsymbol{g}}^* = J_{\boldsymbol{h} \circ \boldsymbol{g}}^c. \tag{1.303}$$

Accordingly the Cauchy-Rieman condition reads $J_{\boldsymbol{f}}^c = 0$ and for **stationary points of real-valued functionals** we have two equivalent conditions:

$$\frac{\partial f(\boldsymbol{z_0}, \boldsymbol{z_0^*})}{\partial \boldsymbol{z}} = \boldsymbol{0}, \quad \frac{\partial f(\boldsymbol{z_0}, \boldsymbol{z_0^*})}{\partial \boldsymbol{z}^*} = \boldsymbol{0}. \tag{1.304}$$

Now consider a functional $f = h \circ g$ with $h : \mathbb{C}^n \to \mathbb{R}$ and $\boldsymbol{g} : \mathbb{R} \to \mathbb{C}^n$. The ordinary $\mathbb{R}$-derivative can be rewritten according to (1.292) as

$$\frac{\partial}{\partial x} = \frac{\partial}{\partial z} + \frac{\partial}{\partial z^*}. \tag{1.305}$$

Therefore we find

$$\begin{aligned}
\frac{\partial f}{\partial x} &= \frac{\partial f}{\partial z} + \frac{\partial f}{\partial z^*} = \frac{\partial h}{\partial \boldsymbol{g}}\frac{\partial \boldsymbol{g}}{\partial z} + \frac{\partial h}{\partial \boldsymbol{g}^*}\frac{\partial \boldsymbol{g}^*}{\partial z} + \frac{\partial h}{\partial \boldsymbol{g}}\frac{\partial \boldsymbol{g}}{\partial z^*} + \frac{\partial h}{\partial \boldsymbol{g}^*}\frac{\partial \boldsymbol{g}^*}{\partial z^*} \\
&= \frac{\partial h}{\partial \boldsymbol{g}}\frac{\partial \boldsymbol{g}}{\partial x} + \frac{\partial h}{\partial \boldsymbol{g}^*}\frac{\partial \boldsymbol{g}^*}{\partial x}.
\end{aligned} \tag{1.306}$$

Now we will **formally extend the $\mathbb{CR}$-calculus to functional derivatives**. We assume the afore deduced properties of the Wirtinger derivatives to be still valid and the functional differential to be an integral operator with the derivative being its kernel.

We formally find with (1.289) that

$$\frac{\delta \widetilde{v}(\boldsymbol{r}, t)}{\delta \Psi(\boldsymbol{r}_1, ... \boldsymbol{r}_N, t_1)} = \delta(t - t_1) f([\Psi]; \boldsymbol{r}, \boldsymbol{r}_1, ..., \boldsymbol{r}_N, t, t_1) \tag{1.307}$$

does not have memory with respect to the wavefunction as the fundamental variable. Analogously this holds for $\delta \widetilde{v}/\delta \Psi^*$.

In order to find memory in the Runge-Gross mapping we need the density as the fundamental variable instead of the wavefunction or the orbitals. We now employ the inverse variable transformation $\widehat{\rho}_{\widehat{\rho}_0}^{-1}$, generating the wavefunctions

$$|\Psi([n]; t)\rangle \tag{1.308}$$

as operators of the density. Analogously we construct the Kohn-Sham orbitals as functionals of the density $\{\phi_i([n]; \boldsymbol{r}, t)\}$. Consider $v_{\widehat{\rho}_0} = \widetilde{v}_{\widehat{\rho}_0} \circ \widehat{\rho}_{\widehat{\rho}_0}$ restricted to pure states,

$$v_{\Psi_0}([n]; \boldsymbol{r}, t) = v_{\Psi_0}([\Psi[n]]; \boldsymbol{r}, t). \tag{1.309}$$

Now we can apply the same reasoning to $|\Psi([n]; t)\rangle$ as was done at the beginning of the section for $v_{\Psi_0}([n]; \boldsymbol{r}, t)$ [42].

We can conclude: In general we need the density $n(\boldsymbol{r}, t)$ on the whole time interval $[t_0, T]$ in order to construct the wavefunction (orbitals) $|\Psi(t)\rangle$ $(\phi_i(\boldsymbol{r}, t))$. One cannot construct the wavefunction (orbitals) from the knowledge of the density at the same time. Therefore $|\Psi[n]\rangle$ $(\phi_i[n])$ has to have "memory" of the density at earlier times.

If we have the differential expressible as an integral operator the associated integral kernel obeys using (1.306)

$$\frac{\delta v_{\Psi_0}([n']; \boldsymbol{r}, t)}{\delta n(\boldsymbol{r}', t')} = \int_{t_0}^{t} \int dt'' d^3 r_1 ... d^3 r_N \left[\frac{\delta \widetilde{v}(\boldsymbol{r}, t)}{\delta \Psi(\boldsymbol{r}_1, ..., \boldsymbol{r}_N, t'')} \frac{\delta \Psi_{\Psi_0}(\boldsymbol{r}_1, ..., \boldsymbol{r}_N, t'')}{\delta n(\boldsymbol{r}', t')} \right. $$
$$\left. + \frac{\delta \widetilde{v}(\boldsymbol{r}, t)}{\delta \Psi^*(\boldsymbol{r}_1, ..., \boldsymbol{r}_N, t'')} \frac{\delta \Psi^*_{\Psi_0}(\boldsymbol{r}_1, ..., \boldsymbol{r}_N, t'')}{\delta n(\boldsymbol{r}', t')} \right]. \tag{1.310}$$

Especially for the Kohn-Sham case we find

$$\frac{\delta v_{\phi_0}([n']; \boldsymbol{r}, t)}{\delta n(\boldsymbol{r}', t')} = \sum_{i=1}^{N} \int_{t_0}^{t} \int dt'' d^3 r'' \left[\frac{\delta \widetilde{v}(\boldsymbol{r}, t)}{\delta \phi_i(\boldsymbol{r}'', t'')} \frac{\delta \phi_{i, \phi_0}(\boldsymbol{r}'', t'')}{\delta n(\boldsymbol{r}', t')} \right. $$
$$\left. + \frac{\delta \widetilde{v}(\boldsymbol{r}, t)}{\delta \phi_i^*(\boldsymbol{r}'', t'')} \frac{\delta \phi^*_{i, \phi_0}(\boldsymbol{r}'', t'')}{\delta n(\boldsymbol{r}', t')} \right]. \tag{1.311}$$

Evidently, the memory, as defined in subsection 1.3.4, resides in the wavefunction (orbitals) as operators of the density n. The derivative with respect to the wavefunction (orbitals) is local in time. Hence, whenever the **wavefunction (orbitals) are locally expressible in terms of the density**, then we have **no memory**. Further, there will be **no initial state dependence of the potential** but an initial state dependence due to the set of the possible potentials and densities which dependend on the initial state chosen. This is evident, as we can construct the potential by only knowing the density in the vicinity of the time t under consideration. An important example is the Kohn-Sham helium spin-singlet state (1.270) with the orbitals

$$\phi_1(\boldsymbol{r}, t) = \phi(\boldsymbol{r}, t)|\uparrow\rangle, \tag{1.312}$$
$$\phi_2(\boldsymbol{r}, t) = \phi(\boldsymbol{r}, t)|\downarrow\rangle, \tag{1.313}$$

and the relation

$$\phi(\boldsymbol{r}, t) = \frac{1}{\sqrt{2}} \sqrt{n(\boldsymbol{r}, t)} \exp\left[\mathrm{i}S(\boldsymbol{r}, t)\right], \tag{1.314}$$

where $S(\boldsymbol{r}, t)$ is a phase function obeying

$$\frac{\boldsymbol{j}}{n} = \boldsymbol{\nabla} S. \tag{1.315}$$

In three and two dimensions we face the problem of determining the rotational part of S. However, for the instructive case of one spatial dimension we immediately find due to

$$j(x, t) = -\int_{-\infty}^{x} dx' \partial_t n(x', t) \tag{1.316}$$

with the boundary condition $j \to 0$ for $|x| \to \infty$

$$S([n]; x, t) = -\int_{-\infty}^{x} dx' \frac{\int_{-\infty}^{x'} dx'' \partial_t n(x'', t)}{n(x', t)} + C(t) \tag{1.317}$$

and $C(t) = \lim_{x \to -\infty} S(x, t)$. The spatial part of the orbitals is locally expressible in terms of the density. Therefore the mapping v_{ϕ_0} will have no memory. In fact it holds that via inversion of the Kohn-Sham-equation we find

$$
\begin{aligned}
v([n]; x, t) \;=\; & \frac{1}{2} \left(\frac{\partial_x^2 n(x, t)}{2n(x, t)} - \left(\frac{\partial_x n(x, t)}{2n(x, t)} \right)^2 \right) \\
& - \frac{1}{2} \left(\frac{\int_{-\infty}^{x} dx' \partial_t n(x', t)}{n(x, t)} \right)^2 \\
& + \partial_t \int_{-\infty}^{x} dx' \frac{\int_{-\infty}^{x'} dx'' \partial_t n(x'', t)}{n(x', t)} - \partial_t C(t).
\end{aligned}
\tag{1.318}
$$

The term $\partial_t C(t)$ can be fixed by the choice of gauge and will be set equal to zero.
If we now want to make contact to a physical system, we have to connect the noninteracting system to the interacting system via the exchange-correlation potential. Hence, the mapping of interest (1.284) consists of three terms, i.e., the mapping v_{ϕ_0}, v_{Ψ_0} and the v_{H}. The Hartree-term is local in time. For the helium spin-singlet case also the term due to v_{ϕ_0} is local in time. For the interacting part with the appropriate boundary conditions, i.e.,

$$
\begin{aligned}
\widetilde{v}_{\Psi_0}([\Psi]; x, t) = & \\
-\int_{-\infty}^{x} dy \frac{\partial_t j(y, t) + \partial_y \langle \Psi(t)|\widehat{T}(y)|\Psi(t)\rangle + \partial_y \langle \Psi(t)|\widehat{W}(y)|\Psi(t)\rangle}{n(y, t)} &
\end{aligned}
\tag{1.319}
$$

we do not know if the wavefunction $|\Psi(t)\rangle$ can be expressed locally in terms of the density. Therefore the exact exchange-correlation potential will have memory in general, i.e., it will be nonlocal in time. Recent numerical simulations showed, however, that memory-effects for a helium singlet system (in an intense laser field) [15] are negligible.

67

An Orbital Fixing Procedure

As pointed out by van Leeuwen [42], the Kohn-Sham-potential without relation to the interacting case cannot be used for propagation. Without fixing the external potential and defining the Hartree-exchange-correlation potential we cannot predict the interacting density. However, one could construct an iteration scheme for the orbital potential $\widetilde{v}_{\phi_0}$ [42]. Suppose we fix the density in the denominator of the integrand in equation (1.319) for the noninteracting case to $n_0(x,t)$. We thus define the potential in terms of the orbitals as

$$\widetilde{v}_{\phi_0,0}([\phi_k];x,t) := -\int_{-\infty}^{x} dy \frac{\partial_t j(y,t) + \partial_y \langle \Phi(t)|\widehat{T}(y)|\Phi(t)\rangle}{n_0(y,t)}.$$

Let us then start with an initial guess $\{\phi_k^{(1)}\}$ of the orbitals and calculate the potential $v^{(1)}(x,t) = \widetilde{v}_{\phi_0,0}([\{\phi_k^{(1)}\}];x,t)$. Then we can use the potential $v^{(1)}$ to propagate the Kohn-Sham-equations and obtain new orbitals $\{\phi_k^{(2)}\}$. These orbitals will not be equal to the original ones unless

$$\widetilde{v}_{\phi_0,0}([\{\phi_k^{(1)}\}];x,t) = \widetilde{v}_{\phi_0}([\{\phi_k^{(1)}\}];x,t), \tag{1.320}$$

i.e., unless the density of the system with orbitals $\{\phi_k^{(1)}\}$ is equal to the fixed density $n_0(x,t)$. We can therefore set up an iteration scheme to generate the Kohn-Sham-potential for a given density. However, it is not clear that this iteration scheme converges.

1.3.5 Criticism on the Foundations of Time-Dependent Density Functional Theory

Density functional theory has been widely accepted and is also mathematically on solid ground. However, its time-dependent counterpart is lacking the same mathematical rigor and its formal foundations have been criticized [44, 45].

The main point of criticism is related to the implementation of the Runge-Gross mapping theorem. It is argued that the time-dependent Kohn-Sham equations, which are a direct consequence of the undisputed one-to-one correspondence between densities and external potentials, may not be used, even in principle, to predict time-dependent densities. Therefore the Kohn-Sham construction may only reproduce given densities via a noninteracting system. If this were true, time-dependent density functional theory would be degraded from a physically exact and predictive theory to an ad hoc approximation in the spirit of a local Hartree-Fock scheme.

In short the line of argumentation is as follows:

In the constructive proof of the extendend Runge-Gross theorem equation (1.109) shows up,

$$\begin{aligned}
\boldsymbol{\nabla}_{\boldsymbol{r}} \cdot \left[n'^{(0)}(\boldsymbol{r})\boldsymbol{\nabla}_{\boldsymbol{r}} v'^{(k)}(\boldsymbol{r}) \right] &= n^{(k+2)}(\boldsymbol{r}) - q'^{(k)}(\boldsymbol{r}) \\
&\quad - \sum_{l=0}^{k-1} \binom{k}{l} \boldsymbol{\nabla}_{\boldsymbol{r}} \cdot \left[n'^{(k-l)}(\boldsymbol{r})\boldsymbol{\nabla}_{\boldsymbol{r}} v'^{(l)}(\boldsymbol{r}) \right],
\end{aligned}$$

which defines with appropriate initial and boundary conditions the Kohn-Sham potential in terms of its Taylor expansion in time. One clearly sees the dependence of the potential on the second time derivative of the density, i.e., $\frac{\partial^2}{\partial t^2} n(\boldsymbol{r}, t) = \sum_{k=0}^{\infty} \frac{1}{k!} n^{(k+2)}(\boldsymbol{r})(t - t_0)^k$. If one now wants to predict the time-evolution via a propagation scheme where at each time step the Kohn-Sham potential is calculated according to the above equation one needs to take the second time derivative of the density into account. At least at the initial time t_0 this cannot be done without further knowledge, e.g., the density at an infinitesimally later time. Therefore it is argued that this construction of the Kohn-Sham potential via the second time-derivative of the density implies a **dependence on the future** [44].

However, the Runge-Gross mapping of a density to its associated local potential — for a noninteracting systems this is the Kohn-Sham potential — does not have any knowledge of the physical system it has to describe. Instead, the Hartree-exchange-correlation potential is required, i.e., equation (1.156),

$$v_{\text{Hxc}}([n]; \boldsymbol{r}, t) \equiv v^{\text{Hxc}}_{\widehat{\rho}_0, \widehat{\rho}'_0}([n]; \boldsymbol{r}, t) := v_{\widehat{\rho}'_0}([n]; \boldsymbol{r}, t) - v_{\widehat{\rho}_0}([n]; \boldsymbol{r}, t).$$

We can define the Hartree-exchange-correlation potential accordingly if we relate the interacting and the noninteracting system via their modified local force balance equations (1.91)

$$\underbrace{\partial_\nu \partial_\mu \Pi_{\mu\nu}(\boldsymbol{r}, t)}_{=:q(\boldsymbol{r}, t)} = \boldsymbol{\nabla}_{\boldsymbol{r}} \cdot [n(\boldsymbol{r}, t) \boldsymbol{\nabla}_{\boldsymbol{r}} v_{\text{Hxc}}([n]; \boldsymbol{r}, t)] + \underbrace{\partial_\nu \partial_\mu tr[\widehat{T}_{\mu\nu}(\boldsymbol{r}) \widehat{\rho}'(t)]}_{=:q'(\boldsymbol{r}, t)}. \tag{1.321}$$

Again we assume Taylor expandability and find for the Hartree-exchange-correlation potential

$$\boldsymbol{\nabla}_{\boldsymbol{r}} \cdot \left[n^{(0)}(\boldsymbol{r}) \boldsymbol{\nabla}_{\boldsymbol{r}} v^{(k)}_{\text{Hxc}}([n]; \boldsymbol{r}) \right] = \tag{1.322}$$

$$q^{(k)}(\boldsymbol{r}) - (q')^{(k)}(\boldsymbol{r}) - \sum_{l=0}^{k-1} \binom{k}{l} \boldsymbol{\nabla}_{\boldsymbol{r}} \cdot \left[n'^{(k-l)}(\boldsymbol{r}) \boldsymbol{\nabla}_{\boldsymbol{r}} v^{(l)}_{\text{Hxc}}([n]; \boldsymbol{r}) \right].$$

The terms $q^{(k)}(\boldsymbol{r})$ and $(q')^{(k)}(\boldsymbol{r})$ are found via successive application of the Ehrenfest theorem for the operators $\widehat{\Pi}_{\mu\nu}(\boldsymbol{r})$ and $\widehat{T}_{\mu\nu}(\boldsymbol{r})$ for the associated initial configurations $\widehat{\rho}_0$ and $\widehat{\rho}'_0$, respectively. The dependence on the second time derivative, and therefore also any future dependence, has vanished via relating the noninteracting system to the interacting one.

However, here another source of criticism arises. In order to define the Hartree-exchange-correlation potential one needs $q^{(k)}(\boldsymbol{r})$. Via the Ehrenfest theorem for the interacting system this expression can be explicitly calculated . This amounts to a solution of the interacting problem [45]. If this route is chosen, nothing is gained, as one has to **simultaneously solve the interacting as well as the noninteracting problem**. Nevertheless via lemma 1.3.3 the expectation value of any operator $\widehat{O}(t)$ acting on the wavefunctions can be described as an operator of the given external potential of the interacting system alone. Especially we have $q(\boldsymbol{r}, t) = \langle \partial_\mu \partial_\nu \widehat{\Pi}_{\mu\nu}(\boldsymbol{r}) \rangle_t \equiv q([v]; \boldsymbol{r}, t)$. Thus we could in principle rewrite the $q^{(k)}(\boldsymbol{r})$ without referring to the solution $\widehat{\rho}(t)$ of the interacting problem, i.e., the solution of the fully interacting Schrödinger equation.

A simultaneous solution of the interacting as well as the noninteracting problem is not required. However, to know this mapping exactly the interacting problem for all external potentials has to be solved in the first place. Hence, this problem remains. It is here where we usually have to use approximations for the internal forces of the interacting system. Nevertheless we have an, in principle, exact way to rewrite the interacting problem in terms of a noninteracting one. Note that similar problems arise in time-independent density functional theory if one wants the exact expression of $E_{xc}[n]$, which can only be given by solution of the corresponding interacting problem.

Beside the usual implementation of time-dependent density functional theory via propagation of the nonlinear Kohn-Sham equations, one could think of using the Kohn-Sham construction as an **iteration scheme** [45, 46]. This would be a possible way to circumvent any problems arising in the usual propagation scheme. Though such a calculation was implemented and converged [47] a general proof of convergence is still missing.

Chapter 2

Intense Laser-Matter Interaction

Laser systems are available over a wide range of wavelengths, intensities and pulse durations. It is already possible to produce attosecond pulses or peak intensities up to 10^{22} W/cm^2 [48–50]. Depending on the wavelength, laser intensity and binding energies of the systems of interest, perturbation theory is in general not applicable anymore. For instance, at 1 μ m wavelength and typical binding energies, perturbation theory is assumed to break down at about 10^{13} W/cm^2. Depending on the intensity and the system, e.g., for highly charged ions, one has to take relativistic effects into account. However, for our purposes we will safely assume relativistic effects being negligible. Usual approaches to (nonperturbative) strong field physics are the Floquet theory, the strong field approximation and ab initio numerical calculations [3]. A very simple approach is the so-called simple man's theory [see [53] for a review]. There one uses classical arguments to describe an electron released from its parent ion and travelling freely in the laser field, i.e., without influence from the residual system. Though very crude, the simple man's theory predicts many phenomena of intense laser-atom interaction qualitatively quite well, e.g., the cut-off laws of above-threshold ionization and harmonic generation. The successes of the simple man's theory indicate that under certain circumstances in strong field physics the electrons behave nearly classical. The importance of classical contributions can be seen if asymptotic expansions of the strong field approximation are considered, or in the theory of quantum orbits [54].

Typically a three-step model is used to explain most of the observed strong field phenomena. In a first step an electron is removed from its parent ion (ionization) by the laser field. The electron then propagates in the continuum. It may recollide with the residual system if the first step happend at a time such that the laser field drives the electron back. High order harmonic generation for instance is due to recombination of an electron of high kinetic energy with the parent system and is well described by the strong field approximation. High order harmonic generation is able to efficiently convert a vast amount of low frequency photons into a single high frequency photon. This process can be used to generate short wavelength radiation and attosecond pulses. In addition, high-order harmonic generation can be used to image molecular orbitals via so-called orbital tomography [55, 56]. Further characteristic strong field processes are over-barrier ionization or above-threshold ionization [48, 51, 52]. Certain strong field phenomena

can only be explained if correlation or collectivity are included in the treatment. The strong field approximation in its standard form is merely a single active electron theory and can therefore not properly describe multi-particle strong field phenomena such as nonsequential double ionization. In this well-studied process [see, e.g., [57] and references therein] the electron comes back to the residual system and frees a second electron by a collision. This gives rise to a much higher yield of doubly charged ions than a sequential treatment, i.e., assuming uncorrelated electrons.

In this chapter we will review the theory for multiphoton processes in dipole approximation. We present the field mode expectation value and relate it to the dipole expectation value. For high intensity lasers we will show a classical description of the photon field to be adequate. Subsequently the strong field approximation will be derived in two different ways. Finally a general many-body S-matrix theory in the spirit of the strong field approximation is introduced.

2.1 Multiphoton Processes in Dipole Approximation

The minimal coupling Hamiltonian in velocity gauge and in the Schrödinger picture is given by [58]

$$\widehat{H} = \frac{1}{2m_{\mathrm{e}}} \sum_{k=1}^{N} \left(-i\hbar \boldsymbol{\nabla}_k - \frac{e}{c} \boldsymbol{A}(\boldsymbol{r}_k) \right)^2 + \widehat{V}(\boldsymbol{r}_1, ..., \boldsymbol{r}_N) + \widehat{H}_{\mathrm{f}}, \tag{2.1}$$

with $\widehat{V}$ the scalar potential describing the interaction with the nuclei and electron-electron repulsion and the vector potential in second quantized notation

$$\boldsymbol{A}(\boldsymbol{r}) = \sum_{\boldsymbol{k},\lambda} \sqrt{\frac{2\pi\hbar c^2}{\omega_k \mathcal{V}}} \boldsymbol{\epsilon}_{\boldsymbol{k},\lambda} \left(\exp(i\delta) a_{\boldsymbol{k},\lambda} \exp(i\boldsymbol{k} \cdot \boldsymbol{r}) + \exp(-i\delta) a_{\boldsymbol{k},\lambda}^{\dagger} \exp(-i\boldsymbol{k} \cdot \boldsymbol{r}) \right) \tag{2.2}$$

where $a_{\boldsymbol{k},\lambda}$, $a_{\boldsymbol{k},\lambda}^{\dagger}$ are the bosonic annihilation and creation operators of a photon with wavevector $\boldsymbol{k}$ and polarization λ, $\boldsymbol{\epsilon}_{\boldsymbol{k},\lambda}$ the polarization unit vector, $\mathcal{V}$ the quantization volume and ω_k the associated angular frequency of mode $\boldsymbol{k}, \lambda$. We choose the arbitrary phase $\delta = 0$ in what follows. Note that we use **Gaussian units**, i.e., $\epsilon_0 = 1/(4\pi)$ and $\mu_0 = 4\pi/c^2$. The field Hamiltonian is defined as

$$\widehat{H}_{\mathrm{f}} = \sum_{\boldsymbol{k},\lambda} \hbar\omega_k \left(a_{\boldsymbol{k},\lambda}^{\dagger} a_{\boldsymbol{k},\lambda} + \frac{1}{2} \right) \tag{2.3}$$

where the zero point energy $\frac{1}{2} \sum_{\boldsymbol{k},\lambda} \hbar\omega_k$ can be discarded if one is only interested in phenomena involving essentially the difference in field energy.

We will now introduce an important approximation, the **dipole approximation**. First the exponentials are expanded in a series

$$\exp(\pm i\boldsymbol{k} \cdot \boldsymbol{r}) = 1 \pm i\boldsymbol{k} \cdot \boldsymbol{r} + ... \tag{2.4}$$

If we assume the wavelength of the laser at consideration to be large compared to the relevant interaction region, e.g., the size of some atomic system, the spatial dependence of the field is negligible, i.e., $|\boldsymbol{k} \cdot \boldsymbol{r}| \ll 1$. Hence we can cut the expansion already after the first term:

$$\boldsymbol{A}(0) \;\; = \;\; \sum_m \sqrt{\frac{2\pi\hbar c^2}{\omega_m \mathcal{V}}} \boldsymbol{\epsilon}_m \left(a_m + a_m^\dagger \right), \tag{2.5}$$

where we used the abbreviation $m = (\boldsymbol{k}, \lambda)$ and $\omega_k = \omega_m$. Note that in this approximation the magnetic field of the laser pulse is ignored because we have with $\boldsymbol{A} = \boldsymbol{A}(0)$, $\boldsymbol{B} = \boldsymbol{\nabla} \times \boldsymbol{A}(0) \equiv 0$. The electric field in dipole approximation reads [58]

$$\boldsymbol{E}(0) \;\; = \;\; \sum_m \sqrt{\frac{2\pi\hbar c^2}{\omega_m \mathcal{V}}} \frac{\omega_m}{c} \boldsymbol{\epsilon}_m \left(\mathrm{i} a_m - \mathrm{i} a_m^\dagger \right), \tag{2.6}$$

which again is found by quantization of the classical expression. We may further rewrite
$$\widehat{H} = \widehat{H}_\mathrm{s} + \widehat{H}_1 + \widehat{H}_2 + \widehat{H}_\mathrm{f}, \tag{2.7}$$

with

$$\widehat{H}_\mathrm{s} \;\; = \;\; -\frac{\hbar^2}{2m_\mathrm{e}} \sum_{k=1}^N \boldsymbol{\nabla}_k^2 + \widehat{V}(\boldsymbol{r}_1, ..., \boldsymbol{r}_N), \tag{2.8}$$

$$\widehat{H}_1 \;\; = \;\; \frac{\mathrm{i} e \hbar}{m_\mathrm{e} c} \sum_{k=1}^N \boldsymbol{\nabla}_k \cdot \boldsymbol{A}(0), \tag{2.9}$$

$$\widehat{H}_2 \;\; = \;\; \frac{Ne^2}{2m_\mathrm{e}c^2} \boldsymbol{A}(0)^2 = \frac{Ne^2}{2m_\mathrm{e}c^2} \left(\sum_m \frac{2\pi\hbar c^2}{\omega_m \mathcal{V}} \left(a_m + a_m^\dagger \right) \boldsymbol{\epsilon}_m \right)^2. \tag{2.10}$$

The next step is to redefine the creation and annihilation operators to omit $\widehat{H}_2$. First we will introduce canonical coordinate and momentum operators

$$q_m \;\; = \;\; \sqrt{\frac{\hbar}{2\omega_m}} \left(a_m + a_m^\dagger \right), \tag{2.11}$$

$$p_m \;\; = \;\; -\mathrm{i}\hbar \frac{d}{dq_m} = -\mathrm{i}\sqrt{\frac{\hbar\omega_m}{2}} \left(a_m - a_m^\dagger \right). \tag{2.12}$$

This is analogous to the usual canonical quantization procedure [58], i.e., the canonical coordinates and momentum are subject to the commutation relation $[p_m, q_{m'}]_- = -\mathrm{i}\hbar\delta_{m,m'}$. Thus we can rewrite the total Hamiltonian in terms of the canonical operators

$$\widehat{H} = \widehat{H}_\mathrm{s} + \widehat{H}_1 + \widehat{H}_\mathrm{f}', \tag{2.13}$$

with

$$\widehat{H}_\mathrm{f}' \;\; = \;\; \widehat{H}_f + \widehat{H}_2 \tag{2.14}$$

$$= \;\; \frac{1}{2} \sum_m \left(-\hbar^2 \frac{d}{dq_m} + \omega_m^2 q_m \right) + \frac{1}{2} \omega_\mathrm{p}^2 \sum_m \sum_{m'} \boldsymbol{\epsilon}_m \cdot \boldsymbol{\epsilon}_{m'} q_m q_{m'}$$

$$\widehat{H}_1 \;\; = \;\; \frac{\mathrm{i} e \hbar}{m_\mathrm{e}} \sum_{k=1}^N \boldsymbol{\nabla}_k \cdot \left(\sum_m \sqrt{\frac{4\pi}{\mathcal{V}}} \, q_m \boldsymbol{\epsilon}_m \right) \tag{2.15}$$

where

$$\omega_{\mathrm{p}} = \sqrt{\frac{4\pi e^2 N}{m_{\mathrm{e}} \mathcal{V}}} \tag{2.16}$$

is the plasma frequency for an electron gas of density $N/\mathcal{V}$. With the definition of the real and symmetric matrix

$$W_{m,m'} = \omega_m^2 \delta_{m,m'} + \omega_{\mathrm{p}}^2 \boldsymbol{\epsilon}_m \cdot \boldsymbol{\epsilon}_{m'} \tag{2.17}$$

we can express $\widehat{H}_{\mathrm{f}}'$ as

$$\widehat{H}_{\mathrm{f}}' = \frac{1}{2} \left(\sum_m p_m^2 + \sum_{m,m'} W_{m,m'} q_m q_{m'} \right). \tag{2.18}$$

The spectral theorem for finite dimensions guarantees that there exists a real orthogonal matrix O, i.e., $O^{\mathrm{T}}O = OO^{\mathrm{T}} = \mathbb{1}$ which diagonalizes W via $\mathrm{diag}(W) = O^{\mathrm{T}}WO$ with eigenvalues $\{\Omega_\mu\}$. Let

$$Q_\mu = \sum_m O_{\mu m} \, q_m, \tag{2.19}$$

$$P_\mu = \sum_m O_{\mu m} \, p_m, \tag{2.20}$$

$$\boldsymbol{\Upsilon}_\mu = \sum_m O_{\mu m} \, \boldsymbol{\epsilon}_m. \tag{2.21}$$

Then one can express $\widehat{H}_{\mathrm{f}}'$ as independent harmonic oscillators

$$\widehat{H}_{\mathrm{f}}' = \frac{1}{2} \left(\sum_m P_m^2 + \sum_m \Omega_m^2 Q_m^2 \right). \tag{2.22}$$

Note that P_m and $Q_{m'}$ are well-defined with respect to the commutation relation $[P_m, Q_{m'}]_- = -\mathrm{i}\hbar \delta_{m,m'}$. Further we have

$$\widehat{H} = \widehat{H}_{\mathrm{s}} + \widehat{H}_{\mathrm{f}}' + \frac{\mathrm{i}e\hbar}{m} \sqrt{\frac{4\pi}{\mathcal{V}}} \sum_k \boldsymbol{\nabla}_k \cdot \sum_m \boldsymbol{\Upsilon}_m Q_m. \tag{2.23}$$

One finds that the term $\widehat{H}_2$ perturbs the photon energy and the polarization of the field modes due to coupling of the field modes among themselves via the electrons. Introducing the dressed annihilation and creation operators defined as

$$\widetilde{a}_m = (2\hbar\Omega_m)^{-\frac{1}{2}} \left(\Omega_m Q_m + \mathrm{i}P_m^\dagger \right), \tag{2.24}$$

$$\widetilde{a}_m^\dagger = (2\hbar\Omega_m)^{-\frac{1}{2}} \left(\Omega_m Q_m - \mathrm{i}P_m^\dagger \right), \tag{2.25}$$

we finally arrive at the **field-dressed Hamiltonian in velocity gauge**

$$\widehat{H} = \widehat{H}_{\mathrm{s}} + \frac{\mathrm{i}e\hbar}{m_{\mathrm{e}}c} \sum_{k=1}^N \boldsymbol{\nabla}_k \cdot \widetilde{\boldsymbol{A}}(0) + \sum_m \hbar\Omega_m \left(\widetilde{a}_m^\dagger \widetilde{a}_m + \frac{1}{2} \right), \tag{2.26}$$

where $\widetilde{\boldsymbol{A}}(0) = \sum_m \sqrt{\frac{2\pi\hbar c^2}{\Omega_m \mathcal{V}}} \boldsymbol{\Upsilon}_m \left(\widetilde{a}_m + \widetilde{a}_m^\dagger\right)$. The missing term $\widehat{H}_2$ is now accounted for by the shifted energies and the changes in polarization of the field modes. However, in most cases the term $\widehat{H}_2$ and thus the energy and polarization modifications are ignored from the beginning. This approximation is well justified if for the limit of infinite quantization volume the condition

$$\omega_{\mathrm{p}} \sim \sqrt{\frac{N}{\mathcal{V}}} \to 0 \tag{2.27}$$

holds. This is, of course, fulfilled for single atom light interactions. For a dense gas, i.e., in the thermodynamic limit, we have $N \to \infty$ if the quantization volume is extended to infinity and therefore ω_{p} may result in important contributions.

For the Hamiltonian (2.13) written in terms of the canonical coordinate and momentum operators, $q_{\boldsymbol{k},\lambda}$ and $p_{\boldsymbol{k},\lambda}$, we may define, using the unitary operator

$$\widehat{U}_{\mathrm{L}} = \exp\left(\mathrm{i}\frac{e}{\hbar c}\sum_k \boldsymbol{r}_k \cdot \boldsymbol{A}(0)\right) = \exp\left(\frac{\mathrm{i}}{\hbar}\sqrt{\frac{4\pi}{\mathcal{V}}}\sum_k e\,\boldsymbol{r}_k \cdot \sum_m \boldsymbol{\epsilon}_m q_m\right), \tag{2.28}$$

the length form of the Hamiltonian $\widehat{H}_{\mathrm{L}}$ by

$$\widehat{H}\widehat{U}_{\mathrm{L}} = \widehat{U}_{\mathrm{L}}\widehat{H}_{\mathrm{L}}. \tag{2.29}$$

Note that the wavefunctions in velocity gauge $|\Psi\rangle$ and in length gauge $|\Psi_{\mathrm{L}}\rangle$ obey the relation

$$|\Psi\rangle = \widehat{U}_{\mathrm{L}}|\Psi_{\mathrm{L}}\rangle. \tag{2.30}$$

We find

$$\begin{aligned}
\widehat{H}_{\mathrm{L}} &= \widehat{H}_{\mathrm{s}} + \frac{1}{2}\sum_m\left(-\hbar^2\frac{d^2}{dq_m^2} + \omega_m^2 q_m\right) + \\
&+ \sqrt{\frac{4\pi}{\mathcal{V}}}\sum_k e\,\boldsymbol{r}_k \cdot \sum_m\left(-\mathrm{i}\hbar\boldsymbol{\epsilon}_m\frac{d}{dq_m}\right) + \frac{2\pi}{\mathcal{V}}\sum m\left(e\sum_k \boldsymbol{r}_k\right)^2.
\end{aligned} \tag{2.31}$$

Transforming back to creation and annihilation operators and defining

$$\boldsymbol{D} \equiv \boldsymbol{D}(\boldsymbol{r}_1, ..., \boldsymbol{r}_N) := \left(-e\sum_k \boldsymbol{r}_k\right) = \sum_k \boldsymbol{d}_k, \tag{2.32}$$

the dipole polarization vector, we finally arrive at the **length (gauge) form of the Hamiltonian**

$$\widehat{H}_{\mathrm{L}} = \widehat{H}_{\mathrm{s}} + \widehat{H}_{\mathrm{f}} + \boldsymbol{D} \cdot \boldsymbol{E}(0) + \underbrace{\frac{2\pi}{\mathcal{V}}\sum_m \boldsymbol{D}^2}_{=\widehat{H}_{\mathrm{Pol}}}. \tag{2.33}$$

The last term $\widehat{H}_{\mathrm{Pol}}$ is the polarization energy operator and describes as $\widehat{H}_2$ above in velocity gauge the back reaction of the laser modes via the electrons. Again we can neglect the back-coupling of the laser modes if for the limit of infinite quantization volume $\mathcal{V}$ we have $\widehat{H}_{\mathrm{Pol}} \to 0$. Accordingly, for the thermodynamic limit the polarization energy operator may give important contributions.

Before we proceed, we make a further transformation of equation (2.33) which is often used. If we assume $\widehat{H}_{\mathrm{Pol}} \to 0$ we can switch to the so-called intermediate picture in which we can eliminate the field Hamiltonian $\widehat{H}_{\mathrm{f}}$. With the Hamiltonian $\widehat{H}$ of equation (2.33) — we will drop the subscript L in our further considerations — the Schrödinger equation reads

$$i\hbar \frac{\partial}{\partial t} |\Psi(t)\rangle = \widehat{H} |\Psi(t)\rangle. \tag{2.34}$$

With the unitary transformation $\widehat{U}_{\mathrm{i}} = \exp\left(-\mathrm{i} \sum_m a_m^\dagger a_m \omega_m t\right) = \exp\left(-\frac{\mathrm{i}}{\hbar} \widehat{H}_{\mathrm{f}} t\right)$, where the zero point energy has been ignored, and

$$|\Psi(t)\rangle = \widehat{U}_{\mathrm{i}} |\Psi_{\mathrm{i}}(t)\rangle \tag{2.35}$$

one finds

$$i\hbar |\Psi_{\mathrm{i}}(t)\rangle = \left\{ \widehat{H}_{\mathrm{s}} + \sum_m \sqrt{\frac{2\pi\hbar\omega_m}{\mathcal{V}}} \boldsymbol{\epsilon}_m \cdot \boldsymbol{D} \widehat{U}_{\mathrm{i}}^\dagger \left(\mathrm{i}a_m - \mathrm{i}a_m^\dagger\right) \widehat{U}_{\mathrm{i}} \right\} |\Psi_{\mathrm{i}}(t)\rangle. \tag{2.36}$$

Using the commutation relations of the bosonic creation and annihilation operators we obtain

$$\exp\left(\mathrm{i}a_m^\dagger a_m \omega_m t\right) a_m^\dagger = a_m^\dagger \exp\left(\mathrm{i}a_m a_m^\dagger \omega_m t\right) \tag{2.37}$$

$$a_m \exp\left(-\mathrm{i}a_m^\dagger a_m \omega_m t\right) = \exp\left(-\mathrm{i}a_m a_m^\dagger \omega_m t\right) a_m. \tag{2.38}$$

leading to the **length gauge Hamiltonian in the intermediate picture**

$$i\hbar |\Psi_{\mathrm{i}}(t)\rangle = \tag{2.39}$$
$$\left\{ \widehat{H}_{\mathrm{s}} + \sum_m \sqrt{\frac{2\pi\hbar\omega_m}{\mathcal{V}}} \boldsymbol{\epsilon}_m \cdot \boldsymbol{D} \left(\mathrm{i}a_m \exp(-\mathrm{i}\omega_m t) - \exp(\mathrm{i}\omega_m t)\mathrm{i}a_m^\dagger\right) \right\} |\Psi_{\mathrm{i}}(t)\rangle.$$

This special form highlights the resemblance between the Schrödinger equation with a quantized photon field and its semi-classical counterpart. We will come back to this equation later when the so-called laser-approximation is deduced.

2.1.1 Field Mode and Dipole Expectation Value

With the above defined Hamiltonian in length gauge (2.33) we will now calculate in accordance to [59] the expectation value of the number of photons in mode $(\boldsymbol{k}', \lambda') = m'$,

$$\langle a_{m',\mathrm{H}}^\dagger(t) a_{m',\mathrm{H}}(t) \rangle_0, \tag{2.40}$$

in the Heisenberg picture at time t. We assume

$$\widehat{H}_{\mathrm{Pol}} \to 0 \tag{2.41}$$

and discard the zero point energy of $\widehat{H}_{\mathrm{f}}$. The system-Hamiltonian $\widehat{H}_{\mathrm{s}}$ and $\boldsymbol{D}$ are expressed in terms of a complete set of energy eigenstates $\{|i\rangle\}$

$$\widehat{H}_{\mathrm{s}}|i\rangle = E_i|i\rangle. \tag{2.42}$$

With the transition operators

$$\sigma_{ij} = |i\rangle\langle j| \tag{2.43}$$

one finds $\widehat{H}_{\mathrm{s}} = \sum_i E_i \sigma_{ii}$ and $\boldsymbol{D} = \sum_{i,j} |i\rangle\langle i|\boldsymbol{D}|j\rangle\langle j| = \sum_{i,j} \boldsymbol{\mu}_{ij}\sigma_{ij}$. This leads to

$$\widehat{H} = \sum_m \hbar\omega_m a_m^\dagger a_m + \sum_i E_i \sigma_{ii} + \mathrm{i}\hbar \sum_{i,j} \sum_m C_{ijm}\sigma_{ij}(a_m - a_m^\dagger), \tag{2.44}$$

with $C_{ijm} = (2\pi\omega_m/\hbar\mathcal{V})^{1/2}\boldsymbol{\mu}_{ij} \cdot \boldsymbol{\epsilon}_m$. The time-dependent annihilation operator of mode m' fulfills the Heisenberg equation

$$-\mathrm{i}\hbar\frac{\partial}{\partial t}a_{m',\mathrm{H}}(t) = \left[\widehat{H}_{\mathrm{H}}(t), a_{m',\mathrm{H}}(t)\right]_- \tag{2.45}$$

with $\widehat{H}_{\mathrm{H}}(t)$ the Hamiltonian in the Heisenberg picture. Calculating the commutator one finds

$$\frac{\partial}{\partial t}a_{m',\mathrm{H}}(t) = -\mathrm{i}\omega_{m'}a_{m',\mathrm{H}}(t) - \sum_{i,j} C_{ijm'}\sigma_{ij,\mathrm{H}}(t), \tag{2.46}$$

and for the creation operator we obtain

$$\frac{\partial}{\partial t}a_{m',\mathrm{H}}^\dagger(t) = \mathrm{i}\omega_{m'}a_{m',\mathrm{H}}^\dagger(t) - \sum_{i,j} C_{ijm'}\sigma_{ij,\mathrm{H}}(t). \tag{2.47}$$

Equations (2.46), (2.47) are two inhomogeneous ordinary differential equations of first order. The homogeneous solution for the annihilation operator is

$$a_{m',\mathrm{H}}(t) = \exp\left(-\mathrm{i}\omega_{m'}t\right) a_{m'}(t_0) \tag{2.48}$$

and a particular inhomogeneous solution is

$$a_{m',\mathrm{H}}(t) = \exp\left(-\mathrm{i}\omega_{m'}t\right) \int_{t_0}^t dt' \sum_{i,j} C_{ijm'} \exp\left(\mathrm{i}\omega_{m'}t'\right) \sigma_{ij,\mathrm{H}}(t'), \tag{2.49}$$

leading to

$$\begin{aligned}
a_{m',\mathrm{H}}(t) &= \exp(-\mathrm{i}\omega_{m'}t)a_{m'}(t_0) \\
&+ \exp(-\mathrm{i}\omega_{m'}t) \int_{t_0}^t dt' \sum_{i,j} C_{ijm'} \exp(\mathrm{i}\omega_{m'}t')\sigma_{ij,\mathrm{H}}(t').
\end{aligned} \tag{2.50}$$

Analogously one finds the general solution for the creation operator. **The expectation value of the number of photons in mode $(\boldsymbol{k}', \lambda') = m'$ follows as**

$$
\begin{aligned}
\langle a_{m',\mathrm{H}}^{\dagger}(t) a_{m',\mathrm{H}}(t) \rangle_0 &= \langle a_{m'}^{\dagger}(t_0) a_{m'}(t_0) \rangle_0 \\
&\quad - 2\sqrt{\frac{2\pi\omega_{m'}}{\hbar\mathcal{V}}} \Re \left\{ \int_{t_0}^{t} dt' \langle a_{m'}(t_0) \boldsymbol{\epsilon}_{m'} \cdot \boldsymbol{D}_{\mathrm{H}}(t') \rangle_0 \exp(-\mathrm{i}\omega_{m'} t') \right\} \\
&\quad + \frac{2\pi\omega_{m'}}{\hbar\mathcal{V}} \int_{t_0}^{t} dt' \int_{t_0}^{t} dt'' \langle \boldsymbol{D}_{\mathrm{H}}(t') \cdot \boldsymbol{D}_{\mathrm{H}}(t'') \rangle_0 \exp(-\mathrm{i}\omega_{m'}(t' - t'')).
\end{aligned}
\tag{2.51}
$$

Here we have used

$$
\sum_{i,j} \boldsymbol{\mu}_{ij} \sigma_{ij,\mathrm{H}}(t) = \boldsymbol{D}_{\mathrm{H}}(t).
\tag{2.52}
$$

A special case, which we will need later on in the context of high-order harmonic generation, is the one where the system is initially in its ground-state and the field mode m' is not occupied, i.e., $|\Psi(t_0)\rangle_{\mathrm{f,s}} = |N_{\mathrm{f}}; ..., 0_{m'}, ...\rangle_{\mathrm{f}} \otimes |\Psi_0\rangle_{\mathrm{s}}$. Therefore only the third term of equation (2.51) survives and we find

$$
\begin{aligned}
\langle a_{m',\mathrm{H}}^{\dagger}(t) a_{m',\mathrm{H}}(t) \rangle_0 &= \frac{2\pi\omega_{m'}}{\hbar\mathcal{V}} \int_{t_0}^{t} dt' \int_{t_0}^{t} dt'' \langle \boldsymbol{D}_{\mathrm{H}}(t') \cdot \boldsymbol{D}_{\mathrm{H}}(t'') \rangle_0 \exp(-\mathrm{i}\omega_{m'}(t' - t'')) \quad (2.53) \\
&= \frac{2\pi\omega_{m'}}{\hbar\mathcal{V}} \sum_{k,k'}^{N} \int_{t_0}^{t} dt' \int_{t_0}^{t} dt'' \langle \boldsymbol{d}_{k,\mathrm{H}}(t') \cdot \boldsymbol{d}_{k',\mathrm{H}}(t'') \rangle_0 \exp(-\mathrm{i}\omega_{m'}(t' - t'')).
\end{aligned}
$$

This term accounts for spontaneous emission and scattering. The term $\langle \boldsymbol{d}_{k,\mathrm{H}}(t') \cdot \boldsymbol{d}_{k',\mathrm{H}}(t'') \rangle_0$ is the two-time dipole correlation function. If we now assume uncorrelated emitters, e.g., in the original work [59] N one-electron atoms being the constituents of a dilute gas, we can approximate

$$
\langle \boldsymbol{d}_{k,\mathrm{H}}(t') \cdot \boldsymbol{d}_{k',\mathrm{H}}(t'') \rangle_0 \simeq \langle \boldsymbol{d}_{k,\mathrm{H}}(t') \rangle_0 \cdot \langle \boldsymbol{d}_{k',\mathrm{H}}(t'') \rangle_0.
\tag{2.54}
$$

Further we can use this approximation to rewrite

$$
\langle a_{m',\mathrm{H}}^{\dagger}(t) a_{m',\mathrm{H}}(t) \rangle_0 \simeq \frac{2\pi\omega_{m'}}{\hbar\mathcal{V}} \left| \sum_{k=1}^{N} \int_{t_0}^{t} dt' \langle \boldsymbol{d}_{k,\mathrm{H}}(t') \rangle_0 \exp(\mathrm{i}\omega_{m'} t') \right|^2
\tag{2.55}
$$

if $N \gg 1$ such that the self-correlation terms contribute negligibly. If further all electrons "see" the same field we obtain the absolute square of N times the single dipole expectation value.

Using the dipole expectation value to describe the field mode expectation value is common in strong field physics. However, one has to make sure that the approximations above are well justified.

2.1.2 Classical Description of the Laser Field

Until now we have treated the laser field in second quantization. However, as will be shown below, in the case of intense laser fields, it is well justified to use a **classical description of the laser field**. The Hamiltonian in length gauge and dipole approximation then reads [58]

$$\widehat{H}(t) = \widehat{H}_{\mathrm{s}} + \boldsymbol{D} \cdot \boldsymbol{E}(t) \tag{2.56}$$

with $\boldsymbol{E}(t) = \sum_m E_m \boldsymbol{\epsilon}_m \sin(\omega_m t + \delta_m)$, E_m the peak field strength and δ_m the phase of field mode m. For a comparison to the photon field in terms of number states $|N_{\mathrm{f}}; n_1, n_2, ..., n_M\rangle_{\mathrm{f}}$ and for the description of transition matrices $\langle N_{\mathrm{f}}; n_1, n_2, ..., n_M|_{\mathrm{f}} \otimes \langle \Psi|_{\mathrm{s}} \Psi(t)\rangle_{\mathrm{fs}}$ the so-called phasors are of importance [see e.g. [58] page 129]. The inner product between number states correspond to the normalized phase integral of δ, i.e.,

$$_{\mathrm{f}}\langle m|n\rangle_{\mathrm{f}} \leftrightarrow \frac{1}{2\pi} \int_0^{2\pi} d\delta \exp(-\mathrm{i}(m-n)\delta). \tag{2.57}$$

Note the similarity between the second term in the Hamiltonian (2.56) and the second quantized form in the intermediate picture (2.39) if we rewrite

$$\boldsymbol{E}(t) = \sum_m (E_m/2)\boldsymbol{\epsilon}_m[\mathrm{i}\exp(-\mathrm{i}(\omega_m t + \delta_m)) - \mathrm{i}\exp(\mathrm{i}(\omega_m t + \delta_m))]. \tag{2.58}$$

One way to validate a classical description of the laser field at high intensities is through the expectation value of the electric field and its uncertainty in the Heisenberg picture. If one assumes a Glauber state and a high mean number of photons, i.e., a high intensity, a classical description is valid [60].

Here we will formally deduce the classical field approximation in a different way. We will make a comparison between the solutions of the Schrödinger equation with Hamiltonian (2.56) and the quantized photon field Hamiltonian (2.33) via their resolvent equations [58]. For $\widehat{H}$ is time-independent in second quantization we use the resolvent equation

$$\left(E - \widehat{H}\right) G(E) = \mathbb{1}. \tag{2.59}$$

The time-dependent wavefunction solution to the Schrödinger equation reads

$$|\Psi(t)\rangle_{\mathrm{fs}} = -\frac{1}{2\pi\mathrm{i}} \int_{-\infty}^{\infty} dE\, G(E)\, \exp(-\mathrm{i}Et/\hbar)|\Psi_0\rangle_{\mathrm{fs}} \tag{2.60}$$

with the initial condition $|\Psi_0\rangle_{\mathrm{fs}} = |N_{\mathrm{f}}; n_0^1, n_0^2, ...\rangle_{\mathrm{f}} \otimes |\Psi_0\rangle_{\mathrm{s}}$. Next consider the matrix elements

$$_{\mathrm{f}}\langle N_{\mathrm{f}}; n_1 + n_0^1, n_2 + n_0^2, ...|(E - \widehat{H})G(E)|N_{\mathrm{f}}; n_0^1, ...\rangle_{\mathrm{f}} = \delta_{n_1|0}\delta_{n_2|0}... \quad . \tag{2.61}$$

Obviously the n_m are the changes in the photon number of mode m with respect to the initial occupation. We define

$$_\text{f}\langle N_\text{f}; n_1 + n_0^1, ...|G(E)|N_\text{f}; n_0^1, ...\rangle_\text{f} = G_{n_1|n_0^1,...}(E). \tag{2.62}$$

Thus one finally ends up with the **second-quantized resolvent equation**

$$\left[E - \widehat{H}_\text{s} - \sum_m (n_m + n_0^m)\hbar\omega_m\right] G_{n_1|n_0^1,...}(E) \tag{2.63}$$

$$= -\boldsymbol{D} \cdot \sum_m \boldsymbol{\epsilon}_m \left(\text{i}F_{n_m+1}G_{n_1|n_0^1,...,n_m+1|n_0^m,...}(E) - \text{i}F_{n_m-1}G_{n_1|n_0^1,...,n_m-1|n_0^m,...}(E)\right)$$

$$+\delta_{n_1,0}...$$

with $F_{n_m} = \sqrt{\frac{2\pi\hbar\omega_m(n_m+n_0^m)}{\mathcal{V}}}$. However, one may derive the same result in a different way which will guide us how to do it in the classical field case, where we do not have a time-independent Hamiltonian or number states.

We begin with the Heitler-Ma equation in second-quantized description, which explicitly takes care of the initial condition, i.e., $|\Psi(t_0)\rangle_\text{fs} = |\Psi_0\rangle_\text{fs}$,

$$\text{i}\hbar\frac{\partial}{\partial t}|\Psi(t)\rangle_\text{fs} = [\widehat{H}_\text{s} + \widehat{H}_\text{f} + \boldsymbol{D} \cdot \boldsymbol{E}(0)]|\Psi(t)\rangle_\text{fs} + \text{i}\hbar\delta(t)|\Psi_0\rangle_\text{fs}. \tag{2.64}$$

We make an expansion of the wavefunction in terms of number states $|N_\text{f}; n_1 + n_0^1, ...\rangle$ of the field,

$$|\Psi(t)\rangle_\text{fs} = \sum_{n_1=-n_0^1,...}^\infty |N_\text{f}; n_1 + n_0^1, ...\rangle_\text{f} \otimes |\Psi_{n_1|n_0^1,...}(t)\rangle_\text{s}, \tag{2.65}$$

where the n_m are the changes in the mode occupation numbers. Plugging this expansion into the Heitler-Ma equation (2.64) and projecting onto $\langle N_\text{f}; n_1' + n_0^1, ...|$ we find

$$\text{i}\hbar\frac{\partial}{\partial t}|\Psi_{n_1|n_0^1,...}(t)\rangle_\text{s} = [\widehat{H}_\text{s} + \sum_m (n_m + n_0^m)\hbar\omega_m]|\Psi_{n_1|n_0^1,...}(t)\rangle_\text{s}$$

$$+ \boldsymbol{D} \cdot \sum_m \sqrt{\frac{2\pi\hbar\omega_m}{\mathcal{V}}}\boldsymbol{\epsilon}_m \left[((n_m + n_0^m) - 1)^{1/2}\text{i}|\Psi_{n_1|n_0^1,...,n_m-1|n_0^m,...}(t)\rangle_\text{s}\right.$$

$$- \left.((n_m + n_0^m) + 1)^{1/2}\text{i}|\Psi_{n_1|n_0^1,...,n_m+1|n_0^m,...}(t)\rangle_\text{s}\right]$$

$$+ \text{i}\hbar\delta(t)\delta_{n_1|n_0^1}...|\Psi_0\rangle_\text{s}. \tag{2.66}$$

With a Fourier expansion as in (2.60),

$$|\Psi_{n_1|n_0^1,...}(t)\rangle_\text{s} = -\frac{1}{2\pi\text{i}} \int_{-\infty}^\infty dE \exp(-\text{i}Et/\hbar)G_{n_1|n_0^1,...}(E)|\Psi_0\rangle_\text{s} \tag{2.67}$$

and the identity

$$\text{i}\hbar\delta(t) = -\frac{1}{2\pi\text{i}} \int_{-\infty}^\infty dE \exp(-\text{i}Et/\hbar) \tag{2.68}$$

we find the second-quantized resolvent equation (2.63).

Now we turn to the classical field case. We again incorporate explicitly the initial condition via the Heitler-Ma version of the Schrödinger equation,

$$i\hbar\frac{\partial}{\partial t}|\Psi(t)\rangle = [\widehat{H}_s + \boldsymbol{D} \cdot \boldsymbol{E}(t)]|\Psi(t)\rangle + i\hbar\delta(t)|\Psi_0\rangle. \tag{2.69}$$

In order to reduce this Schrödinger equation without approximation to stationary equations we expand $|\Psi(t)\rangle$ in a generalized "integral+series" Fourier expansion

$$|\psi(t)\rangle = -\frac{1}{2\pi i}\sum_{n_1,...=-\infty}^{\infty}\int_{-\infty}^{\infty}dE \ \exp\left(-\frac{iEt}{\hbar} + i(n_1\omega_1 + ...)t\right) \tag{2.70}$$
$$\times \exp(i(n_1\delta_1 + ...))G_{n_1|0,...}(E)|\Psi_0\rangle,$$

as well as the δ-distribution in time

$$i\hbar\delta(t) = -\frac{1}{2\pi i}\sum_{n_1,...=-\infty}^{\infty}\int_{-\infty}^{\infty}dE \ \exp\left(-\frac{iEt}{\hbar} + i(n_1\omega_1 + ...)t\right) \tag{2.71}$$
$$\times \exp(i(n_1\delta_1 + ...))\delta_{n_1,0}... \quad .$$

The phasors $\exp[i(n_1\delta_1 + ...)]$ correspond in accordance to (2.57) to the number states. If we plug the wavefunction in this expanded form into equation (2.69) and compare the coefficients of $\exp\left[-\frac{i}{\hbar}Et + i(n_1\omega_1 + ...)t + i(n_1\delta_1 + ...)\right]$ on both sides the **first-quantized resolvent equation**

$$\left[E - \widehat{H}_s - \sum_m n_m\hbar\omega_m\right]G_{n_1|0,...}(E) \tag{2.72}$$
$$= -\boldsymbol{D} \cdot \sum_m \frac{E_m\boldsymbol{\epsilon}_m}{2}\left(iG_{n_1|0,...,n_m+1|0,...}(E) - iG_{n_1|0,...,n_m-1|0,...}(E)\right)$$
$$+ \delta_{n_1,0}...$$

results. The subindices 0 are chosen to remind us of the initial condition and for a stronger analogy to the second-quantized case.

To **compare both descriptions** we first redefine the initial number state

$$|N_f; n_0^1, ..., n_0^m, ...\rangle_f \rightarrow |0_f; 0, ..., 0, ...\rangle_f \tag{2.73}$$

as the new "vacuum" state. Hence, we also change the notation

$$G_{n_1|n_0^1,...,n_m|n_0^m,...}(E) \rightarrow G_{n_1|0,...,n_m|0,...}(E) \tag{2.74}$$

in (2.63). Further we note the difference in the prefactors of the $G_{n_1|0,...}(E)$. While for equation (2.63) we have occupation number and mode-dependent prefactors F_{n_m}, for the classical field case (2.72) we find occupation number-independent (however, mode-dependent) prefactors $E_m/2$. We will now introduce the **laser approximation** where we assume $n_0^m \gg n_m$, i.e., the initial mode occupation of photons is much bigger then the

changes in the photon number in that mode. As the field modes of an intense laser are highly populated this approximation is well justified, leading to

$$F_{n_m} \approx F_{n_m \pm 1} \quad \approx \quad \sqrt{\frac{2\pi n_0^m \hbar \omega_m}{\mathcal{V}}} = F_{n_0^m} \tag{2.75}$$

$$(n_m + n_0^m)\hbar\omega_m \quad \approx \quad n_0^m \hbar\omega_m \tag{2.76}$$

Because for the initial energy density $\mathcal{W}_0^m = n_0^m \hbar\omega_m/\mathcal{V}$ holds we can associate $F_{n_0^m}$ with the classical field strength,

$$E_m = \sqrt{\frac{2\mathcal{W}_0^m}{\epsilon_0}} = 2F_{n_0^m}. \tag{2.77}$$

Thus the first quantized description will be very accurate as long as $n_m/n_0^m \ll 1$ holds for those modes responsible for the most important physical processes involved in the evolution of the system. For moderate intensities of about 1 W/cm^2 at optical frequencies the initial number density $n_0/\mathcal{V}$ is about 10^7/cm^3 while the change in the photon number hardly exceeds several hundreds [58]. In this work we typically consider intensities higher then 10^{13} W/cm^2.

2.2 Strong Field Approximation

The strong field approximation or Keldysh-Faisal-Reiss theory [4–6] is one of the main tools to treat strong field laser-atom and laser-molecule interaction. Though merely a single active electron approximation, i.e., one electron may interact with the laser field while the residual system is treated as a frozen background, it describes most high field phenomena [3] well, at least qualitatively. Besides, it offers a rather physically intuitive interpretation. Of course, such an approximate theory also has its limits and drawbacks. The main problem beside the incompatibility with many-particle phenomena, lies within the loss of gauge invariance [61] introduced by the approximations made.
We will derive the strong field approximation in two different ways. Beside a Keldysh-Faisal-Reiss like description there is another derivation of the strong field approximation following Lewenstein [7]. Finally, the strong field approximation is generalized to multi-particle phenomena [8]. This intense-field many-body S-matrix theory is cabable of describing nonsequential double ionization.

2.2.1 Keldysh-Faisal-Reiss Theory

First we will turn to the Keldysh-Faisal-Reiss theory of the strong field approximation and use **atomic units** again. Further we will apply the laser approximation, i.e., a classical field description

$$\widehat{H}_{\mathrm{L}}(t) = \widehat{H}_s + \underbrace{\boldsymbol{r} \cdot \boldsymbol{E}(t)}_{=\widehat{H}_{\mathrm{I,L}}(t)} \tag{2.78}$$

where $\widehat{H}_s = -\frac{1}{2}\boldsymbol{\nabla}^2 + V(\boldsymbol{r})$. Although we have derived the the laser approximation in length gauge we may, in first quantized description, switch to velocity gauge by the gauge transformation

$$|\psi_{\mathrm{V}}(t)\rangle = \exp\left(-\mathrm{i}\boldsymbol{r}\cdot\boldsymbol{A}(t)\right)|\Psi_{\mathrm{L}}(t)\rangle \tag{2.79}$$

with $-\frac{\partial}{\partial t}\boldsymbol{A}(t) = \boldsymbol{E}(t)$. The associated Hamiltonian in velocity gauge reads

$$\widehat{H}_{\mathrm{V}}(t) = \frac{1}{2}\left[\boldsymbol{p} + \boldsymbol{A}(t)\right]^2 + V(\boldsymbol{r}) = \widehat{H}_{\mathrm{s}} + \widehat{H}_{\mathrm{I,V}}(t). \tag{2.80}$$

Note that we have included the factor $1/c$ of the Hamiltonian (2.1) in $\boldsymbol{A}(t)$. The difference between length and velocity gauge amounts to a translation in momentum space. While in velocity gauge the kinetic momentum $\boldsymbol{p}_{\mathrm{kin}} = \boldsymbol{p} + \boldsymbol{A}(t)$ and the canonical momentum $\boldsymbol{p}$ are different in length gauge they are the same. Note here that via a further transformation

$$|\widetilde{\Psi}_{\mathrm{V}}(t)\rangle = \exp\left(\mathrm{i}\int_{t_0}^t d\tau \boldsymbol{A}(\tau)^2/2\right)|\Psi_{\mathrm{V}}(t)\rangle \tag{2.81}$$

one can get rid of the $\boldsymbol{A}(t)^2/2$-term in the Hamiltonian in velocity gauge. Nevertheless we will keep this term. Note that there were some disputes in the literature concerning its importance [see refs. in [3]].

We begin with the Dyson equation for the evolution operator [see equation (1.154)] where we suppress the gauge index which will be restored later on,

$$\widehat{U}(t,t_0) = \widehat{U}_s(t,t_0) - \mathrm{i}\int_{t_0}^t dt'\widehat{U}_s(t,t')\widehat{H}_{\mathrm{I}}(t')\widehat{U}(t',t_0) \tag{2.82}$$

$$= \widehat{U}_s(t,t_0) - \mathrm{i}\int_{t_0}^t dt'\widehat{U}(t,t')\widehat{H}_{\mathrm{I}}(t')\widehat{U}_s(t',t_0), \tag{2.83}$$

with $\widehat{U}_{\mathrm{s}}(t,t_0) = \mathcal{T}_{\mathrm{D}}\left\{\exp\left(-\mathrm{i}\int_{t_0}^t dt'\widehat{H}_{\mathrm{s}}\right)\right\}$ being the system evolution operator. A Dyson like expansion can be constructed with respect to the **Volkov evolution operator** $\widehat{U}^{(V)}(t,t_0)$, which is a solution for a freely propagating electron in a laser field

$$\mathrm{i}\frac{\partial}{\partial t}\widehat{U}^{(V)}(t,t_0) = \widehat{H}^{(V)}\widehat{U}^{(V)}(t,t_0), \tag{2.84}$$

$\widehat{H}^{(V)}(t) = \frac{p^2}{2} + \widehat{H}_{\mathrm{I}}(t)$. The Dyson expansion of (2.82) then reads

$$\widehat{U}(t,t_0) = \widehat{U}^{(V)}(t,t_0) - \mathrm{i}\int_{t_0}^t dt'\widehat{U}^{(V)}(t,t')V\widehat{U}^{(V)}(t',t_0) \tag{2.85}$$

$$- \int_{t_0}^t dt''\int_{t''}^t dt'\widehat{U}^{(V)}(t,t')V\widehat{U}^{(V)}(t',t'')V\widehat{U}^{(V)}(t'',t_0) + \dots \quad .$$

One may rewrite the limits of integration using $\int_{t_0}^t dt''\int_{t''}^t dt' = \int_{t_0}^t dt'\int_{t_0}^t dt''\Theta(t'-t'') = \int_{t_0}^t dt'\int_{t_0}^{t'} dt''$. The Volkov wavefunction reads $|\Psi_{\mathrm{V}}^{(V)}(t)\rangle = \exp\left(-\mathrm{i}S_p(t,t_0)\right)|\boldsymbol{p}\rangle$ with $\langle\boldsymbol{r}|\boldsymbol{p}\rangle = \exp\left(\mathrm{i}\boldsymbol{p}\cdot\boldsymbol{r}\right)/(2\pi)^{3/2}$ and

$$S_p(t,t_0) = \frac{1}{2}\int_{t_0}^t dt'\left[\boldsymbol{p} + \boldsymbol{A}(t')\right]^2, \tag{2.86}$$

where $\widehat{U}^{(V)}(t, t_0) = \exp(-iS_p(t, t_0))$. In length gauge the Volkov wavefunction reads $|\Psi_L^{(V)}(t)\rangle = \exp(-iS_p(t, t_0))|\boldsymbol{p} + \boldsymbol{A}(t)\rangle$.

If we now plug equation (2.85) into the Dyson equation (2.82) we find the still formally exact expression

$$
\begin{aligned}
\widehat{U}(t, t_0) &= \widehat{U}_s(t, t_0) - i \int_{t_0}^t dt' \widehat{U}^{(V)}(t, t') \widehat{H}_I(t') \widehat{U}_s(t', t_0) \\
&\quad - \int_{t_0}^t dt' \int_{t_0}^{t'} dt'' \widehat{U}^{(V)}(t, t') V \widehat{U}^{(V)}(t', t'') \widehat{H}_I(t'') \widehat{U}_s(t'', t_0) + \ldots \quad .
\end{aligned}
\tag{2.87}
$$

These terms have an intuitive physical interpretation. They describe different pathways of the electron. The first one is due to no interaction at all with the laser field, the second term accounts for the electron interacting with the laser field at time t', being emitted at that instant. The third term describes ionization at time t'', propagation in the laser-dressed continuum until time t' where the electron interacts with the residual system, and again free propagation in the laser field afterwards. The standard strong field approximation is now found by truncating the expansion after the second term, leading to the strong field approximation wavefunction

$$
|\Psi(t)\rangle^{(\text{SFA})} = |\Psi_0(t)\rangle - i \int_{t_0}^t dt' \widehat{U}^{(V)}(t, t') \widehat{H}_I(t') |\Psi_0(t')\rangle
\tag{2.88}
$$

with $|\Psi_0(t_0)\rangle$ the eigenstate of $\widehat{H}_s$ from which the dynamics starts. Thus we assume that the electron is ejected into the continuum at time t' and is no longer influenced by the binding potential. This is not a rigorous perturbation theory. Instead, one assumes the binding potential is initially governing the evolution of the electron, and after ionization the laser field dominates. The strong field approximation wavefunction is usually not the primary object of interest. One rather is interested in matrix elements of the form

$$
M_{\boldsymbol{p}}(t_1, t_0) = \langle \Psi_{\boldsymbol{p}}(t_1) | \widehat{U}(t_1, t_0) | \Psi_0(t_0) \rangle
\tag{2.89}
$$

with $|\Psi_{\boldsymbol{p}}(t)\rangle$ a scattering state of asymptotic momentum $\boldsymbol{p}$, or

$$
\boldsymbol{d}(t) = \langle \Psi(t) | \boldsymbol{r} | \Psi(t) \rangle,
\tag{2.90}
$$

the dipole matrix element. The matrix element (2.89) is of interest for **above-threshold ionization**, (2.90) for **high-order harmonic generation**. In both matrix elements one now uses the strong field approximation wavefunction. The dipole moment is used as an approximation for the field mode expectation value in accordance to subsection 2.1.1.

First we will calculate $M_{\boldsymbol{p}}(t_1, t_0)$ in strong field approximation. The exact scattering state $|\Psi_{\boldsymbol{p}}(t)\rangle$ is perpendicular to the initial state, leading to

$$
\langle \Psi_{\boldsymbol{p}}(t_1) | \widehat{U}_s(t_1, t_0) | \Psi_0(t_0) \rangle = 0.
\tag{2.91}
$$

The approximated matrix element thus reads

$$
M_{\boldsymbol{p}}(t_1, t_0) \simeq -i \int_{t_0}^{t_1} dt' \langle \Psi_{\boldsymbol{p}}(t_1) | \widehat{U}^{(V)}(t_1, t') \widehat{H}_I(t') \widehat{U}_s(t', t_0) | \Psi_0(t_0) \rangle.
\tag{2.92}
$$

The associated physical interpretation is: ionization at time t' and subsequent electron motion in the laser field until time t_1 without a rescattering event. In a final approximation, we substitute $|\Psi_{\boldsymbol{p}}(t_1)\rangle \to |\boldsymbol{p}\rangle$ and find

$$M_{\boldsymbol{p}}^{(\text{SFA})}(t_1, t_0) = -\mathrm{i} \int_{t_0}^{t_1} dt' \langle \Psi_{\boldsymbol{p}}^{(V)}(t') | \widehat{H}_{\mathrm{I}}(t') | \Psi_0(t') \rangle, \tag{2.93}$$

the **strong field approximation matrix element**. One may rewrite the matrix element via $\widehat{H}_{\mathrm{I}}(t') = \widehat{H}^{(V)}(t') - \widehat{H}_{\mathrm{s}} + V$ as

$$M_{\boldsymbol{p}}^{(\text{SFA})}(t_1, t_0) = - \left. \langle \Psi_{\boldsymbol{p}}^{(V)}(t') | \Psi_0(t') \rangle \right|_{t_0}^{t_1} - \mathrm{i} \int_{t_0}^{t_1} dt' \langle \Psi_{\boldsymbol{p}}^{(V)}(t') | V | \Psi_0(t') \rangle. \tag{2.94}$$

In most cases one has t_0 and t_1 such that the laser is switched off at that times, and one neglects the contribution of the first term as it would vanish without the approximation $|\Psi_{\boldsymbol{p}}(t_1)\rangle \to |\boldsymbol{p}\rangle$ because of orthogonality,

$$M_{\boldsymbol{p}}^{(\text{SFA})}(t_1, t_0) = -\mathrm{i} \int_{t_0}^{t_1} dt' \langle \Psi_{\boldsymbol{p}}^{(V)}(t') | V | \Psi_0(t') \rangle. \tag{2.95}$$

At a first glance this outcome seems to be strange because the laser field does not mediate the transition anymore. However, ionization can be interpreted as time-reversed recombination, which is governed by the potential of the system. The only difference between length and velocity gauge now lies in the Volkov wavefunctions. The question of which of the gauges should be chosen for atomic ionization is treated in [61]. This work shows qualitative differences between the gauges and concludes that the length gauge leads to a better agreement with numerical ab initio results.

Now we turn to the derivation of the matrix element

$$\boldsymbol{d}(t) = \langle \Psi(t) | \boldsymbol{r} | \Psi(t) \rangle \tag{2.96}$$

in the strong field approximation. If we plug the strong field approximation wavefunction into the matrix element (2.96) we find (for a spherically symmetric potential) the Keldysh dipole moment

$$
\begin{aligned}
\boldsymbol{d}^{(\text{K})}(t) = \; & \underbrace{\langle \Psi_0(t) | \boldsymbol{r} | \Psi_0(t) \rangle}_{=0} \\
& -\mathrm{i} \int_{t_0}^{t} dt' \langle \Psi_0(t) | \boldsymbol{r} \widehat{U}^{(V)}(t, t') \widehat{H}_{\mathrm{I}}(t') | \Psi_0(t') \rangle + c.c. \\
& + \int_{t_0}^{t} dt' \int_{t_0}^{t} dt'' \langle \Psi_0(t'') | \widehat{H}_{\mathrm{I}}(t'') \widehat{U}^{(V)}(t'', t) \boldsymbol{r} \widehat{U}^{(V)}(t, t') \widehat{H}_{\mathrm{I}}(t') | \Psi_0(t') \rangle,
\end{aligned} \tag{2.97}
$$

where $c.c.$ denotes the complex conjugate. Again a simple intuitive explanation of the different terms can be given. The first two terms account for ionization via the laser pulse at time t', followed by free propagation in the laser-dressed continuum without further influence of the binding potential, and finally recombination into the initial state

via emission of harmonic radiation at time t, in accordance to the simple man's three-step model. The third term describes continuum-continuum interaction where the freed electron emits radiation but stays in the continuum interacting with the laser field. The continuum-continuum transitions corresponding to Thomson scattering are disregarded in the so-called Lewenstein-dipole moment. With the Volkov-Schrödinger equation (2.84) and, once again $\widehat{H}_{\mathrm{I}}(t') = \widehat{H}^{(V)}(t') - \widehat{H}_{\mathrm{s}} + V$, we can recast

$$-\mathrm{i} \int_{t_0}^{t} dt' \, \langle \Psi_0(t) | \boldsymbol{r} \widehat{U}^{(V)}(t,t') \widehat{H}_{\mathrm{I}}(t') | \Psi_0(t') \rangle \tag{2.98}$$

$$= - \langle \Psi_0(t) | \boldsymbol{r} \widehat{U}^{(V)}(t,t') | \Psi_0(t') \rangle \Big|_{t_0}^{t} - \mathrm{i} \int_{t_0}^{t} dt' \langle \Psi_0(t) | \boldsymbol{r} \widehat{U}^{(V)}(t,t') V | \Psi_0(t') \rangle.$$

The third term, using the same procedure as above and defining $|\Psi_0^{(V)}(t)\rangle = \widehat{U}^{(V)}(t,t_0) |\Psi_0(t_0)\rangle$, yields

$$\langle \Psi_0(t) | \boldsymbol{r} \widehat{U}^{(V)}(t,t') | \Psi_0(t') \rangle \Big|_{t_0}^{t} - \langle \psi_0^{(V)}(t) | \boldsymbol{r} \widehat{U}^{(V)}(t,t') | \psi_0(t') \rangle \Big|_{t_0}^{t}$$

$$+\mathrm{i} \int_{t_0}^{t} dt' \langle \Psi_0(t) | \boldsymbol{r} \widehat{U}^{(V)}(t,t') V | \Psi_0(t') \rangle$$

$$-\mathrm{i} \int_{t_0}^{t} dt' \langle \Psi_0^{(V)}(t) | \boldsymbol{r} \widehat{U}^{(V)}(t,t') V | \Psi_0(t') \rangle$$

$$-\mathrm{i} \int_{t_0}^{t} dt' \langle \Psi_0(t') | V \widehat{U}^{(V)}(t',t) \boldsymbol{r} | \Psi_0(t) \rangle$$

$$+\mathrm{i} \int_{t_0}^{t} dt' \langle \Psi_0(t') | V \widehat{U}^{(V)}(t',t) \boldsymbol{r} | \Psi_0^{(V)}(t) \rangle$$

$$+ \int_{t_0}^{t} dt' \int_{t_0}^{t} dt'' \langle \Psi_0(t') | V \widehat{U}^{(V)}(t',t) \boldsymbol{r} \widehat{U}^{(V)}(t,t'') V | \Psi_0(t'') \rangle.$$

Collecting all terms of equation (2.97) gives

$$\begin{aligned}
\boldsymbol{d}^{(\mathrm{K})}(t) &= \langle \Psi_0^{(V)}(t) | \boldsymbol{r} | \Psi_0^{(V)}(t) \rangle \tag{2.99}\\
&\quad -\mathrm{i} \int_{t_0}^{t} dt' \langle \Psi_0^{(V)}(t) | \boldsymbol{r} \widehat{U}^{(V)}(t,t') V | \Psi_0(t') \rangle\\
&\quad +\mathrm{i} \int_{t_0}^{t} dt' \langle \Psi_0(t') | V \widehat{U}^{(V)}(t',t) \boldsymbol{r} | \Psi_0^{(V)}(t) \rangle\\
&\quad + \int_{t_0}^{t} dt' \int_{t_0}^{t} dt'' \langle \Psi_0(t') | V \widehat{U}^{(V)}(t',t) \boldsymbol{r} \widehat{U}^{(V)}(t,t'') V | \Psi_0(t'') \rangle.
\end{aligned}$$

The Volkov time-evolution leads to dispersion of the initial wavefunction $|\Psi_0\rangle$ [62]. Hence, if we take $t_0 \to -\infty$ we can neglect the contributions due to the terms with $|\Psi_0^{(V)}(t)\rangle$ and finally end up with the **Keldysh dipole moment**

$$\boldsymbol{d}^{(\mathrm{K})}(t) = \lim_{t_0 \to -\infty} \int_{t_0}^{t} dt' \int_{t_0}^{t} dt'' \langle \Psi_0(t') | V \widehat{U}^{(V)}(t',t) \boldsymbol{r} \widehat{U}^{(V)}(t,t'') V | \Psi_0(t'') \rangle. \tag{2.100}$$

2.2.2 Lewenstein Theory

A different way to approximate a single active electron in an intense laser field was introduced by Lewenstein et al. in [7]. They started with a single particle Hamiltonian in laser approximation and length gauge. The Lewenstein ansatz for the electronic wavefunction reads

$$|\Psi(t)\rangle = \exp\left[-iE_0(t-t_0)\right]\left(\widetilde{b}(t)|\Psi_0\rangle + \int d^3p\, b(\boldsymbol{p},t)|\boldsymbol{p}\rangle\right) \tag{2.101}$$

where $\widehat{H}_{\mathrm{s}}|\Psi_0\rangle = E_0|\Psi_0\rangle$. Plugging this ansatz into the Schrödinger equation (2.78) one finds

$$E_0|\Psi(t)\rangle + i\exp\left[-iE_0(t-t_0)\right]\left(\frac{\partial}{\partial t}\widetilde{b}(t)|\Psi_0\rangle + \int d^3p\frac{\partial}{\partial t}b(\boldsymbol{p},t)|\boldsymbol{p}\rangle\right) \tag{2.102}$$

$$= \exp\left[-iE_0(t-t_0)\right]\left\{[E_0 + \boldsymbol{r}\cdot\boldsymbol{E}(t)]\widetilde{b}(t)|\Psi_0\rangle + \int d^3p\left[\widehat{H}_{\mathrm{s}} + \boldsymbol{r}\cdot\boldsymbol{E}(t)\right]b(\boldsymbol{p},t)|\boldsymbol{p}\rangle\right\}.$$

We will now make the assumption that the depletion of the initial state is negligible, i.e.,

$$\widetilde{b}(t) \simeq 1 \Rightarrow \frac{\partial}{\partial t}\widetilde{b}(t) \simeq 0. \tag{2.103}$$

By projecting onto $\exp\left[iE_0(t-t_0)\right]|\boldsymbol{p}'\rangle$ we therefore find

$$i\frac{\partial}{\partial t}b(\boldsymbol{p}',t) = \left(-E_0 + \frac{\boldsymbol{p}'^2}{2}\right)b(\boldsymbol{p}',t) + \langle\boldsymbol{p}'|\int d^3p\, V(\boldsymbol{r})b(\boldsymbol{p},t)|\boldsymbol{p}\rangle + \langle\boldsymbol{p}'|\boldsymbol{r}\cdot\boldsymbol{E}(t)|\Psi_0\rangle$$

$$+\langle\boldsymbol{p}'|\int d^3p\,\boldsymbol{r}\cdot\boldsymbol{E}(t)b(\boldsymbol{p},t)|\boldsymbol{p}\rangle. \tag{2.104}$$

Neglecting the continuum-continuum matrix element $\langle\boldsymbol{p}'|V(\boldsymbol{r})b(\boldsymbol{p},t)|\boldsymbol{p}\rangle$, $\boldsymbol{d}(\boldsymbol{p}') = \langle\boldsymbol{p}'|\boldsymbol{r}|\psi_0\rangle$ and

$$\langle\boldsymbol{p}'|\boldsymbol{r}|\boldsymbol{p}\rangle = i\boldsymbol{\nabla}_{p'}\delta^3(\boldsymbol{p}'-\boldsymbol{p}) \tag{2.105}$$

we find

$$i\frac{\partial}{\partial t}b(\boldsymbol{p}',t) = \left(-E_0 + \frac{\boldsymbol{p}'^2}{2}\right)b(\boldsymbol{p}',t) + \boldsymbol{E}(t)\cdot\boldsymbol{d}(\boldsymbol{p}') + i\boldsymbol{E}(t)\cdot\boldsymbol{\nabla}_{p'}b(\boldsymbol{p}',t).$$

Defining $a(p) = (-E_0 + \frac{\boldsymbol{p}^2}{2})$ and $\kappa(\boldsymbol{p},t) = +\boldsymbol{E}(t)\cdot\boldsymbol{d}(\boldsymbol{p})$ we arrive at the **Lewenstein equation**

$$\frac{\partial}{\partial t}b(\boldsymbol{p},t) - \boldsymbol{E}(t)\cdot\boldsymbol{\nabla}_p b(\boldsymbol{p},t) = -ia(p)b(\boldsymbol{p},t) - i\kappa(\boldsymbol{p},t). \tag{2.106}$$

This is a first order semilinear partial differential equation of Cauchy type. A unique solution can be constructed with the **method of characteristics** [63]. Via the parameter

s of the characteristics to be constructed we transform the partial differential equation into a set of ordinary differential equations

$$\frac{dt}{ds}(s, \boldsymbol{p^0}) \quad = \quad 1 \tag{2.107}$$

$$\frac{dp_1}{ds}(s, \boldsymbol{p^0}) \quad = \quad -E_1(t) \tag{2.108}$$

$$\frac{dp_2}{ds}(s, \boldsymbol{p^0}) \quad = \quad -E_2(t) \tag{2.109}$$

$$\frac{dp_3}{ds}(s, \boldsymbol{p^0}) \quad = \quad -E_3(t) \tag{2.110}$$

$$\frac{db}{ds}(s, \boldsymbol{p^0}) \quad = \quad -\mathrm{i}a(p)b(s, \boldsymbol{p^0}) - \mathrm{i}\kappa(\boldsymbol{p}, t) \tag{2.111}$$

where $d_s \equiv (\partial t/\partial s)\partial_t + (\partial p_i/\partial s)\partial_{p_i} \equiv \partial_t - \boldsymbol{E}(t) \cdot \boldsymbol{\nabla}_p$. Here the initial data lies on

$$\Gamma = \{(\gamma(\boldsymbol{p^0}), p_1^0, p_2^0, p_3^0)\}, \tag{2.112}$$

with $\phi : \mathbb{R}^3 \to \mathbb{R}^4 : (p_1^0, p_2^0, p_3^0) \mapsto (\gamma(\boldsymbol{p^0}), p_1^0, p_2^0, p_3^0))$ the associated atlas for the description of the three-dimensional hyperspace:

$$t(s = 0, \boldsymbol{x}) \quad = \quad \gamma(\boldsymbol{x}) = t_0 \tag{2.113}$$

$$p_1(s = 0, \boldsymbol{x}) \quad = \quad p_1^0 \tag{2.114}$$

$$p_2(s = 0, \boldsymbol{x}) \quad = \quad p_2^0 \tag{2.115}$$

$$p_3(s = 0, \boldsymbol{x}) \quad = \quad p_3^0. \tag{2.116}$$

Here $\boldsymbol{x}$ are the parameters for the initial data. The initial data is

$$b(\boldsymbol{p}, t)|_\Gamma = b(\boldsymbol{p}(s = 0, \boldsymbol{p^0}), t(s = 0, \boldsymbol{p^0})) \equiv b(s = 0, \boldsymbol{p^0}). \tag{2.117}$$

In order to have a unique solution the projected characteristics $(1, -E_1(t(s = 0, \boldsymbol{p^0})), -E_2(t(s = 0, \boldsymbol{p^0})), -E_3(t(s = 0, \boldsymbol{p^0})))$ have to be nowhere tangent to the hyperspace of the initial data Γ, i.e., they should be noncharacteristic. Hence, the scalar product of the normal vector $N(\Gamma)$ and the projected characteristics should be nowhere equal to zero:

$$N(\Gamma) \cdot (1, -E_1(t_0), -E_2(t_0), -E_3(t_0)) \quad = \quad (1, 0, 0, 0) \cdot (1, -E_1(t_0), -E_2(t_0), -E_3(t_0))$$
$$= \quad 1. \tag{2.118}$$

Hence the solutions of the ordinary differential equations read

$$t(s, \boldsymbol{p^0}) \quad = \quad t_0 + s \tag{2.119}$$

$$p_1(s, \boldsymbol{p^0}) \quad = \quad p_1^0 - \int_{t_0}^{t_0+s} d\tau\, E_1(\tau) = p_1^0 + A_1(t_0 + s) - A_1(t_0) \tag{2.120}$$

$$p_2(s, \boldsymbol{p^0}) \quad = \quad p_2^0 + A_2(t_0 + s) - A_2(t_0) \tag{2.121}$$

$$p_3(s, \boldsymbol{p^0}) \quad = \quad p_3^0 + A_3(t_0 + s) - A_3(t_0) \tag{2.122}$$

$$b(s, \boldsymbol{p^0}) \quad = \quad -\mathrm{i} \int_0^s d\tau\, \kappa(\boldsymbol{p}, t_0 + \tau) \exp\left(-\mathrm{i} \int_\tau^s d\tau'\, a(p)\right). \tag{2.123}$$

In a final step we rewrite the implicit solution (2.123) in an explicit way by $\boldsymbol{p}(\tau, \boldsymbol{p^0}) = \boldsymbol{p^0} + \boldsymbol{A}(t_0 + \tau) - \boldsymbol{A}(t_0) \equiv \boldsymbol{p} - \boldsymbol{A}(t) + \boldsymbol{A}(t_0 + \tau)$ and change the variables of integration $\tau = t' - t_0$, $\tau' = t'' - t_0$, leading to

$$
b^{(L)}(\boldsymbol{p}, t) \quad = \tag{2.124}
$$
$$
-\mathrm{i} \int_{t_0}^{t} dt' \kappa(\boldsymbol{p} - \boldsymbol{A}(t) + \boldsymbol{A}(t'), t') \exp\left(-\mathrm{i} \int_{t'}^{t} dt'' a(\boldsymbol{p} - \boldsymbol{A}(t) + \boldsymbol{A}(t''))\right).
$$

The Lewenstein wavefunction with $\boldsymbol{p'} = \boldsymbol{p} - \boldsymbol{A}(t)$ and $S_{p'}(t, t') = \int_{t'}^{t} dt'' \left(\frac{(\boldsymbol{p'} + \boldsymbol{A}(t''))^2}{2}\right)$ then reads

$$
|\Psi(t)\rangle^{(L)} \quad = \quad |\Psi_0(t)\rangle \tag{2.125}
$$
$$
-\mathrm{i} \int_{t_0}^{t} dt' \int d^3 p' |\boldsymbol{p'} + \boldsymbol{A}(t)\rangle \exp\left(-\mathrm{i} S_{p'}(t, t')\right) \langle \boldsymbol{p'} + \boldsymbol{A}(t')|\boldsymbol{r} \cdot \boldsymbol{E}(t')|\Psi_0(t')\rangle.
$$

Though the derivation appears to be quite different to the strong field approximation one finds with $\widehat{U}^{(V)}(t, t') = \int d^3 p' |\boldsymbol{p'} + \boldsymbol{A}(t)\rangle \exp\left(-\mathrm{i} S_{p'}(t, t')\right) \langle \boldsymbol{p'} + \boldsymbol{A}(t')|$ in length gauge and equation (2.88) that

$$
|\Psi(t)\rangle^{(L)} = |\Psi(t)\rangle^{(SFA)}. \tag{2.126}
$$

The so-called **Lewenstein dipole moment** is, due to negligence of the continuum-continuum transition in equation (2.97),

$$
\boldsymbol{d}^{(L)}(t) \quad = \quad \int d^3 p' \, b^{(L)}(\boldsymbol{p'}, t) \langle \Psi_0 | \boldsymbol{r} | \boldsymbol{p'} \rangle + c.c. \tag{2.127}
$$
$$
= \quad -\mathrm{i} \int_{t_0}^{t} dt' \int d^3 p' \langle \Psi_0 | \boldsymbol{r} | \boldsymbol{p'} + \boldsymbol{A}(t) \rangle \exp\left(-\mathrm{i} S_{p'}(t, t')\right)
$$
$$
\langle \boldsymbol{p'} + \boldsymbol{A}(t') | \boldsymbol{r} \cdot \boldsymbol{E}(t') | \Psi_0(t') \rangle + c.c..
$$

2.2.3 Intense-Field Many-Body S-Matrix Theory

We start with a many-body Hamiltonian in laser approximation (we again suppress the index of the gauge)

$$
\widehat{H}(t) = \widehat{H}_s + \widehat{H}_I(t). \tag{2.128}
$$

The idea we pursue is analogous to the strong field approximation. According to our physical understanding, we rearrange the Hamiltonian into two parts, an evolution guiding part $\widehat{H}^0(t)$ and an evolution perturbing part $\widehat{H}^p(t)$. This will be done for the initial state of the system and the assumed final state. As we usually start with an eigenstate of the system Hamiltonian we use as **initial partition of the Hamiltonian**

$$
\widehat{H}_i^0(t) = \widehat{H}_s \quad \text{and} \quad \widehat{H}_i^p(t) = \widehat{H}_I(t). \tag{2.129}
$$

Then we have in accordance to equation (2.82)

$$|\Psi(t)\rangle = |\Psi_0(t)\rangle - \mathrm{i} \int_{t_0}^{t} dt' \widehat{U}(t, t') \widehat{H}_i^p(t') |\Psi_0(t')\rangle. \tag{2.130}$$

In a further step we will rearrange the Hamiltonian according to the **final state** we assume the system to be in after the evolution. With

$$\left(\mathrm{i} \frac{\partial}{\partial t} - \widehat{H}_f^0(t) \right) \widehat{U}_f^0(t, t_0) = 0 \tag{2.131}$$

we define the Dyson equation

$$\widehat{U}(t, t_0) = \widehat{U}_f^0(t, t_0) - \mathrm{i} \int_{t_0}^{t} dt' \widehat{U}_f^0(t, t') \widehat{H}_f^p(t') \widehat{U}(t', t_0) \tag{2.132}$$

and write the wavefunction of the system as

$$\begin{aligned} |\Psi(t)\rangle = \ & |\psi_0(t)\rangle - \mathrm{i} \int_{t_0}^{t} dt' \widehat{U}_f^0(t, t') \widehat{H}_i^p(t') |\Psi_0(t')\rangle \\ & - \int_{t_0}^{t} dt' \int_{t_0}^{t'} dt'' \widehat{U}_f^0(t, t') \widehat{H}_f^p(t') \widehat{U}(t', t'') \widehat{H}_i^p(t'') |\Psi_0(t'')\rangle. \end{aligned} \tag{2.133}$$

Now let us examine the S-Matrix element

$$\begin{aligned} M_f(t_1, t_0) = \ & \langle \Psi_f(t_1) | \Psi_0(t_1) \rangle - \mathrm{i} \int_{t_0}^{t_1} dt' \langle \Psi_f(t') | \widehat{H}_i^p(t') | \Psi_0(t') \rangle \\ & - \int_{t_0}^{t_1} dt' \int_{t_0}^{t'} dt'' \langle \Psi_f(t') | \widehat{H}_f^p(t') \widehat{U}(t', t'') \widehat{H}_i^p(t'') | \Psi_0(t'') \rangle, \end{aligned} \tag{2.134}$$

which is still exact. Now we introduce an **intermediate partition** of the evolution operator. Remember the single active electron case of the strong field approximation. There one used as intermediate (virtual) state the Volkov state of the electron. In the many electron case one will in general find some electrons removed from its parent ion, some still bound. Analogously to the strong field approximation one will describe those electrons detached from the residual system by a Volkov wavefunction. This concept will become more clear when we rearrange the Hamiltonian of a two-electron system to describe nonsequential double ionization below.

The intermediate partitioning reads as

$$\widehat{H}(t) = \widehat{H}^0(t) + \widehat{H}^p(t). \tag{2.135}$$

We rewrite the corresponding evolution operator as

$$\begin{aligned} \widehat{U}(t, t_0) = \ & \widehat{U}^0(t, t_0) - \mathrm{i} \int_{t_0}^{t} dt' \widehat{U}^0(t, t') \widehat{H}^p(t') \widehat{U}^0(t', t_0) \\ & - \int_{t_0}^{t} dt'' \int_{t''}^{t} dt' \widehat{U}^0(t, t') \widehat{H}^p(t') \widehat{U}^0(t', t'') \widehat{H}^p(t'') \widehat{U}^0(t'', t_0) + ..., \end{aligned} \tag{2.136}$$

plug this into equation (2.134), leading to the **scattering-matrix expansion**

$$M_f(t_1, t_0) = \sum_{k=0}^{\infty} M_f^{(k)}(t_1, t_0) \tag{2.137}$$

with

$$M_f^{(0)}(t_1, t_0) = \langle \Psi_f(t_1) | \Psi_0(t_1) \rangle \tag{2.138}$$

$$M_f^{(1)}(t_1, t_0) = -\mathrm{i} \int_{t_0}^{t_1} dt' \langle \Psi_f(t') | \widehat{H}_i^p(t') | \Psi_0(t') \rangle$$

$$M_f^{(2)}(t_1, t_0) = - \int_{t_0}^{t_1} dt' \int_{t_0}^{t'} dt'' \langle \Psi_f(t') | \widehat{H}_f^p(t') \widehat{U}^0(t', t'') \widehat{H}_i^p(t'') | \Psi_0(t'') \rangle$$

$$\dots = \dots .$$

The interpretation of the different matrix elements works in an analogous manner as in the single active electron case. The afore-derived strong field approximation can be recovered with an appropriately chosen partitioning of an one-body Hamiltonian. One may associate Feynman-like diagrams with every matrix element in the S-matrix expansion (2.137) and establish a diagrammatic approach to the intense-field many-body S-matrix theory [8].

A very important process, which cannot be explained in a single active electron description and is in need of a proper inclusion of electron-electron correlation, is **nonsequential double ionization**. By nonsequential it is meant that the ionization processes of the first and the second electron are not independent of each other. In fact, the inelastic scattering of one electron at the parent system may cause the ejection of the second electron. The importance of the nonsequential mechanism for double ionization is wavelength dependent [3,8]. In a certain intensity regime it dominates double ionization for near infrared wavelengths while for ultra-violet wavelengths the sequential process is the by far dominating mechanism.

Here we will not go through all the calculations. We want to give an example of the above described partitioning scheme for a physical process and point out, which of the generated terms are of importance and give its interpretation. For an extensive consideration of nonsequential double ionization we refer to [3, 8, 57].

The Hamiltonian of helium in a laser field in velocity gauge reads

$$\widehat{H}(t) = \frac{p_1^2 + p_2^2}{2} + (\boldsymbol{p}_1 + \boldsymbol{p}_2) \cdot \boldsymbol{A}(t) + \boldsymbol{A}^2(t) - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}} \tag{2.139}$$

with Z the charge of the nucleus and $r_{12} = |\boldsymbol{r}_1 - \boldsymbol{r}_2|$. As we assume our system to be in its ground-state initially, we use accordingly the associated initial partitioning

$$\widehat{H}_i^0 = \frac{p_1^2 + p_2^2}{2} - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}, \quad \widehat{H}_i^p = (\boldsymbol{p}_1 + \boldsymbol{p}_2) \cdot \boldsymbol{A}(t) + \boldsymbol{A}^2(t). \tag{2.140}$$

In the final configuration we assume both electrons emitted and freely traveling in the laser field. The core potential as well as the interaction potential are treated as perturbations,

91

i.e.,

$$\widehat{H}_f^0 = \frac{p_1^2 + p_2^2}{2} + (\boldsymbol{p}_1 + \boldsymbol{p}_2) \cdot \boldsymbol{A}(t) + \boldsymbol{A}^2(t), \quad \widehat{H}_i^p = -\frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}. \qquad (2.141)$$

The intermediate partitioning is chosen according to our physical intuition that one electron is freely propagating while the other is still bound to the ion. Of course, there are a lot of other possible path ways but this one is assumed to be the most important for arriving at the final state. Hence,

$$\begin{aligned}
\widehat{H}^0 &= \frac{p_1^2 + p_2^2}{2} + \boldsymbol{p}_1 \cdot \boldsymbol{A}(t) + \frac{\boldsymbol{A}^2(t)}{2} - \frac{Z}{r_2}, \\
\widehat{H}^p &= \boldsymbol{p}_2 \cdot \boldsymbol{A}(t) + \frac{\boldsymbol{A}^2(t)}{2} - \frac{Z}{r_1} + \frac{1}{r_{12}}.
\end{aligned} \qquad (2.142)$$

The evolution operator for the Hamiltonian $\widehat{H}^0$ is a direct product of the Volkov evolution operator for a single electron $\widehat{U}_1^V(t, t_0)$ and a single-electron bound state evolution operator $\widehat{U}_2^B(t, t_0)$,

$$\widehat{U}^0(t, t_0) = \widehat{U}_1^V(t, t_0) \otimes \widehat{U}_2^B(t, t_0). \qquad (2.143)$$

If we plug this into equation (2.137), assume the zeroth order to be zero, we obtain two terms for $M_f^{(1)}(t_1, t_0)$ and six terms for $M_f^{(2)}(t_1, t_0)$ [8]. If we consider infrared to near-optical wavelengths we can neglect almost all terms. The two terms of $M_f^{(1)}(t_1, t_0)$ stand for a "shake-off" process, where the first electron leaves so quickly that the second electron is shaken off. However, for low frequency strong field ionization the emitted electrons are usually slow such that this process is negligible. Four of the six terms of $M_f^{(2)}(t_1, t_0)$ do not have correlation during the double ionization process and hence contribute insignificantly. A further term corresponds to the unlikely event in which one electron interacts with the laser while the second electron goes into the intermediate Volkov state. The main contribution comes from

$$\begin{aligned}
M_f(t_1, t_0) \simeq & \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (2.144) \\
& \int_{t_0}^{t_1} dt' \int_{t_0}^{t'} dt'' \langle \Psi_f(t')| \frac{1}{r_{12}} U^0(t', t'')(\boldsymbol{p}_1 \cdot \boldsymbol{A}(t'') + \frac{\boldsymbol{A}^2(t'')}{2})|\Psi_0(t'')\rangle.
\end{aligned}$$

The physical interpretation is that one electron interacts with the laser at time t'' and is ejected into the continuum, traveling freely in the laser pulse while the other electron stays at the ion. At time t' the first electron comes back to the residual system and interacts with the still bound one. Finally both electrons leave the system in accordance to the simple man's three-step model. This approximation leads to reasonable quantitative agreement with experimental data [3, 8, 57].

Chapter 3

Many-Body Quantum Dynamics in Intense Laser Fields

After a broad introduction to both fields, i.e., density functional theory as an approach to the quantum many-body problem and intense-laser matter interaction theory, we will try to tackle the problem of nonperturbative dynamics of many-particle systems via time-dependent density functional theory. With the increasing interest in real-time quantum dynamics of matter exposed to short and intense laser light time-dependent density functional theory beyond linear response attracts more and more attention (see [11] and references therein). Until now we have shown that a classical description of the laser field in dipole approximation is valid. Note here that the dipole approximation introduces an external field, which becomes infinite as $|\boldsymbol{r}| \to \infty$. From a formal point of view one usually looks at external potentials, which go to zero for $|\boldsymbol{r}| \to \infty$. However, one could introduce some damping of the external laser potential far away from the system without influencing the actual dynamics. Therefore time-dependent density functional theory can be applied to solve the complex many-body dynamics. In order to circumvent this formal problem one could think of switching to velocity gauge. However, then one has to use time-dependent current density functional to establish a mapping between vector potentials and current densities [64].

Though time-dependent density functional theory seems to be a natural choice, the treatment of atomic and molecular systems in intense laser fields poses various challenging problems. Our approach to time-dependent density functional theory so far did only consider fundamental problems. In a next step characteristics of an explicit exchange-correlation potential have to be investigated. There have been various interesting discoveries concerning time-dependent density functional theory for intense laser-matter interaction [11]. If one looks at ionization processes, recent findings suggest that one has to take into account a discontinuity in the exchange-correlation potential whenever ionization occurs [65]. This agrees with the time-independent theory, where the energy functional shows discontinuous behavior whenever the number of particles in the system assumes integer values [9]. This property of the functional explains why two well separated atomic systems have minimal combined ground-state energy with zero net charge for each system. Another challenge in the practical application of time-dependent density functional theory is to express the

observables of interest as functionals of the density (or Kohn-Sham orbitals) alone. It was shown, that one needs highly nontrivial functionals to calculate, e.g., the double ionization probability [66] or momentum distributions [67].

Here we will focus on the question, which features of the exchange-correlation potentials are important in resonant light-matter interaction. The resonant population transfer between eigenstates of a system is fundamental. Any approach to the calculation of quantum dynamics should be able to handle this process. Though for time-dependent density functional theory this is the case, at least in principle, approximations for the exchange-correlation potential capable of reproducing population transfer density-dynamics are yet unknown. We investigate Rabi oscillations in a one dimensional model system of helium in an intense laser field. We employ a simple adiabatic approximation for the exchange-correlation potential and analyze the behavior of the resonantly driven self-consistent system. Further the possibility of a few-level approximation for time-dependent density functional theory is explored.

Finally we apply time-dependent density functional theory to a complex system in an intense laser field. We consider the C_{60} fullerene which exhibits strong collective behavior. The question whether collective modes are excited even though the incident laser field is far off resonant is considered. Strong radiation by collective modes of a system would hinder the novel approaches to orbital imaging, as those rely on the assumption that mainly high-order harmonic radiation is emitted [see [55] and [56] for a review]. Extensions of the strong field approximation including collective behavior are deduced to estimate the relative efficiency of the collective response compared to the "standard" harmonic radiation.

3.1 Resonant Dynamics and Excited States

Resonant interactions are of fundamental importance in physics. Naturally, a density functional reformulation of quantum mechanics should be able to describe such processes. However, from a density functional point of view even excited state densities and their corresponding eigenenergies are not easy to determine as they do not obey a simple energy minimization property like the ground-state. The usual ground-state density functional theory has to be modified to exactly determine all eigendensities of a quantum system. Hence, we expect resonant interactions to require quite involved approximations for the exchange-correlation potential to be adequately reproduced. How does the exchange-correlation potential know about the eigenstates and eigenvalues of the interacting system? What mechanism leads to resonant dynamics, i.e., Rabi-oscillations?

First we will give an overview of how excited states in density functional theory are calculated and how excitation energies are extracted from linear response time-dependent density functional theory. In a next step we employ a one-dimensional helium model which we are able to solve numerically both exactly and within a time-dependent Kohn-Sham framework. We show that the time-dependent Kohn-Sham dipole indeed shows Rabi-type oscillations for the widely used exact-exchange approximation. However, the time-dependent density of the population transfer to the excited state is not properly

described. The Rabi-type oscillations are attributed to classical effects, and we argue that the population transfer density-dynamics needs a proper inclusion of correlations and nonadiabatic effects in the exchange-correlation potential. Further we discuss the incompatibility of few-level approximations and time-dependent density functional theory.

3.1.1 Excited States in Density Functional Theory

As seen in section 1.3.2 the ground-state density can be found by energy minimization of the corresponding energy functional. However, excited state densities and their excitation energies were not discussed. There is no straightforward minimization principle for excited states. Nevertheless, one can rigorously deduce all eigenstates also in a density functional approach.

First we take a closer look at ground-state density functional theory. The Hohenberg-Kohn functional F_{HK} (1.139) was defined on the set of pure-state-v-representable densities. Extending its domain to the set

$$\mathcal{I}_N := \left\{ n \left| 0 \leq n,\ \sqrt{n} \in H^1(\mathbb{R}^3),\ \int d^3r\, n(\boldsymbol{r}) = N \right. \right\} \tag{3.1}$$

we define

$$Q[n] = \min_{\Psi} \left\{ \langle \Psi | \widehat{T} + \widehat{V}_{\mathrm{int}} | \Psi \rangle \, | \psi \mapsto n \in \mathcal{I}_N,\ \Psi \in \mathcal{W}_N \right\} \tag{3.2}$$

with $\mathcal{W}_N := \{ \Psi | \|\Psi\|_2 = 1, \sum_{k=1}^N \int |\nabla_k \Psi|^2 < \infty \}$, which is well-defined and existing [30]. With this we can define the energy functional

$$\widetilde{E}_v[n] := Q[n] + \int d^3r\, v(\boldsymbol{r})\, n(\boldsymbol{r}). \tag{3.3}$$

If we have the excited states $|\Psi_i\rangle$, which are extrema with respect to the associated energies $E_i = \langle \Psi_i | \widehat{H} | \Psi_i \rangle$, we immediately find that

$$E_i \geq \widetilde{E}_v[n_i], \tag{3.4}$$

where n_i is the corresponding density. The equality holds if and only if $|\Psi_i\rangle$ delivers the (local) minimal energy of its corresponding one-particle density, i.e., $\langle \Psi_i | \widehat{T} + \widehat{V}_{\mathrm{int}} | \Psi_i \rangle = Q[n_i]$. Thus, both functionals have the same extremum E_i, i.e.,

$$\delta \widetilde{E}_v[n_i] = \delta \langle \Psi_i | \widehat{H} | \Psi_i \rangle = 0. \tag{3.5}$$

However, if $|\Psi_i\rangle$ does not lead to the minimum of its own density, then $\widetilde{E}_v[n]$ does not know about that excited state and hence the excited state density n_i does not extremize the corresponding energy functional. Not every stationary state density n_i extremizes the corresponding energy functional. The global minimum for some v, i.e., one searches over all densities, is the ground-state. Thus we can conclude [68] **that every (local) extremum of $\widetilde{E}_v[n]$ is a stationary state density**. One can show [30] that the functional

$\widetilde{E}_v[n]$ is nonconvex (at least in three spatial dimensions). Thus we will at least find *some* excited states. Otherwise we would have no extremum beside the global minimum. This happens if we extend the domain from wavefunctions to ensembles [68], i.e., we define some $Q'[n]$ and $\widetilde{E}_v'[n]$, for which convexity holds,

$$\widetilde{E}_v'[n_i + x(n_0 - n_i)] \leq \widetilde{E}_v'[n_i] + x\left(\widetilde{E}_v'[n_0] - \widetilde{E}_v'[n_i]\right), \tag{3.6}$$

with $0 \leq x \leq 1$. Then for $\widetilde{E}_v'[n_0] < \widetilde{E}_v'[n_i]$ we find

$$\frac{\widetilde{E}_v'[n_i] - \widetilde{E}_v'[n_i + x(n_0 - n_i)]}{x} \geq \widetilde{E}_v'[n_i] - \widetilde{E}_v'[n_0] > 0. \tag{3.7}$$

If one introduces a Kohn-Sham system of noninteracting electrons and defines the exchange-correlation energy functional in accordance to the Kohn-Sham theorem 1.3.6 it holds [68] that **every density which extremizes $\widetilde{E}_v[n]$ may be constructed from a self-consistent solution. However, not every self-consistent solution yields a density extremizing $\widetilde{E}_v[n]$.** If the non-extremizing self-consistent solutions actually have some physical meaning is, to the best of our knowledge, unknown. Therefore we may conclude that the ground-state exchange-correlation potential has knowledge of (at least some) excited states. This is also of importance if we want to use an adiabatic approximation in the time-dependent theory. Even for such a simple approximation we can assume that some eigenvalues, i.e., resonance-frequencies, may influence the dynamics of the time-dependent system. However, also possibly unphysical self-consistent solutions may have some influence on the approximated dynamics.

Still we do not know if we can construct all excited state densities just by using the ground-state energy functional. A proper approach to successively generating all excited state densities is **ensemble density functional theory** [9, 69–72]. We will outline the ideas of [69].

For any M-dimensional subspace $\mathcal{R}$ spanned by determinantal (noninteracting) wavefunctions $\{|\Phi_i\rangle\}$ we define the equally distributed density

$$n_\mathcal{R} = G_{\widehat{n}}^M(\mathcal{R}) = \frac{1}{M}\sum_{i=1}^M \langle\Phi_i|\widehat{n}|\Phi_i\rangle. \tag{3.8}$$

Note that such a subspace can be found for every density. If we further define the M-dimensional subspace $\mathcal{S}$ spanned via general wavefunctions $\{|\Psi_i\rangle\}$ it can be shown that

$$G_{\widehat{T}}^M(\mathcal{R}_\mathcal{R}') := \min_{\mathcal{R}'}\left\{\frac{1}{M}\sum_{i=1}^M \langle\Phi_i'|\widehat{T}|\Phi_i'\rangle\,|\dim\mathcal{R}' = M, \mathcal{R}' \to n_\mathcal{R}\right\}, \tag{3.9}$$

$$G_{\widehat{T}+\widehat{V}_{\text{int}}}^M(\mathcal{S}_\mathcal{R}') := \min_{\mathcal{S}'}\left\{\frac{1}{M}\sum_{i=1}^M \langle\Psi_i'|\widehat{T}+\widehat{V}_{\text{int}}|\Psi_i'\rangle\,|\dim\mathcal{S}' = M, \mathcal{S}' \to n_\mathcal{R}\right\} \tag{3.10}$$

exist and are well-defined [69]. With this we can define

$$H^M(\mathcal{R}) = \frac{1}{M}\sum_{i=1}^{M}\langle\Phi_i|\widehat{T}|\Phi_i\rangle + \int d^3r\, v(\boldsymbol{r})n_{\mathcal{R}}(\boldsymbol{r}) \tag{3.11}$$

$$+ \frac{1}{2}\int d^3r\, d^3r'\frac{n_{\mathcal{R}}(\boldsymbol{r})n_{\mathcal{R}}(\boldsymbol{r'})}{|\boldsymbol{r}-\boldsymbol{r'}|} + E_{\text{xc}}^M(\mathcal{R}), \tag{3.12}$$

where

$$E_{\text{xc}}^M(\mathcal{R}) := G_{\widehat{T}+\widehat{V}_{\text{int}}}^M(\mathcal{S}'_{\mathcal{R}}) - G_{\widehat{T}}^M(\mathcal{R}'_{\mathcal{R}}) \tag{3.13}$$

$$- \frac{1}{2}\int d^3r\, d^3r'\frac{n_{\mathcal{R}}(\boldsymbol{r})n_{\mathcal{R}}(\boldsymbol{r'})}{|\boldsymbol{r}-\boldsymbol{r'}|}. \tag{3.14}$$

We find [69] that

$$\min_{\mathcal{R}} H^M(\mathcal{R}) = \frac{E_1 + ... + E_M}{M} \tag{3.15}$$

exists with $E_1, ..., E_M$ the first M eigenvalues of the Hamiltonian $\widehat{H}$. Moreover, if $\mathcal{R}_0$ is such that $\min_{\mathcal{R}} H^M(\mathcal{R}) = H^M(\mathcal{R}_0)$ we have

$$n_1 + ... + n_M = MG_{\widehat{n}}^M(\mathcal{R}_0) \tag{3.16}$$

with $n_1, ..., n_M$ the corresponding densities of the eigenstates of $\widehat{H}$. Thus the route to all excited eigenstate densities and energies is clear. One has to successively apply the above minimization to first generate (E_1, n_1) and then $(1/2(E_1 + E_2), 1/2(n_1 + n_2))$. From this one can infer (E_2, n_2). In a next step we calculate the 3rd order to get (E_3, n_3) and so forth. Via the usual Kohn-Sham scheme this minimization procedure amounts to solve the nonlinear single-particle equations

$$\left[-\frac{1}{2}\boldsymbol{\nabla}_{\boldsymbol{r}}^2 + v(\boldsymbol{r}) + \int d^3r'\,\frac{n(\boldsymbol{r'})}{|\boldsymbol{r}-\boldsymbol{r'}|} + \frac{\delta E_{\text{xc}}^M}{\delta n(\boldsymbol{r})}\right]\phi_k(\boldsymbol{r}) = \epsilon_k\phi_k(\boldsymbol{r}) \tag{3.17}$$

with

$$n(\boldsymbol{r}) = \frac{1}{M}\sum_{i=1}^{M}\sum_{k=1}^{N}w_{ik}|\phi_k(\boldsymbol{r})|^2 \tag{3.18}$$

and $w_{ik} = 0, 1$. Note that the derived exchange-correlation potentials will be different for every M. Therefore the usual approximations for the (ground-state) theory will not necessarily give good results [72]. If E_{xc}^M is approximated by the Slater-exchange (exact exchange) this approach corresponds to the Slater transition state theory [9]. Further one may extend the distribution of the densities to fractional occupations [70], i.e.,

$$n_{\mathcal{R}} = \sum_{i=1}^{M}\eta_i\langle\Phi_i|\widehat{n}|\Phi_i\rangle \tag{3.19}$$

with $\eta_1 \geq \eta_2 \geq ... \geq \eta_M \geq 0$.

In time-dependent density functional theory one extracts excitation energies typically via **linear response** calculations [11]. For a weak perturbing field one does not need to know the full time-dependent exchange-correlation potential but only its linear response, i.e., the first functional derivative at the ground-state density (1.287). The central equation of linear response time-dependent density functional theory in frequency space is [11]

$$\chi(\boldsymbol{r}, \boldsymbol{r}', \omega) = \chi_{\mathrm{KS}}(\boldsymbol{r}, \boldsymbol{r}', \omega) \tag{3.20}$$
$$+ \int d^3 r_1 \, d^3 r_2 \chi_{\mathrm{KS}}(\boldsymbol{r}, \boldsymbol{r}_1, \omega) \left\{ \frac{1}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} + f_{\mathrm{xc}}([n_{\mathrm{GS}}], \boldsymbol{r}_1, \boldsymbol{r}_2, \omega) \right\} \chi(\boldsymbol{r}_2, \boldsymbol{r}', \omega)$$

with $\chi(\boldsymbol{r}, \boldsymbol{r}', \omega)$ the point-wise susceptibility of the interacting system, i.e, $\chi = \delta n_{\widehat{\rho}_0}/\delta v$, and $\chi_{\mathrm{KS}}(\boldsymbol{r}, \boldsymbol{r}', \omega)$ the noninteracting counterpart. The Kohn-Sham linear response kernel can be written as [11]

$$\chi_{\mathrm{KS}}(\boldsymbol{r}, \boldsymbol{r}', \omega) = 2 \lim_{\eta \to 0^+} \sum_{a,i} \left\{ \frac{\phi_i^*(\boldsymbol{r})\phi_a(\boldsymbol{r})\phi_a^*(\boldsymbol{r}')\phi_i(\boldsymbol{r}')}{\omega - (\epsilon_a - \epsilon_i) + i\eta} - \frac{\phi_a^*(\boldsymbol{r})\phi_i(\boldsymbol{r})\phi_i^*(\boldsymbol{r}')\phi_a(\boldsymbol{r}')}{\omega + (\epsilon_a - \epsilon_i) - i\eta} \right\} \tag{3.21}$$

where the index i represents all occupied Kohn-Sham orbitals ϕ_i and a all unoccupied orbitals ϕ_a with their Kohn-Sham energy ϵ_i and ϵ_a. The pure Kohn-Sham transitions occur whenever the frequency hits one of the energy differences. These poles represent single-particle excitations. The Hartree-exchange-correlation kernel shifts the transitions to their true (interacting) values and also describes multi-particle excitations if it is accurately known [76].

3.1.2 Resonant Dynamics in the Interacting Theory

We now consider resonant dynamics in an interacting system. To that end we employ a one dimensional model system. The generalization to the three dimensional case is straightforward. For one dimension we have via the local force balance equation [see section 1.2.1]

$$\begin{aligned} \partial_t^2 n(x,t) &= \partial_x[n(x,t)\partial_x v(x,t)] \\ &+ \underbrace{\langle \Psi(t)|\partial_x^2 \widehat{T}(x) + \partial_x \widehat{W}(x)|\Psi(t)\rangle}_{=:q([n];x,t)} \end{aligned} \tag{3.22}$$

with the one dimensional momentum-stress tensor

$$\widehat{T}(x) := \sum_\sigma \{(\partial_x \widehat{\psi}_\sigma^\dagger(x))\partial_x \widehat{\psi}_\sigma(x) - \frac{1}{4}\partial_x^2(\widehat{\psi}_\sigma^\dagger(x)\widehat{\psi}_\sigma(x))\} \tag{3.23}$$

and the one dimensional interaction term

$$\widehat{W}(x) := \sum_{\sigma,\sigma'} \int dx' \widehat{\psi}_\sigma^\dagger(x)\widehat{\psi}_{\sigma'}^\dagger(x')(\partial_x v_{\mathrm{ee}}(|x - x'|))\widehat{\psi}_{\sigma'}(x')\widehat{\psi}_\sigma(x). \tag{3.24}$$

An interacting spin-singlet state can be written according to (1.49) as

$$|\Psi(t)\rangle = \widehat{U}(t, t_0)|\Psi(t_0)\rangle = \int dx \int dx' \, \psi(x, x', t)\widehat{\psi}_\uparrow(x)\widehat{\psi}_\downarrow(x')|0\rangle. \qquad (3.25)$$

Let us introduce the widely used one-dimensional model helium [73]. We assume that both electrons move only along the laser polarization direction. Softening the Coulomb interaction,

$$\frac{1}{|\boldsymbol{r}|} \rightarrow \frac{1}{\sqrt{1 + x^2}}, \qquad (3.26)$$

we obtain for the Hamiltonian $\widehat{H}(t) = \widehat{T} + \widehat{V}_{\text{int}} + \widehat{V}(t)$ with

$$\widehat{T} = -\frac{1}{2}\left[\partial_x^2 + \partial_{x'}^2\right], \qquad (3.27)$$

$$\widehat{V}_{\text{int}} = \frac{1}{\sqrt{1 + (x - x')^2}} \qquad (3.28)$$

and

$$\widehat{V}(t) = -\frac{2}{\sqrt{1 + x^2}} - \frac{2}{\sqrt{1 + x'^2}} + E(t)[x + x']. \qquad (3.29)$$

Here, the coupling to the laser field is described by the electric field in dipole approximation $E(t)$, $\widehat{T}$ is the kinetic energy, and $\widehat{V}_{\text{int}}$ the electron-electron interaction. The corresponding potential in equation (3.22) thus reads $v(x, t) = v_0(x) + v_{\text{L}}(x, t)$ with $v_0(x) = -2/\sqrt{1 + x^2}$ and $v_{\text{L}}(x, t) = xE(t)$. We start from the spin-singlet ground-state. Since there is no spin-dependent potential in our model the state will remain a spin-singlet state, i.e.,

$$\langle x, x'|\Psi(t)\rangle = \frac{1}{\sqrt{2}}\psi(x, x', t)[|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle] \qquad (3.30)$$

with $\psi(x, x', t)$ being symmetric under the exchange of x and x', and a time-evolution according to the time-dependent Schrödinger equation $i\partial_t\psi(x, x', t) = \widehat{H}\psi(x, x', t)$. The ground-state energy in this system is $E_0 = -2.238$, the first excited spin-singlet state is at $E_1^{\uparrow\downarrow} = -1.705$.

The linear response of the exact model helium is calculated by "kicking" the system gently [74] using a δ-like electric field (corresponding to a step-like vector potential) and Fourier-transforming the dipole $d(t) = \int dx \, xn(xt)$. The result is shown in figure 3.1 below. The strongest line corresponds to the transition between the ground state and the first excited singlet-state at $\omega = E_1^{\uparrow\downarrow} - E_0 = 0.533$, followed by transitions to higher excited states and the first continuum. The time-dependent Schrödinger equation spectrum also shows transitions to (and between) doubly excited states and the corresponding continua. Such transitions will be absent in linear response time-dependent density functional theory employing simple, adiabatic exchange-correlation potentials [76]. If we now resonantly drive the interacting system we can induce Rabi oscillations between the ground-state
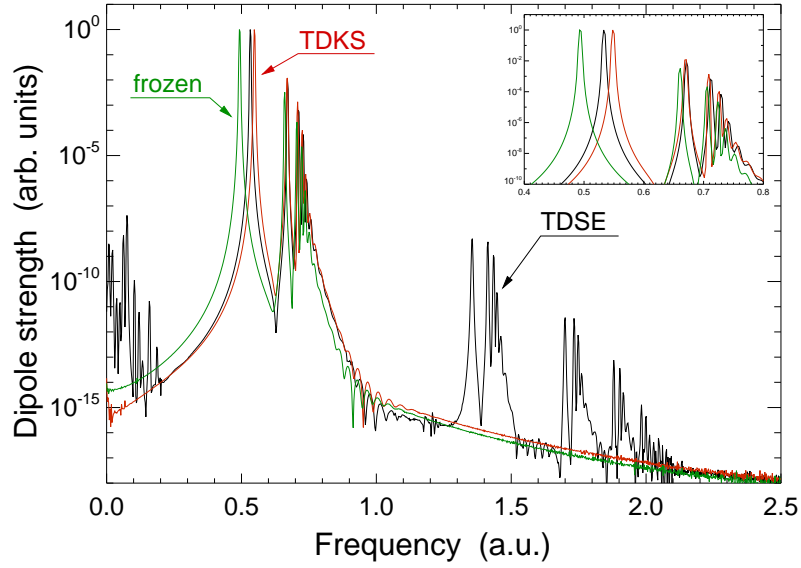
Figure 3.1: Linear response of the helium model atom as obtained from the full time-dependent Schrödinger calculation (black, labelled 'TDSE'), from the exact-exchange time-dependent Kohn-Sham calculation (red, labelled 'TDKS'), and the frozen exact-exchange Kohn-Sham potential (green, labelled 'frozen'). The insert shows a close-up of the transitions to singly excited states.

and an excited state of opposite parity. An approximate description of this resonant dynamics is possible via a two-level description where only the ground-state $|\Psi_0\rangle$ and the addressed excited state $|\Psi_1\rangle$ are taken into account, i.e., $|\Psi(t)\rangle \simeq a(t)\exp(-iE_0t)|\Psi_0\rangle + b(t)\exp(-iE_1t)|\Psi_1\rangle$ [2]. The corresponding Hamiltonian reads

$$
\begin{aligned}
\widehat{H}(t) &= E_0|\Psi_0\rangle\langle\Psi_0| + E_1|\Psi_1\rangle\langle\Psi_1| \\
&\quad + 2E(t)\langle\Psi_0|x|\Psi_1\rangle|\Psi_0\rangle\langle\Psi_1| + 2E(t)\langle\Psi_0|x|\Psi_1\rangle|\Psi_1\rangle\langle\Psi_0|.
\end{aligned} \tag{3.31}
$$

Further, for our problem

$$
\langle\Psi_0|x|\Psi_1\rangle = \langle\Psi_1|x|\Psi_0\rangle =: D. \tag{3.32}
$$

The density of the interacting model helium is well approximated by $n(x,t) = |a(t)|^2 n_0(x) + |b(t)|^2 n_1(x) + 2\Re\{a^*(t)b(t)\exp(-i\omega t)\Delta n(x)\}$, with $\Delta n(x) = \langle\Psi_0|\hat{n}(x)|\Psi_1\rangle$ real. Note that the two-level Hamiltonian (3.31) is nonlocal, which will be the origin of inconsistencies with time-dependent density functional theory later on. The solutions of these equations are analytically known if one further introduces the rotating wave approximations [2]. Of special interest is the time-dependend dipole $d(t)$ of the resonantly driven two-particle system, which is proportional to the emitted power of the driven system in a semiclassical picture. Via the Ehrenfest theorem one can deduce the equation

$$
\ddot{d}(t) = -2E(t)[2\omega D^2(|a(t)|^2 - |b(t)|^2)] - \omega d(t). \tag{3.33}
$$

100
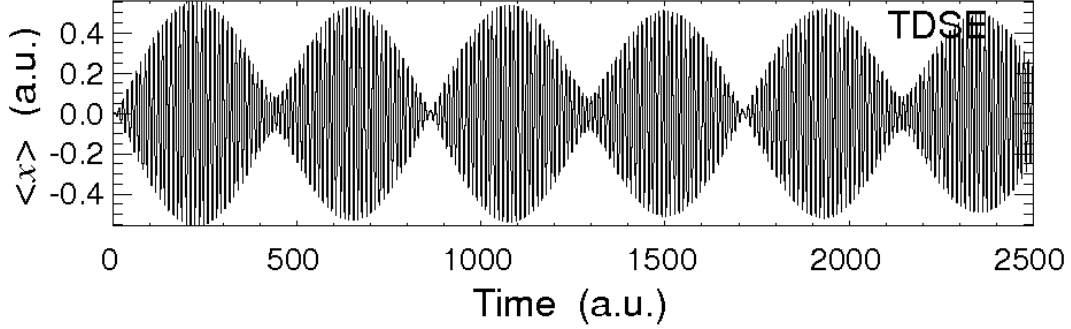
Figure 3.2: Expectation value $\langle x \rangle$ vs time for a resonant excitation with $\widehat{A} = 0.0125$ and $\omega = 0.533$ for the time-dependent Schrödinger equation

With the initial conditions $a(t_0) = 1$ and $b(t_0) = 0$ and the rotating wave approximation a solution for $E(t) = \widehat{E}\cos((\omega + \epsilon)t)$ reads [2]

$$d(t) \simeq B(\epsilon)\Re\left\{i\left[\cos\left(\frac{\Omega t}{2}\right) + i\frac{\epsilon}{\Omega}\sin\left(\frac{\Omega t}{2}\right)\right]\sin\left(\frac{\Omega t}{2}\right)\exp(i\phi + i(\omega + \epsilon)t)\right\}, \quad (3.34)$$

with ϵ the detuning from the exact resonance frequency, $\Omega_R = |D|\widehat{E}$ the Rabi frequency and $\Omega = \sqrt{\Omega_R^2 + \epsilon^2}$. The amplitude of the dipole moment (3.34) B depends on the detuning ϵ:

$$B(\epsilon) = 2\frac{\Omega_R}{\sqrt{\Omega_R^2 + \epsilon^2}}D. \quad (3.35)$$

The dipole acceleration calculated with equation (3.22) in length gauge reads

$$\ddot{d}(t) = -2E(t) - \int dx\, n(x,t)\, \partial_x v_0(x). \quad (3.36)$$

Although both descriptions of the dipole acceleration, i.e., (3.33) and (3.36), should be equal approximately, they are based on different footings. While in the initial two-level approximation we have spatially nonlocal potentials, the derivation of equation (3.36) involved local potentials. We will come back to this issue below in the context of few-level approximations within time-dependent density functional theory.

In the numerical calculations a laser field of vector potential amplitude $\widehat{A} = 0.0125$, i.e., electric field amplitude $\widehat{E} = \omega\widehat{A}$, was ramped up over two laser cycles and then held constant. The laser frequency was tuned to the resonance $\omega = E_1^{\uparrow\downarrow} - E_0$, i.e., $\omega = 0.533$ for the time-dependent Schrödinger equation calculation. The time-dependent Schrödinger equation result shown in figure 3.2 displays Rabi oscillations of the envelope of frequency $\Omega = \widehat{A}\omega D = 0.0075$, as expected. At $t = \pi/\Omega \simeq 420$ the excited state is maximally populated and the envelope of the excursion is close to zero. At $t = 2\pi/\Omega \simeq 840$ the system is mostly in the ground state again. A closer inspection of the time-dependent Schrödinger equation result shows that because of ionization and excitation of other states the population of the first excited state after half the Rabi period is only 0.975 instead of unity. The population of the ground state after a full Rabi cycle is 0.96.

3.1.3 Resonant Dynamics in the Noninteracting Theory

For the noninteracting Kohn-Sham state we have for a spin-singlet

$$|\Phi(t)\rangle = \int dx \int dx' \phi(x,t)\phi(x',t)\widehat{\psi}_\uparrow^\dagger(x)\widehat{\psi}_\downarrow^\dagger(x')|0\rangle \tag{3.37}$$

and $n(x,t) = 2|\phi(x,t)|^2$. From the requirement that the interacting and the noninteracting density should be the same we find with

$$\partial_t^2 n(x,t) = \partial_x\left[n(x,t)\partial_x(v(x,t) + v_{\text{Hxc}}([n];x,t))\right] \tag{3.38}$$
$$+\langle\Phi(t)|\widehat{T}(x)|\Phi(t)\rangle \tag{3.39}$$

the analogon for the noninteracting case of (3.22)

$$v_{\text{Hxc}}([n];x,t) = \int_{-\infty}^x \frac{dx'}{n(x',t)} \quad \left\{\partial_{x'}\langle\Psi(t)|\widehat{T}(x')|\Psi(t)\rangle + \langle\Psi(t)|\widehat{W}(x')|\Psi(t)\rangle\right.$$
$$\left. -\partial_{x'}\langle\Phi(t)|\widehat{T}(x')|\Phi(t)\rangle\right\} + c_1(t)\int_{-\infty}^x \frac{dx'}{n(x',t)}$$
$$+c_2(t) \tag{3.40}$$

where $c_1(t)$ and $c_2(t)$ are constants of integration and are assumed to be zero due to the usual boundary conditions, i.e., $v_{\text{Hxc}} \to 0$ for $|\boldsymbol{r}| \to \infty$. The above proposed procedure to derive the exact noninteracting Hartree-exchange-correlation potential v_{Hxc} is equivalent to an inversion scheme [14]. For our case having the solution of the Schrödinger equation, we find as an explicit operator of the interacting wavefunction $\psi(x,y,t)$ and the Kohn-Sham orbitals $\varphi(x,t)$

$$v_{\text{Hxc}}([\psi,\phi];x,t) = \int_{-\infty}^x 2\frac{dx'}{n(x',t)} \quad \left\{\partial_{x'}\left[\int dy\partial_{x'}\psi^*(x',y,t)\partial_{x'}\psi(x',y,t)\right.\right.$$
$$\left. -(\partial_{x'}\phi^*(x',t))(\partial_{x'}\phi(x',t))\right] \tag{3.41}$$
$$\left. + \int dy\psi^*(x',y,t)\psi(x',y,t)\partial_{x'}v_{\text{int}}(|x'-y|)\right\}.$$

Note here that all possible memory effects reside in the Kohn-Sham orbitals and the interacting wavefunctions if rewritten in terms of the density, i.e., $\phi([n];x,t)$ and $\psi([n];x,y,t)$. Therefore the exact orbital-dependent Kohn-Sham equation reads

$$\mathrm{i}\partial_t\phi(x,t) = \left\{-\frac{1}{2}\partial_x^2 + v(x,t) + v_{\text{Hxc}}([\psi,\phi];x,t)\right\}\phi(x,t). \tag{3.42}$$

Again we may derive an equation for the dipole acceleration. Independently of the interaction we also find (3.36), i.e., all the information about the interaction is found in the time-dependent density.

Until now we just have rewritten the interacting problem as a noninteracting Kohn-Sham problem. Via a solution of the exact interacting problem $\psi(x,x',t)$ we are now able to calculate the exact noninteracting one. However, the goal would be to find some approximate scheme for the Kohn-Sham system to solve the Rabi problem without knowledge of the dynamics of the interacting system.
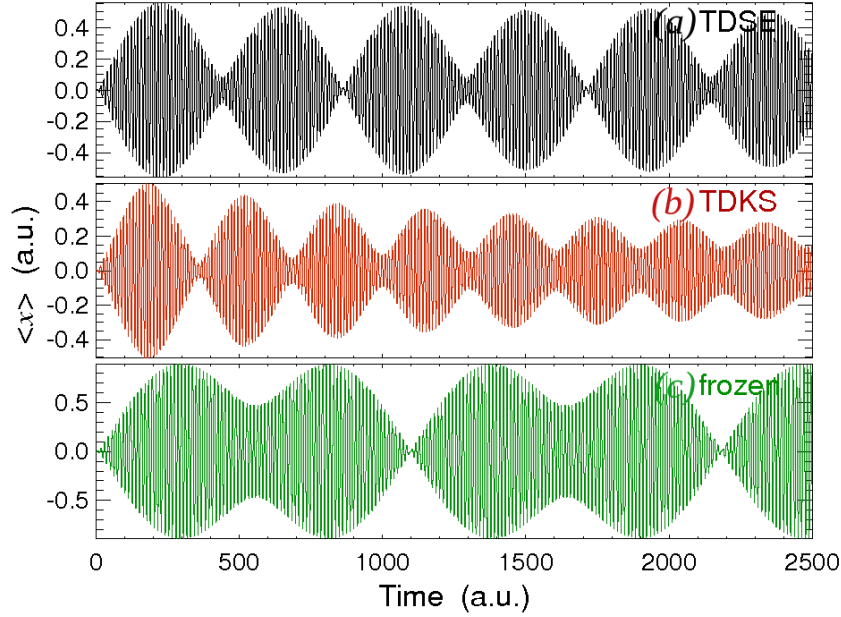
Figure 3.3: Expectation values $\langle x \rangle$ vs time for a resonant excitation with $\widehat{A} = 0.0125$ and (a) $\omega = 0.533$ for the time-dependent Schrödinger calculation, (b) $\omega = 0.549$ for the time-dependent Kohn-Sham calculation, and (c) $\omega = 0.492$ for the frozen Kohn-Sham calculation.

Resonant Dynamics in Exact-Exchange Approximation

Now let us specialize in the so-called exact-exchange approximation. For the spin singlet case we recover equation (1.272), i.e.,

$$v_{\text{Hx}}([n]; x, t) = \int \frac{|\phi(x', t)|^2 \, dx'}{\sqrt{1 + (x - x')^2}}.$$

This adiabatic approximation neglects any correlation effects, and the time-dependent Kohn-Sham equation equals the time-dependent Hartree-Fock equation in this case. The time-dependent Hartree-Fock wavefunction is a Slater-determinant,

$$\langle x, x' | \Phi(t) \rangle = \frac{1}{\sqrt{2}} \phi(x', t) \phi(x, t) [| \uparrow \downarrow \rangle - | \downarrow \uparrow \rangle]. \tag{3.43}$$

Analogous to the interacting case we calculate the linear dipole response of the exact-exchange approximation. The result is shown in figure 3.1 above where we also included the linear response spectrum for the "frozen" Kohn-Sham ground state potential $v_{\text{KS}}^{(0)}(x) = -2/\sqrt{1 + x^2} + \int (n_0(x') \, dx')/(2\sqrt{1 + (x - x')^2})$ (commonly called "bare" Kohn-Sham response). The difference between the time-dependent Kohn-Sham and the "frozen" Kohn-Sham result is due to $v_{\text{KS}}(x, t) - v_{\text{KS}}^{(0)}(x)$, which shifts the peaks closer to the correct positions. One finds that the exact-exchange approximation leads to good result concerning single excitations. However, as expected double excitations are missing.

103
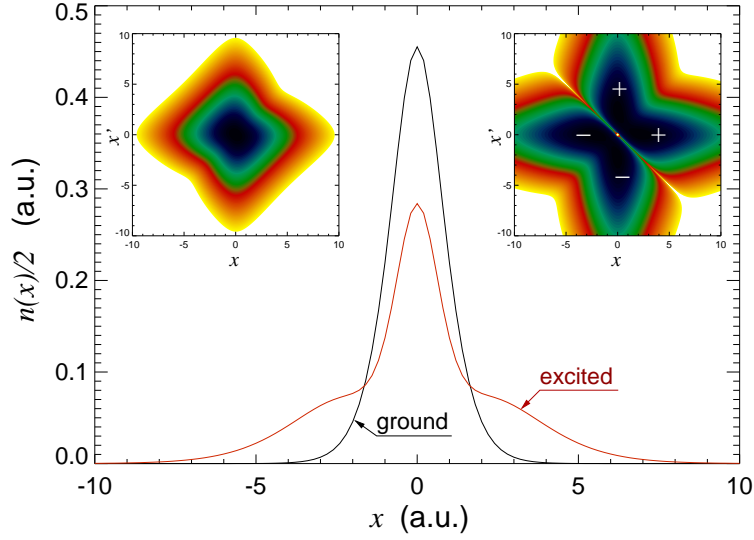
Figure 3.4: Groundstate density $n_0(x)/2 = \int dx' \, |\psi_0(x,x')|^2$ (black, labelled 'ground') and excited state density $n_1(x)/2 = \int dx' \, |\psi_1(x,x')|^2$ (red, labelled 'excited'). The two inserts show contour plots of $|\psi_0(x,x')|^2$ (left) and $|\psi_1(x,x')|^2$ (right). The signs of $\psi_1(x,x')$ are indicated in the right insert.

Figure 3.3 shows $\langle x \rangle(t) = d(t)/2$ as it results from the time-dependent Schrödinger equation, time-dependent Kohn-Sham, and frozen Kohn-Sham calculations. The same amplitude of the vector potential and the same pulse shape as for the time-dependent Schrödinger equation case was used, however tuned to the "exact" transition frequency $\omega = 0.549$ for the time-dependent Kohn-Sham, and $\omega = 0.492$ for the frozen Kohn-Sham calculation. In the frozen Kohn-Sham calculation ionization and the population of other excited states is more pronounced. As a consequence, the excursion envelope does not go to zero at $t = \pi/\Omega$ and the excursion amplitude is overestimated. The time-dependent Kohn-Sham calculation shows oscillations of the right amplitude. The Rabi period one infers from the envelope-oscillations is close to the exact result in. For nonresonant driving the amplitude oscillations are absent, as they should.

Figure 3.3 suggests that there are Rabi oscillations in the time-dependent Kohn-Sham system. If this were true the time-dependent Kohn-Sham density should oscillate between the ground state density and the first excited state density, both shown in figure 3.4. Unfortunately, this is not the case. Examining the time-dependent Kohn-Sham density at time $t \simeq 350$ reveals that it does not assume the shape of the excited state density of figure 3.4 but rather resembles the ground state Kohn-Sham density again! Hence, **despite an erroneous time-dependent Kohn-Sham density we observe the Rabi-like oscillations** of figure 3.3 in its first moment, i.e., **in the time-dependent Kohn-Sham dipole**. As for our two-electron system the exact Kohn-Sham orbital corresponding to the excited state density is given by $\phi_1(x) = \sqrt{n_1(x)/2}$ and thus, according to figure 3.4, has no nodes, the exact Kohn-Sham orbital representing this excited state density must be the *ground-state* of a Kohn-Sham potential $v_{\mathrm{KS}}[n_1]$. Obviously, the exact exchange-only

approximation used above is not capable of "guiding" the density towards the stationary, "new" groundstate density n_1 during a π-pulse. Correlation is needed to describe the density dynamics of the population transfer properly, and it is unlikely that any adiabatic Hartree-exchange-correlation potential $v_{\mathrm{Hxc}}[n(t)] = v_{\mathrm{Hx}}[n(t)] + v_{\mathrm{c}}[n(t)]$ is capable of doing so. Instead, memory effects are expected [13].

Let us now investigate the origin of the Rabi-like oscillations in the time-dependent Kohn-Sham dipole of figure 3.3. Since it is not due to population transfer to the excited state there must be another explanation.

Assume that the evolution of the system may be approximated by a classical point particle, which is located at the center of mass of the density. It then moves in good approximation in an anharmonic potential

$$v(x) = \frac{\omega^2}{2} x^2 + \frac{\alpha}{3} x^3 + \frac{\beta}{4} x^4 \tag{3.44}$$

with α and β some constants, driven by an external force of the form $E(t) = \widehat{E} \cos[(\omega + \epsilon)t]$. We may also introduce a damping λ [77]. By successive approximations one finds the true resonance frequency being shifted

$$\omega \mapsto \omega + \underbrace{\left(\frac{3\beta}{8\omega} - \frac{5\alpha^2}{12\omega^3} \right)}_{=:\kappa} b^2. \tag{3.45}$$

The excursion amplitude squared of the corresponding solution in terms of the detuning ϵ is given by a third order equation,

$$B(\epsilon)^2 \left[(\epsilon - \kappa B(\epsilon))^2 + \lambda \right]^2 = \frac{\widehat{E}^2}{4\omega^2}. \tag{3.46}$$

One finds three different regimes, depending on the strength of the driver. For $\epsilon \to 0$ one has

$$B(\epsilon) \simeq \frac{\widehat{E}}{2\omega\sqrt{\lambda^2 + \epsilon^2}}. \tag{3.47}$$

For a higher driving force the maximum will be displaced until one finds for $\widehat{E} > \frac{8\omega^2\lambda^2}{|\kappa|}$ more than one real solution for equation (3.46). Thus, unlike the two-level quantum case, i.e., equation (3.35), the initially symmetric lineshape is shifted and becomes asymmetric with increasing strength of the driving force $\widehat{E}$ and develops a characteristic discontinuity in the excursion amplitude. Figure 3.5 shows that the amplitude of the time-dependent Kohn-Sham dipole as a function of the laser frequency displays these features. The oscillations can intuitively be understood in the following way: The particle is resonantly driven until it feels the anharmonicity of the potential due to the increasing excursion. Then the driving force no longer is in resonance and the excursion decreases. Therefore we conclude that the **Rabi-like oscillations of the time-dependent Kohn-Sham system are due to classical effects** [78].
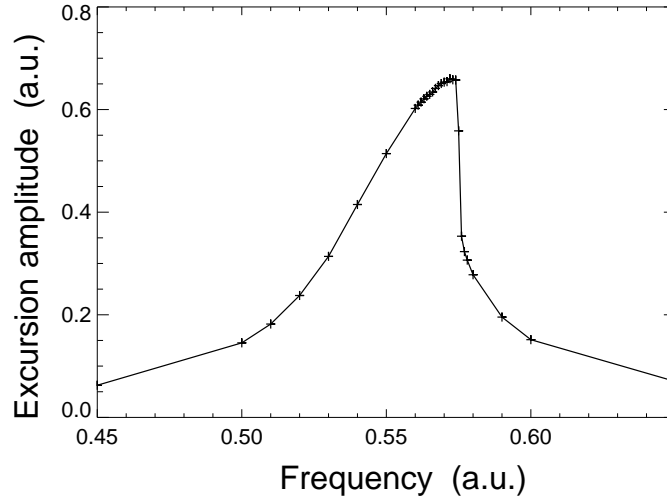
105

Figure 3.5: Time-dependent Kohn-Sham calculation excursion amplitude $B = \max x$ vs laser frequency for a driver with $\widehat{A} = 0.0125$. Discontinuity and asymmetric peak structure are characteristic of classical anharmonic oscillations.

Few-Level Approximation in Time-Dependent Density Functional Theory

As shown above the simple exact-exchange approximation is not capable of reproducing the correct density-dynamics. One is in need of a more elaborate approximation for the exchange-correlation potential. Therefore we will take a step back and look at equation (3.41). One might think that a good approximation of the interacting wavefunction should also lead to a good approximation for the Hartree-exchange-correlation potential. We know that the interacting wavefunction is well approximated by a two-level scheme. In order to make this approximation self-contained one would have to find some way to determine $a(t)$ and $b(t)$ in terms of the noninteracting system. Although this seems a good route to follow such an approximation will lead to wrong predictions independent of $a(t)$ and $b(t)$, because the **two-level approximation is in conflict with the very basis of time-dependent density functional theory**.
Note first that the dipole acceleration of an N-particle system [equation (3.36)] reads $\ddot{d}(t) = -NE(t) - \int dx\, n(x,t)\partial_x v_0(x)$. Here the term depending on $\partial_x v_{\text{Hxc}}([n]; x, t)$ vanishes in accordance with the zero-force theorem [11, 79]. With $n_0(x)$ and $n_1(x)$ symmetric as well as $v_0(x)$ even, we find owing to

$$\int dx\, n_0(x)\partial_x v_0(x) = \int dx\, n_1(x)\partial_x v_0(x) = 0 \tag{3.48}$$

that a two-level approximated Hartree-exchange-correlation potential yields to

$$\ddot{d}(t) = -NE(t) - cd(t), \tag{3.49}$$

with $c = \int dx(\partial_x v_0(x))\Delta n(x)/\int dx\, x\Delta n(x)$. This is the driven harmonic oscillator which [for initial conditions $d(0) = \dot{d}(0) = 0$] does not exhibit oscillations of the excursion amplitude as a function of the driver amplitude, i.e., no Rabi-like oscillations. The extension

to three dimensions is straightforward.

The introduction of the two-level approximation in equation (3.41) leads to inconsistencies with respect to the corresponding Hilbert spaces and Hamiltonians. In order to illustrate this fact it is sufficient to consider the Heisenberg equation (1.60) for some general, time-independent operator $\widehat{O}$,

$$
\begin{aligned}
\partial_t \widehat{O}_{\mathrm{H}}(t) &= \mathrm{i}[\widehat{H}_{\mathrm{H}}(t), \widehat{O}_{\mathrm{H}}(t)]_- \\
&= \mathrm{i}\left(\widehat{U}^{-1}(t, t_0)[\widehat{H}(t), \widehat{O}]_- \widehat{U}(t, t_0)\right),
\end{aligned}
\tag{3.50}
$$

with $\widehat{O}_{\mathrm{H}}(t) = \widehat{U}^{-1}(t, t_0)\widehat{O}\widehat{U}(t, t_0)$ and the time evolution operator (1.154) on the infinite-dimensional Hilbert space. The afore-mentioned application of a two level approximation amounts to

$$
\mathrm{i}\left(\widehat{U}_2^{-1}(t, t_0)[\widehat{H}(t), \widehat{O}]\widehat{U}_2(t, t_0)\right)
\tag{3.51}
$$

$$
= \mathrm{i}\left\{\widehat{U}_2^{-1}(t, t_0)\widehat{\mathbb{1}}_2\left(\widehat{H}(t)\widehat{\mathbb{1}}\widehat{O} - \widehat{O}\widehat{\mathbb{1}}\widehat{H}(t)\right)\widehat{\mathbb{1}}_2\widehat{U}_2(t, t_0)\right\},
$$

with $\widehat{\mathbb{1}} = \sum_{k=0}^{\infty} |\Psi_k\rangle\langle\Psi_k|$, $\widehat{\mathbb{1}}_2 = \sum_{k=0}^{1} |\Psi_k\rangle\langle\Psi_k|$ and

$$
\widehat{U}_2(t, t_0) = \mathcal{T}\left(\exp(-\mathrm{i}\int_{t_0}^{t} dt'\widehat{\mathbb{1}}_2\widehat{H}(t')\widehat{\mathbb{1}}_2)\right),
\tag{3.52}
$$

i.e., calculating the commutator in the infinite-dimensional Hilbert space while the time evolution is restricted to two Hilbert space dimensions. Instead, for a consistent two-level approximation we should have

$$
\partial_t\left(\widehat{U}_2^{-1}(t, t_0)\widehat{O}\widehat{U}_2(t, t_0)\right)
\tag{3.53}
$$

$$
= \mathrm{i}\left\{\widehat{U}_2^{-1}(t, t_0)\widehat{\mathbb{1}}_2\left(\widehat{H}(t)\widehat{\mathbb{1}}_2\widehat{O} - \widehat{O}\widehat{\mathbb{1}}_2\widehat{H}(t)\right)\widehat{\mathbb{1}}_2\widehat{U}_2(t, t_0)\right\},
$$

leading to a different commutator. Thus the two-level approximation applied to equation (3.41) leads to a mixing of different Hilbert spaces and is inconsistent with the derivation of equation (3.41). One has to include contributions from states outside the two-level subspace [80]. Obviously, our analysis not only applies to a two-level approximation but to any few-level approximation.

However, by the usual inversion scheme [14] one could construct some Kohn-Sham potential v_{KS} generating the two level density $n(x, t)$. The associated dipole acceleration would be

$$
\ddot{d}(t) = -\int dx n(x, t)\partial_x v_{\mathrm{KS}}([n]; x, t).
\tag{3.54}
$$

If we define v_{Hxc} by subtracting from the Kohn-Sham the physical external potentials we end up with

$$
\ddot{d}(t) = -NE(t) - cd(t) - \int dx\, n(x, t)\partial_x v_{\mathrm{Hxc}}([n]; x, t).
\tag{3.55}
$$

By construction, this two-level density has the right dipole acceleration. This can only be possible if the term depending on v_{Hxc} contributes. Otherwise the same problem as with equation (3.49) discussed above arises. However, a nonvanishing contribution from $\int dx\, n(x,t)\, \partial_x v_{\mathrm{Hxc}}([n];x,t)$ is only possible if v_{Hxc} does not describe internal forces only and thus violates the zero-force theorem [11,79]. As a consequence, the external potentials of the interacting and the noninteracting system cannot be kept equal. In fact, there is no local external potential $v(x)$ that supports just two levels.

3.2 Recollision Induced Plasmon Emission

A typical interaction scenario in strong field laser atom or molecule interaction involves three steps: (i) the removal of an electron from a target (ionization), (ii) motion of this electron in the continuum, and, possibly, (iii) a recollision with the "parent" atom or molecule if step (i) occurred at a time such that the laser field drives the electron back. The recollision in the third step is responsible for the plateaus in photoelectron and high harmonic spectra, and nonsequential multiple ionization, corresponding to the three pathways (i) scattering in the presence of a laser field, (ii) recombination and emission of a photon, and (iii) laser-induced collisional ionization (see, e.g., [49,52,81] for reviews). Structural information about the target is encoded in both photoelectron and harmonics spectra. Hence, besides the potential of high-order harmonic generation as an efficient source of short wavelength radiation and attosecond pulses [49], the so-called "tomographic imaging" of molecular orbitals [see [55] and [56] for a review] has attracted considerable attention. It is clear that whatever is "imaged" in this procedure is supposed to be representation-independent, i.e., should not depend on the basis in which one expands the multielectron wavefunction. This requirement is difficult to fulfill within the simple and commonly adopted single active electron approximation [82].

Here we study the recollision dynamics and the emitted radiation for the case of the C_{60} fullerene, which is an example for a multielectron system displaying collective modes and an interesting dynamics when exposed to fs laser pulses [83,84] (other such systems are, e.g., metal clusters or biomolecules). The laser frequency is kept well below the surface and volume plasmon frequency of C_{60} so that only the recolliding electron may excite the collective modes efficiently but not the laser itself. In the context of "orbital imaging" it is vital to know whether the structural information encoded in the high-order harmonic generation spectra is "contaminated" by emission at collective frequencies. In other words, we are interested in the **relative efficiency of the collective response with respect to the "standard" harmonic generation**.

First the C_{60} jellium model we use in the time-dependent density functional theory calculations is reviewed, and its collective modes are identified. Then the high-order harmonic generation spectra are presented for three different wavelengths, ranging from the typical 800 nm up to 3508 nm. The transition from the linear to the nonlinear excitation regime is discussed, enhancements in the dipole spectra due to plasmon excitation are evidenced, and their origin is investigated. Further we compare the time-dependent

density functional theory results with the predictions of a simple, single active electron approximated Lewenstein-like model of high-order harmonic generation from C_{60}. Finally we develop analytical models which take collective modes into account and enable us to predict the relative efficiency of harmonic emission due to recollision-induced plasmon excitation with respect to standard harmonic generation.

3.2.1 Model

The C_{60} fullerene is modelled using density functional theory employing a **jellium potential for the ionic background** of inner and outer radius R_i, R_o, respectively, [85,86], i.e.,

$$v_0(r) = \begin{cases} -\kappa\dfrac{3}{2}\left(R_o^2 - R_i^2\right), & r \leq R_i \\ -\kappa\left(\dfrac{3}{2}R_o^2 - \left[\dfrac{r^2}{2} + \dfrac{R_i^3}{r}\right]\right) - V_0, & R_i < r < R_o \\ -\kappa\dfrac{R_o^3 - R_i^3}{r}, & r \geq R_o \end{cases} \tag{3.56}$$

where $\kappa = r_s^{-3}$, $R_i = 5.3$, $R_o = 8.1$, $r_s^{-3} = N/(R_o^3 - R_i^3)$, $N = 250$ Kohn-Sham electrons, and $V_0 = 0.68$ (atomic units are used unless noted otherwise). The solution of the time-independent Kohn-Sham equation

$$\epsilon_j \phi_j(\boldsymbol{r}) = \left(-\frac{1}{2}\boldsymbol{\nabla}_{\boldsymbol{r}}^2 + v_0(r) + v_{\mathrm{H}}([n]; \boldsymbol{r}) + v_{\mathrm{xc}}([n]; \boldsymbol{r})\right)\phi_j(\boldsymbol{r}) \tag{3.57}$$

according theorem 1.3.6 yields the ground state configuration from which we start the propagation. Here, ϕ_j, $j = 1 \ldots N$ are the N Kohn-Sham orbitals, ϵ_j are the Kohn-Sham orbital energies,

$$v_{\mathrm{H}}([n]; \boldsymbol{r}) = \int d^3 r' \frac{n(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} \tag{3.58}$$

is the Hartree potential, and

$$v_{\mathrm{xc}}([n]; \boldsymbol{r}) = v_{\mathrm{x}}([n]; \boldsymbol{r}) = -\left[\frac{3n(\boldsymbol{r})}{\pi}\right]^{1/3} \tag{3.59}$$

is the exchange-correlation potential in exchange-only local density approximation in accordance to equation (1.228). The $N = 250$ Kohn-Sham electrons lead to a spin-neutral, closed-shell ground state of spherical symmetry. More precisely, we obtain 200 σ-electrons (without node in the radial wavefunctions) and 50 π-electrons [with one node in the radial wavefunction located close to the C_{60}-radius $R = (R_i + R_o)/2 = 6.7$]. The free parameter $V_0 = 0.68$ is used to adjust the Kohn-Sham energy of the highest occupied molecular orbital (HOMO) to the ionization potential of C_{60}, $-\epsilon_{\mathrm{HOMO}} = I_p \simeq 0.28$. The HOMO of our model is a π-orbital of angular momentum quantum number $\ell = 4$. Figure 3.6 illustrates and summarizes the ground state configuration from which we start the
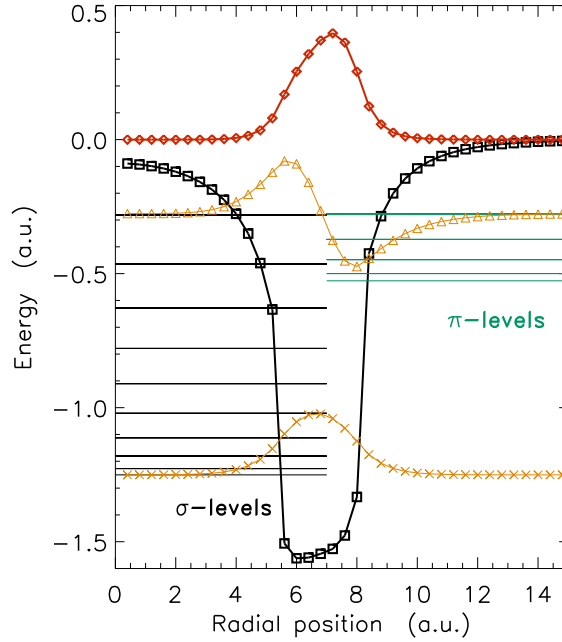
Figure 3.6: Net Kohn-Sham potential (black, squares), total density (red, diamonds), wavefunctions of the lowest Kohn-Sham orbital and the HOMO (orange, crosses and triangles, respectively). The σ- and π-levels are indicated. Density and wavefunctions are scaled to fit into the plot.

time-dependent calculations.

In order to characterize the **collective response** of the model C_{60} we apply the real-time method proposed in reference [74], as done in the previous section. To that end we solve the time-dependent Kohn-Sham equation in exchange-only local density approximation [75] [see theorem 1.3.8]

$$i\partial_t \phi_j(\boldsymbol{r}, t) = \left(-\frac{1}{2} \boldsymbol{\nabla}_{\boldsymbol{r}}^2 + v_0(r) + v_{\mathrm{L}}(\boldsymbol{r}, t) + v_{\mathrm{H}}([n]; \boldsymbol{r}, t) + v_{\mathrm{x}}([n]; \boldsymbol{r}, t) \right) \phi_j(\boldsymbol{r}, t) \quad (3.60)$$

with

$$v_{\mathrm{L}}(\boldsymbol{r}, t) = \widehat{A}\delta(t)z$$

a δ-like electric field $\boldsymbol{E}(t) = -\partial \boldsymbol{A}/\partial t = \widehat{A}\delta(t)$ in dipole approximation for $\widehat{V} = \boldsymbol{A}(t) \cdot \boldsymbol{p}$ and $\boldsymbol{A}(t) = \widehat{A}\boldsymbol{e}_z\Theta(t)$. From the Fourier-transform of the dipole

$$d_z(t) = \int d^3r \; z \, n(\boldsymbol{r}, t) \quad (3.61)$$

the spectrum $S(\omega) = |d_z(\omega)|^2$ is calculated. Figure 3.7 shows that the linear dipole response consists of several narrow lines (single-particle transitions) that sit on top of two broad structures (the surface and volume plasmon, respectively). Closer inspection shows that transitions of the type $\sigma\ell \to \pi(\ell \pm 1)$, $\pi\ell \to \sigma(\ell \mp 1)$ contribute to the surface (or Mie) plasmon ω_{Mie} and transitions between σ-states and (initially unoccupied) δ-states (with two radial nodes) to the volume plasmon ω_{p}.
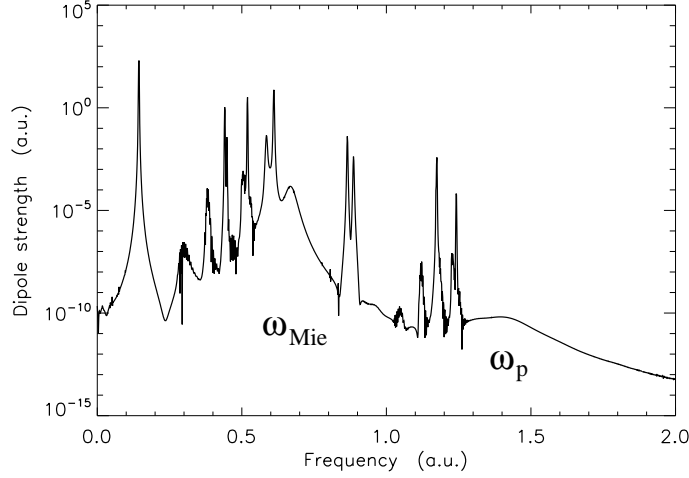
Figure 3.7: Dipole response of the C_{60} model system. Narrow lines (single-particle transitions) on top of two broad structures (surface or Mie plasmon $\omega_{\text{Mie}} \simeq 0.7$ and volume plasmon $\omega_{\text{p}} \simeq 1.4$) are observed. The Mie plasmon corresponds to homogeneous dipole-like oscillations of the electron density with respect to the ions. The volume plasmon (in general a breathing mode) is visible in our dipole spectra since it contains a nonvanishing dipole component. The dipole strength is normalized such that its integral equals $N = 250$.

3.2.2 Results

In this subsection we shall present and discuss our results for dipole spectra $S(\omega)$ of the model C_{60} when exposed to Gaussian and trapezoidal laser pulses of various peak intensities and wavelengths.

From linear to nonlinear plasmon excitation

We solved the time-dependent Kohn-Sham equation (3.60) for Gaussian pulses with a vector potential of the form

$$A(t) = -\frac{\widehat{E}}{\omega} \sin(\omega_{\text{l}} t) \exp(-a^2(t)) \tag{3.62}$$

with

$$a(t) = 3 \left[\frac{\omega_{\text{l}} t}{n\pi} - 1 \right]. \tag{3.63}$$

There are $0.278\,n$ cycles within the FWHM of the Gaussian pulse (with respect to the electric field or the vector potential) centered around $t = (2\pi/\omega_{\text{l}})(n/2)$. We started the simulation from the ground state at $t = 0$ and stopped at $t = (2\pi/\omega_{\text{l}})n$ with $n = 8$.

Figure 3.8 shows the transition from the linear to the nonlinear regime. At very

low field amplitude ($\widehat{E} = 0.0025$ and 0.005 at 2280 and 800 nm, respectively) the dipole spectra display replicas of the linear response profile on a very low level, depending on the bandwidth of the applied laser pulse. Upon doubling the field amplitude ($\widehat{E} = 0.005$ and 0.01 at 2280 and 800 nm, respectively) the signal in the dipole spectrum is quadrupled, as expected in the linear regime. The corresponding values of intensity are $0.9 \cdot 10^{12} \mathrm{W/cm^2}$ and $3.5 \cdot 10^{12} \mathrm{W/cm^2}$. However, with further increasing laser intensity, plateaus develop and the high harmonic-signal increases rapidly over a wide frequency range. One may argue that this increase of the harmonic signal is just due to the standard harmonic generation mechanism while the collective response is still within the linear regime and thus not visible at higher laser intensities. The next part is hence devoted to identify plasmon enhancements and their wavelength dependence.
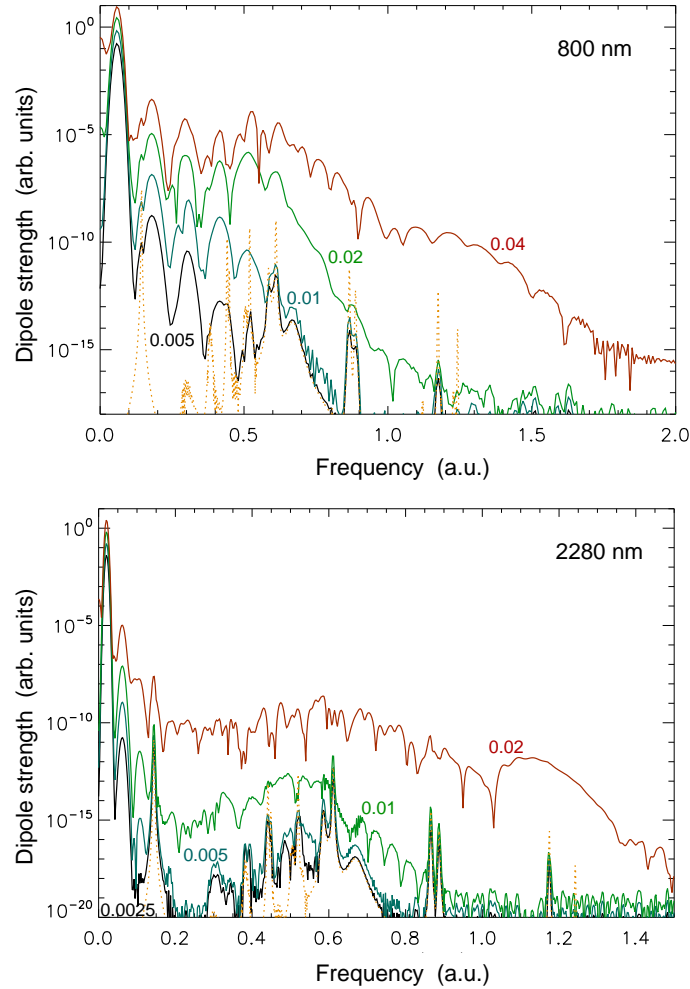
Figure 3.8: Harmonic spectra of the C_{60} model for Gaussian laser pulses with $\omega_\mathrm{l} = 0.057$ ($\lambda = 800\,\mathrm{nm}$, upper panel) and $\omega_\mathrm{l} = 0.02$ ($\lambda = 2280\,\mathrm{nm}$, lower panel). The values of $\widehat{E}$ are given in the plots. The linear response profile from figure 3.7 is included (dotted). The field amplitude $\widehat{E} = 0.04$ corresponds to the intensity $5.6 \cdot 10^{13} \mathrm{W/cm^2}$.

Plasmon enhancements and wavelength dependence

Figure 3.9 shows the harmonic spectra $S(\omega)$ as calculated from the full dipole and the outermost orbital density only ('HOMO only') for an 8-cycle, (2,4,2) trapezoidal 800-nm laser pulse, i.e., with 2-cycles up and down ramps and 4 cycles of constant amplitude $\widehat{E} = 0.05$. Trapezoidal pulses have the advantages (i) that the comparison with the semi-analytical results for constant amplitude pulses of section 3.2.4 is more straightforward, and (ii) that cut-off positions do less sensitively depend on the carrier-envelope phase since $\widehat{E}$ is constant over several cycles [see reference [52] for a discussion of carrier-envelope phase-effects]. We checked that all our findings are qualitatively insensitive to the pulse shape. The difference between the two harmonic spectra clearly indicates that not just the valence electron contributes to the emission. **Enhancements** by two orders of magnitude **around frequencies at which the system displays collective modes** are visible. The standard cut-off known from atomic high-order harmonic generation is at $3.17U_{\mathrm{p}} + |\epsilon_{\mathrm{HOMO}}|$ (with $U_{\mathrm{p}} = \widehat{E}^2/(4\omega_{\mathrm{l}}^2)$ the ponderomotive energy) and indicated by an arrow. The real **cut-off**, however, **is extended** to higher harmonic frequencies **because recombination into orbitals with higher ionization potentials** $|\epsilon_j| > |\epsilon_{\mathrm{HOMO}}|$ takes place. Note that the latter is possible without violation of the Pauli principle (unless Kohn-Sham electrons are frozen in the respective states). An extension of the standard harmonic plateau in a multielectron system—presumably of the same origin—has also been observed in reference [87].
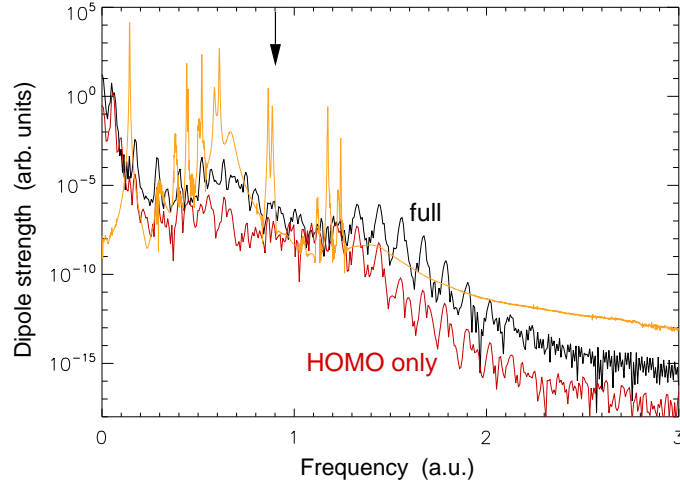

Figure 3.9: Harmonic spectra of the C_{60} model for $\widehat{E} = 0.05$, $\omega_{\mathrm{l}} = 0.057$ ($\lambda = 800\,\mathrm{nm}$), and an 8-cycle trapezoidal laser pulse with 2-cycles up and down ramps. The full spectrum and the one just from the valence Kohn-Sham electron ("HOMO only") are shown. The linear dipole response from figure 3.7 is included (shifted vertically). The vertical arrow indicates the standard cut-off $3.17U_{\mathrm{p}} + |\epsilon_{\mathrm{HOMO}}|$.

In the following we show that with increasing laser wavelength the emission spectra become more and more single active electron like in the sense that all collective response is less efficient than the standard harmonic generation by the outermost electron at the re-

spective frequency. In the single active electron calculations we also start from the density functional theory ground-state but freeze the potentials v_H and v_xc for the propagation of the valence Kohn-Sham orbital.

Figure 3.10 shows that at $\lambda = 2280\,\mathrm{nm}$ there are still substantial differences between the single active electron result and the full time-dependent Kohn-Sham calculation. First, the single active electron approximation yield is higher because the ionization step in the three-step scenario described above is more efficient for a frozen potential since there is no polarization which counteracts the laser field. Second, the plasmon emission included in the full result obscures the oscillatory structure from which structural information (i.e., in our case the C_{60} radius and the width of the spherical jellium shell) could be obtained. Only in the (extended) cut-off region full and single active electron result agree very well because there are no collective modes at such high frequencies.
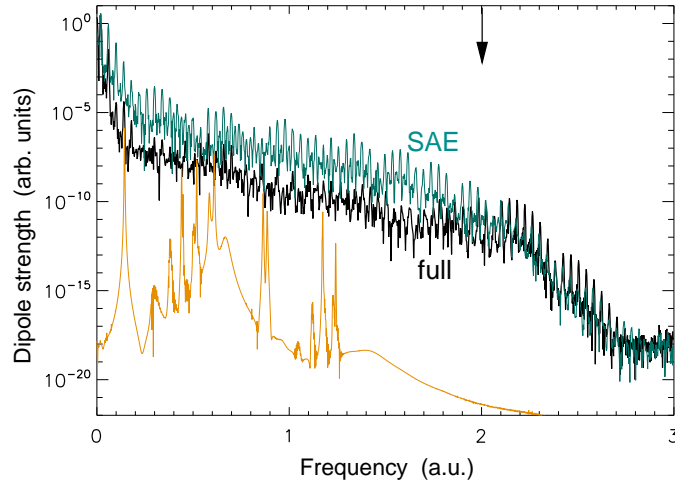
Figure 3.10: Emission for $\omega_\mathrm{l} = 0.02$ ($\lambda = 2280\,\mathrm{nm}$) and $\widehat{E} = 0.03$ (other parameters as in figure 3.9). The results from the full time-dependent Kohn-Sham calculation ('full') and the single active electron approximation simulation are shown. The linear dipole response from figure 3.7 is included (shifted vertically). The vertical arrow indicates the standard cut-off.

At the even **longer wavelength $\lambda = 3508\,\mathrm{nm}$ the full time-dependent Kohn-Sham result agrees well with the single active electron result**, as is shown in figure 3.11. Also the cut-off is at the expected position, indicating that recombination into states with orbital energies $|\epsilon| > |\epsilon_\mathrm{HOMO}|$ is insignificant. A closer inspection of the individual response of all the Kohn-Sham electrons shows that the standard high-order harmonic generation of the HOMO Kohn-Sham electrons (i.e., the two spin-degenerate ones with $\ell = 4$ and $m = 0$) clearly dominates. Hence, long wavelengths are advantageous for imaging schemes which are based on interference structures in the high-order harmonic generation spectra predicted by strong field-theoretical treatments [65] in single active electron approximation. However, the efficiency of high-order harmonic generation also decreases with increasing laser wavelength [88]. The fact that the **efficiency of the collective response decreases even faster than the efficiency of high-order har-**
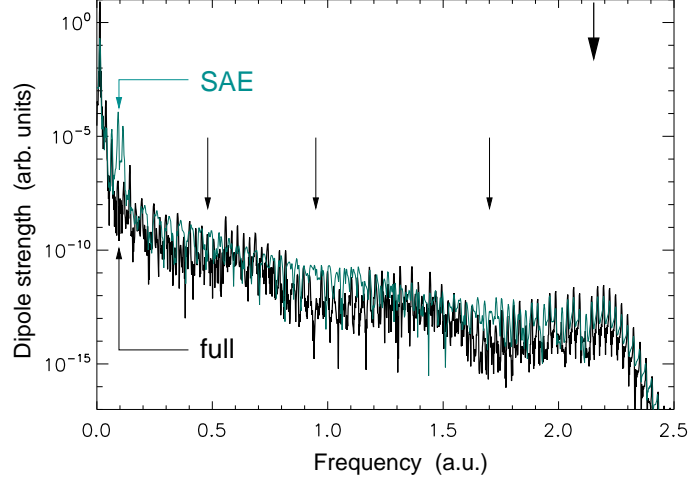
114

Figure 3.11: Emission for $\omega_l = 0.013$ ($\lambda = 3508\,\text{nm}$) and $\widehat{E} = 0.02$. The results from a full time-dependent Kohn-Sham calculation ('full') and a single active electron simulation are shown. The bold vertical arrow indicates the standard cut-off, the three thin vertical arrows local minima in the envelope of the full spectrum.

monic generation is one of the main results in this section.

3.2.3   Identifying the Mechanism

In section 3.2.2 we showed that at low field strengths the collective response increases linearly with the field strength (i.e., the signal in the dipole spectra quadratically) while at higher intensities the standard high harmonic plateau develops, which is an entirely nonlinear phenomenon. Further we showed that plasmon enhancements are present, although they decrease relative to the standard high harmonic plateau with increasing wavelength. This means that there must be some nonlinear effect at work which is able to generate a collective response of comparable strength as the standard high harmonics. The latter are due to returning electrons which recombine. The obvious guess is to attribute the collective response also to the returning electrons so that the similar efficiency of harmonic emission via the single active electron approximation and via the collective mechanism can be understood if recombination with emission of a photon and with excitation of a plasmon (followed by emission of a photon) are similarly efficient. In this subsection we support the viewpoint that **the recolliding electrons indeed excite collective modes** by analyzing our numerical results in more detail.

In our time-dependent density functional theory simulations we use a spherically symmetric imaginary potential $W(r) = -\mathrm{i}W_0(r/R_g)^{16}$ with $W_0 = 100$ and R_g the radius of the numerical grid. The imaginary potential serves as an absorber of probability density approaching the boundary of the numerical grid [75]. Usually the grid is chosen big enough so that only the probability density corresponding to never-returning electrons is absorbed and thus the imaginary potential does not affect the relevant dynamics taking place in

the interior of the numerical grid where $W(r)$ is negligible. However, in order to test whether recolliding electrons are responsible for *both* the standard harmonic generation *and* the plasmon enhancements, we may absorb probability density representing electrons of a certain excursion amplitude $\widehat{z}$ by moving the imaginary potential closer to the C_{60}. If the plasmon enhancements are due to recolliding electrons we then expect the harmonic signal and the plasmon signal to drop. If, instead, the plasmon enhancements are due to some other yet unknown nonlinear effect which does not require *returning* electrons, then the harmonic signal should drop while the plasmon signal sustains.

Figure 3.12 shows dipole spectra for $\lambda = 2280$ nm and $\widehat{E} = 0.01$ (i.e., the second highest intensity shown in the lower panel of figure 3.1) for two grid sizes. The excursion amplitude of a free electron in this case is $\widehat{z} = \widehat{E}/\omega_l^2 = 25$. Hence we expect the $R_g = 100$-grid to comprise all the relevant electron dynamics whereas on the $R_g = 40$-grid some electrons will be already inhibited from returning to the C_{60} because the corresponding probability density is absorbed. In fact, figure 3.12 shows that parts of the plateau are removed in the spectrum for the smaller grid. Only the single particle transition lines close to $\omega = 0.6$ are unaffected by the absorbing boundary, showing that these transitions are not excited by recolliding electrons but—presumably—by multiphoton resonances. However, besides these resonant transitions the whole plateau is suppressed. We thus conclude that the returning electrons are essential for the excitation of the collective modes. This
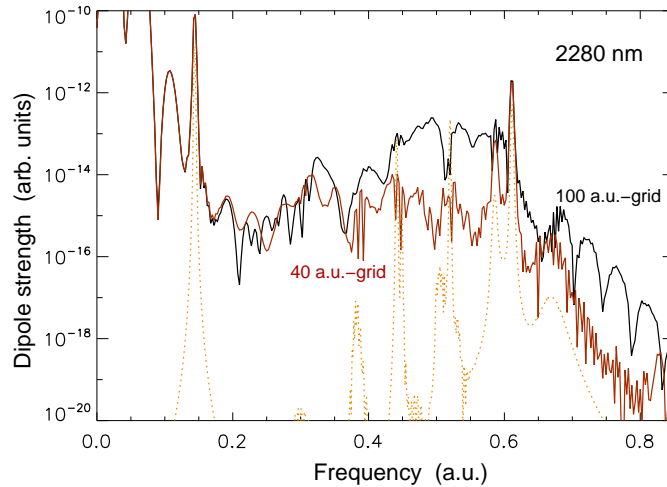

Figure 3.12: Same as in figure 3.8, lower panel, for $\widehat{E} = 0.01$ but two different grid sizes (indicated in the plot). The linear response profile from figure 3.7 is included again (dotted).

conclusion is further supported by a time-frequency analysis of the dipole $d_z(t)$. To that end a spectral window is applied to $d_z(\omega)$. The result is transformed back, which corresponds to the spectral filtering of certain harmonics for the generation of attosecond pulses in experiments [49]. The result is shown in figure 3.13. The emission follows overall nicely the classical "simple man's theory": the classical return-times of electrons with return-energy E_{ret} (which contribute to the emission of harmonic radiation at a frequency $\omega = E_{\text{ret}} + |\epsilon_{\text{HOMO}}|$) are indicated by white trajectories in the frequency-time plane. It is
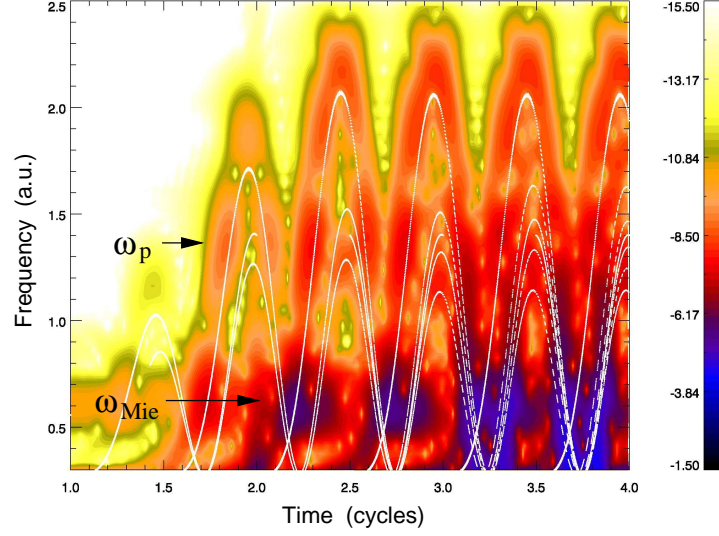
Figure 3.13: Logarithmically scaled contour plot of the time-frequency analyzed dipole emission $\log_{10}|d_z(t,\omega)|^2$ for the parameters of figure 3.10. The white lines indicate the classical solutions of returning electrons (see text). The positions of the Mie surface plasmon and the volume plasmon are indicated.

seen that the plasmon emission is correlated with the return of electrons. Whenever there are recolliding electrons having the right energy to excite a plasmon, enhanced emission is observed. Due to the large width of the collective resonances the emission decays before the next returning electron collides.

3.2.4 Strong Field Approximation vs long-wavelength Time-Dependent Density Functional Theory Result

We now show that the **structure in the high-order harmonic generation spectrum (of long wavelengths)** of figure 3.11 is indeed **similar to what one expects from the strong field approximation** applied to high-order harmonic generation, i.e., the so-called Lewenstein-model of subsection 2.2.2. Within the Lewenstein-model the dipole expectation value for an infinite, linearly polarized laser pulse

$$\boldsymbol{E}(t) = \widehat{E}\boldsymbol{e}_z\cos(\omega_1 t), \qquad E(t) = -\partial_t A(t) \tag{3.64}$$

is given by equation (2.127), i.e.,

$$
\begin{aligned}
d_z^{(L)}(t) &= \int d^3 p'\, b^{(L)}(\boldsymbol{p}',t)\langle\Psi_0|z|\boldsymbol{p}'\rangle + c.c. \\
&= -\lim_{t_0\to-\infty} \mathrm{i}\int_{t_0}^t dt' \int d^3 p' \langle\Psi_0|z|p_z' + A(t)\rangle \exp\left(-\mathrm{i}S_{\boldsymbol{p}'}(t,t')\right) \\
&\qquad\qquad \langle p_z' + A(t')|z\widehat{E}\cos(\omega_1 t')|\Psi_0(t')\rangle + c.c.
\end{aligned}
\tag{3.65}
$$

117

with $S_{\boldsymbol{p}'}(t,t') = 1/2 \int_{t'}^{t} dt''(\boldsymbol{p}' + \boldsymbol{A}(t''))^2$. Now we asymptotically approximate the $\boldsymbol{p}$-integration [93]. The saddel-point of the highly oscillating integrand can be found by $\boldsymbol{\nabla}_{\boldsymbol{p}}[S_{\boldsymbol{p}'}(t,t') + \epsilon_{\text{HOMO}}t'] = \boldsymbol{0}$, leading to

$$k(t,\tau) = -\widehat{E}\,\frac{\cos\omega_{\text{l}}t - \cos\omega_{\text{l}}(t-\tau)}{\omega_{\text{l}}^2 \tau}, \tag{3.66}$$

where $\tau = t - t'$ is the travel-time of the electron between ionization and recombination and $\boldsymbol{k}(t,\tau) = k(t,\tau)\boldsymbol{e}_z$. In order for the asymptotic approximation to be well-defined we need to have $\det(\partial_{p_i}\partial_{p_j}S) > 0$. Here we find $\det(\partial_{p_i}\partial_{p_j}S) = \tau^3$ for $0 < \tau < \infty$. With a change of the variable of integration $t' \to \tau$ we hence find for the asymptotically approximated expression

$$\begin{aligned} d_z^{(L)}(t) &\simeq \mathrm{i}\int_0^\infty d\tau \left(\frac{2\pi}{\mathrm{i}\tau}\right)^{3/2} \mu_z^*[k(t,\tau) + A(t)] \\ &\quad \times \exp[-\mathrm{i}S(t,\tau)]\widehat{E}\cos[\omega_{\text{l}}(t-\tau)] \\ &\quad \times \mu_z[k(t,\tau) + A(t-\tau)] + \text{c.c.} \end{aligned} \tag{3.67}$$

where

$$\mu_z(p_z) = \langle p_z|z|\Psi_0\rangle, \tag{3.68}$$

$S(t,\tau)$ the saddle-point action defined as

$$\begin{aligned} S(t,\tau) &= (U_{\text{p}} - \epsilon_{\text{HOMO}})\tau - \frac{2U_{\text{p}}(1 - \cos\omega_{\text{l}}\tau)}{\omega_{\text{l}}^2\tau} \\ &\quad - \frac{U_{\text{p}}C(\tau)\cos[(2t-\tau)\omega_{\text{l}}]}{\omega_{\text{l}}} \end{aligned} \tag{3.69}$$

with

$$C(\tau) = \sin\omega_{\text{l}}\tau - \frac{4}{\omega_{\text{l}}\tau}\sin^2(\omega_{\text{l}}\tau/2) \tag{3.70}$$

and $U_{\text{p}} = \widehat{E}^2/(4\omega_{\text{l}}^2)$.

The target-dependence of the high-order harmonic generation spectra enters in (3.67) via the initial state $|\Psi_0\rangle$ through the ionization and recombination matrix elements $\mu_z[k(t,\tau) + A(t-\tau)]$ and $\mu_z^*[k(t,\tau) + A(t)]$, respectively [89]. We assume an initial state of the form $\psi_0(\boldsymbol{r}) = \phi_0(r)Y_{\ell,0}(\theta,\varphi)/r$ with $Y_{\ell,m}(\theta,\varphi)$ a spherical harmonic and model the valence π-orbital using a radial wavefunction $\phi_0(r)/r = (2\Delta)^{-1/2}$ for $R - \Delta < r \le R$, $-(2\Delta)^{-1/2}$ for $R < r \le R + \Delta$, and zero otherwise. Here, Δ is half the thickness of the C_{60}-shell, i.e., $\Delta = (R_o - R_i)/2 = 1.4$. Assuming further $|p_z\Delta| \ll 1$ and, e.g., $\ell = 0$, we obtain

$$\mu_z(p_z) \sim \frac{1}{p_z^2}(\sin p_z R - p_z R\cos p_z R + p_z^2 R^2 \sin p_z R) \tag{3.71}$$

and a similar but more lengthy expressions for $\ell = 4$. One clearly sees that structural information (i.e., the C_{60}-radius R) is "encoded" in $\mu_z(p_z)$. If the approximation $|p_z\Delta| \ll 1$
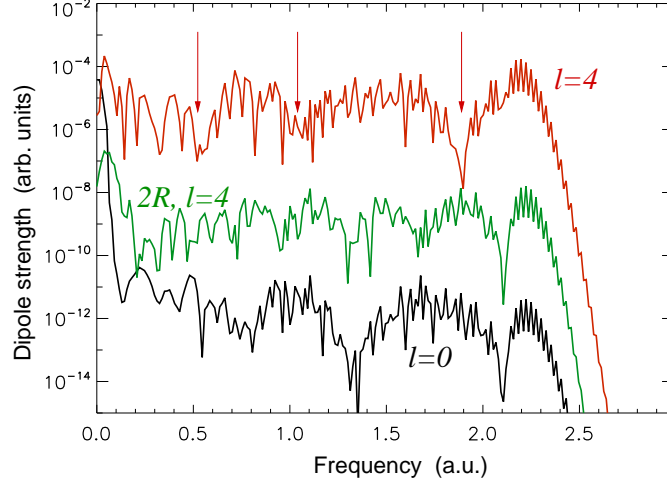
Figure 3.14: Harmonic spectra $S(\omega)$, calculated from equation 3.67 for $\ell = 4$, $\ell = 0$, and $\ell = 4$ but twice the radius R. The laser parameters are the same as in figure 3.11 [$\omega_l = 0.013$ ($\lambda = 3508\,\text{nm}$) and $\widehat{E} = 0.02$]. $R = 6.7$ and $\Delta = 1.4$ was used. The three thin vertical arrows indicate local minima in the envelope of the spectrum for $\ell = 4$.

is not made, also information about the shell thickness 2Δ is included in the matrix element $\mu_z(p_z)$.

Figure 3.14 shows the harmonic spectra obtained from the Fourier-transform $d_z^{(\text{L})}(\omega)$ of equation (3.67) for $\ell = 4$ and $\ell = 0$ and the laser parameters of figure 3.11. The positions of the minima in the envelope of the high-order harmonic generation spectra depend on the initial ℓ quantum number and the C_{60} radius R. In order to illustrate this dependency the spectra for $\ell = 0$, $\ell = 4$, and $\ell = 4$ but with the radius doubled are shown. The minima indicated in the $\ell = 4$-spectrum by vertical arrows may be compared with those of the time-dependent density functional theory result in figure 3.11. The latter are at $\omega \simeq 0.5$, 0.95, and 1.7. The arrows in figure 3.14 are at $\omega \simeq 0.52$, 1.05, and 1.9, which is in reasonable agreement. Note that the agreement would be worse if one attempted to compare with the $\ell = 0$-spectrum, let alone with the spectrum for $\ell = 4$ and doubled radius, which is qualitatively different since there is at least one more pronounced minimum in the envelope.

3.2.5 Strong Field Approximation including Recollision-Induced Collective Excitations

For systems with a single active electron, harmonic spectra are usually analyzed using the strong field approximation (or Lewenstein model) [7, 90], as we did in the previous section. Emission into a mode with frequency ω and polarization $\boldsymbol{e}_\lambda$, $\lambda = 1, 2$, by a system with only a single active electron can also be described by the amplitude

$$M_{\text{SAE}}(\omega, \lambda) = -\int d^3p \int_{-\infty}^{\infty} dt \, \langle \Psi_0, 1_{\omega,\lambda} | \widehat{V}_{\text{rad}}^\dagger | 0_{\omega,\lambda}, \boldsymbol{p} \rangle \int_{-\infty}^{t} dt' \, \langle \boldsymbol{p} | \widehat{V}_{\text{L}}(t') | \Psi_0 \rangle. \qquad (3.72)$$

Here, $|\Psi_0\rangle$ is the single-electron ground state, $|\boldsymbol{p}\rangle$ is the Volkov state of drift momentum $\boldsymbol{p}$, $|n_{\omega,\lambda}\rangle$ is the Fock state of the harmonic radiation field with n photons in the respective mode ($n = 0, 1$ in our case) and $\widehat{V}^{\dagger}_{\mathrm{rad}}$ and $\widehat{V}_{\mathrm{L}}(t')$ are the interaction operators coupling to the radiation and the laser field, respectively,

$$\widehat{V}^{\dagger}_{\mathrm{rad}} = -\mathrm{i}\sqrt{\frac{2\pi\omega}{\mathcal{V}}}\boldsymbol{r} \cdot \boldsymbol{e}_{\lambda}a^{\dagger}_{\omega,\lambda} \ \exp(\mathrm{i}\omega t), \tag{3.73}$$

$$\widehat{V}_{\mathrm{L}}(t) = E(t)z, \tag{3.74}$$

with $a^{\dagger}$ the photon creation operator and $\mathcal{V}$ the quantization volume. The amplitude (3.72) describes an electron which is lifted from the ground state to a Volkov state by the laser field at time t' and emits a harmonic photon upon recombination at time $t > t'$. The harmonic spectrum is given by the square modulus of (3.72) and appears to be virtually identical to the spectrum found from the dipole (3.67) [90]. In the dipole approximation we use here the wavevector $\boldsymbol{K}$ of the emitted photon does not appear in the amplitude (3.72).

Now we **introduce a similar amplitude which accounts for the collective modes**: in addition to the pathway described by (3.72) the recombining electron may excite collective modes which then relax upon emission of a harmonic photon. The amplitude for such a process reads

$$\begin{aligned} M_{\mathrm{coll}}(\omega, \lambda) &= \sum_{j}\sum_{L}\int_{-\infty}^{\infty}dt \, \langle 0_j, 1_{\omega,\lambda}|\widehat{V}^{\dagger}_{\mathrm{rad}}|0_{\omega,\lambda}, L_j\rangle \\ &\times \int d^3p \int_{-\infty}^{t}dt' \, \langle \Psi_0, L_j|\widehat{U}|0_j, \boldsymbol{p}\rangle \int_{-\infty}^{t'}dt'' \, \langle \boldsymbol{p}|\widehat{V}_{\mathrm{L}}(t'')|\Psi_0\rangle. \end{aligned} \tag{3.75}$$

Here, $|0_j\rangle$ and $|L_j\rangle$ are the ground and the L-th excited state of a collective mode, labelled by j (e.g., surface or volume oscillations). The **interaction energy between the electron and the residual electron cloud** is described by the operator $\widehat{U}$. The amplitude (3.76) is a straightforward generalization of the Lewenstein model to the case when collective modes can be involved in the emission process.

To evaluate the collective amplitude (3.76) a certain model for the description of the collective modes and their interaction $\widehat{U}$ with the active electron is required. In order to estimate the relative contribution of the single active electron approximation and the collective pathways to the radiation spectrum we use a simple model which takes collective degrees of freedom into account as two noninteracting harmonic oscillators with eigenfrequencies $\omega_{\mathrm{Mie}} \simeq 0.7$ and $\omega_{\mathrm{p}} \simeq 1.4$ (i.e., the surface and the volume plasmon in the C_{60}-model above). The respective widths of the plasmons are taken as $\Gamma_{\mathrm{Mie(p)}} \approx 0.2$. The main physical mechanism which generates these widths is a coupling between collective and single-electron degrees of freedom. This can also be interpreted as collisionless or Landau damping of collective modes in a finite system [91,92]. To obtain an explicit form for the interaction operator $\widehat{U}$ we **employ a rigid sphere model** in which the electron cloud is treated as an incompressible homogeneous sphere which may oscillate around its

equilibrium position. Note that on the level of modelling in this subsection it does not matter whether we consider a homogeneous sphere or a spherical shell. Within the rigid sphere model the interaction operator has the form

$$
U(\boldsymbol{r}, \boldsymbol{X}) = \frac{(N-1)}{R} \begin{cases} \dfrac{3}{2} - \dfrac{(\boldsymbol{r}-\boldsymbol{X})^2}{2R^2}, & |\boldsymbol{r}-\boldsymbol{X}| \leq R, \\[2mm] \dfrac{R}{|\boldsymbol{r}-\boldsymbol{X}|}, & |\boldsymbol{r}-\boldsymbol{X}| > R, \end{cases} \tag{3.76}
$$

where $N = 240$ is the number of electrons, $\boldsymbol{r}$ is the active electron's position and $\boldsymbol{X}$ is the center-of-mass displacement of the electron cloud. Because of the relatively high energies of the plasmons only the first excited collective states are relevant in the sum over L in (3.76). For a first excited state $X \simeq 1/\sqrt{(N-1)\omega_{\mathrm{Mie(p)}}} \ll R$ so that with high accuracy (e.g., taking $N = 240$ and $\omega_{\mathrm{Mie}} = 0.7$ one estimates $X \simeq 0.08$) one may simplify (3.76) keeping only the linear term with respect to the center-of-mass displacement $\boldsymbol{X}$:

$$
U(\boldsymbol{r}, \boldsymbol{X}) \simeq U_0(r) + \frac{N-1}{R^3} \boldsymbol{r} \cdot \boldsymbol{X} \begin{cases} 1, & r \leq R, \\ R^2/r^3, & r > R \end{cases}. \tag{3.77}
$$

Next, we assume that the electron excursion amplitude in the laser field $\widehat{z} = \widehat{E}/\omega_{\mathrm{l}}^2$ is less than or comparable to the cluster size R. Then, with reasonable accuracy, we may use

$$
U(\boldsymbol{r}, \boldsymbol{X}) \simeq \frac{N-1}{R^3} \boldsymbol{r} \cdot \boldsymbol{X} \tag{3.78}
$$

instead of (3.77). Within this approximation an explicit relation between the amplitudes (3.76) and (3.72) can be derived. To this end we first evaluate the emission matrix element in (3.72),

$$
\langle \Psi_0, 1_{\omega,\lambda} | \widehat{V}_{\mathrm{rad}}^\dagger | 0_{\omega,\lambda}, \boldsymbol{p} \rangle = -\mathrm{i}\sqrt{\frac{2\pi\omega}{\mathcal{V}}} \langle \Psi_0 | \boldsymbol{r} \cdot \boldsymbol{e}_\lambda | \boldsymbol{p} \rangle \ \exp(\mathrm{i}\omega t). \tag{3.79}
$$

Here we used the standard relation $\langle a | \boldsymbol{p} | b \rangle = -\mathrm{i}m\omega_{ab}\langle a | \boldsymbol{r} | b \rangle$ which is only correct if the states $|a\rangle$ and $|b\rangle$ are eigenstates of the same Hamiltonian. Within our model this is not strictly the case for the states $|\Psi_0\rangle$ and $|\boldsymbol{p}\rangle$. In deriving (3.79) we have further taken into account that in a linearly polarized field $\boldsymbol{A} = A\boldsymbol{e}_0$, after integration over all momenta $\boldsymbol{p}$ in (3.72), the unit vector $\boldsymbol{e}_0$ along the polarization direction should appear so that we may replace $\boldsymbol{r} \cdot \boldsymbol{e}_{\boldsymbol{K},\lambda}$ by the product $(\boldsymbol{e}_0 \cdot \boldsymbol{e}_{\boldsymbol{K},\lambda})(\boldsymbol{r} \cdot \boldsymbol{e}_0)$. A similar procedure for the emission matrix element in (3.76) yields

$$
\langle 0_{\mathrm{Mie(p)}}, 1_{\omega,\lambda} | \widehat{V}_{\mathrm{rad}}^\dagger | 0_{\omega,\lambda}, 1_{\mathrm{Mie(p)}} \rangle \tag{3.80}
$$

$$
= -\mathrm{i}\sqrt{\frac{\pi(N-1)\omega}{\mathcal{V}\omega_{\mathrm{Mie(p)}}}} \boldsymbol{e}_z \cdot \boldsymbol{e}_\lambda \ \exp(\mathrm{i}(\omega - \omega_{\mathrm{Mie(p)}})t - \Gamma_{\mathrm{Mie(p)}}t/2).
$$

Here we used the fact that for the harmonic oscillator $\langle 0 | z | 1 \rangle = 1/\sqrt{2M\Omega}$ with $M = (N-1)m$ and $\Omega = \omega_{\mathrm{Mie(p)}}$ in our case. Also we take into account that the oscillator is

excited along the polarization direction given by the unit vector $\boldsymbol{e}_z$.

Rearranging the time-integrations, the amplitude (3.76) can be also written as

$$
\begin{aligned}
M_{\text{coll}}(\omega, \lambda) = \sum_j \sum_{\text{Mie,p}} \int d^3 p \int_{-\infty}^{\infty} dt' \, \langle \Psi_0, 1_{\text{Mie(p)}} | \widehat{U} | 0_{\text{Mie(p)}}, \boldsymbol{p} \rangle \\
\times \int_{t'}^{\infty} dt \, \langle 0_{\text{Mie(p)}}, 1_{\omega,\lambda} | \widehat{V}_{\text{rad}}^{\dagger} | 0_{\omega,\lambda}, 1_{\text{Mie(p)}} \rangle \int_{-\infty}^{t'} dt'' \, \langle \boldsymbol{p} | \widehat{V}_{\text{L}}(t'') | \Psi_0 \rangle.
\end{aligned}
\tag{3.81}
$$

Now the inner integral over t can be evaluated explicitly using (3.80). The result reads

$$
\int_{t'}^{\infty} dt \, \langle 0_{\text{Mie(p)}}, 1_{\omega,\lambda} | \widehat{V}_{\text{rad}}^{\dagger} | 0_{\omega,\lambda}, 1_{\text{Mie(p)}} \rangle \tag{3.82}
$$

$$
= -\mathrm{i} \sqrt{\frac{\pi(N-1)\omega}{\mathcal{V}\omega_{\text{Mie(p)}}}} \, \frac{\boldsymbol{e}_z \cdot \boldsymbol{e}_\lambda \, \exp(\mathrm{i}(\omega - \omega_{\text{Mie(p)}})t')}{\Gamma_{\text{Mie(p)}}/2 - \mathrm{i}(\omega - \omega_{\text{Mie(p)}})}.
$$

Finally, using the standard expression for the coordinate matrix element of the harmonic oscillator $\langle 0 | z | 1 \rangle = 1/\sqrt{2M\Omega}$ and (3.78) one obtains for the first matrix element in (3.82)

$$
\langle \Psi_0, 1_{\text{Mie(p)}} | \widehat{U} | 0_{\text{Mie(p)}}, \boldsymbol{p} \rangle = \frac{1}{R^3} \sqrt{\frac{N-1}{2\omega_{\text{Mie(p)}}}} \langle \Psi_0 | z | \boldsymbol{p} \rangle \, \exp(\mathrm{i}\omega_{\text{Mie(p)}}t). \tag{3.83}
$$

Collecting equations (3.79)–(3.83), we may express the amplitude (3.76) via (3.72) as

$$
M_{\text{coll}} = \mathrm{i} \frac{N-1}{2R^3} \left\{ \frac{\omega_{\text{Mie}}^{-1}}{\Gamma_{\text{Mie}}/2 - \mathrm{i}(\omega - \omega_{\text{Mie}})} + \frac{\omega_{\text{p}}^{-1}}{\Gamma_{\text{p}}/2 - \mathrm{i}(\omega - \omega_{\text{p}})} \right\} M_{\text{SAE}}. \tag{3.84}
$$

Equation (3.84) shows that collective modes may lead to enhancements in the high-order harmonic generation spectrum around the respective plasmon frequencies. For the plasmon enhancements to be detectable $|M_{\text{coll}}|^2 > |M_{\text{SAE}}|^2$ should hold. For the **ratio of collective to single active electron high-order harmonic generation efficiency** we obtain

$$
\boxed{\frac{|M_{\text{coll}}|^2}{|M_{\text{SAE}}(\omega = \omega_{\text{Mie(p)}})|^2} \simeq \left[\frac{N-1}{R^3 \omega_{\text{Mie(p)}} \Gamma_{\text{Mie(p)}}} \right]^2} \tag{3.85}
$$

For $N = 240$, $R = 6.7$, $\Gamma_{\text{Mie}} = \Gamma_{\text{p}} = 0.2$ the ratio (3.85) is above 10 for the surface and about unity for the volume plasmon.

The ratio (3.85) **does not depend on the laser parameters anymore** whereas in our time-dependent density functional theory results we observe a wavelength-dependent relative efficiency of the plasmon enhancements. With increasing laser intensity or wavelength the electron's excursion amplitude is increasing and the approximation (3.78) for the interaction between the active electron and the electron cloud becomes invalid. Without the assumption of small excursion amplitudes (as compared to the cluster radius) a simple relationship of the type (3.84) cannot be established. Qualitatively it is quite obvious, however, that with increasing excursion amplitude distances $r \simeq R$ [for which

(3.77) is sizeable] contribute less and less to the spatial matrix element (3.83). As a consequence the standard single-electron high-order harmonic generation spectrum dominates for $\widehat{E}/\omega_l^2 \gg R$. In fact, $\widehat{E}/\omega_l^2 = 15.4$, 75.0, and 118.3 in figure 3.9, 3.10, and 3.11, respectively, supporting our statement.

The results (3.84) and (3.85) were derived making several approximations besides the one of small excursion amplitudes. For example, the surface and the volume plasmons were treated as independent. This makes sense if they are well separated from each other, i.e., $|\omega_{\mathrm{Mie}} - \omega_{\mathrm{p}}| \gg (\Gamma_{\mathrm{Mie}} + \Gamma_{\mathrm{p}})/2$, which is actually not fulfilled in the case of C_{60}. Another simplification was that we applied the rigid sphere model for the description of the electron cloud. Within this model the volume plasmon simply does not exist. In a more realistic description one should use two different interaction potentials instead of (3.76) alone, which will lead to two different coefficients in (3.85) for approximating the relative efficiency.

3.2.6 Linear Response induced by a Single Active Orbital

In the above derivation we introduced a very simple model for the collective response of the system. We analyzed the shortcomings of this approach. Time-dependent density functional theory is routinely used to calculate the collective response of large systems. Usually one employs a linear response approach to calculate excitation spectra and finds good agreement with experiment (see subsection 3.1.1).

For a bound electron with the initial state $|\Psi_0\rangle$ having the binding energy ϵ_{HOMO} and $\boldsymbol{A}(t)$ the vector potential of the laser pulse in dipole approximation the strong field approximation wavefunction reads in length gauge [see equation (2.125) and subsection 3.2.4 for the definition of the travel time τ]

$$
\begin{aligned}
|\Psi(t)\rangle &= |\Psi_0(t)\rangle - \int d^3p \, |\boldsymbol{p} + \boldsymbol{A}(t)\rangle \int_0^t d\tau \, \boldsymbol{E}(t-\tau) \\
&\quad \cdot \langle \boldsymbol{p} + \boldsymbol{A}(t-\tau)|\boldsymbol{z}|\Psi_0\rangle \, e^{-\mathrm{i}(S_{\boldsymbol{p}}(t,\tau)+\epsilon_{\mathrm{HOMO}}(t-\tau))}.
\end{aligned}
\tag{3.86}
$$

$\boldsymbol{E}(t) = -\partial_t \boldsymbol{A}(t)$ is the electric field of the laser, $S_{\boldsymbol{p}}(t,\tau) + \epsilon_{\mathrm{HOMO}}(t - \tau) = [\int_{t-\tau}^t dt'' \frac{1}{2}(\boldsymbol{p} + \boldsymbol{A}(t''))^2 + \epsilon_{\mathrm{HOMO}}(t - \tau)]$ the quasi classical action and the variable of integration τ is the travel-time between ionization and recollision. Note that the validity of this approximation in the Lewenstein derivation assumes the ionization to be weak. The strong field approximation wavefunction mainly occupies its initial state.

In order to derive an analytic approximation for recollision induced plasmon emission we will describe the outermost orbital, which excites the plasmon via recollision, in terms of the strong field approximation wavefunction. Further we will deduce within the framework of time-dependent density functional theory the **effective potential change due to the strong field approximation orbital**. This change will be treated as an perturbation for the residual system, which then may radiate. From this we will infere some approximations for the dipole radiation of the collective modes excited via the returning orbital. The main advantage is that linear response time-dependent density functional theory gives very good approximations for the collective response of the system.

We begin with the time-dependent Kohn-Sham equation [see theorem 1.3.8]

$$i\frac{\partial}{\partial t}\phi_i(\boldsymbol{r},t) = \left(-\frac{1}{2}\boldsymbol{\nabla}^2 + v(\boldsymbol{r},t) + v_\mathrm{H}([n];\boldsymbol{r},t) + v_\mathrm{xc}([n],\boldsymbol{r},t)\right)\phi_i(\boldsymbol{r},t), \qquad (3.87)$$

where $v(\boldsymbol{r},t) = v_0(r) + v_\mathrm{L}(\boldsymbol{r},t)$ and $v_0(r)$ the ionic background and $v_\mathrm{L}(\boldsymbol{r},t)$ the laser field in dipole approximation. If the initial state $|\Phi_0\rangle$ is a ground state we loose the initial state dependence, which is assumed. The N occupied orbitals constitute the density, i.e.,

$$n(\boldsymbol{r},t) = \sum_{i=1}^{N} |\phi_i(\boldsymbol{r},t)|^2. \qquad (3.88)$$

Now we adopt the strong field approximation for time-dependent density functional theory. We **describe the outermost orbital** $\phi_N(\boldsymbol{r},t) \equiv \psi(\boldsymbol{r},t)$ within this approximation. The corresponding density change

$$\delta n(\boldsymbol{r},t) \simeq \delta n^\mathrm{SFA}(\boldsymbol{r},t) \qquad (3.89)$$

leads to a variation of the Hartree and exchange-correlation potential

$$\begin{aligned}
\delta v(\boldsymbol{r},t) &= \int d^3r' \frac{\delta n^\mathrm{SFA}(\boldsymbol{r}'t)}{|\boldsymbol{r}-\boldsymbol{r}'|} \\
&+ \underbrace{\left(v_\mathrm{xc}([n_0+\delta n^\mathrm{SFA}];\boldsymbol{r},t) - v_\mathrm{xc}([n_0];\boldsymbol{r})\right)}_{=:\delta v_\mathrm{xc}([\delta n^\mathrm{SFA}];\boldsymbol{r},t)}.
\end{aligned} \qquad (3.90)$$

The exchange-correlation variation depends now on the choice of approximation for the exchange-correlation potential. We assume the contribution of the exchange-correlation variation to the dynamics to be negligible, leading to

$$\delta v(\boldsymbol{r},t) \simeq \int d^3r' \frac{\delta n^\mathrm{SFA}(\boldsymbol{r}'t)}{|\boldsymbol{r}-\boldsymbol{r}'|}. \qquad (3.91)$$

The **effective Kohn-Sham potential** in this approximation then reads

$$\begin{aligned}
v_\mathrm{KS}([n];\boldsymbol{r},t) &\simeq v_0(\boldsymbol{r}) + \int d^3r' \frac{n_0(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} + v_\mathrm{xc}([n_0];\boldsymbol{r}) \qquad (3.92)\\
&+ v_\mathrm{L}(\boldsymbol{r},t) + \delta v(\boldsymbol{r},t). \qquad (3.93)
\end{aligned}$$

The density change is induced by $v_\mathrm{L}(\boldsymbol{r},t) + \delta v(\boldsymbol{r},t)$. For the plasmon excitation, i.e., the collective density variation, only $\delta v(\boldsymbol{r},t)$ will contribute, as we have assumed the laser to be far-off resonant.

If we are interested in how the emission of collective modes obscures the spectrum of high harmonics we need to know the radiation of those collective modes. The main contribution of the plasmon emission, if expanded in multipoles, will be the dipole radiation. Thus we need to calculate the dipole radiation of the excited collective motion.

In our considerations the field due to the recollision of the outermost orbital $\delta v(\boldsymbol{r}, t)$ is perturbative. One should not be confused at this point. We have a strong laser pulse which cannot be treated as a perturbation. However, we assume the laser pulse to be far-off resonant with respect to the plasmon modes. So only the recolliding electron, treated non-perturbatively, may excite these modes. The effective field of the returning electron $\delta v(\boldsymbol{r}, t)$ is responsible for the excitations of collective modes.

The dipole response in z direction due to the collective density variation $\delta n_{\mathrm{coll}}(\boldsymbol{r}', t)$ induced by $\delta v(\boldsymbol{r}, t)$ is

$$
\begin{aligned}
d_z(\omega) &= \frac{1}{\sqrt{2\pi}} \int dt\, e^{-i\omega t} \int d^3r\, z\, \delta n_{\mathrm{coll}}(\boldsymbol{r}, t) \tag{3.94} \\
&\simeq \int d^3r \int d^3r'\, z\, \chi_{\mathrm{KS}}(\boldsymbol{r}, \boldsymbol{r}', \omega)\delta v(\boldsymbol{r}', \omega),
\end{aligned}
$$

where $\chi_{\mathrm{KS}}(\boldsymbol{r}, \boldsymbol{r}', \omega)$ is the Kohn-Sham linear response kernel of the system and $\delta v(\boldsymbol{r}', \omega) = \mathcal{F}(\delta v)(\boldsymbol{r}, \omega)$ the Fourier transformed Hartree potential. Further, with

$$
\Gamma_z(\boldsymbol{r}', \omega) := \int d^3r\, z\, \chi_{\mathrm{KS}}(\boldsymbol{r}, \boldsymbol{r}', \omega), \tag{3.95}
$$

we find with a multipole expansion of $\delta v(\boldsymbol{r}, \omega)$

$$
d_z(\omega) \simeq \sum_{i=0}^{\infty} \int d^3r' \Gamma_z(\boldsymbol{r}', \omega)\delta v_i(\boldsymbol{r}', \omega). \tag{3.96}
$$

The linear dipole moment may be calculated by applying a δ-like electric field in dipole approximation $\boldsymbol{E}(t) = \widehat{A}\delta(t)$, which is equivalent to give the ground-state wavefunctions a coherent velocity field, i.e., $|\psi_i\rangle \to e^{ikz}|\psi_i\rangle$ [74]. This is analogous to the assumption that the main contribution to the dipole response is due to the dipole of the perturbing field. With the Fourier transform $\mathcal{F}(\widehat{A}\delta(t)) = \frac{\widehat{A}}{\sqrt{2\pi}}$ we find the linear dipole response

$$
\begin{aligned}
d_z^{\mathrm{dr}}(\omega) &= \int d^3r' \Gamma_z(\boldsymbol{r}', \omega)\frac{\widehat{A}}{\sqrt{2\pi}}z' \tag{3.97} \\
&+ \int d^3r' \int d^3r\, \Gamma_z(\boldsymbol{r}', \omega)\left[\frac{1}{|\boldsymbol{r} - \boldsymbol{r}'|}\right. \\
&+ \left. f_{\mathrm{xc}}(\boldsymbol{r}, \boldsymbol{r}', \omega)\right]\delta n_{\mathrm{dr}}(\boldsymbol{r}', t).
\end{aligned}
$$

Here $f_{\mathrm{xc}}(\boldsymbol{r}, \boldsymbol{r}', \omega)$ is the exchange-correlation kernel. In leading order we may approximate the dipole response by

$$
d_z^{\mathrm{dr}}(\omega) \simeq \underbrace{\int d^3r' \Gamma_z(\boldsymbol{r}', \omega)z'}_{=:D(\omega)} \frac{\widehat{A}}{\sqrt{2\pi}}. \tag{3.98}
$$

For $\delta v(\boldsymbol{r}, \omega)$ in dipole approximation $\delta v(\boldsymbol{r}, \omega) \simeq z\delta v(\omega)$ we find in leading order the **collective dipole response**

$$
d_z(\omega) \simeq d_z^{\mathrm{dr}}(\omega)\frac{\sqrt{2\pi}}{\widehat{A}}\delta v(\omega) \simeq D(\omega)\delta v(\omega). \tag{3.99}
$$

In order to derive the density variation due to the SFA wavefunction we will further simplify equation (3.86). We will **approximate the p-integration by an asymptotic expansion** [93]. Asymptotic approximations, above all the saddle-point approximation, are widely and very successfully used within strong field physics. Returning to equation (3.86) the exponent, which will be subject to a saddle-point approximation in coordinate space, is

$$
\begin{aligned}
S(\boldsymbol{p}, t, \tau) & = (\boldsymbol{p} + \boldsymbol{A}(t)) \cdot \boldsymbol{r} + \frac{1}{2} \int_{t-\tau}^{t} dt'' \, (\boldsymbol{p} + \boldsymbol{A}(t''))^2 \\
& + \epsilon_{\mathrm{HOMO}}(t - \tau) - (\boldsymbol{p} + \boldsymbol{A}(t - \tau)) \cdot \boldsymbol{x}.
\end{aligned}
\tag{3.100}
$$

The critical points of the exponent are found by solving

$$
\boldsymbol{\nabla}_p S(\boldsymbol{p}, t, \tau) \overset{!}{=} 0,
\tag{3.101}
$$

leading to the saddle-point

$$
\begin{aligned}
\boldsymbol{k}(\boldsymbol{r}, \boldsymbol{x}, t, \tau) & = -\frac{\int_{t-\tau}^{t} dt'' \, \widehat{A}(t'')}{\tau} + \frac{\boldsymbol{x} - \boldsymbol{r}}{\tau} \\
& = \boldsymbol{k}(t, \tau) + \frac{\boldsymbol{x} - \boldsymbol{r}}{\tau}.
\end{aligned}
\tag{3.102}
$$

Here $\boldsymbol{k}(t, \tau)$ is the saddle-point from the SFA treatment of high-order harmonic generation, i.e., equation (3.66). For the asymptotic expansion to be valid the determinant $\det(\partial_{p_i} \partial_{p_j} \widehat{S}) = \tau^3 \neq 0$. With

$$
\begin{aligned}
\mu(\boldsymbol{r}, t, \tau) & := \left\langle \boldsymbol{k}(t, \tau) + \boldsymbol{A}(t - \tau) - \frac{\boldsymbol{r}}{\tau} + \frac{\boldsymbol{x}}{2\tau} \Big| z \big| \psi_0 \right\rangle, \\
f(t, \tau) & := \left(\frac{2\pi}{\mathrm{i}\tau} \right)^{\frac{3}{2}} e^{-\mathrm{i} \int_{t-\tau}^{t} dt'' \frac{1}{2} (\boldsymbol{k}(t, \tau) + \boldsymbol{A}(t''))^2} \\
& \quad E(t - \tau) e^{\mathrm{i}\epsilon_{\mathrm{HOMO}}\tau}
\end{aligned}
\tag{3.103}
$$

the asymptotically expanded SFA wavefunction then reads

$$
\begin{aligned}
\psi(\boldsymbol{r}, t) & \simeq \psi_0(\boldsymbol{r}, t) - \mathrm{i} \int_0^t d\tau \frac{e^{-\mathrm{i}(\boldsymbol{k}(t,\tau) + \boldsymbol{A}(t)) \cdot \boldsymbol{r}}}{(2\pi)^{3/2}} \\
& \times \mu(\boldsymbol{r}, t, \tau) e^{-\mathrm{i}\epsilon_{\mathrm{HOMO}}t} e^{\frac{\mathrm{i}r^2}{2\tau}} f(t, \tau).
\end{aligned}
\tag{3.104}
$$

The associated density is

$$
\begin{aligned}
n(\boldsymbol{r}, t) & = \psi^*(\boldsymbol{r}, t) \psi(\boldsymbol{r}, t) \simeq n_0(\boldsymbol{r}) \\
& - 2\Re \left\{ \mathrm{i}\psi_0^*(\boldsymbol{r}) \int d\tau e^{\frac{\mathrm{i}r^2}{2\tau}} \frac{e^{-\mathrm{i}(\boldsymbol{k}(t,\tau) + \boldsymbol{A}(t)) \cdot \boldsymbol{r}}}{(2\pi)^{3/2}} \mu(\boldsymbol{r}, t, \tau) f(t, \tau) \right\},
\end{aligned}
\tag{3.105}
$$

with $n_0(\boldsymbol{r}) = |\psi_0(\boldsymbol{r})|^2$ the initial orbital density. Here we have neglected the modulus square of the continuum part of the wavefunction. This term is assumed to be negligible

due to the Lewenstein assumption of weak ionization. We will further use initial orbitals of the form

$$\psi_0(\boldsymbol{r}) = \psi_0(r, \theta, \varphi) = \frac{\phi_0(r)}{r} Y_{k,0}(\theta, \varphi) \tag{3.106}$$

with $\phi_0(r)$ contributing mostly around $r = R$. Here $Y_{k,0}(\theta, \varphi)$ is a spherical harmonic of order $(k, 0)$.

The **Hartree-potential due to the density variation**

$$\begin{aligned} \delta n^{\mathrm{SFA}}(\boldsymbol{r}, t) & \equiv & \delta n(\boldsymbol{r}, t) \\ & = & n(\boldsymbol{r}, t) - n_0(\boldsymbol{r}) \end{aligned} \tag{3.107}$$

expanded in multipoles [94] is

$$\delta v(\boldsymbol{r}, t) = 4\pi \sum_{i=1}^{\infty} \sum_{j=-i}^{j=i} \frac{1}{2i+1} \left(\int d^3 r' \frac{r'^i_<}{r'^{i+1}_>} Y^*_{i,j}(\boldsymbol{r}') Y_{i,j}(\boldsymbol{r}) \delta n(\boldsymbol{r}', t) \right). \tag{3.108}$$

Here $Y_{i,j}(\boldsymbol{r})$ are the spherical harmonics of order i, j expressed in Cartesian coordinates and $r'_{(<,>)} := (\min, \max)\{r', r\}$.
We may rewrite the potential variation in the form

$$\begin{aligned} \delta v(\boldsymbol{r}, t) = & -\frac{4}{\sqrt{2\pi}} \Re \left\{ i \int d\tau d^3 r' e^{-i(\widetilde{\boldsymbol{k}}(t,\tau)\cdot\boldsymbol{r}' - \frac{r'^2}{2\tau})} \right. \\ & \left. \times \sum_{i,j} \frac{1}{2i+1} \frac{r'^i_<}{r'^{i+1}_>} Y^*_{i,j}(\boldsymbol{r}') Y_{i,j}(\boldsymbol{r}) \psi^*_0(\boldsymbol{r}') \mu(\boldsymbol{r}', t, \tau) f(t, \tau) \right\}, \end{aligned} \tag{3.109}$$

with $\widetilde{\boldsymbol{k}}(t, \tau) := \boldsymbol{k}(t, \tau) + \boldsymbol{A}(t)$.
In the appendix we asymptotically expand the potential variation. However, the final result is not very intuitive. Therefore we will proceed deducing another approximate solution for the potential variation.

This other derivation makes use of the **special behavior of the spherical Bessel functions** $j_l(x)$. Though the approximation we derive within this section will not be as general as the asymptotically expanded Hartree potential variation, it will be of a very simple form.
First we will calculate $\mu(\boldsymbol{r}', t, \tau)$ for equation (3.109). We will make use of the expansions [94]

$$e^{i\boldsymbol{k}'\cdot\boldsymbol{x}} = \sum_{\ell=0}^{\infty} i^\ell \sqrt{4\pi(2\ell+1)} j_\ell(|k'|x) Y_{\ell,0}(\theta, \varphi), \tag{3.110}$$

$$e^{i\frac{\boldsymbol{x}\cdot\boldsymbol{r}'}{\tau}} = 4\pi \sum_{m=0}^{\infty} i^m j_m\left(\frac{xr'}{\tau}\right) \sum_{n=-m}^{n=m} Y^*_{m,n}(\theta, \varphi) Y_{m,n}(\theta', \varphi'), \tag{3.111}$$

and

$$z = 2\sqrt{\frac{\pi}{3}}Y_{1,0}(\theta, \varphi)x, \tag{3.112}$$

where $\boldsymbol{k}' := \boldsymbol{k}(t, \tau) + \boldsymbol{A}(t - \tau)$. Thus we have with the measure $d\Omega = d\varphi d\theta \sin\theta$

$$
\begin{aligned}
\mu(\boldsymbol{r}', t, \tau) &= \left(\frac{8}{3}\right)^{1/2}\sum_{\ell,m,n} i^{\ell+m}\sqrt{4\pi(2\ell+1)}Y_{m,n}(\theta', \varphi') \\
&\times \int_0^\infty dx x^2 j_\ell(|k'|x)j_m\left(\frac{xr'}{\tau}\right)e^{i\frac{x^2}{2\tau}}\phi_0(x) \\
&\times \int d\Omega Y_{\ell,0}(\theta, \varphi)Y_{m,n}^*(\theta, \varphi)Y_{1,0}(\theta, \varphi)Y_{k,0}(\theta, \varphi).
\end{aligned}
\tag{3.113}
$$

Using the Wigner 3j-symbols $\begin{pmatrix} \ell_1\,\ell_2\,\ell_3 \\ m_1 m_2 m_3 \end{pmatrix}$ [94] we find

$$
\begin{aligned}
\mu(\boldsymbol{r}', t, \tau) &= \sum_{\ell,m} i^{\ell+m}(2\ell+1)\sqrt{\frac{2}{\pi}(2m+1)(2k+1)} \\
&\times Y_{m,n}(\theta', \varphi')\int_0^\infty dx x^2 j_\ell(|k'|x)j_m\left(\frac{xr'}{\tau}\right)e^{i\frac{x^2}{2\tau}}\phi_0(x) \\
&\times \left((2k-1)\begin{pmatrix} 1\ k\ (k-1) \\ 0\ \ 0\ \ 0 \end{pmatrix}^2\begin{pmatrix} \ell\ (k-1)\ m \\ 0\ \ 0\ \ 0 \end{pmatrix}^2 \right. \\
&\left. + (2k+3)\begin{pmatrix} 1\ k\ (k+1) \\ 0\ \ 0\ \ 0 \end{pmatrix}^2\begin{pmatrix} \ell\ (k+1)\ m \\ 0\ \ 0\ \ 0 \end{pmatrix}^2\right).
\end{aligned}
\tag{3.114}
$$

If we now apply the same procedure, i.e., the same expansions and the Wigner 3j-symbols, to the rest of the Hartree potential variation we end up with

$$
\begin{aligned}
\delta v(\boldsymbol{r}, t) &= -\frac{2}{\pi^{3/2}}\Re\left\{\sum_{h,i,j,\ell,m=0}^\infty i^{\ell+m+h}(-1)^h Y_{i,0}(\theta, \varphi) \right. \\
&\times\frac{(2h+1)(2\ell+1)(2k+1)(2j+1)(2m+1)}{\sqrt{(2i+1)}} \\
&\times i\int_0^t d\tau f(t, \tau)\left[\int_0^\infty dr' r' e^{i\frac{r'^2}{2\tau}}\phi_0^*(r')\frac{r_<^{'i}}{r_>^{'i+1}}j_h(|\widetilde{k}|r')\right] \\
&\times\begin{pmatrix} k\ m\ j \\ 0\ 0\ 0 \end{pmatrix}^2\begin{pmatrix} h\ j\ i \\ 0\ 0\ 0 \end{pmatrix}^2\left[\int_0^\infty dx x^2\phi_0(x)e^{i\frac{x^2}{2\tau}}j_\ell(|k'|x)\right. \\
&\times \left. j_m\left(\frac{r'x}{\tau}\right)\right]\left((2k-1)\begin{pmatrix} 1\ k\ (k-1) \\ 0\ \ 0\ \ 0 \end{pmatrix}^2\begin{pmatrix} \ell\ (k-1)\ m \\ 0\ \ 0\ \ 0 \end{pmatrix}^2\right. \\
&\left.\left. +(2k+3)\begin{pmatrix} 1\ k\ (k+1) \\ 0\ \ 0\ \ 0 \end{pmatrix}^2\begin{pmatrix} \ell\ (k+1)\ m \\ 0\ \ 0\ \ 0 \end{pmatrix}^2\right)\right\}.
\end{aligned}
\tag{3.115}
$$

For comparison we express the strong field approximation dipole moment for high-order harmonic generation (3.67) in terms of the Wigner 3j-symbols:

$$d_z^{(L)}(t) = -\frac{2k+1}{3\pi^2}\Re\left\{\mathrm{i}\int_0^t d\tau \underbrace{f(t,\tau)\kappa(\tau,\widetilde{k})(\kappa(\tau,k'))^*}_{=:\kappa^{\mathrm{SFA}}(t,\tau)}\right\} \tag{3.116}$$

and

$$\kappa(\tau,\widetilde{k}) := \int dr\, r^2\phi_0^*(r)\left[\mathrm{i}^{(k-1)}(2(k-1)+1)\begin{pmatrix}1 & k & (k-1)\\0 & 0 & 0\end{pmatrix}^2 j_{k-1}(|\widetilde{k}|r) \tag{3.117}$$
$$+"(k-1)\leftrightarrow(k+1)"\Big].$$

Now we will examine the x-integration of equation (3.115). Note that for $\omega_\mathrm{l}\tau \ll 1$ we have $|k'|\sim 0$ because

$$|k'| = \left|-\frac{\int_{t-\tau}^t dt''A(t'')}{\tau}+A(t-\tau)\right| \tag{3.118}$$
$$\overset{\omega_\mathrm{l}\tau\ll 1}{\simeq} |-A(t)+A(t)| = 0.$$

The argument of the second spherical Bessel function in the x-integration is $\frac{xr'}{\tau}\sim\frac{R^2}{\tau}$. For a general laser pulse $|k'|\lesssim\widehat{A}$ with $\widehat{A}$ the field-strength. As we have a localized orbital around $x=R$ we find $|k'|x\lesssim\widehat{A}R$ for the non-zero contributions in the x-integration. Thus we have

$$|k'|x\to 0 \quad\text{for}\quad \tau\ll\frac{1}{\omega_\mathrm{l}} \quad\text{or}\quad \widehat{A}R\ll 1, \tag{3.119}$$
$$\frac{r'x}{\tau}\to 0 \quad\text{for}\quad \tau\gg R^2.$$

If the argument of the spherical Bessel functions $x\to 0$, only $j_0(x)\to 1$ will have a non-vanishing contribution. If we further concentrate on the dipole term of the multipole expansion of the Hartree potential we have

$$\begin{pmatrix}h & j & 1\\0 & 0 & 0\end{pmatrix}^2 \to h = \{j-1,j+1\}. \tag{3.120}$$

Assume now that the parameters R and ω_l fulfill

$$R^2\ll\frac{1}{\omega_\mathrm{l}} \tag{3.121}$$

such that for $T\in[R^2,\frac{1}{\omega}]$, $R^2\ll T\ll\frac{1}{\omega_\mathrm{l}}$

$$j_0\left(\frac{r'x}{\tau}\right)j_{\ell>0}(|k'|x) \simeq \Theta(\tau-T)j_{\ell>0}(|k'|x) \tag{3.122}$$
$$j_{m>0}\left(\frac{r'x}{\tau}\right)j_{\ell>0}(|k'|x) \simeq 0.$$

Therefore only $m = 0$ will lead to a non-vanishing contribution:

$$\begin{pmatrix} k & 0 & j \\ 0 & 0 & 0 \end{pmatrix}^2 \quad \rightarrow \quad k = j, \tag{3.123}$$

$$\begin{pmatrix} \ell & k \pm 1 & 0 \\ 0 & 0 & 0 \end{pmatrix}^2 \quad \rightarrow \quad \ell = k \pm 1.$$

With this choice of parameters, i.e., $R^2 \ll T \ll \frac{1}{\omega_l}$ and $\tau > T$

$$\exp\left(i\frac{r'^2}{2\tau}\right) \simeq 1 \simeq \exp\left(i\frac{x^2}{2\tau}\right) \tag{3.124}$$

and owing to the localized orbital around $r' = R$ we can set

$$\frac{r'_<}{r'^2_>}Y_{1,0}(\theta, \varphi) \sim \sqrt{\frac{3}{4\pi}}\frac{r'}{R^3}z. \tag{3.125}$$

Collecting all this we find with

$$\kappa_1(\tau, k') := \int dr\, r^2 \phi_0(r) \left(i^{(k-1)}\sqrt{2(k-1)+1}\begin{pmatrix} 1 & k & (k-1) \\ 0 & 0 & 0 \end{pmatrix}^2\right.$$
$$\times j_{k-1}(|k'|r) + "(k-1) \leftrightarrow (k+1)") \tag{3.126}$$

and

$$\kappa_2(\tau, \widetilde{k}) := \int dr\, r^2 \phi_0^*(r) \left(-i^{(k-1)}(2(k-1)+1)\begin{pmatrix} 1 & k & (k-1) \\ 0 & 0 & 0 \end{pmatrix}^2\right.$$
$$\times j_{k-1}(|\widetilde{k}|r) + "(k-1) \leftrightarrow (k+1)") \tag{3.127}$$

$$\delta v(\boldsymbol{r}, t) \sim -\frac{2k+1}{\pi^2}\Re\left\{i\int_0^t d\tau\, \Theta(\tau - T)f(t, \tau)\kappa_1(\tau, k')\kappa_2(\tau, \widetilde{k})\right\}\frac{z}{R^3}. \tag{3.128}$$

As we have $f(t, \tau)\kappa_1(\tau, k')\kappa_2(\tau, \widetilde{k}) \simeq \kappa^{\mathrm{SFA}}(t, \tau)$, the standard strong field approximation integrand for high-order harmonic generation, we can rewrite

$$\delta v(\boldsymbol{r}, t) \sim -\frac{2k+1}{\pi^2}\Re\left\{i\int_0^t d\tau\, \Theta(\tau - T)\kappa^{\mathrm{SFA}}(t, \tau)\right\}\frac{z}{R^3}.$$

Note that due to the behavior of the spherical Bessel functions $\kappa^{\mathrm{SFA}}(t, \tau) \rightarrow 0$ for $\widehat{A}R \ll 1$. This is just the physical condition that the deBroglie-wavelength becomes too long to disturb the system as a whole. This approximation should work well even for $R^2 \sim \frac{1}{\omega}$, leading to

$$d_z(\omega) \sim -D(\omega)\frac{2k+1}{\pi^2 R^3}\mathcal{F}\left\{\Re\left[i\int d\tau\, \Theta(\tau - T)\kappa^{\mathrm{SFA}}(t, \tau)\right]\right\}. \tag{3.129}$$

Finally we may **approximate**

$$d_z(\omega) \sim D(\omega)\frac{3}{R^3}d_z^{(L)}(\omega), \tag{3.130}$$

in accordance to the afore deduced strong field approximation model including recollision-induced collective excitations of subsection 3.2.5. Note that the dipole spectrum is proportional to $|d_z(\omega)|^2$. Hence, for the **ratio of collective to single active electron high-order harmonic generation efficiency** we obtain

$$\boxed{\frac{|d_z(\omega)|^2}{|d_z^{(L)}(\omega)|} \equiv \frac{|M_{\mathrm{coll}}|^2}{|M_{\mathrm{SAE}}(\omega)|^2} \simeq \left|D(\omega)\frac{3}{R^3}\right|^2}, \tag{3.131}$$

where $D(\omega)$ is the normalized dipole response of the system (3.99). This generalizes the result of subsection 3.2.5. Accordingly, the ratio can be of the order of one or even higher. However, again the ratio (3.131) **does not depend on the laser parameters anymore** whereas in our full time-dependent density functional theory results we observe a wavelength-dependent relative efficiency of the plasmon enhancements.

Conclusion and Outlook

In conclusion, we presented an ab initio approach to time-dependent density functional theory. We defined the set of v-representable densities and the associated external potentials and gave simple conditions for the existence of the different orders of the Taylor expansions of the densities as well as the external potentials. With this knowledge we stated a rigorous formulation of the extended Runge-Gross theorem. A formal definition of "quantum memory" in terms of functional derivatives was given. The question of functional differentiability of the potential-mapping was found to be connected with the properties of the set of possible density variations. The possibility of an ab initio time-local approximation for the exact exchange-correlation potential was discussed. In particular we found the potentials to be independent of previous densities and of the initial state if the associated wavefunctions were expressible in terms of the instantaneous density and their time-derivatives.

After an introduction into intense laser-matter interaction we studied the problem of resonant dynamics from a density functional point of view. We found for a simple adiabatic approximation the dipole of the Kohn-Sham system to exhibit Rabi-like oscillations. Nevertheless, the density-dynamics of the population transfer were not well reproduced. We could attribute this behavior to a classical effect and argued that only a proper inclusion of correlation and nonadiabatic effects should be able to describe the Rabi density-dynamics. Furthermore, any few-level approximation was found to be in conflict with the very basis of time-dependent density functional theory. Finally, we applied the Kohn-Sham-scheme to C_{60} subject to an intense laser pulse far off-resonant with respect to the collective modes. A strong enhancement of the harmonic radiation at the plasmon resonances and an extension of the usual cut-off was observed. We attributed the enhancement to recollision-induced plasmon excitation, followed by emission. The contribution of recollision-induced plasmon emission to the usual harmonic radiation becomes smaller for longer wavelengths, i.e., the efficiency for this recollision process drops faster than for the recollision process responsible for high-order harmonic generation. In order to predict the relative efficiency we developed two simple analytical models in the spirit of the strong field approximation.

Future work: We have found that the initial state dependence of the mapping vanishes if the mapping depends locally on the density. The question arises whether the opposite conclusion is also valid. The implementation of the Kohn-Sham scheme as an iteration scheme and the associated convergence properties also pose an interesting challenge. Additionally, the developement of an exchange-correlation potential

capable of reproducing the density-dynamics of Rabi oscillations will be pursued. In time-independent systems one uses ensemble density functional theory to find the excited state densities and the excitation energies. This concept may be useful for the description of resonant dynamics in time-dependent density functional theory. Furthermore, it is known that several excited states can be described by the ground-state energy functional. It is assumed that the corresponding Kohn-Sham scheme may generate in addition to these physical excited state densities also unphysical self-consistent solutions. This can be investigated with the help of our one-dimensional helium model system.

Appendix A

Asymptotically Expanded Potential Variation

We apply an **asymptotic expansion for the r'-integration** of equation (3.109) of subsection 3.2.6. If we want to use the saddle-point approximation we have to make sure that the integrand is at least one-time differentiable. However, in this case, due to $\frac{r'^i_<}{r'^{i+1}_>}$, the integrand is not differentiable at $r = r'$.

In order to **properly define the asymptotic expansion** of equation (3.109), we assume the order of integration to be interchangeable and the $\boldsymbol{x}$-integration is left unevaluated. Further we divide the regions of the r'-integration into $\mathcal{D}_A := \{\boldsymbol{r}'|r' \leq r\}$ and $\mathcal{D}_B := \{\boldsymbol{r}'|r' > r\}$, in which the integrand will be differentiable, leading to

$$
\begin{aligned}
I(r) &= \int d^3r' e^{-\mathrm{i}\widetilde{S}(\boldsymbol{r}',\boldsymbol{x})} g_0(r,\boldsymbol{r}',\boldsymbol{x},t,\tau) \qquad\qquad\text{(A.1)} \\
&= I^A(r) + I^B(r),
\end{aligned}
$$

with $g_0(r,\boldsymbol{r}',\boldsymbol{x},t,\tau)$ the remaining integrand and $I^{A,B}(r)$ integrals over the regions $\mathcal{D}_A$ and $\mathcal{D}_B$, respectively. The region $\mathcal{D}_A$ is bound by $\partial\mathcal{D}_A := \{\boldsymbol{r}'|r' = r\} = S^2(r)$, the sphere of radius r. Region $\mathcal{D}_B$ has the same boundary but is not bound from above as $r' \to \infty$. Nevertheless we can assume $\mathcal{D}_B$ to be bound. As the integrand goes to zero for large values of r' we can choose an outer boundary $\partial\mathcal{D}_{B,\text{out}}$ which will not contribute to the asymptotic expansion and thus may be neglected.

Critical points beside the saddle-point $\boldsymbol{r}'_s = \boldsymbol{x} + \tau\widetilde{\boldsymbol{k}}(t-\tau)$ are the points on the boundary $\partial\mathcal{D}_A$. Note that the saddle-point may also lie on $\partial\mathcal{D}_A$ itself. With this we find the following possible cases:

1. saddle-point in $\mathcal{D}_A$ and boundary-critical points from $\mathcal{D}_A$ and $\mathcal{D}_B$,

2. saddle-point in $\mathcal{D}_B$ and boundary-critical points from $\mathcal{D}_A$ and $\mathcal{D}_B$,

3. saddle-point on the boundary $\partial\mathcal{D}_A$.

APPENDIX A: Asymptotically Expanded Potential Variation

From [93] we know that the contribution of a saddle-point lying in the interior in leading order is

$$I_0^{A,B}(r) \sim (\mathrm{i}2\pi\tau)^{\frac{3}{2}} g_0(r, \boldsymbol{r}'_s, \boldsymbol{x}, t, \tau) e^{-\mathrm{i}\widetilde{S}(\boldsymbol{r}'_s, \boldsymbol{x})}. \tag{A.2}$$

If the saddle-point is on the boundary between the two regions its contribution is

$$I_{\partial\mathcal{D}_A,s}^{A,B}(r) \sim \frac{1}{2}(\mathrm{i}2\pi\tau)^{\frac{3}{2}} g_0(r, \boldsymbol{r}'_s, \boldsymbol{x}, t, \tau) e^{-\mathrm{i}\widetilde{S}(\boldsymbol{r}'_s, \boldsymbol{x})}. \tag{A.3}$$

For the boundary-critical terms from region $\mathcal{D}_A$ and $\partial\mathcal{D}_A$ we have to define a parametric representation of the boundary itself:

$$\sigma : \mathcal{P} := [0, \pi[\times[0, 2\pi[\quad \rightarrow \quad S^2(r) \tag{A.4}$$
$$(\Theta, \phi) \quad \mapsto \quad \boldsymbol{r}'(\Theta, \phi). \tag{A.5}$$

With σ we can define the 3×2 Jacobian matrix $\mathcal{J} := \frac{\partial r_i}{\partial \sigma_j}$ and the determinant

$$W := \left|\det(\mathcal{J}^T \mathcal{J})\right|^{\frac{1}{2}}, \tag{A.6}$$

where $\mathcal{J}^T$ is the transposed matrix. Further $\vartheta(\sigma) := \widetilde{S}(\boldsymbol{r}'(\sigma), \boldsymbol{x})$ and

$$\boldsymbol{H}_0 := g_0(\boldsymbol{r}', \boldsymbol{r}, t, \tau) \frac{\boldsymbol{\nabla}'\widetilde{S}}{|\boldsymbol{\nabla}'\widetilde{S}|^2}. \tag{A.7}$$

The outward pointing unit normal vector on the boundary $\partial\mathcal{D}_A$ is different for both regions:

$$\boldsymbol{N}^A = -\boldsymbol{N}^B. \tag{A.8}$$

The boundary contribution in leading order is

$$I_{\partial\mathcal{D}_A}^A(r) \sim -\mathrm{i} \int_{\mathcal{P}} \left(\boldsymbol{H}_0 \cdot \boldsymbol{N}^A\right) W e^{-\mathrm{i}\vartheta(\sigma)} d\sigma \sim -I_{\partial\mathcal{D}_A}^B(r). \tag{A.9}$$

If we collect all contributions for the different cases we obtain

1. $I(r) \sim I_0^A(r) + I_{\partial\mathcal{D}_A}^A(r) + I_{\partial\mathcal{D}_A}^B(r)$,

2. $I(r) \sim I_0^B(r) + I_{\partial\mathcal{D}_A}^A(r) + I_{\partial\mathcal{D}_A}^B(r)$,

3. $I(r) \sim I_{\partial\mathcal{D}_A,s}^A(r) + I_{\partial\mathcal{D}_A,s}^B(r)$.

Thus regardless of the position of the saddle-point the integral is asymptotically approximated by

$$I(r) \sim (\mathrm{i}2\pi\tau)^{\frac{3}{2}} g_0(r, \boldsymbol{r}'_s, \boldsymbol{x}, t, \tau) e^{-\mathrm{i}\widetilde{S}(\boldsymbol{r}'_s, \boldsymbol{x})}, \tag{A.10}$$

which is just the standard saddle-point approximation expression.

Therefore with

$$\boldsymbol{\nabla}_{r'}\widetilde{S}(\boldsymbol{r}',\boldsymbol{x}) \;:=\; \boldsymbol{\nabla}'\left(\widetilde{\boldsymbol{k}}(t,\tau)\cdot\boldsymbol{r}' - \frac{r'^2}{2\tau} + \frac{\boldsymbol{x}\cdot\boldsymbol{r}'}{\tau}\right) = 0$$

$$\Rightarrow \boldsymbol{r}'_s \;=\; \boldsymbol{x} + \tau\widetilde{\boldsymbol{k}}(t,\tau) := \boldsymbol{x}' \tag{A.11}$$

and $\det(\partial_i'\partial_j'\widetilde{S}(\boldsymbol{r}')) = -(1/\tau)^3 \neq 0$ we find

$$\delta v(\boldsymbol{r},t) \;\sim\; -4\pi\sum_{i,j}\frac{Y_{i,j}(\boldsymbol{r})}{2i+1}\Re\left\{\mathrm{i}\int_0^t d\tau(2\pi\mathrm{i}\tau)^{\frac{3}{2}}f(t,\tau)\right. \tag{A.12}$$

$$\left.\times\int d^3x Y_{i,j}^*(\boldsymbol{x}')\psi_0^*(\boldsymbol{x}')\frac{x_<'^i}{x_>'^{i+1}}\frac{e^{-\mathrm{i}\widetilde{\boldsymbol{k}}\cdot\boldsymbol{x}'}}{(2\pi)^{3/2}}e^{\mathrm{i}\frac{\boldsymbol{x}'^2}{2\tau}}e^{-\mathrm{i}\frac{\boldsymbol{x}'\cdot\boldsymbol{x}}{\tau}}\frac{e^{\mathrm{i}\boldsymbol{k}'\cdot\boldsymbol{x}}}{(2\pi)^{3/2}}e^{-\mathrm{i}\frac{\boldsymbol{x}^2}{2\tau}}z\psi_0(x)\right\}.$$

Here we have used $\boldsymbol{k}' = \boldsymbol{k}(t,\tau) + \boldsymbol{A}(t-\tau)$. If we want to make use of the properties of the spherical harmonics involved in the $\boldsymbol{x}$-integration we first have to note that the first two spherical harmonics $Y_{i,j}^*(\boldsymbol{x}')Y_{k,0}(\boldsymbol{x}')$, where the second is due to the assumed form of our initial orbital, are displaced with regard to the integration variable $\boldsymbol{x}$. The displacement of a spherical harmonic due to a coordinate change

$$\boldsymbol{x}' = \boldsymbol{x} - \boldsymbol{q} \tag{A.13}$$

with $\boldsymbol{q} = \boldsymbol{q}(q,\Theta,\Phi)$ can be rewritten as [94]

$$Y_{\ell'm'}\left[\boldsymbol{x}'(x',\theta',\varphi')\right] \tag{A.14}$$

$$= \sum_{\ell=0}^{\ell'}(-1)^{\ell'+1}\left[\frac{4\pi(2\ell+1)(2\ell'-2\ell+1)}{2\ell'+1}\right]^{\frac{1}{2}}\left(\frac{q}{x'}\right)^{\ell'}\left(\frac{x}{q}\right)^{\ell}\{Y_\ell(\theta,\varphi)\otimes Y_{\ell'-\ell}(\Theta,\Phi)\}_{\ell'm'}.$$

The irreducible tensor product $\{Y_\ell(\theta,\varphi)\otimes Y_{\ell'-\ell}(\Theta,\Phi)\}_{\ell'm'}$ is defined via the Wigner 3j-symbols $\left(\begin{smallmatrix}\ell_1\,\ell_2\,\ell_3\\m_1m_2m_3\end{smallmatrix}\right)$

$$\{Y_\ell(\theta,\varphi)\otimes Y_{\ell'-\ell}(\Theta,\Phi)\}_{\ell'm'} := \tag{A.15}$$

$$\sum_{M_1M_2}(-1)^{2\ell-\ell'+m'}\sqrt{2\ell'+1}\begin{pmatrix}\ell\;(\ell'-\ell)\;\ell'\\M_1\;M_2\;m'\end{pmatrix}Y_{\ell M_1}(\theta,\varphi)Y_{(\ell-\ell')M_2}(\Theta,\Phi).$$

As we have a translation in z-direction we find with $\Theta \equiv 0$

$$q = -\widetilde{k}\tau, \quad r_s = x' = \left(x^2 + \widetilde{k}^2\tau^2 + 2x\widetilde{k}\tau\cos\theta\right)^{\frac{1}{2}}. \tag{A.16}$$

In order to use the spherical harmonics we will introduce a further approximation. As we have assumed a well localized wavefunction at $x = R > 1$ for ϕ_0 the main contribution for $\widetilde{k}\tau < R$ to x' will be due to x^2 and for $\widetilde{k}\tau > R$ will be $\widetilde{k}\tau$ itself. Thus we will further use

$$x' \simeq \left(x^2 + \widetilde{k}^2\tau^2\right)^{\frac{1}{2}}. \tag{A.17}$$

137

With the condition $m_1 + m_2 = -m_3$ of the Wigner 3j-symbols and the knowledge that a spherical harmonic equals zero for $\Theta \equiv 0$ if $M_2 \neq 0$ we find

$$
\begin{aligned}
Y^*_{i,j}(\boldsymbol{x}') \; \simeq \; & \sum_{a=0}^{i} (-1)^{2a+1} \sqrt{4\pi(2a+1)(2i-2a+1)} \left(\frac{q}{x'}\right)^i \\
& \times \left(\frac{x}{q}\right)^a \begin{pmatrix} i \; a \; (i-a) \\ -j \; j \; 0 \end{pmatrix} Y_{a,j}(\theta,\varphi) Y_{(i-a),0}(0)
\end{aligned} \tag{A.18}
$$

and

$$
\begin{aligned}
Y_{k,0}(\boldsymbol{x}') \; \simeq \; & \sum_{b=0}^{i} (-1)^{2b+1} \sqrt{4\pi(2b+1)(2k-2b+1)} \left(\frac{q}{x'}\right)^k \\
& \times \left(\frac{x}{q}\right)^b \begin{pmatrix} k \; b \; (k-b) \\ 0 \; 0 \; 0 \end{pmatrix} Y_{b,0}(\theta,\varphi) Y_{(k-b),0}(0).
\end{aligned} \tag{A.19}
$$

Now we have expressed the translated spherical harmonics in terms of the integration variable $\boldsymbol{x}(x,\theta,\varphi)$. Turning to the angular integration in spherical coordinates with the measure $d\Omega = d\varphi d\theta \sin\theta$ we find via the spherical Bessel functions $j_e(x)$

$$
e^{i(\boldsymbol{A}(t)-\boldsymbol{A}(t-\tau))\cdot\boldsymbol{x}} \; = \; \sum_{e=0}^{\infty} i^e \sqrt{4\pi(2e+1)} j_e(|\boldsymbol{A}(t)-\boldsymbol{A}(t-\tau)|x) Y_{e,0}(\theta,\varphi) \tag{A.20}
$$

and

$$
z = 2\sqrt{\frac{\pi}{3}} Y_{1,0}(\theta,\varphi)x \tag{A.21}
$$

the integral

$$
\int d\Omega Y_{a,j}(\theta,\varphi) Y_{b,0}(\theta,\varphi) Y_{1,0}(\theta,\varphi) Y_{k,0}(\theta,\varphi) Y_{e,0}(\theta,\varphi) \tag{A.22}
$$

$$
= \sum_{c,d=0}^{\infty} \frac{(2c+1)(2d+1)}{4\pi} \sqrt{3(2b+1)(2e+1)(2k+1)} \begin{pmatrix} 1 \; c \; k \\ 0 \; 0 \; 0 \end{pmatrix}^2 \begin{pmatrix} b \; d \; e \\ 0 \; 0 \; 0 \end{pmatrix}^2 \begin{pmatrix} a \; c \; d \\ 0 \; 0 \; 0 \end{pmatrix}^2 \delta_{j,0}.
$$

Using the Wigner 3j-symbols one can reduce the infinite series expansions of equation (A.12)-(A.22) to finite ones, leading altogether to

$$
\begin{aligned}
\delta v(\boldsymbol{r}t) \sim & -8\pi \sum_{i=1}^{\infty}\sum_{a=0}^{i}\sum_{b=0}^{k}\sum_{c=k-1}^{k+1}\sum_{d=a-c}^{a+c}\sum_{e=b-d}^{b+d} \\
& \frac{\sqrt{(2a+1)(2i-2a+1)(2k-2b+1)(2k+1)}}{2i+1} \\
& Y_{(i-a),0}(0)Y_{(k-b),0}(0)(2b+1)(2c+1)(2d+1) \\
& (2e+1)Y_{i,0}(\boldsymbol{r})\Re\left\{ \mathrm{i}\int_0^t d\tau f(t,\tau)(2\pi\mathrm{i}\tau)^{\frac{3}{2}}e^{-\mathrm{i}\frac{\hat{k}^2\tau}{2}} \right. \\
& \left[\int_0^{\infty} dx x\frac{x_<'^i}{x_>'^{i+1}}\phi_0^*(x')e^{-\mathrm{i}\frac{x^2}{\tau}}\left(\frac{q}{x'}\right)^{i+k+1}\right. \\
& \left.\left(\frac{x}{q}\right)^{a+b+1}\phi_0(x)j_e(|\boldsymbol{A}(t)-\boldsymbol{A}(t-\tau)|x)\right] \\
& \begin{pmatrix} i\ a\ (i-a) \\ -j\ \ j\ \ 0 \end{pmatrix}\begin{pmatrix} k\ b\ (k-b) \\ 0\ \ 0\ \ 0 \end{pmatrix}\begin{pmatrix} a\ c\ d \\ 0\ 0\ 0 \end{pmatrix}^2\begin{pmatrix} 1\ c\ k \\ 0\ 0\ 0 \end{pmatrix}^2 \\
& \left.\begin{pmatrix} b\ d\ e \\ 0\ 0\ 0 \end{pmatrix}^2\right\}.
\end{aligned}
\tag{A.23}
$$

The dipole term is the most important one for the recollision induced plasmon emission process. Thus we find, for instance, in the case of $\psi_0(\boldsymbol{x}) = \frac{\phi_0(x)}{x}Y_{0,0}(\theta,\phi)$ the **simple approximation**

$$
\begin{aligned}
\delta v(\boldsymbol{r}t) \sim & -\sqrt{\frac{1}{\pi}}z\Re\left\{ \int_0^t d\tau\left(\frac{\mathrm{i}\tau}{2\pi}\right)^{\frac{3}{2}}f(t,\tau)e^{-\frac{\mathrm{i}}{2}\tilde{k}^2\tau} \right. \\
& \left[\int_0^{\infty} dx\frac{x_<'}{x_>'^2}\frac{\phi_0^*(x')}{R}\frac{x^2}{x'^2}e^{-\mathrm{i}\frac{x^2}{\tau}}\phi_0(x)\right. \\
& \left(\tilde{k}(t,\tau)j_1(|A(t)-A(t-\tau)|x)\right. \\
& -\frac{1}{3}xj_0(|A(t)-A(t-\tau)|x) \\
& \left.\left.\left.-\frac{2}{3}xj_2(|A(t)-A(t-\tau)|x)\right)\right]\right\}
\end{aligned}
\tag{A.24}
$$

so that with equation (3.99) and the Fourier transform of the above expression

$$
d_z(\omega) \sim D(\omega)\delta v(\omega).
\tag{A.25}
$$

Although the asymptotically approximated potential variation (A.23) is in principle more general then the approximation (3.129) it does not lead to a simple and intuitive ratio of the collective to the single active electron high-order harmonic generation efficiency similar to (3.131).

Bibliography

[1] W. Kohn, Rev. Mod. Phys **71**, 1253 (1999)

[2] M.O. Scully and M. Suhail Zubairy, *Quantum Optics*, (Cambridge University Press, 2001)

[3] D. Bauer, *Intense laser-field induced multiphoton processes in single- and many-electron systems*, (Habilitationsschrift, TU Darmstadt, 2002)

[4] L.V. Keldysh, Zh. Eksp. Teor. Fiz **47**, 1945 (1964)

[5] F.H.M. Faisal, J. Phys. B: Atom. Molec. Phys. **6**, L89 (1973)

[6] H.R. Reiss, Phys. Rev. A **22**, 1786 (1980)

[7] M. Lewenstein, Ph. Balcou, M.Yu. Ivanov, Anne L'Huillier and P.B. Corkum, Phys. Rev. A **49** 2117

[8] A. Becker and F.H.M. Faisal, J. Phys. B: At. Mol. Opt. Phys **38** R1 (2005)

[9] R.M. Dreizler and E.K.U. Gross, *Density Functional Theory - An Approach to the Quantum Many-Body Problem*, (Springer, Berlin Heidelberg, 1990)

[10] E. Runge and E.K.U. Gross, Phys. Rev. Lett. **52**, 997 (1984)

[11] M.A.L. Marques *et al.*, *Time-Dependent Density Functional Theory*, Lect. Notes Phys. **706** (Springer, Heidelberg, 2006)

[12] R. van Leeuwen, Int. J. Mod. Phys. B **15**, 1969 (2001)

[13] N.T. Maitra, K. Burke and C. Woodward, Phys. Rev. Lett. **89**, 023002 (2002)

[14] M. Lein and S. Kümmel, Phys. Rev. Lett. **94**, 143003 (2005)

[15] M. Thiele, E.K.U. Gross and S. Kümmel, Phys. Rev. Lett **100**, 153004 (2008)

[16] P. Coleman, Ann. Henri Poincare **4**, 1 (2003)

[17] D.N. Fittinghoff, P.R. Bolton, B. Chang and K.C. Kulander, Phys. Rev. Lett. **69**, 2642 (1992)

[18] W. Nolting, *Viel-Teilchen-Theorie*, 5.Auflage, (Springer, Berlin Heidelberg, 2002).

[19] H. Haken, *Quantenfeldtheorie des Festkoerpers* (B.G. Teubner, Stuttgart, 1973)

[20] I.V. Tokatly, Phys. Rev. B **71**, 165104 (2005)

[21] I.V. Tokatly, Phys. Rev. B **71**, 165105 (2005)

[22] P.C. Martin and J. Schwinger, Rhys. Rev. **115**, 1342 (1959)

[23] R. van Leeuwen, Phys. Rev. Lett. **82**, 3863 (1999)

[24] D. Werner, *Funktionalanalysis*, (Springer, Berlin Heidelberg, 2000)

[25] M.M. Vainberg, *Variational Methods for the Study of Nonlinear Operators*, (Holden-Day, Inc., San Francisco London Amsterdam, 1964)

[26] P. Blanchard and E. Bruening, *Mathematical Methods in Physics: Distributions, Hilbert Space Operators and Variational Methods*, (Birkhaeuser Bosten, 2003)

[27] L.H. Thomas, Proc. Cambridge Phil. Soc. **23**, 542 (1927)

[28] E. Fermi, Rend. Accad. Naz. Linzei **6**, 602 (1927)

[29] P. Hohenberg and W. Kohn, Phys. Rev. **136B**, 864 (1964)

[30] E.H. Lieb, Int. J. Quant. Chem. **24**, 243 (1983)

[31] H. Englisch and R. Englisch, Phys. Stat. Sol (b) **124**, 373 (1984)

[32] G. Hellwig, *Differentialoperatoren der mathematischen Physik*, (Springer, Berlin, Heidelberg 1964)

[33] J.E. Harriman, Phys. Rev. A **24**, 680 (1981)

[34] N.T. Maitra, Int. J. Quant. Chem **102**, 573 (2005)

[35] R. van Leeuwen, Phys. Rev. Lett. **80**, 1280 (1998)

[36] N.D. Mermin, Phys. Rev **137**, A1441 (1965)

[37] G. Vignale, Phys. Rev. A **77**, 062511 (2008)

[38] B.A. Dubrovin, A.T. Fomenko and S. P. Novikov *Modern Geometry I*, (Springer, Berlin, Heidelberg, 1984)

[39] C.A. Ullrich and I.V. Tokatly, Phys. Rev. B **73**, 235102 (2006)

[40] J. B. Krieger, Y. Li and G. J. Iafrate, Phys. Rev. A **45**, 101 (1992)

[41] P.W. Payne, J. Chem. Phys. **71**, 490 (1979)

[42] R. van Leeuwen, *Private Communication* (2008)

[43] K. Kreutz-Delgado, *The Complex Gradient Operator and the $\mathbb{CR}$-Calculus*, (ECE275A-Lecture Supplement-Fall 2006, Version ECE275CG-F05v1.3d)

[44] J. Schirmer and A. Dreuw, Phys. Rev. A **75**, 022513 (2007)

[45] J. Schirmer and A. Dreuw, Phys. Rev. A **78**, 056502 (2008)

[46] N.T. Maitra, R. van Leeuwen and K. Burke, Phys. Rev. A **78**, 056501 (2008)

[47] H.O. Wijewardane and C.A. Ullrich, Phys. Rev. Lett. **100**, 056404 (2008)

[48] T. Brabec and F. Krausz, Rev. Mod. Phys. **72**, 545 (2000)

[49] P. Agostini and L.F. DiMauro, Rep. Prog. Phys. **67**, 813 (2004).

[50] F. Krausz and M. Ivanov, Rev. Mod. Phys. **81**, 163 (2009)

[51] M. Protopapas, C.H. Keitel and P.L. Knight, Rep. Prog. Phys **60**, 389 (1997)

[52] D.B. Milošević, G.G. Paulus, D. Bauer, and W. Becker, J. Phys. B: At. Mol. Opt. Phys. **39**, R203 (2006).

[53] D. Bauer, D.B. Milosevic and W. Becker, J. Mod. Opt **53**, 135 (2006)

[54] D. Bauer, Phys. Rev. Lett. **94**, 113001 (2005)

[55] J. Itatani, J. Levesque, D. Zeidler, Hiromichi Niikura, H. Pépin, J.C. Kieffer, P.B. Corkum, D.M. Villeneuve, Nature **432**, 867 (2004).

[56] M. Lein, J. Phys. B: At. Mol. Opt. Phys. **40**, R135 (2007).

[57] A. Becker and F.H.M. Faisal, Phys. Rev. A **59**, R1742 (1999),: A. Becker, R. Dörner and R. Moshammer, J. Phys. B **38**, S753 (2005)

[58] F.H.M. Faisal, *Theory of Multiphoton Processes*, (Plenum, New York, 1987)

[59] P.L. Knight and P.W. Milonni, Phys. Rep. **66**, 21 (1980)

[60] R. Loudon, *The Quantum Theory of Light*, (Clarendon Press, 1985)

[61] D. Bauer, D.B. Milosevic and W. Becker, Phys. Rev. A **72**, 023415 (2005)

[62] W. Becker *et al.*, Phys. Rev. A **56**, 645 (1996)

[63] D. Zwillinger, *Handbook of Differential Equations*, (Academic Press, San Diego, 1998)

[64] G. Vignale, Phys. Rev. B **70**, 201102 (2004)

[65] M. Lein and S. Kümmel, Phys. Rev. Lett. **94**, 143003 (2005)

[66] F. Wilken and D. Bauer, Phys. Rev. Lett. **97**, 203001 (2006)

[67] F. Wilken and D. Bauer, Phys. Rev. A **76**, 023409 (2007)

[68] J. P. Perdew and M. Levy, Phys. Rev. B **31**, 6264 (1985)

[69] N. Hadjisavvas and A. Theophilou, Phys. Rev. A **32**, 720 (1985)

[70] E.K.U. Gross, L.N. Oliveira and W. Kohn, Phys. Rev. A **37**, 2805 (1988)

[71] E.K.U. Gross, L.N. Oliveira and W. Kohn, Phys. Rev. A **37**, 2809 (1988)

[72] L.N. Oliveira, E.K.U. Gross and W. Kohn, Phys. Rev. A **37**, 2821 (1988)

[73] See, e.g., R. Grobe and J.H. Eberly, Phys. Rev. Lett. **68**, 2905 (1992); S.L. Haan, R. Grobe, and J.H. Eberly, Phys. Rev. A **50**, 378 (1994); D. Bauer, Phys. Rev. A **56**, 3028 (1997); D.G. Lappas and R. van Leeuwen, J. Phys. B: At. Mol. Opt. Phys. **31**, L249 (1998); M. Lein, E.K.U. Gross, and V. Engel, Phys. Rev. Lett. 8**5**, 4707 (2000).

[74] K. Yabana and G.F. Bertsch, Phys. Rev. B **54**, 4484 (1996)

[75] D. Bauer and P. Koval, Comp. Phys. Comm. **174**, 396 (2006)

[76] N.T. Maitra, F. Zhang and R.J. Cave, J. Chem. Phys **120**, 5932 (2004)

[77] L.D. Landau and E.M. Lifschiz, *Mechanik*, (Akademie Verlag Berlin, 1962)

[78] S.N. Shevchenko, A.N. Omelyanchouk, A.M. Zagoskin, S. Savel'ev and Franco Nori, New J. Phys. **10**, 073026 (2008)

[79] G. Vignale, Phys. Rev. Lett. **74**, 3233 (1995)

[80] P.R. Berman, Am. J. Phys. **42**, 992 (1973)

[81] A. Becker and F.H.M. Faisal, J. Phys. B: At. Mol. Opt. Phys. **38**, R1 (2005).

[82] Serguei Patchkovskii, Zengxiu Zhao, Thomas Brabec, and D.M. Villeneuve, Phys. Rev. Lett **97**, 123003 (2006); J. Chem. Phys. **126**, 114306 (2007).

[83] I.V. Hertel, T. Laarmann, and C.P. Schulz, Adv. At. Mol. Opt. Phys. **50**, 219 2005.

[84] Ihar Shchatsinin, Tim Laarmann, Gero Stibenz, Günter Steinmeyer, Andrei Stalmashonak, Nick Zhavoronkov, Claus Peter Schulz, and Ingolf V. Hertel, J. Chem. Phys. **125**, 194320 (2006).

[85] M.J. Puska and R.M. Nieminen, Phys. Rev. A **47**, 1181 (1993).

[86] D. Bauer, F. Ceccherini, A. Macchi, and F. Cornolti, Phys. Rev. A **64**, 063203 (2001).

[87] J. Zanghellini, Ch. Jungreuthmayer, and T. Brabec, J. Phys. B: At. Mol. Opt. Phys. **39**, 709 (2006).

[88] K. Schiessl, K.L. Ishikawa, E. Persson, and J. Burgdörfer, Phys. Rev. Lett. **99**, 253903 (2007).

[89] M.F. Ciappina, A. Becker, and A. Jaroń-Becker, Phys. Rev. A **76**, 063406 (2007).

[90] W. Becker, S. Long, and J.K. McIver, Phys. Rev. A **50**, 1540 (1994).

[91] Yu.A. Malov and D.F. Zaretsky, Phys. Lett. A **177**, 379 (1993).

[92] U. Kreibig and M. Vollmer, *Optical Properties of Metal Clusters* (Springer, Berlin, 1995).

[93] N. Bleistein and R.A. Handelsman, *Asymptotic Expansions of Integrals*, (Dover, 1986)

[94] D.A. Varshalovich, A.N. Moskalev and V.K. Khersonskii, *Quantum Theory of Angular Momentum*, (World Scientific, Singapore, 1988)

Acknowledgment

Three years, three months and sixteen days. This is the amount of time I came to calculate when thinking about my thesis. However, in best agreement with the theory of relativity, my personal "proper" feeling of time tells me something completely different. Good times go by much faster than bad ones, and I really enjoyed the last years.
Foremost I owe my supervisor **Dieter Bauer** a debt of gratitude. Without his support and counsel this work would not have been possible. Beside his expertise in physics I appreciate most his sense of humor and his encouraging personality.
Further I have to thank my family [**Peter, Maria and Martin Ruggenthaler**]. They were a perpetual source of support and good advice. Especially, I want to thank my girlfriend, **Monika Schachenhofer**, who accepted more inconveniences than anyone else due to my doctoral thesis.

Furthermore:

Sergei Popruzhenko [Extension of the SFA to collective phenomena], Robert van Leeuwen [Foundations of TDDFT], Gebhard Grübl [Introduction to theoretical physics], Univ.-Prof. Dr. Monika Ritsch-Marte [Keeping me in theoretical physics], Adriana Pálffy [PhD-style, English, roommate,...], Markus Penz [English, mathematical questions, InfMathPhys,...], Matthias Ruf [Mathematical questions, die Bettwurst, humor, ...], Bruno Ebner [Mathematical questions, humor, parties,...], Ursula Schachenhofer [Art, culture, parties,...], Stefan Pieper [Lifestyle, the art of humor, Kohlfahrt,...], Rainer Silbernagl [History, law, Avernion,...], Felix Mackenroth [Roommate, humor, coffee,...], Benedikt Wundt [Roleplaying, song of ice and fire, Kohlfahrt extreme,...], Sarah Müller [Cigarettes, philosophy, beer,...], Stephan Schnez [Heidelberg, playstation, beer,...], Henrik Hetzheim [PhD-questions, roleplaying, rides,...], Christian Sternagel [Roleplaying, holidays, books,...], Thomas Sternagel [Roleplaying, holidays, beer,...], Nicola Blassnig [Holidays, die Gottheit, biology,...], Daniel Sürth [Rides home, C&C++, roleplaying,...], Maria Schachenhofer [Elias, Elias, Elias,...], Mario Hechenblaikner [Elias, Elias, Elias,...], Johann, Margret and Clemens Schachenhofer [Hospitality], Philipp Waldburger [Operation dance sensation, roleplaying, beer,...], Stefan Langebner [UNKUMIGM, Vögelebichl, beer,...], RMU Bosra, In Flames.

Erklärung

Diese Arbeit ist von mir selbstständig verfasst worden, und ich habe keine anderen als die angegebenen Quellen und Hilfsmittel benutzt.

Michael Ruggenthaler, März 2009