

A UNIFYING APPROXIMATION SCHEME FOR DENSITY FUNCTIONAL
THEORIES: A FORCE BALANCE BASED APPROACH

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Vorgelegt von:
Mary-Leena Martine Tchenkoue Djouom

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Mary-Leena Tchenkoue

Gutachter der Dissertation:	Prof. Dr. Angel Rubio Dr. Michael Ruggenthaler
Zusammensetzung der Prüfungskommission:	Prof. Dr. Angel Rubio Dr. Michael Ruggenthaler Prof. Dr. Nina Rohringer Prof. Dr. Michael Rübhausen Prof. Dr. Carsten Ullrich
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Leiter des Fachbereichs Physik:	Prof. Dr. Wolfgang Hansen
Dekan der Fakultät MIN:	Prof. Dr. Heinrich Graener

ABSTRACT

First-principle methods as a way of understanding various fundamental phenomena that occur in nature is an active field of research in condensed matter physics and other related fields. There is great interest in the study of how a system or a property changes when an external perturbation is applied to it, say, by switching on a magnetic field or probing the system with a laser. Many successful theoretical developments have been made over the years to specifically treat these different situations. However using one of these theories out of its assigned setting, by construction, does not always guarantee a suitable outcome and some interesting features may not be captured. This is partly due to the approximations that are used in these methods which are geared to only specific external perturbations or properties. It is therefore of importance to have a theory that can, in a consistent way, treat these various settings and allow for the qualitative study of the changes that occur when different external stimuli (magnetic fields, lasers,...) are applied to a system. We propose here such an approach that contains all the ingredients necessary to perform such a qualitative study.

In this thesis we present a unifying scheme to determine exchange correlation potentials in density and current density functional theories including vector potentials. The standard energy-based approach to determine functionals is not used here. Instead this approach relies on the equations of motion of particular current densities and is viable both for the ground state and the time-dependent setting. We aim at directly approximating the density-potential mapping thereby avoiding subtleties that arise from functional differentiability and also the costly optimized effective potential procedure of orbital-dependent energy functionals. We then show that the different density functional theories are connected through these equations of motion and demonstrate this for a local-exchange approximation. We show how these exchange-type approximations reduce to the usual local density approximation in the case of a homogeneous system. We highlight what is not captured when approximations for simple settings are used in more complex ones. In addition, these equations of motion provide a way to numerically construct density-potential mappings for different density functional theories and we show this particularly for a ground state lattice setting including the Peierl's phase.

All these show that this equation-of-motion-based approach bears many interesting advantages and provides a new path for approximations in density functional theories. Moreover, it sets a path for a more complete understanding of the properties of molecules or solids subject to different external stimuli.

ZUSAMMENFASSUNG

Ab-initio Methoden zum Verständnis grundlegender Phänomene, die in der Natur auftreten, sind ein aktives Forschungsfeld in der Festkörperphysik und anderen verwandten Bereichen. Eine der Hauptfragestellungen hierbei ist, wie sich ein System und seine Eigenschaften ändern, wenn sich eine externe Größe ändert, beispielsweise indem ein Magnetfeld eingeschaltet oder das System mit einem Laser getrieben wird. Im Laufe der Jahre wurden viele erfolgreiche Theorien entwickelt, um spezifische solche Situationen zu behandeln. Die Verwendung dieser Theorien in anderen Situationen führt jedoch häufig nicht zu einem zufriedenstellenden Ergebnis, da wichtige Merkmale nicht erfasst werden. Dies ist teilweise auf die Näherungen zurückzuführen, die bei diesen Methoden verwendet werden, und welche nur für spezielle externe Störungen oder spezifische Eigenschaften zulässig sind. Es ist daher wichtig, eine Theorie zu haben, die alle Spezialfälle auf konsistente Art und Weise behandelt. Wir stellen einer Herangehensweise vor, die alle Bestandteile enthält, die zur Durchführung einer solchen qualitativen Studie erforderlich sind.

Wir stellen in dieser Arbeit ein einheitliches Schema von Näherungen zur Bestimmung von Austauschkorrelationspotentialen (einschließlich Vektorpotentialen) in Dichte- und Stromdichtefunktionaltheorien vor. Der standardmäßige energiebasierte Ansatz zur Bestimmung von Funktionalen wird hier nicht verwendet. Stattdessen beruht dieser Ansatz auf den Bewegungsgleichungen bestimmter Stromdichten und ist sowohl für den Grundzustand als auch für die zeitabhängige Situation gültig. In dem Ansatz wollen wir die Dichte-Potential-Abbildung direkt approximieren, wodurch Probleme vermieden werden, die sich aus der funktionalen Differenzierbarkeit ergeben, sowie das kostspielige optimierte effektive Potentialverfahren von orbitalabhängigen Energiefunktionalen. Wir zeigen dann, dass die verschiedenen Dichtefunktionaltheorien durch diese Bewegungsgleichungen verbunden sind, und demonstrieren dies für eine lokale Austauschnäherung. Wir zeigen, wie sich diese Näherungen vom Austauschtyp bei einem homogenen System auf die übliche lokale-Dichte-Näherung reduzieren. Durch das Anwenden dieser komplexeren Näherungen auf einfachere Systeme ergeben sich Effekte, die in den anderen Theorien nicht sichtbar werden. Darüber hinaus bieten diese Bewegungsgleichungen eine Möglichkeit, Dichte-Potential-Abbildungen für verschiedene Dichtefunktionaltheorien numerisch zu untersuchen, und wir zeigen dies insbesondere für ein simplest System realisiert auf einem Gitter im Grundzustand welches eine Peierl-Phase enthält.

All dies zeigt, dass dieser auf Bewegungsgleichungen basierende Ansatz viele interessante Vorteile bietet und einen neuen Weg für Approximationen in Dichtefunktionaltheorien bietet. Darüber hinaus zeigt die neue Näherungstheorie wie

man die Untersuchung von Eigenschaften von Molekülen und Festkörpern unter dem Einfluß von verschiedenen externen Störungen vereinheitlichen kann.

PUBLICATIONS

Some results of the work done during my PhD have been published prior to this thesis. The following research paper is a part of this thesis:

- [1] Mary-Leena M. Tchenkoue, Markus Penz, Iris Theophilou, Michael Ruggenthaler, and Angel Rubio. "Force balance approach for advanced approximations in density functional theories." In: *The Journal of Chemical Physics* 151.15 (2019), p. 154107. DOI: [10.1063/1.5123608](https://doi.org/10.1063/1.5123608).

The following publication is not part of this thesis

- [1] Davis Welakuh, Michael Ruggenthaler, Mary-Leena M. Tchenkoue, Heiko Appel, and Angel Rubio. "Two-photon down conversion in ab-initio non-relativistic electrostatics." In: in preparation ()

Contributions to publications

- [1] M-L. Tchenkoue did the derivations of the work following the ideas discussed with M. Ruggenthaler and A. Rubio. M. Penz, I. Theophilou and M. Ruggenthaler contributed to shape the storyline and prepare a first draft. All authors discussed the results and edited the manuscript.
- [2] Following ideas that arose within discussions together with M. Ruggenthaler H. Appel and A. Rubio, D. Welakuh did the derivations of the work and H. Appel and M-L. Tchenkoue contributed in implementing the work and doing numerical simulations. All authors were resourceful during various discussions on the analytic and numerical problems encountered, discussion of the results and editing of the manuscript. D. Welakuh and M. Ruggenthaler prepared a first draft.

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INTRODUCTION

The electronic many-body problem is ubiquitous in modern quantum physics [1]. It is important for atoms, molecules and materials science and determines many structural, transport, optoelectronic and other important properties of these systems, such as absorption and emission spectra, chemical bonds or their conductive behavior. Yet it is also one of the hardest problems. The reason being that while we have an equation that potentially informs us about all the details of the electronic state of a microscopic system – the interacting multi-electron Schrödinger equation – finding solutions to this equation is extremely hard. Since there are only a handful of analytic solutions known, most famously for the hydrogen atom [2], we have to resort to numerical approaches. However, a straightforward numerical solution is prohibitively expensive. The reason being the so-called “exponential wall” [3], which indicates the exponential increase in dimension of the problem with the number of particles. Since the dimension of the problem correlates with the time it takes a computer to solve the problem, only very small systems can be solved within a reasonable time. The problem gets even harder once we consider explicitly time-dependent problems [4] or systems under influence of magnetic fields [5]. For instance, for strongly driven systems, where perturbation theory is no longer applicable, the solution of the helium atom is already extremely challenging [6, 7]. Therefore many approximation schemes or even full reformulations of the many-electron problem have been developed over the years [8].

Most prominent among these is ground state density functional theory (DFT) [9]. It relies on the fact that the ground state of the interacting multi-electron Schrödinger equation can be found by minimizing the total energy of the system. This minimization, however, can be performed with the density of the total system instead of with the full multi-electron wavefunction [10]. And a minimization with just the density, which corresponds to the locally resolved charge density of the system, can be done numerically very efficiently. The price we pay is that we no longer know the form of the energy expression we need to minimize exactly. Only for specifically simple systems we can express the energy in terms of the density alone. So in general we need to approximate these energy expressions.

The approximation of these energy expressions can be done quite accurately with an idea that Kohn and Sham introduced [11]. Indeed, if we perform the minimization with respect to the density by using the simplest non-trivial wavefunctions – non-interacting Slater determinants – as representatives, we can use the respective non-interacting energy expressions as a first guess. Only small modifications of the non-interacting energy are enough to get reasonable agreements between approximate DFT predictions and experimental values [9]. The solution

of these modified Schrödinger equations – the Kohn-Sham (KS) equations – is numerically feasible for very large systems and hence it became the workhorse of modern electronic structure theory. Yet the most simple of these approximations are also known to have several limitations. This is true especially for strongly correlated systems, that is, the interacting system is very different to a non-interacting system and thus the first guess is quite bad [12]. But also other situations are challenging for simple DFT approximations [13].

Our focus in the following will, however, not be to provide more accurate DFT approximations for the ground state (although we highlight a possible interesting and appealing way in the course of this thesis). Although this is the most important and most widely considered case, there are other interesting situations to which DFT has been extended. It will be the connection between these extensions, approximation schemes within these extensions and also how these approximation schemes are connected. Of these extensions the most important one is time-dependent density functional theory (TDDFT) [14]. Although it formally looks very similar to ground state DFT it is not connected to the minimum energy principle. Instead it rests upon the equation of motion (EOM) of the density and the current density. Nevertheless, using these EOMs we can also recast the time-dependent multi-electron Schrödinger equation in terms of a simplified KS equation and get access to non-equilibrium situations for complex system. To find the form of these effective potentials, we instead of modifying the energy of the non-interacting problem, need to modify the forces of the non-interacting system [15]. Yet this fact is almost never used but instead one adopts approximations from ground state DFT derived from the minimum-energy principle. This procedure – known as the adiabatic approximation – introduces a further level of approximation and the resulting equations are known to have further deficiencies [16]. A different situation is the case of magnetic fields, for which either a static version similar to DFT can be formulated or a time-dependent formulation similar to TDDFT is available. But even in these more involved situations it is mainly the approximations from ground state DFT that are employed, accordingly we expect that they are even less reliable.

In this thesis we want to present a remedy for this situation by introducing a novel approximation scheme that unifies all these different versions of DFT. The main idea is that also for the ground state (with or without the magnetic field) the exact solutions need to fulfill the EOMs of the time-dependent formulations and thus we can use the EOMs to provide approximations. This result highlights that an energy minimum corresponds to a force balance between all the particles. Since we will show that all these different DFTs are connected via the same EOMs, we can connect approximations from different DFTs. We highlight this for a local-exchange approximation, where we use a Slater determinant to approximate the interaction forces. In this way we highlight how DFTs from more complex situations, e.g., including the magnetic field, can be used consistently for simpler situations, e.g., without magnetic field. On the other hand we show what is not

captured when applying approximations from simpler situations to more complex ones. Since we do no longer have an energy expression that we minimize, the proposed local-exchange approximation is not straightforwardly connected to standard energy-based approximations. We, however, demonstrate that it reduces to known approximations for a homogeneous setting. Finally we highlight a further advantage of the EOM-based approach to DFTs. The EOMs allow for a numerical construction of the basic mapping theorems of the different DFT settings. This holds not only for the time-dependent case [15], but we demonstrate that we can also use it as a novel way to investigate the mappings for static situations. We do so specifically in the case of lattice DFTs where there is less knowledge about the existence and properties of these mappings. All of the above shows that EOM-based approaches to DFTs have many appealing advantages and we hope that it provides novel impulses in the ongoing quest for ever more accurate DFT approximations.

THEORETICAL BACKGROUND

In this chapter we introduce the most important situations that describe many-electron systems subject to different electromagnetic fields and their corresponding density-functional reformulations. This builds the basis of our later considerations where we connect all of the different density-functional theories (DFTs) via general equations of motion (EOMs). We divide the chapter into four parts that correspond to different physical situations. The first part (Sec. 2.1) is dedicated to the description of the ground state of many-electron systems, such as atoms and molecules in free space. So the electrons only experience, besides their mutual Coulomb interaction, the attractive scalar potential of the nuclei. This is the most widely investigated situation. We then discuss the Hartree-Fock approximation of the static Schrödinger equation in Sec. 2.1.1 before introducing in detail ground state DFT in Sec. 2.1.2. In the next part (Sec. 2.2) we consider the case when the electronic system is time-dependent and subject to a further general time-dependent scalar potential, such as a laser pulse in dipole approximation. We discuss the time-dependent Schrödinger equation and focus then on its reformulation in terms of TDDFT in Sec. 2.2.1. We then consider the situation where the many-electron system is influenced by a static magnetic field and its new ground state (Sec. 2.3). For this we investigate the static magnetic Schrödinger equation and discuss reformulations based on the current density in Sec. 2.3.1. Finally in Sec. 2.4 we look at the most general case, where a system is perturbed by a general time-dependent electromagnetic field, that is, an atom or molecule that is subject to a time-dependent magnetic and electric field. We consider the time-dependent magnetic Schrödinger equation before talking about its density-functional reformulation in Sec. 2.4.1.

2.1 STATIC SCHRÖDINGER EQUATION

In this section and in the rest of the work we always work within the Born-Oppenheimer approximation [17] and only investigate the electronic properties of microscopic systems for fixed ion positions. That is, we treat the nuclei as classical particles that are clamped, and only the electrons are treated quantum mechanically. We further use atomic units (au) throughout the work ($\hbar = e = m = \frac{4\pi}{\epsilon_0} = 1$ [18]). We here focus on the ground state of microscopic systems in free space and thus the electrons are only subject to the attractive potentials of the (classical) nuclei. The Hamiltonian for this case takes the form

$$\hat{H} = \hat{T} + \hat{V} + \hat{W}. \quad (1)$$

Here,

$$\hat{T} = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 \quad (2)$$

is the kinetic-energy operator of the N electrons and ∇_i is the gradient operator acting on the i th particle coordinate. The external potential due to nuclei is

$$\hat{V} = \sum_{i=1}^N v_{\text{ext}}(\mathbf{r}_i), \quad (3)$$

with $v_{\text{ext}}(\mathbf{r}) = -\sum_{\alpha=1}^M Z_{\alpha} / |\mathbf{R}_{\alpha} - \mathbf{r}|$ and Z_{α} the charge as well as \mathbf{R}_{α} the fixed position of the nucleus α . Finally, the electron-electron interaction energy operator is given by

$$\hat{W} = \frac{1}{2} \sum_{i \neq j} w(|\mathbf{r}_i - \mathbf{r}_j|), \quad (4)$$

where $w(|\mathbf{r}_i - \mathbf{r}_j|) = 1/|\mathbf{r}_i - \mathbf{r}_j|$ is the electrostatic Coulomb interaction.

We then want to find the ground state of the above Hamiltonian, which is the lowest energy eigenstate that fulfills the static Schrödinger equation

$$\hat{H}\Psi_0(\mathbf{r}_1\sigma_1, \dots, \mathbf{r}_N\sigma_N) = E_0\Psi_0(\mathbf{r}_1\sigma_1, \dots, \mathbf{r}_N\sigma_N). \quad (5)$$

Here $\Psi_0(\mathbf{r}_1\sigma_1, \dots, \mathbf{r}_N\sigma_N)$ is an N -electron wavefunction which depends not only on the N particle coordinates but also on the spin $\sigma \in \{\uparrow, \downarrow\}$ of each particle. Since electrons are spin-1/2 particles they are fermions and thus they are described by anti-symmetric wavefunctions [19]. That is, if we exchange two spin-space coordinates $(\mathbf{r}_i\sigma_i) = \mathbf{x}_i \leftrightarrow (\mathbf{r}_j\sigma_j) = \mathbf{x}_j$ then we have

$$\Psi_0(\mathbf{x}_1, \dots, \mathbf{x}_i, \dots, \mathbf{x}_j, \dots, \mathbf{x}_N) = -\Psi_0(\mathbf{x}_1, \dots, \mathbf{x}_j, \dots, \mathbf{x}_i, \dots, \mathbf{x}_N). \quad (6)$$

This implies the Pauli exclusion principle [20]. That is, two electrons cannot occupy the same quantum state. In the following, this symmetry is always implied but we will not always explicitly indicate the dependence on space and spin. To solve Eq. (5) uniquely we need to impose further conditions. Besides the fermionic symmetry we only allow wavefunctions that decay sufficiently fast to infinity, such that they are normalizable. That is, we restrict to wavefunctions Ψ that obey

$$\langle \Psi | \Psi \rangle = \int \Psi^* \Psi d\mathbf{x}_1 d\mathbf{x}_2 \dots d\mathbf{x}_N = 1. \quad (7)$$

Here $\int d\mathbf{x}_1 \dots d\mathbf{x}_N$ implies integration over the $3N$ spatial coordinates and summation over N spin coordinates. Furthermore, the wavefunctions should be well-behaved at every point in space [15]. These conditions allow us by using the definition of expectation values of a Hermitean operator \hat{O}

$$\langle \hat{O} \rangle = \langle \Psi | \hat{O} | \Psi \rangle = \int \Psi^* \hat{O} \Psi d\mathbf{x}_1 \dots d\mathbf{x}_N \quad (8)$$

to find the ground state by the variational principle [2]

$$E_0 = \min_{\Psi} \langle \Psi | \hat{H} | \Psi \rangle. \quad (9)$$

The ground state is therefore the one state that minimizes the expectation value of the total energy operator \hat{H} given in Eq. (1). This result is especially important for the formulation of the static Schrödinger problem in terms of a density-functional theory.

Although in principle we now have everything we need to determine the ground state of a given Hamiltonian, in practice this is a very challenging task. In principle we just need to vary over all wavefunctions that fulfill the above conditions and once we have found the one with the lowest energy, we are done (we exclude here and in the following the possibility of non-normalizable scattering states such as when $v_{\text{ext}}(\mathbf{r}) = 0$). But due to the large dimension of the configuration space ($3N$ from the space coordinates and multiplied by two due to the spin) it becomes very hard to parameterize the many-body wavefunction. The parameters grow exponentially with the number of electrons. This fact is called the "exponential wall" [3] and makes a direct numerical solution of the many-body Schrödinger equation impossible in practice when more than a few electrons are treated. This can already be seen from the sheer size of data that one would need to store. For instance, for $N = 10$ and a small real-space grid (we represent \mathbb{R} by just a few discrete points, say 10) of 10^3 for each particle, we have about 10^{30} numbers to store (ignoring symmetries). This is more than a yotta-byte of data.

However, a number of methods have been devised over the years to tackle this quantum "exponential wall" problem. Here we only look into *ab initio* or *first-principles* methods. For these methods only the fundamental Hamiltonian of the system with physical constants and mathematical principles are used to construct approximations. We do not consider simplified models of the original problem. *Ab initio* methods can be roughly divided into two categories:

1. In a first approach, approximations are made directly at the level of the wavefunction. We will briefly introduce one of these methods, namely *Hartree-Fock theory*, but many other wavefunction methods exist (also for finite systems) such as configuration interaction expansions [21], quantum Monte-Carlo approaches [22–25], many-body perturbation theory [26, 27] and tensor networks [28, 29]. Most of these methods still remain numerically costly and work best for rather small systems.
2. A second approach aims at using an object of much lower-dimension than the wavefunction that still holds all necessary information about the system. In the following, we will consider ground state DFT, which bases everything on the one-particle density. Once more complex situations are investigated, other objects become necessary, e.g., the current for the case of magnetic fields (see Sec. 2.3.1). Other approaches consider from the start more com-

plex objects like the reduced density matrix [9, 30, 31] or the single-particle Green's function [26, 32, 33]

2.1.1 Wavefunction approximations: the Hartree-Fock theory

Let us first consider the simplest wavefunction-based theory, which is called Hartree-Fock theory. Many concepts introduced here will become important later in this thesis. In Hartree-Fock theory [34] the many-body wavefunction Ψ is assumed to be a single Slater determinant of N orthonormal spin orbitals $\phi_i(\mathbf{r}\sigma)$

$$\Phi = \frac{1}{\sqrt{N!}} \det \begin{pmatrix} \phi_1(\mathbf{r}_1\sigma_1) & \dots & \phi_N(\mathbf{r}_1\sigma_1) \\ \vdots & & \vdots \\ \phi_1(\mathbf{r}_N\sigma_N) & \dots & \phi_N(\mathbf{r}_N\sigma_N) \end{pmatrix}. \quad (10)$$

Each spin orbital can be written as a product of a spatial and a spin wavefunction, i.e., $\phi_i(\mathbf{x}) = \phi_i(\mathbf{r})\chi_i(\sigma)$. We will always denote determinantal wavefunctions by Φ to differentiate them from the correlated N -electron wavefunction Ψ . The N spin orbitals are obtained by invoking the variational principle for the ground state (see Eq. (9)) while restricting the form of the wavefunction to a Slater determinant [8]. Therefore by doing this minimization with respect to the spin orbitals, which obey the orthonormalization conditions

$$\int \phi_i^*(\mathbf{x})\phi_j(\mathbf{x})d\mathbf{x} = \delta_{ij}, \quad (11)$$

the many-body problem is reduced to a set of N -coupled non-linear differential equations

$$\hat{F}\phi_i(\mathbf{x}) = \sum_{j=1}^N \epsilon_{ij}\phi_j(\mathbf{x}). \quad (12)$$

The Fock operator \hat{F} is an effective one-electron operator defined as

$$\hat{F} = -\frac{1}{2}\nabla^2 + v_{\text{ext}} + \hat{g}, \quad (13)$$

where the Coulomb-exchange operator $\hat{g}(x_1)$ given by

$$\hat{g} = \hat{j} - \hat{k} \quad (14)$$

represents the average potential which is felt by the i th electron due to the presence of the other electrons. The Hartree and exchange operators are

$$\hat{j}(\mathbf{x}_1)f(\mathbf{x}_1) \equiv \sum_{i=1}^N \int \phi_i^*(\mathbf{x}_2)\phi_i(\mathbf{x}_2) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} f(\mathbf{x}_1) d\mathbf{x}_2, \quad (15)$$

$$\hat{k}(\mathbf{x}_1)f(\mathbf{x}_1) \equiv \sum_{i=1}^N \int \phi_i^*(\mathbf{x}_2)f(\mathbf{x}_2) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \phi_i(\mathbf{x}_1) d\mathbf{x}_2 \quad (16)$$

respectively, where $f(\mathbf{x}_1)$ is an arbitrary function. The Hartree-Fock equations (13) must be solved through an iterative scheme, since the orbitals ϕ_i that are solutions to the problem appear in the Fock operator \hat{F} . This scheme is known as the self-consistent-field (SCF) method [8, 35]. The basic idea behind this scheme is simple: From an initial guess for the spin orbitals, the average potential \hat{g} experienced by each electron is calculated. Then the eigenvalue equation (13) is solved to get a new set of spin orbitals. With these new set of spin orbitals, one calculates again \hat{g} and the procedure is repeated until self-consistency is attained. That is, once we have attained self-consistency \hat{g} does no longer change by the above procedure. The Slater determinant obtained from these spin orbitals is the Hartree-Fock ground-state wavefunction. Every observable of the system can then be obtained as expectation values with respect to this wavefunction.

The Hartree-Fock method is simple, however, the wavefunction does not take into account the correlation resulting from the interaction between electrons. To take the Coulomb correlation into account, one needs to go beyond the single Slater representation. Methods developed to handle this belong to the well known post Hartree-Fock methods [21, 36]. Although present day computation power makes the application of these correlated wavefunction-based *ab initio* methods possible, the algebraic formulation of these various many-body methods formally scale as $\sim M^4$, with M being the number of basis states. While it is difficult to properly assess the exact range of applicability of these methods, some systems of interest will most certainly be beyond their reach.

An entirely different approach with an optimum scaling behaviour is therefore needed to handle large systems. The question is then whether there exists some kind of effective non-interacting approach involving only single-particle operators which could capture the fully interacting many-body problem in a more complete manner, while still accounting for correlation. DFT [9], which is the focus of this thesis, is indeed such an approach.

2.1.2 Density Functional Theory

We saw that the complexity of the wavefunction scales exponentially with the number of electrons. Therefore most systems of interest, since they contain many electrons, will become computationally impossible to treat for wavefunction-based methods. On the other hand, we note that the Hamiltonian \hat{H} consists of one-body (\hat{T}, \hat{V}) or at most two-body (\hat{W}) operators, regardless of the size of the system. Thus one may pose the question whether it is really necessary to use the complicated wavefunction to compute the energy and other properties of the system. Is it possible that the wavefunction contains way more information explicitly than one actually needs such that a less complicated quantity is still sufficient to investigate most properties of the system? This is indeed the case. The one-particle density

$$n_0(\mathbf{r}) = N \int d\mathbf{x}_2 \dots d\mathbf{x}_N \Psi_0^*(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) \Psi_0(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N), \quad (17)$$

where we have summed over all spins and we use also in the following that the first coordinate $\mathbf{x}_1 = (\mathbf{r}\sigma_1)$, is such a quantity. Due to the anti-symmetrization of the wavefunction, all coordinates are equivalent and we use the first one in the following for convenience. Unlike the wavefunction, the density depends only on three coordinates independently of the size (number of electrons) of the system. This makes the density a computationally manageable quantity to use in order to describe a physical system. DFT tells us that the density contains *implicitly* all the information of the many-body wavefunction.

Already before the formal definition of DFT, attempts were made to use the density instead of the wavefunction as a descriptor of many-body systems. The earliest attempts actually date back to works of Thomas and Fermi, 1927 [37, 38]. To briefly introduce their approach we start by stating that, originally, it is a quantum statistical formulation in which only the kinetic energy is taken into account while the nuclear-electron and electron-electron contributions are treated completely classically. With this the Thomas-Fermi model leads to a simple expression for the kinetic energy based on the homogeneous electron gas [9], which is a simple model of a system with constant electron density. Together with the classical expressions for the nuclear-electron and electron-electron contributions, the Thomas-Fermi energy is given as

$$E_{\text{TF}}[n] = \frac{3}{10}(3\pi^2)^{2/3} \int n^{5/3}(\mathbf{r})d\mathbf{r} - Z \int \frac{n(\mathbf{r})}{\mathbf{r}}d\mathbf{r} + \frac{1}{2} \int \int \frac{n(\mathbf{r}_1)n(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}d\mathbf{r}_1d\mathbf{r}_2, \quad (18)$$

where the first term is the Thomas-Fermi kinetic energy $T_{\text{TF}}[n]$. To determine the right density that goes in Eq. (18), the Thomas-Fermi model makes use of the variational principle and minimizes the energy $E_{\text{TF}}[n]$. The accuracy of this model to describe atoms or molecules is limited due to the fact that the kinetic-energy expression $T_{\text{TF}}[n]$ is only approximate and also exchange and correlation effects are completely neglected. However, this was an important first step towards representing a quantum system in terms of the density $n(\mathbf{r})$ only.

Despite the numerous modifications and improvements made to the Thomas-Fermi theory [39–42] the method remained rather inaccurate for most applications.

The Hohenberg-Kohn Theorem

This changed with the landmark paper by Hohenberg and Kohn [10] and the introduction of DFT, which showed how to make the approaches of Thomas and Fermi formally exact. Modern DFT rests upon two ideas put forward in this landmark paper. Firstly, Hohenberg and Kohn showed that one can exchange under certain conditions the wavefunction as a descriptor of the many-body system by only its density. In a more precise form, the first Hohenberg-Kohn theorem reads [16]

Theorem 1 *In a finite, interacting N -electron system with a given particle-particle interaction, there exists a one-to-one correspondence between the external potential $v_{\text{ext}}(\mathbf{r})$ and*

the ground state density $n_0(\mathbf{r})$. In other words, the external potential $v[n_0](\mathbf{r})$ (up to an arbitrary additive constant) is a unique functional of the ground state density.

More formally we can express this result in terms of a one-to-one (bijective) mapping between all external potentials that allow for a non-degenerate ground state, all non-degenerate ground state wavefunctions and all ground state densities

$$v_{\text{ext}}(\mathbf{r}) \xleftrightarrow{1:1} \Psi_0 \xleftrightarrow{1:1} n_0(\mathbf{r}). \quad (19)$$

This shows that in principle we can express the wavefunction by its density $\Psi_0 = \Psi_0[n_0]$ and thus any observable described by an operator \hat{O} becomes a functional of the density n_0 . Again, more formally

$$\Psi_0 = \Psi_0[n_0] \implies O[n_0] = \langle \Psi_0[n_0] | \hat{O} | \Psi_0[n_0] \rangle. \quad (20)$$

In addition to the one-to-one mapping between ground state densities, wavefunctions and potentials, Hohenberg and Kohn showed how to determine the ground state density for a given system described by a Hamiltonian of the form of Eq. (1). The energy functional, which in the standard formulation of DFT is the most important density functional, is given for some arbitrary ground state density n associated to a ground state wavefunction $\Psi = \Psi[n]$ (note that we here write n and Ψ instead of n_0 and Ψ_0 to not overload notation) by

$$E_{v_{\text{ext}}}[n] = \langle \Psi[n] | \hat{H} | \Psi[n] \rangle = \underbrace{\langle \Psi[n] | \hat{T} + \hat{W} | \Psi[n] \rangle}_{=F[n]} + \int d\mathbf{r} v_{\text{ext}}(\mathbf{r}) n(\mathbf{r}), \quad (21)$$

where $F[n]$ is called the universal functional as it is the same for all N -electron systems with the same electron-electron interaction, regardless of the external potential acting on it. It is then shown that the exact ground state density n_0 for a given external potential v_{ext} is the one that minimizes the energy functional

$$E[n_0] = \min_n E_{v_{\text{ext}}}[n]. \quad (22)$$

This result can be inferred from the variational principle of Eq. (9). The main drawback of the minimization via the density instead of via the wavefunction is that we do not know the exact form of the universal functional $F[n]$. Besides some mathematical subtleties that make a generalization of the universal functional to more than just ground state densities necessary [43], the main problem in DFT is that we need to find a way to accurately and efficiently approximate $F[n]$.

Kohn-Sham theory for DFT

In practice, the most successful approach to approximate $F[n]$ is then based on a further seminal work by Kohn and Sham [11], where they introduced the KS method. The point of the KS formulation [12] is to replace the original many-body

system by a suitable effective non-interacting system that is assumed to have the same density as the interacting system. Based on the simple to compute expressions of the non-interacting system, approximations for the exact $F[n]$ are then constructed.

The calculations in KS theory are performed for a non-interacting system of N electrons with a Hamiltonian of the form

$$\hat{H}_{KS} = \hat{T} + \hat{V}_{KS}, \quad (23)$$

where $\hat{V}_{KS} = \sum_{i=1}^N v_{KS}(\mathbf{r}_i)$. The Hohenberg-Kohn theorem is valid also in this case, and ensures a one-to-one correspondence between v_{KS} and the ground state density of the non-interacting system. The solution (assuming no degeneracy) to the non-interacting Schrödinger equation is a Slater determinant of the form of Eq. (10). This can be seen by just realizing that each particle $i = 1, \dots, N$ is just subject to an external potential of the form v_{KS} , and its minimal energy is obtained if we just fill the N -lowest spin orbitals while obeying the Pauli exclusion principle. Thus instead of working with the N -electron Slater determinant we can just consider the single-particle equations (as in the case of Hartree-Fock) and directly work with the orbitals $\phi_i(\mathbf{x})$. The equation for each spatial orbital is then a single-particle Schrödinger equation of the form

$$\left(-\frac{1}{2} \nabla^2 + v_{KS}(\mathbf{r}) \right) \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r}) \quad (24)$$

and the ground state density is constructed from the N -lowest single-particle orbitals as

$$n_s(\mathbf{r}) = \sum_{\sigma=\uparrow,\downarrow} \sum_{i=1}^N |\phi_i(\mathbf{x})|^2. \quad (25)$$

The non-interacting energy functional then becomes

$$E_s[n_s] = \underbrace{\sum_{i,\sigma} \int \phi_i^*(\mathbf{x}) \frac{-\nabla^2}{2} \phi_i(\mathbf{x}) d\mathbf{r}}_{=T_s[n_s]} + \int d\mathbf{r} v_{KS}(\mathbf{r}) n_s(\mathbf{r}), \quad (26)$$

where $T_s[n_s]$ is the non-interacting universal functional. Similar to the interacting case, n_s is the non-interacting ground state density that minimizes the energy functional for a given v_{KS} .

The main problem is to know which density is the density of the interacting system. The whole point of DFT is to predict this density by minimizing the energy functional. Kohn and Sham solved this by a self-consistency condition between the interacting and non-interacting system. For this one usually assumes that any interacting ground state density can be represented by a non-interacting KS system. This assumption is called non-interacting v -representability. More generally,

a density is said to be v -representable if it corresponds to the density of an anti-symmetric ground state wavefunction of a Hamiltonian of the form of Eq. (1) [44–49]. If the Hamiltonian happens to be non-interacting, we call such a density non-interacting v -representable. With this assumption we can re-express the exact energy functional for an arbitrary interacting ground state density with the help of the non-interacting energy functional as

$$E_{v_{\text{ext}}}[n] = T_s[n] + E_H[n] + \int d\mathbf{r} v_{\text{ext}}(\mathbf{r})n(\mathbf{r}) + \underbrace{F[n] - T_s[n] - E_H[n]}_{=E_{xc}[n]}. \quad (27)$$

Here we have introduced the classical Hartree energy expression

$$E_H[n] = \frac{1}{2} \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' \quad (28)$$

and the exchange-correlation (xc) energy term $E_{xc}[n]$. This term is unknown and in practice needs to be approximated. The exact ground state density n_0 is then found by minimizing over all ground state densities n . Assuming differentiability of the functionals this minimum can be found by making a functional derivative with respect to n and setting it to zero. Using that we represent the density by a Slater determinant of orthonormal orbitals, this leads to a set of non-linear coupled equations (similar to the case of the Hartree-Fock theory) of the form [11]

$$\left(-\frac{1}{2}\nabla^2 + v_{\text{ext}}(\mathbf{r}) + v_H[n](\mathbf{r}) + v_{xc}[n](\mathbf{r}) \right) \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r}), \quad (29)$$

where the Hartree potential is

$$v_H[n](\mathbf{r}) = \frac{\delta E_H[n]}{\delta n(\mathbf{r})} = \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \quad (30)$$

and the unknown xc potential is defined by

$$v_{xc}[n](\mathbf{r}) = \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})}. \quad (31)$$

Equations (25) and (29) for all occupied orbitals need to be solved self-consistently. The self-consistent solution n_0 is then the density that minimizes $E_{v_{\text{ext}}}[n]$ and is thus the sought after interacting density. For the self-consistent solution the single-particle KS potential $v_{KS} = v_{\text{ext}}(\mathbf{r}) + v_H[n_0](\mathbf{r}) + v_{xc}[n_0](\mathbf{r})$ reproduces exactly the interacting density n_0 .

We have not solved anything at this point, we have just rewritten the minimization of the energy functional $E_{v_{\text{ext}}}[n]$ in an implicit way. However, we take into account the non-interacting kinetic energy and the Hartree interaction energy explicitly and have shifted the unknown expression into the xc energy. As it turns out, simple approximations to $E_{xc}[n]$ and with this $v_{xc}[n_0]$ are already very accurate in most cases [12].

Local Density Approximation

The oldest and most widely used approximation in DFT is the local density approximation (LDA) [9]. It approximates the xc energy expression of an inhomogeneous system by the xc energy of the homogeneous electron gas, evaluated at the local density. This is the standard energy-based approach for the derivation of xc functionals [12]. In the second part of the thesis (Sec. 3.2), we will show an alternative way to directly directly the xc potentials from a force-based description of many-body systems circumventing the xc energy expressions. The LDA takes the form

$$\begin{aligned}
 E_{\text{xc}}^{\text{LDA}}[n] &= \int n(\mathbf{r}) \epsilon_{\text{xc}}^{\text{hom}}(n(\mathbf{r})) d\mathbf{r} \\
 &= \int n(\mathbf{r}) \left(\epsilon_{\text{x}}^{\text{hom}}(n(\mathbf{r})) + \epsilon_{\text{c}}^{\text{hom}}(n(\mathbf{r})) \right) d\mathbf{r} \\
 &= E_{\text{x}}^{\text{LDA}}[n] + E_{\text{c}}^{\text{LDA}}[n],
 \end{aligned} \tag{32}$$

where the xc energy density $\epsilon_{\text{xc}}^{\text{hom}}(n(\mathbf{r}))$ is solely a function of the density at the corresponding point and decomposed into exchange energy density $\epsilon_{\text{x}}^{\text{hom}}(n(\mathbf{r}))$ and correlation energy density $\epsilon_{\text{c}}^{\text{hom}}(n(\mathbf{r}))$. The LDA exchange energy functional makes use of the exchange energy density $\epsilon_{\text{x}}^{\text{hom}}(n(\mathbf{r}))$ pointwise and is given analytically as [12]

$$\begin{aligned}
 E_{\text{x}}^{\text{LDA}}(n) &= \int n(\mathbf{r}) \epsilon_{\text{x}}^{\text{hom}}(n(\mathbf{r})) d\mathbf{r} \\
 &= -\frac{3}{4} \left(\frac{3}{\pi} \right)^{1/3} \int n(\mathbf{r})^{4/3} d\mathbf{r},
 \end{aligned} \tag{33}$$

where

$$\epsilon_{\text{x}}^{\text{hom}}(n(\mathbf{r})) = -\frac{3}{4} \left(\frac{3}{\pi} \right)^{1/3} n(\mathbf{r})^{1/3}. \tag{34}$$

For the correlation energy of the homogeneous electron gas, analytic expressions are not known except in the low density [9, 50] and high density [51, 52] limit which corresponds to infinitely strong and infinitely weak correlations. One usually employs highly accurate numerical data from wavefunction-based methods to fit expressions for the correlation energy density of the homogeneous electron gas [50, 53]. The LDA is easily implemented in the KS equations, as the corresponding xc potential is a simple function of the local density

$$\begin{aligned}
 v_{\text{xc}}^{\text{LDA}}(\mathbf{r}) &= \frac{\delta E_{\text{xc}}^{\text{LDA}}[n]}{\delta n(\mathbf{r})} \\
 &= \epsilon_{\text{xc}}(n(\mathbf{r})) + n(\mathbf{r}) \frac{d\epsilon_{\text{xc}}(n(\mathbf{r}))}{dn(\mathbf{r})}.
 \end{aligned} \tag{35}$$

The exchange part of $v_{xc}^{\text{LDA}}(\mathbf{r})$ is thus obtained from the differentiation of Eq. (33) as

$$v_x^{\text{LDA}} = -\frac{(3\pi^2)^{1/3}}{\pi}n^{1/3}(\mathbf{r}). \quad (36)$$

We note that in the literature [54] there exists some variant of the LDA exchange potential. One of these is the *Slater exchange*

$$v_x^{\text{Slater}}(\mathbf{r}) = \frac{3}{2}v_x^{\text{LDA}}(\mathbf{r}) \quad (37)$$

which was obtained as a free-electron approximation to the exchange potential to make a simplification of the Hartree-Fock method. Thus the average exchange energy was replaced by the value one should get for a free-electron gas with local density given by the density at the position in question. This then led to a simple expression for the average potential field. In application, v_x^{Slater} is often multiplied by an adjustable prefactor α which defines the so-called $X\alpha$ -method [55]

$$v_x^{X\alpha}(\mathbf{r}) = \frac{3}{2}\alpha v_x^{\text{LDA}}(\mathbf{r}). \quad (38)$$

By comparison to some empirical values, it was found that multiplying v_x^{Slater} by a prefactor α that minimizes the energy, gave good results. The value of α often used is 0.7 which leads back to the usual LDA exchange. In Sec. 3.3 we will show how the force-based approximations to xc potentials for the homogeneous electron gas reduce to a form of the $X\alpha$ variant of LDA (which in our case we denote with λ instead). Then we show that by setting λ to 1/2 we get exactly the LDA exchange potential $v_x^{\text{LDA}}(\mathbf{r})$ and give a clear meaning to our choice of λ .

A number of more accurate approximations based not only on the density but also on its spatial gradient have been derived over the years. These build up the group of generalized gradient approximations (GGAs) [56–58] which have been revised and modified [59–61]. Other approximations involving higher derivatives of the density and sometimes orbital-dependent quantities such as the kinetic energy density $\tau(r)$ are grouped under meta-GGAs [62–64]. Some more recent functionals of this type have been derived by Perdew and others [65–68]. Further, a higher level of accuracy is achieved by taking into account exact exchange contributions to the xc energy functionals of LDA, GGA and meta-GGAs to form hybrid and meta-hybrid functionals [69–72]. This detailed hierarchy of approximations is known as Jacob’s ladder of density functional approximations [73]. In Chap. 3 we will devise orbital-dependent approximations based on the local-force equations of quantum mechanics which are on the fourth level of this Jacob’s ladder. The main advantage of these approximations is, however, that they are consistent with all the different situations (to be) discussed in this introductory chapter as well.

2.2 TIME-DEPENDENT SCHRÖDINGER EQUATION

So far we have discussed how quantum mechanics and then DFT is used to predict the properties of electronic systems in the presence of an attractive static scalar external potential, for instance, the attractive Coulomb potentials of static classical nuclei. However, in many situations the static picture is not sufficient and the actual dynamics of the electrons upon radiation or when a chemical reaction happens become important. In this case we need to consider the time-dependent Schrödinger equation instead of the static one. That means we no longer look for the wavefunction or eigenfunctions of a time-independent Hamiltonian but investigate an evolution equation of the form of [27]

$$i\partial_t\Psi(\mathbf{x}_1, \dots, \mathbf{x}_N, t) = \hat{H}(t)\Psi(\mathbf{x}_1, \dots, \mathbf{x}_N, t). \quad (39)$$

To solve such an evolution equation, which is first-order in time, we need to choose an initial state $\Psi(t_0) \equiv \Psi_0$ at t_0 . In the following we will, without loss of generality, assume $t_0 = 0$. Under certain conditions [27] we can then solve this equation and from this determine the wavefunction $\Psi(t)$ at each instant in time. In analogy to the static Schrödinger equation given in Eq. (1) we choose in this section the time-dependent Hamiltonian to be of the form of

$$\hat{H}(t) = \hat{T} + \hat{V}_{ext}(t) + \hat{W}. \quad (40)$$

The kinetic part and interaction potential are given by Eqs (2) and (4), respectively. The only explicitly time-dependent operator is the external scalar potential

$$\hat{V}(t) = \sum_i v_{ext}(\mathbf{r}_i, t). \quad (41)$$

In most practical cases, the time-dependent external scalar potential consists of two parts. One that describes static attractive potentials, such as due to static nuclei, and an explicit external time-dependent potential, such as an external laser pulse in dipole approximation. More formally we therefore usually have

$$v(\mathbf{r}, t) = v_0(\mathbf{r}) + v_1(\mathbf{r}, t), \quad (42)$$

where, for instance, we could have $v_1(\mathbf{r}, t) = E_0 x \sin(\omega t)$ which describes a continuous-wave laser with frequency ω and polarization direction \mathbf{e}_x [74]. Similarly to the static case, also for the time-dependent case the numerical solution of the time-dependent Schrödinger equation with interaction \hat{W} among the electrons is only possible for simple systems with only a few electrons. In the case that the external time-dependent perturbation v_1 is as strong or even stronger than the binding potential v_0 , this becomes even more severe. In such strong-field cases already the helium atom with 2 interacting electrons becomes very challenging [6]. Therefore an effective reformulation of time-dependent quantum mechanics in a similar way

as DFT for the static case becomes highly desirable. Before we discuss such a reformulation, let us consider a few further details of the time-dependent Schrödinger equation that become important in the following.

The one-particle density is determined by the wavefunction $\Psi(t)$ similar to the time-independent case as

$$n(\mathbf{r}, t) = N \int |\Psi(\mathbf{x}_1, \dots, \mathbf{x}_N, t)|^2 d\mathbf{x}_2 \dots \mathbf{x}_N. \quad (43)$$

If we now make use of the time-dependent Schrödinger equation of Eq. (39) together with the form of the Hamiltonian of Eq. (40), we find for the time-derivative of the density that

$$\begin{aligned} \partial_t n &= N \int (\partial_t \Psi^*) \Psi + \Psi^* (\partial_t \Psi) d\mathbf{x}_2 \dots \mathbf{x}_N \\ &= -\frac{1}{2i} \int \Psi^* \nabla^2 \Psi - (\nabla^2 \Psi^*) \Psi d\mathbf{x}_2 \dots \mathbf{x}_N \\ &= -\nabla \cdot \mathbf{j}. \end{aligned} \quad (44)$$

Here we have defined the total one-particle current density as

$$\mathbf{j}(\mathbf{r}, t) = N \Im \int \Psi^*(\mathbf{x}_1, \dots, \mathbf{x}_N, t) \nabla \Psi(\mathbf{x}_1, \dots, \mathbf{x}_N, t) d\mathbf{x}_2 \dots \mathbf{x}_N, \quad (45)$$

with ∇ only acting on the first particle position and \Im being the imaginary part. As in the static case we only consider fermionic wavefunctions. Eq. (44) is the continuity equation, which corresponds to the local conservation of particles. That is, the flux of the particle current across the boundary of a given volume determines how the particle number changes in that given volume. Simply put, in time-dependent quantum mechanics particles (or equivalently charges) cannot be created or destroyed. Most easily we see that once we integrate the continuity equation over all of space such that

$$\int \partial_t n(\mathbf{r}, t) d\mathbf{r} = \int \nabla \cdot \mathbf{j}(\mathbf{r}, t) d\mathbf{r} = 0. \quad (46)$$

Also for the current density we can derive how it changes in time for a Hamiltonian of the form of Eq. (40). In this case we find that

$$\begin{aligned} \partial_t \mathbf{j} &= N \Im \int ((\partial_t \Psi^*) \nabla \Psi + \Psi^* \nabla (\partial_t \Psi)) d\mathbf{r}_2 \dots \mathbf{r}_N \\ &= N \Re \int ((\hat{H} \Psi^*) \nabla \Psi - \Psi^* \nabla (\hat{H} \Psi)) d\mathbf{r}_2 \dots \mathbf{r}_N \\ &= N \Re \int ((\hat{H} \Psi^*) \nabla \Psi - \Psi^* \hat{H} \nabla \Psi - \Psi^* (\nabla \hat{H}) \Psi) d\mathbf{r}_2 \dots \mathbf{r}_N \\ &= -n \nabla v - \mathbf{F}_T - \mathbf{F}_W, \end{aligned} \quad (47)$$

where \Re is the real part and $\mathbf{F}_T(\mathbf{r}, t)$ and $\mathbf{F}_W(\mathbf{r}, t)$ are the internal force densities of the many-body system associated to kinetic and interaction effects, respectively.

They can be expressed in the form of the divergence of stress tensors [75, 76]. We give the exact expression of the force terms $\mathbf{F}_T(\mathbf{r}, t)$ and $\mathbf{F}_W(\mathbf{r}, t)$ in Sec. 3.3. If we now consider the total momentum of the system which is connected to the current by

$$\mathbf{P}(t) = \int \mathbf{j}(\mathbf{r}, t) d\mathbf{r}, \quad (48)$$

we find from Eq. (47) that

$$\partial_t \mathbf{P}(t) = \int n(\mathbf{r}, t) \nabla v(\mathbf{r}, t) d\mathbf{r}, \quad (49)$$

since the internal (divergence) contributions integrate to zero. We see that this is the quantum version of Newton's third law. For a many-body system, the rate of change of the total momentum is equal to the external force acting on it. We therefore see that Eq. (47) is a local force equation and locally the internal forces \mathbf{F}_T and \mathbf{F}_W can give an important contribution.

Similarly to Eq. (49), the rate of change of the total angular momentum is given solely by the torque due to external forces, while the net torque due to electron interaction and stress forces vanishes [16]. These relations (in a more general form) describing the net force and net torque will be important in determining conditions on approximations in Sec. 2.4.1 and later in our force-based approach to approximations in DFTs in Sec. 3.2. Further, Eqs. (44) and (47) are the basis of the time-dependent extension of DFT as discussed in the next Sec. 2.2.1 and also provide the foundation for a hydrodynamical perspective of quantum many-body systems [75, 77]. They show an equivalence to two main theories that describe the dynamics of continuous media, that is, elasticity in the case of solids and hydrodynamics for fluids. In these theories the many-body forces are expressed as divergences of stress tensors, which are themselves dependent on the velocity or the displacement field. In hydrodynamics, for instance, the current density satisfies the Navier-Stokes equation [78], which describes the motion of viscous fluids and is given in terms of the divergence of a stress tensor due to viscosity and pressure. This gives relations between densities and potentials without going through the energy.

As said before, solving the time-dependent Schrödinger equation (39) is an extremely challenging task due to the high dimensional wavefunction. As in the static case, approximations have been devised to circumvent this issue either based on wavefunctions [79–82] or on reduced quantities [16, 27, 83, 84]. For wavefunction methods, we here only mention the time-dependent extension of the Hartree-Fock method as discussed in Sec. 2.1.1. One can make the Hartree-Fock equations time-dependent by making the external potential time-dependent and then one finds approximate solutions to the time-dependent Schrödinger equation [85, 86]. In the following, we will focus on extending DFT to the time domain.

2.2.1 Time-Dependent Density Functional Theory

The idea of DFT to replace the wavefunction by the density as basic descriptor of the system can be extended to the time-dependent case. Although mathematically quite different, since it employs EOMs and no variational principle, Runge and Gross provided an analog of the Hohenberg-Kohn theorem for the time-dependent case in 1984 [14]. The Runge-Gross (RG) theorem provides a one-to-one correspondence between the time-dependent external potential of a system and its time-dependent density, for a given initial many-body wavefunction. This allows to recast the time-dependent many-body problem in terms of the time-dependent density as defined in Eq. (43). This gives rise to time-dependent DFT (TDDFT) and allows to determine efficiently not only the excitation spectra of complex molecules [16] but we can also access highly non-linear electron dynamics such as in the case of high-harmonic generation [74, 87–89]

The Runge-Gross Theorem

The basics of TDDFT and the fundamental idea of the RG theorem is to invert the mapping that is induced by the time-dependent Schrödinger equation with a Hamiltonian of the form of Eq. (40) with different external potential $v(\mathbf{r}, t)$ and for a given initial state Ψ_0 . Formally this mapping can be written as

$$v(\mathbf{r}, t) \xrightarrow{i\partial_t \Psi = \hat{H}[v](t)\Psi} \Psi(t) \xrightarrow{n} n(\mathbf{r}, t). \quad (50)$$

That is, for a fixed initial state Ψ_0 we solve the time-dependent Schrödinger equation for all possible external potentials $v(\mathbf{r}, t)$ [14] and from this get then all possible time-dependent wavefunctions $\Psi(t)$ that are connected to the initial state. All these wavefunctions are different since the evolution equation has a unique solution for a given initial state under certain conditions [15]. All these wavefunctions then allow to determine via Eq. (43) all possible time-dependent densities that are connected to the initial state. It is, however, not apriori clear that all the different wavefunctions also lead to different densities. If this would be the case, we could invert the mapping and express the wavefunction in terms of the initial state and the time-dependent density only. This would in turn allow to express all observables in terms of the density and the initial state. The RG theorem tells us that this is indeed the case under certain conditions.

Theorem 2 *Given the initial many-body state Ψ_0 of an N -particle system that evolves under the effect of two different potentials $v(\mathbf{r}, t)$ and $v'(\mathbf{r}, t) \neq v(\mathbf{r}, t) + c(t)$, the densities $n(\mathbf{r}, t)$ and $n'(\mathbf{r}, t)$ will start to differ infinitesimally after t_0 . Hence, there exists a one-to-one mapping between densities and external potentials defined up to a merely additive time-dependent function, given an initial wavefunction. [16]*

We want to highlight that in the context of TDDFT and the RG theorem, two potentials are considered different only if they differ by more than just a purely

time-dependent constant $c(t)$. Since such a time-dependent constant amounts to merely a gauge choice (which is the only gauge freedom left if we only have a scalar potential, see also Sec. 2.4 for further details) all physical observables should be independent of this gauge choice. Indeed, since a time-dependent constant function $c(t)$ just adds a time-dependent phase to the wavefunction $\Psi'(t) = \exp(i \int_0^t dt' c(t')) \Psi(t)$ all observables and specifically the density stay unchanged since it cancels in the inner product.

The proof of the RG theorem gives us already some hints on how to connect to the different DFTs in the coming Chap. 3. This is the reason why unlike with the Hohenberg-Kohn theorem in DFT, here we give a brief recap on the proof of the RG theorem. We follow hereby closely Ref. [16]. There are alternative proofs of the RG theorem available that lift certain of the below restrictions [15, 90, 91], but we stick to this more simple way of showing the invertibility of the mapping of Eq. (50). As a first restriction we consider only potentials that are Taylor expandable about the initial time $t_0 = 0$,

$$v(\mathbf{r}, t) = \sum_{k=0}^{\infty} \frac{1}{k!} v_k(\mathbf{r}) t^k. \quad (51)$$

Thus also a different potential $v'(\mathbf{r}, t)$ is determined uniquely by its expansion coefficients $v'_k(\mathbf{r})$. Therefore, there must exist a smallest integer $k \geq 0$ such that

$$v_k(\mathbf{r}) - v'_k(\mathbf{r}) \neq \text{const}. \quad (52)$$

We will next make two steps. In a first step, the uniqueness between current densities and potentials are established by making use of the EOM of the current density of Eq. (47). To do so we consider the difference between the EOM for the different external potentials at the initial time

$$\partial_t(\mathbf{j}(\mathbf{r}, t) - \mathbf{j}'(\mathbf{r}, t))|_{t=0} = -n(\mathbf{r}, 0) \nabla(v(\mathbf{r}, 0) - v'(\mathbf{r}, 0)). \quad (53)$$

Here we have used Eq. (47) and the fact that both EOMs start from the same initial state such that both systems have the same internal stress forces (see also Sec. 3.1 for the explicit form of the stress forces). If now $v(\mathbf{r}, 0) - v'(\mathbf{r}, 0) \neq \text{const}$ then the current densities will be different. If, on the other hand, they are the same up to a constant, then we go to the next order. Calculating the second time-derivative of the current differences at $t = 0$ *provided* that $v(\mathbf{r}, 0) - v'(\mathbf{r}, 0) = \text{const}$ we find

$$\partial_t^{k+1}(\mathbf{j}(\mathbf{r}, t) - \mathbf{j}'(\mathbf{r}, t))|_{t=0} = -n(\mathbf{r}, 0) \nabla(v_k(\mathbf{r}) - v'_k(\mathbf{r})), \quad (54)$$

with $k=1$. If again the expansion coefficients are the same of both potentials we can go up until the smallest k where they differ and we again have Eq. (54). Since such a k exists by assumption we have shown that $\mathbf{j}(\mathbf{r}, t) \neq \mathbf{j}'(\mathbf{r}, t)$ for $t > 0$.

In the next step we show that the same conclusion holds also for the densities. To do so we use the continuity equation (44) and apply it to Eq. (54). This leads (having the same assumption that for all previous k we have $v_k - v'_k = \text{const}$) to

$$\begin{aligned} \partial_t^{k+2}(n(\mathbf{r}, t) - n'(\mathbf{r}, t))|_{t=0} &= -\nabla \partial_t^{k+1}(\mathbf{j}(\mathbf{r}, t) - \mathbf{j}'(\mathbf{r}, t))|_{t=0} \\ &= -\nabla \cdot (n(\mathbf{r}, 0) \nabla (v_k(\mathbf{r}) - v'_k(\mathbf{r}))). \end{aligned} \quad (55)$$

It is left to show that if $v_k(\mathbf{r}) - v'_k(\mathbf{r}) \neq \text{const}$ the left hand side of Eq. (55) is non-zero. This is done by use of Green's integral theorem. If we define $w_k(\mathbf{r}) = v_k(\mathbf{r}) - v'_k(\mathbf{r})$ we see that

$$\begin{aligned} &\int d\mathbf{r} n(\mathbf{r}, 0) (\nabla w_k(\mathbf{r}))^2 \\ &= -\int d\mathbf{r} w_k(\mathbf{r}) \nabla \cdot (n(\mathbf{r}, 0) \nabla w_k(\mathbf{r})) + \oint d\mathbf{S} \cdot (n(\mathbf{r}, 0) w_k(\mathbf{r}) \nabla w_k(\mathbf{r})). \end{aligned} \quad (56)$$

The second term on the right hand side of Eq. (56) vanishes for all physically realistic potentials, since the density decays exponentially to zero at infinity. Since the integrand on the left hand side is nonnegative, the integral on the left hand side is non-zero as well. From this together with the surface integral vanishing we can conclude that the first term on the right hand side is also non-vanishing, and therefore $\nabla \cdot (n(\mathbf{r}, 0) \nabla w_k(\mathbf{r})) \neq 0$. We have thus shown under certain assumptions that if potentials differ then $n(\mathbf{r}, t) \neq n'(\mathbf{r}, t)$ for $t > 0$.

The RG theorem is the fundamental existence theorem of TDDFT which shows that for a given initial state, the time-dependent density is a unique functional of the potential and vice versa. This implies that also the wavefunction is a functional of the density and the initial state. More formally we can write

$$v(\mathbf{r}, t) = v[n, \Psi_0](\mathbf{r}, t) \implies \hat{H}(t) = \hat{H}[n, \Psi_0](t) \implies \Psi(t) = \Psi[n, \Psi_0](t). \quad (57)$$

This implies that all physical observables become functionals of the density as well by

$$O(t) = \langle \Psi[n, \Psi_0](t) | \hat{O}(t) | \Psi[n, \Psi_0](t) \rangle = O[n, \Psi_0](t) \quad (58)$$

This tells us that one only needs the time-dependent density in order to evaluate any observable of a time-dependent many-body system.

At this point we want to make a few remarks. Firstly, the RG theorem in the above form relies on the Taylor expandability of potentials and observables. This can exclude certain interesting situations and hence there are reformulations of the theorem as well as the proof based on fixed point constructions [90] and non-linear Schrödinger equations [91] that are more general. Further, the theorem can be extended to periodic systems [92]. What is important for our further considerations is that the proof relies on the EOMs for the current density and the density. The EOMs take over the role of the energy minimization in ground state DFT. Their role will become even more prominent in the next paragraph, where we discuss the

time-dependent KS scheme and the extended RG theorem. While the variational principle does not hold for time-dependent quantum mechanics, the EOMs hold for both, the time-dependent and static quantum mechanics. This already gives a hint that if we want to find an encompassing formulation of DFT and TDDFT, the EOMs are a possible way to go. However, the current formulation is geared towards scalar external potentials only. If we also include external magnetic fields, then it needs to be generalized. This will be discussed in Sec. 2.4.1.

As in the case of DFT, also TDDFT is employed almost exclusively together with the KS scheme. In the time-dependent case the KS formalism is based on an extension of the RG theorem introduced by van Leeuwen [93]. Since it again highlights the importance of the EOMs we briefly discuss it in the next paragraph.

The time-dependent Kohn-Sham Scheme

We have shown in the previous section that for a given fixed initial many-body state Ψ_0 , the time-dependent particle density $n(\mathbf{r}, t)$ of a system with interaction $w(|\mathbf{r} - \mathbf{r}'|)$ is a unique functional of the time-dependent potential $v(\mathbf{r}, t)$. For more practical applications, we use the time-dependent KS scheme which entails replacing the interacting system with a non-interacting one such that both yield the same density. Such a system, known as the KS system, is obtained by choosing an effective potential $v_{\text{KS}}(\mathbf{r}, t)$, in general different from that of the target system of course, that mimics all interaction effects and is unique up to a purely time-dependent function. The RG theorem in the above form, however, does not show that this is actually possible.

What one needs to find out is whether two many-body systems with different particle-particle interactions $w(|\mathbf{r} - \mathbf{r}'|)$ (this could also be zero) and different external potentials $v(\mathbf{r}, t)$ and $v'(\mathbf{r}, t)$ starting from different initial states can reproduce exactly the same density $n(\mathbf{r}, t)$. If it is the case, then we need to determine whether the potential is unique up to a purely time-dependent function. This is the question of non-interacting v -representability which was answered in the affirmative by van Leeuwen in Ref. [93] under some mild conditions.

Theorem 3 (extended Runge-Gross theorem) *Given the initial state Ψ_0 of a many-body system evolving under the interaction potential $w(|\mathbf{r} - \mathbf{r}'|)$ and external potential $v(\mathbf{r}, t)$, there exists a different many-body system with initial wavefunction Ψ'_0 evolving under an interaction potential $w'(|\mathbf{r} - \mathbf{r}'|)$ and a unique external potential $v'(\mathbf{r}, t)$ (up to a purely time-dependent function) such that both systems yield the same density. The initial wavefunction Ψ'_0 must be chosen such that it yields the given density and its time-derivative at the initial time. [16]*

The proof relies again on the EOMs of the density and the current subject to some initial conditions [16]. However, in contrast to the RG proof it is not the difference in EOMs that is Taylor expanded (see Eq. (54) and (55)) up to a certain order, but it is the full EOMs that are Taylor expanded. This gives a direct relation

between the Taylor coefficients of the potential v_k and of the density n_k . Without going into detail, the proof shows that given a Taylor expandable density $n(\mathbf{r}, t) = \sum_k \frac{1}{k!} n_k(\mathbf{r}) t^k$ and a compatible initial state, the corresponding potential is uniquely determined up to a purely time-dependent function by combining the EOM of the density (44) and of the current density (47), which leads to

$$-\nabla(n(\mathbf{r}, t)\nabla v(\mathbf{r}, t)) = -\nabla(\mathbf{F}_T(\mathbf{r}, t) + \mathbf{F}_W(\mathbf{r}, t)) - \partial_t^2 n(\mathbf{r}, t). \quad (59)$$

Using the same equation but now for a non-interacting system then allows to give a defining equation for the Hartree-exchange-correlation (Hxc) potential directly as [93]

$$-\nabla(n(\mathbf{r}, t)\nabla v_{Hxc}(\mathbf{r}, t)) = -\nabla(\mathbf{F}_T^s(\mathbf{r}, t) - \mathbf{F}_T(\mathbf{r}, t) - \mathbf{F}_W(\mathbf{r}, t)). \quad (60)$$

Here we denote with $\mathbf{F}_T^s(\mathbf{r}, t)$ the kinetic stress forces of the KS system and with $\mathbf{F}_T(\mathbf{r}, t)$ the kinetic stress forces of the interacting system as well as $\mathbf{F}_W(\mathbf{r}, t)$ the interaction forces of the interacting system (see also Eqs. (126) and (127)). The extended RG theorem is therefore a way to answer in an affirmative way the question of v -representability in TDDFT. A more detailed discussion on the finer details of the v -representability question in TDDFT can be found in [15]. For lattice systems further details are discussed in Refs. [94] and [95].

We can now move on to the practical time-dependent KS scheme. The KS initial wavefunction Φ_0 is taken as a Slater determinant of single particle orbitals $\phi_i^0(\mathbf{x})$ usually obtained from a DFT calculation. The time-dependent (spatial part of the) orbitals are then determined by the self-consistent solution of the non-linear single-particle evolution equation [16]

$$i\partial_t \phi_i(\mathbf{r}, t) = \left(-\frac{\nabla^2}{2} + v_{KS}[n, v, \Psi_0, \Phi_0](\mathbf{r}, t) \right) \phi_i(\mathbf{r}, t), \quad (61)$$

with initial condition

$$\phi_i(\mathbf{r}, 0) = \phi_i^0(\mathbf{r}) \quad (62)$$

and the time-dependent density is given by

$$n(\mathbf{r}, t) = \sum_{i=1}^N |\phi_i(\mathbf{r}, t)|^2. \quad (63)$$

The KS effective potential v_{KS} is defined such that it includes the external potential from the interacting system $v(\mathbf{r}, t)$, the Hartree potential v_H that accounts for some effects due to interaction and only depends on the density at the same time t and finally the xc potential $v_{xc} = v_{Hxc} - v_H$

$$v_{KS}[n, v, \Psi_0, \Phi_0](\mathbf{r}, t) = v(\mathbf{r}, t) + \int d\mathbf{r}' \frac{n(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|} + v_{xc}[n, \Psi_0, \Phi_0](\mathbf{r}, t). \quad (64)$$

In principle this time-dependent KS scheme yields the time-dependent density of the many-body system evolving in time under the influence of an external potential of the form of Eq. (42). However the scheme is not complete without making an approximation to the xc potential. Using Eq. (60) we see that we would need to approximate the internal force densities \mathbf{F}_T and \mathbf{F}_W of the interacting system. A more detailed look [96, 97] shows that these terms depend on the entire history of the time-dependent density and not just on the instantaneous value of the density. Therefore, at point \mathbf{r} and time t the xc potential has a functional dependence not just on $n(\mathbf{r}, t)$ but also on every $n(\mathbf{r}', t')$ for arbitrary point \mathbf{r}' in space and for $0 \leq t' \leq t$ as well as on the initial states Φ_0 and Ψ_0 of the KS and the interacting system, respectively. Thus the xc potential has "memory" (it depends on all the previous densities) and initial state dependence. It is, however, not so easy to devise approximations that have both, "memory" and initial state dependence. These memory effects are well-known to be important for the capture of physical effects such as double excitations and charge transfer reactions [98, 99]. Their importance can be understood from the linear response perspective of double excitations where the memory is responsible for shifting the bare KS resonances and generating new resonances. For, in the calculation for a non-interaction system, that is without a memory dependent kernel, not only will you get excitations at the wrong spots but you will also be missing multiple excitations [97, 100]. It is therefore common practice not to use specific time-dependent approximations but to just employ approximations from the ground state theory.

The Adiabatic Local Density approximation

The standard level of approximations in TDDFT are adiabatic approximations. That is, one uses an approximate energy functional $E_{xc}[n]$ from which one gets an approximate xc potential $v_{xc}[n]$ and uses this in Eq. (61). It is clear that in this way the xc potential only depends on the density $n(\mathbf{r}, t)$ at the same instant of time t and does not depend on the initial states. So these adiabatic functionals miss all the "memory" and the initial state dependence the exact xc potential should have. It is then usually argued that such an adiabatic approximation is good if the density changes slowly, that is, adiabatically. The reason for a failure of the adiabatic approximation in this case can again be understood from linear-response TDDFT, where the functional derivative of the xc potential is used to define a linear-response xc kernel [16]. If there is no memory, such a kernel is frequency independent (due to the Fourier transformation of the delta function in time to frequency, which results in a constant in frequency) and thus these types of excitations are not captured [16]. Yet, despite these drawbacks the adiabatic approximations work surprisingly well in many other situations, such as in the case of strong field physics and plasmonics [74, 101].

Following this logic, the most common adiabatic approximation in TDDFT is the adiabatic LDA (ALDA). It is obtained by using Eq. (35) with the time-dependent density

$$v_{\text{xc}}^{\text{ALDA}}[n](\mathbf{r}, t) = \frac{\delta E_{\text{xc}}^{\text{LDA}}[n]}{\delta n(\mathbf{r}, t)}. \quad (65)$$

Using the LDA in exchange approximation leads to

$$v_{\text{x}}^{\text{ALDA}}[n](\mathbf{r}, t) = -\frac{(3\pi^2)^{1/3}}{\pi} n^{1/3}(\mathbf{r}, t). \quad (66)$$

2.3 STATIC MAGNETIC SCHRÖDINGER EQUATION

Up to now we have discussed the description of many-electron systems influenced only by static or time-dependent scalar potentials. These are the most common situations, yet the external electromagnetic field can be more general. In the case where we are interested in static situations, the most general electromagnetic field takes the form [12]

$$\mathbf{E}(\mathbf{r}) = -\nabla v(\mathbf{r}) \quad (67)$$

$$\mathbf{B}(\mathbf{r}) = \nabla \times \mathbf{A}(\mathbf{r}) \quad (68)$$

with $\mathbf{E}(\mathbf{r})$ and $\mathbf{B}(\mathbf{r})$ being the static electric and magnetic field, respectively. We thus see that we can also have external magnetic fields that influence our electronic system. Such situations also gained much attention over the years [102] and are specifically important, for instance, for astro-chemistry where molecules under the influence of strong magnetic fields are investigated [103]. It is, however, important to realize that to every $\mathbf{B}(\mathbf{r})$ field, we have several possible vector potentials due to the intrinsic gauge freedom of the electromagnetic field [2]. That is, if we choose $\Lambda(\mathbf{r})$ a differentiable function of \mathbf{r} , then besides $\mathbf{A}(\mathbf{r})$,

$$\mathbf{A}'(\mathbf{r}) = \mathbf{A}(\mathbf{r}) + \nabla \Lambda(\mathbf{r}), \quad (69)$$

also describes the same magnetic field. The physics should stay the same, irrespective whether we choose $\mathbf{A}(\mathbf{r})$ or $\mathbf{A}'(\mathbf{r})$ to describe the problem. That is the basic idea of the minimal-coupling prescription [12], where a change of the external electromagnetic field by a gauge transformation of the form of Eq. (69) leads to a local phase that is added to a static wavefunction

$$\Psi' = \Psi e^{-i \sum_{i=1}^N \Lambda(\mathbf{r}_i)}. \quad (70)$$

Any physical observable should stay unaffected by this gauge change in the wavefunction. Therefore one adopts the definition of the momentum, which being a derivative has a dependence on this spatially dependent phase, and uses instead the canonical momentum

$$-i\nabla_i \rightarrow -i\nabla_i + \mathbf{A}(\mathbf{r}_i) \quad (71)$$

in the Schrödinger equation. This leads to the static magnetic Hamiltonian [12], which describes a system of N electrons in the presence of an external electrostatic field $\mathbf{E}(\mathbf{r})$ and a magnetostatic field $\mathbf{B}(\mathbf{r})$,

$$\hat{H} = \frac{1}{2} \sum_{i=1}^N (-i\nabla_i + \mathbf{A}(\mathbf{r}_i))^2 + \hat{V} + \hat{W}. \quad (72)$$

Here \hat{V} and \hat{W} are the scalar and the interaction potentials as defined before in Eqs. (3) and (4), respectively. Having an eigenstate of Eq. (72), we find the corresponding eigenstate when replacing $\mathbf{A} \rightarrow \mathbf{A}' = \mathbf{A} + \nabla\Lambda$ by Eq. (70). Also note that, the trivial gauge freedom we had in the static Schrödinger case, that is, the fact that we could replace $v(\mathbf{r}) \rightarrow v(\mathbf{r}) + \text{const}$, is valid here as well. This can be best seen by Eq. (67), where adding a constant to the potential is canceled by the gradient.

The definition of the density stays the same as before in Eq. (17), since the phase function $\Lambda(\mathbf{r})$ just cancels out. Yet the current, which is connected to the momentum and the forces (see Eq. (49)), is changed. In order to be gauge invariant and in order to obey the continuity equation we have (see Sec. 3.1 for a general derivation)

$$\begin{aligned} \mathbf{j}(\mathbf{r}) &= N\mathfrak{S} \int \Psi^* (\nabla - i\mathbf{A}(\mathbf{r})) \Psi d\mathbf{r}_2 \dots \mathbf{r}_N \\ &= N\mathfrak{S} \int \Psi^* \nabla \Psi d\mathbf{r}_2 \dots \mathbf{r}_N - n(\mathbf{r}, t) \mathbf{A}(\mathbf{r}) \\ &= \mathbf{j}_{\text{para}}(\mathbf{r}) + \mathbf{j}_{\text{dia}}(\mathbf{r}). \end{aligned} \quad (73)$$

Here the first and second term are the paramagnetic and diamagnetic current densities, respectively. We note here that, while the full current \mathbf{j} is gauge-independent, the individual parts are gauge dependent.

We have now defined the basic ingredients corresponding to many electron systems in the presence of a static magnetic field. However, solving the Schrödinger equation remains a tedious task in this setting as well. The Hartree-Fock method has also been adapted to this setting in order to approximate the wavefunction directly [104–106]. A number of approximations have also been developed to approach this issue based on reduced quantities [107–109] associated to systems involving magnetic fields. In the next part will focus on current DFT (CDFT) where the density and certain forms of the current density are the reduced quantities of interest.

2.3.1 Current Density Functional Theory

On a first glance not much seems different when considering the magnetic Hamiltonian of Eq. (72) in DFT instead of the usual Schrödinger equation. It seems reasonable to assume that one now only needs to swap the density n by the current density \mathbf{j} as reduced quantity to set up a CDFT framework. This was indeed

tried by several authors [110–113]. The problem, however, is that due to Eq. (73) we know that the physical current contains an explicit external part in its definition. This is a more severe issue than it seems, since this makes variations with respect to \mathbf{j} not anymore independent of \mathbf{A} . This means that, besides a lack of a formal Hohenberg-Kohn theorem for CDFT with the physical current, the usual way of obtaining the xc potentials becomes problematic. Several ways around this issue, for instance, by introducing an adapted variational principle [114, 115], have been proposed. But in practice a different solution, based on the work of Vignale and Rasolt [107] is used. Instead of a quantity that contains part of the external field, one uses only the parts of the current density that are determined by the wavefunction only. That is, the paramagnetic current \mathbf{j}_{para} and the density n , which appears in the definition of the diamagnetic term. It can then be shown that there is a one-to-one correspondence between the set of ground states Ψ_0 and the set of densities $(n, \mathbf{j}_{\text{para}})$ [116]. The major difference, however, is that there is no uniqueness between the external potentials and the ground state, since for the Pauli equation different external fields (v, \mathbf{A}) can have the same ground state wavefunction [117]. Nevertheless, the above result is enough to re-express the wavefunction only in terms of the paramagnetic current and the density as $\Psi[n, \mathbf{j}_{\text{para}}]$ and thus all observables obey (we denote \mathbf{j}_{para} here as \mathbf{j}_p to avoid an overload of notation)

$$O[n, \mathbf{j}_p] = \langle \Psi[n, \mathbf{j}_p] | \hat{O} | \Psi[n, \mathbf{j}_p] \rangle \quad (74)$$

In particular the energy is obtained as

$$E[n, \mathbf{j}_p] = \underbrace{\langle \Psi[n, \mathbf{j}_p] | \hat{T} + \hat{W} | \Psi[n, \mathbf{j}_p] \rangle}_{F[n, \mathbf{j}_p]} + \underbrace{\int d\mathbf{r} \mathbf{j}_p(\mathbf{r}) \cdot \mathbf{A}(\mathbf{r}) + \int d\mathbf{r} \left(v_{\text{ext}}(\mathbf{r}) + \frac{\mathbf{A}^2(\mathbf{r})}{2} \right) n(\mathbf{r})}_{E_{\text{ext}}[n, \mathbf{j}_p]}. \quad (75)$$

Here the last two terms can be found directly from Eq. (72) using the definition of the paramagnetic current density. From the variational principle the functional $E[n, \mathbf{j}_p]$ has then a minimum for the true density and current $(n, \mathbf{j}_{\text{para}})$.

Having established CDFT, we can follow the usual way and introduce an auxiliary system that we use to devise approximations. Assuming non-interacting v -representability, the ground state densities $(n, \mathbf{j}_{\text{para}})$ are expressed in terms of the KS orbitals. Following a similar procedure as in DFT the total energy functional is obtained as

$$E[n, \mathbf{j}_p] = T_s[n, \mathbf{j}_p] + E_{\text{ext}}[n, \mathbf{j}_p] + E_{\text{H}}[n] + E_{\text{xc}}[n, \mathbf{j}_p], \quad (76)$$

where T_s and E_{H} are given by Eqs. (26) and (28), respectively. By minimizing $E[n, \mathbf{j}_p]$ with respect to the KS orbitals under proper normalization and orthogonality conditions, one arrives at the KS equations of CDFT [107]

$$\{(-i\nabla + \mathbf{A}_{\text{KS}}(\mathbf{r}))^2 + v_{\text{KS}}(\mathbf{r})\} \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r}), \quad (77)$$

where the KS potentials are defined up to a gauge transform by

$$v_{\text{KS}}(\mathbf{r}) = v_{\text{ext}}(\mathbf{r}) + v_{\text{H}}(\mathbf{r}) + v_{\text{xc}}(\mathbf{r}) \quad (78)$$

$$\mathbf{A}_{\text{KS}}(\mathbf{r}) = \mathbf{A}_{\text{ext}}(\mathbf{r}) + \mathbf{A}_{\text{xc}}(\mathbf{r}). \quad (79)$$

The xc potentials are given as

$$v_{\text{xc}}(\mathbf{r}) = \left. \frac{\delta E_{\text{xc}}[n, \mathbf{j}_{\text{p}}]}{\delta n(\mathbf{r})} \right|_{\mathbf{j}_{\text{p}}}, \quad (80)$$

$$\mathbf{A}_{\text{xc}}(\mathbf{r}) = \left. \frac{\delta E_{\text{xc}}[n, \mathbf{j}_{\text{p}}]}{\delta \mathbf{j}_{\text{p}}(\mathbf{r})} \right|_n, \quad (81)$$

where the notation implies that the variation of E_{xc} with respect to one density is done while keeping the other density constant. Vignale and Rasolt also show that, the xc energy functional which now is a functional of the density and the paramagnetic current, can also be expressed in terms of the gauge-invariant vorticity, $E_{\text{xc}}[n, \mathbf{j}_{\text{p}}] \equiv E_{\text{xc}}[n, \mathbf{v}]$ with

$$\mathbf{v}(\mathbf{r}) = \nabla \times \frac{\mathbf{j}_{\text{p}}(\mathbf{r})}{n(\mathbf{r})}. \quad (82)$$

We further note that due to the nonuniqueness issues, it is expected that in paramagnetic CDFT the functionals exhibit non-differentiabilities [12, 117]. A more detailed investigation, however, shows that the same is already true for standard DFT [118]. We will comment on this issues later in Chap. 3.

As with TDDFT, CDFT as well does not have many known approximate xc functionals [119, 120]. So in practice one uses functionals from DFT. Besides, if one would like to use the physical current instead of the paramagnetic current, then there is no clear way to even define formally the corresponding xc potentials. In both cases, we will see in Sec. 3.2.2 how one can overcome these issues.

2.4 TIME-DEPENDENT MAGNETIC SCHRÖDINGER EQUATION

Similarly to the case of the usual Schrödinger equation, the time-dependent situations of the magnetic Schrödinger equation are also important yet use slightly different concepts. Again, instead of a minimum-energy principle and the corresponding ground state we have an evolution equation that needs to have a prescribed initial state. The main difference to the Schrödinger case is that we have a general electromagnetic field. Therefore, before we consider the time-dependent magnetic Schrödinger equation, let us briefly recall the time-dependent Maxwell's equations and how the gauge freedom appears in this case.

A time-dependent electromagnetic field can in general be represented by a time-dependent scalar potential $v(\mathbf{r}, t)$ and vector potential $\mathbf{A}(\mathbf{r}, t)$ as

$$\mathbf{E}(\mathbf{r}, t) = -\nabla v(\mathbf{r}, t) - \partial_t \mathbf{A}(\mathbf{r}, t), \quad (83)$$

$$\mathbf{B}(\mathbf{r}, t) = \nabla \times \mathbf{A}(\mathbf{r}, t). \quad (84)$$

The electric field $\mathbf{E}(\mathbf{r}, t)$ and magnetic field $\mathbf{B}(\mathbf{r}, t)$ do not change under the general gauge transformation

$$\begin{aligned} v'(\mathbf{r}, t) &= v(\mathbf{r}, t) + \frac{\partial \Lambda(\mathbf{r}, t)}{\partial t} \\ \mathbf{A}'(\mathbf{r}, t) &= \mathbf{A}(\mathbf{r}, t) + \nabla \Lambda(\mathbf{r}, t), \end{aligned} \quad (85)$$

where $\Lambda(\mathbf{r}, t)$ is now a differentiable function of \mathbf{r} as well as t . Following our previous discussion in the static case, the wavefunction of the electrons changes by

$$\Psi'(t) = \Psi(t) e^{-i \sum_{i=1}^N \Lambda(\mathbf{r}_i, t)}. \quad (86)$$

As a consequence, we have to use the now explicitly time-dependent canonical momentum

$$-i\nabla \rightarrow -i\nabla + \mathbf{A}(\mathbf{r}_i, t) \quad (87)$$

and we get from the time-derivative acting on $\Psi'(t)$ a scalar modification

$$v(\mathbf{r}_i, t) \rightarrow v(\mathbf{r}_i, t) + \frac{\partial \Lambda(\mathbf{r}_i, t)}{\partial t}. \quad (88)$$

This actually allows to remove the scalar potential altogether by choosing

$$\frac{\partial \Lambda(\mathbf{r}_i, t)}{\partial t} = -v(\mathbf{r}_i, t). \quad (89)$$

In general, though, we have the time-dependent magnetic Schrödinger equation given in some gauge as

$$\hat{H}(t) = \frac{1}{2} \sum_{i=1}^N (-i\nabla_i + \mathbf{A}(\mathbf{r}_i, t))^2 + \hat{V}(t) + \hat{W}, \quad (90)$$

where the first term is the square of the canonical momentum, $\hat{V}(t)$ is given in terms of the scalar potential for the specific gauge and \hat{W} is the usual Coulomb interaction among the particles. The Coulomb interaction is not affected by the gauge transformations of the external field $(v(\mathbf{r}, t), \mathbf{A}(\mathbf{r}, t))$ since it comes from the internal photon field described by quantum electrodynamics in the Coulomb gauge [2]. In order to change the gauge of the internal photon field, one would need to consider full quantum electrodynamics. The time-dependent density is defined as in the time-dependent setting by Eq. (43) and the gauge-invariant physical current density from the continuity equation is

$$\begin{aligned} \mathbf{j}(\mathbf{r}, t) &= N \int \Psi^* (\nabla - i\mathbf{A}(\mathbf{r}, t)) \Psi d\mathbf{r}_2 \dots \mathbf{r}_N \\ &= N \int \Psi^* \nabla \Psi d\mathbf{r}_2 \dots \mathbf{r}_N - n(\mathbf{r}, t) \mathbf{A}(\mathbf{r}, t) \\ &= \mathbf{j}_{\text{para}}(\mathbf{r}, t) + \mathbf{j}_{\text{dia}}(\mathbf{r}, t). \end{aligned} \quad (91)$$

As in the static case we have a paramagnetic and diamagnetic current density that contributes to the full physical current. The continuity equation in this case becomes

$$\partial_t n(\mathbf{r}, t) = -\nabla \cdot (\mathbf{j}_{\text{para}}(\mathbf{r}, t) + \mathbf{j}_{\text{dia}}(\mathbf{r}, t)). \quad (92)$$

As in the purely longitudinal (only scalar potentials) case, we can now derive how the physical current changes in time as

$$\begin{aligned} \partial_t \mathbf{j}(\mathbf{r}, t) &= N \Im \int ((\partial_t \Psi^*) \nabla \Psi + \Psi^* \nabla (\partial_t \Psi)) d\mathbf{r}_2 \dots \mathbf{r}_N - \dot{\mathbf{A}}(\mathbf{r}, t) n(\mathbf{r}, t) - \mathbf{A}(\mathbf{r}, t) \dot{n}(\mathbf{r}, t) \\ &= N \Re \int ((\hat{H} \Psi^*) \nabla \Psi - \Psi^* \nabla (\hat{H} \Psi)) d\mathbf{r}_2 \dots \mathbf{r}_N - \dot{\mathbf{A}}(\mathbf{r}, t) n(\mathbf{r}, t) - \mathbf{A}(\mathbf{r}, t) (\nabla \cdot \mathbf{j}) \\ &= -n(\dot{\mathbf{A}} + \nabla v) + \mathbf{A}(\nabla \cdot \mathbf{j}) + (\nabla \otimes \mathbf{A}) \mathbf{j} + (\mathbf{j}_{\text{para}} \otimes \mathbf{A}) \overleftarrow{\nabla} + \mathbf{F}_T[\psi] + \mathbf{F}_W[\psi], \end{aligned} \quad (93)$$

where \mathbf{F}_T and \mathbf{F}_W are the stress forces due to the kinetic and interaction potentials, respectively (see Sec 3.1 for details).

2.4.1 Time-Dependent Current Density Functional Theory

Let us next consider the according generalization of (TD)DFT to the above time-dependent magnetic Schrödinger equation. A first question that arises, especially after the discussion about the basic quantities in CDFT in Sec. 2.3.1, is which quantity should one pick? In the following we will take the full physical current density $\mathbf{j}(\mathbf{r}, t)$, which is the standard choice in the time-dependent case. To establish the basis of time-dependent CDFT (TDCDFT) we follow Vignale [121]. Similar to his derivation we will directly consider the extended RG theorem for TDCDFT, which implies a RG result for TDCDFT. That is, We first consider the more general question of \mathbf{A} -representability, i.e., under which conditions can we reproduce a given time-dependent current density with a Hamiltonian (90)? From this we can then deduce the fundamental one-to-one correspondence of TDCDFT.

Let us assume that we have a given time-dependent current density $\mathbf{j}(\mathbf{r}, t)$ and some general interaction \hat{W}' (not necessarily the Coulomb interaction). We then ask the question, whether we can reproduce this current density as expectation value of a time-dependent wavefunction $\Psi'(t)$ that is the solution to a time-dependent magnetic Schrödinger equation. Without loss of generality we choose a gauge where we fix $\Lambda(\mathbf{r}, t)$ such that any scalar potential vanishes (see Eq. (89)), which is called the radiation gauge [2, 121]. We therefore have a Hamiltonian of the form of

$$\hat{H}'(t) = \frac{1}{2} \sum_{i=1}^N (-i \nabla_i + \mathbf{A}'(\mathbf{r}_i, t))^2 + \hat{W}'. \quad (94)$$

By controlling the current density, we also control the change of the density through time by the continuity equation. We, however, do not control the total time-dependent

density, which depends on the initial state. That is, by choosing a specific initial state $\Psi'(0)$ to give a specific density $n(\mathbf{r}, 0)$ at $t = 0$, we can also control $n(\mathbf{r}, t)$, which leads to the control of the full current four vector $(n(\mathbf{r}, t), \mathbf{j}(\mathbf{r}, t))$ [121]. If we then consider the EOM for the current density (93) for the chosen initial state, we can follow a similar construction as in the case of the extended RG theorem based on the EOM for the density. That is, if we assume that all quantities are Taylor expandable in time about $t = 0$ with finite convergence radius, we can construct a unique external vector potential $\mathbf{A}'(\mathbf{r}, t)$ that reproduces a given four current density $(n(\mathbf{r}, t), \mathbf{j}(\mathbf{r}, t))$ [121]. The vector potential will depend on the initial state. We therefore have again initial state dependence. If we then perform a gauge transformation, which can also affect the initial state, we can from the above determine in general the pair $(v(\mathbf{r}, t), \mathbf{A}(\mathbf{r}, t))$ that reproduce the given time-dependent densities $(n(\mathbf{r}, t), \mathbf{j}(\mathbf{r}, t))$ in another gauge.

This \mathbf{A} -representability result has two immediate consequences. Firstly, since for a given gauge and initial state the pair $(v(\mathbf{r}, t), \mathbf{A}(\mathbf{r}, t))$ is uniquely determined, we find

$$(n(\mathbf{r}, t), \mathbf{j}(\mathbf{r}, t)) \xleftrightarrow{1:1} (v(\mathbf{r}, t), \mathbf{A}(\mathbf{r}, t)) \xleftrightarrow{1:1} \Psi(t). \quad (95)$$

Therefore the wavefunction becomes uniquely determined by the external pair and initial state, i.e.

$$\Psi(t) = \Psi[\Psi_0, v, \mathbf{A}](t), \quad (96)$$

and so do all observables. This is the extension of the RG result to the time-dependent magnetic Schrödinger equation, which was obtained already before by Ghosh and Dhara [122]. Secondly, if we choose an initial state Ψ_0 and propagate this initial state with the Pauli Hamiltonian of Eq. (90) with all (inequivalent) pairs $(v(\mathbf{r}, t), \mathbf{A}(\mathbf{r}, t))$, we generate all possible pairs $(n(\mathbf{r}, t), \mathbf{j}(\mathbf{r}, t))$. If we then choose a non-interacting initial state Φ_0 that obeys

$$\langle \Psi_0 | \hat{n}(\mathbf{r}) | \Psi_0 \rangle = \langle \Phi_0 | \hat{n}(\mathbf{r}) | \Phi_0 \rangle, \quad (97)$$

where we used the definition $\hat{n}(\mathbf{r}) = \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i)$ for the density operator, we can reproduce all these pairs with the help of an auxiliary non-interacting magnetic Hamiltonian of the form

$$\hat{H}_s(t) = \sum_{i=1}^N \left(\frac{1}{2} (-i\nabla_i + \mathbf{A}_s(\mathbf{r}_i, t))^2 + v_s(\mathbf{r}_i, t) \right), \quad (98)$$

and appropriately chosen effective fields

$$v_s(\mathbf{r}, t) = v_s[\Phi_0, n, \mathbf{j}](\mathbf{r}, t), \quad (99)$$

$$\mathbf{A}_s(\mathbf{r}, t) = \mathbf{A}_s[\Phi_0, n, \mathbf{j}](\mathbf{r}, t). \quad (100)$$

This allows us to define in analogy to TDDFT in Sec. 2.2.1, the KS scalar and vector potentials as

$$v_{\text{KS}}[v, \Psi_0, \Phi_0, n, \mathbf{j}](\mathbf{r}, t) = v(\mathbf{r}, t) + v_H[n](\mathbf{r}, t) + v_{\text{xc}}[\Psi_0, \Phi_0, n, \mathbf{j}](\mathbf{r}, t), \quad (101)$$

$$\mathbf{A}_{\text{KS}}[\mathbf{A}, \Psi_0, \Phi_0, n, \mathbf{j}](\mathbf{r}, t) = \mathbf{A}(\mathbf{r}, t) + \mathbf{A}_{\text{xc}}[\Psi_0, \Phi_0, n, \mathbf{j}](\mathbf{r}, t), \quad (102)$$

and we can predict the interacting density by self-consistently solving the time-dependent KS equations in TDCDFT (suppressing functional dependencies)

$$i\partial_t\phi_i(\mathbf{r}, t) = \left(\frac{1}{2} (-i\nabla_i + \mathbf{A}_{\text{KS}}(\mathbf{r}_i, t))^2 + v_{\text{KS}}(\mathbf{r}_i, t) \right) \phi_i(\mathbf{r}, t) \quad (103)$$

together with the density given by Eq. (43) and the gauge-invariant physical current density by Eq. (91). Note again that these fields are only defined up to a gauge transformation and thus by choosing, for instance, the above radiation gauge (see Eq. (89)), we can even get rid of the scalar part $v_{\text{KS}}(\mathbf{r}, t)$. At this point the question arises whether one could actually avoid the vector potential as well and just work with a scalar potential as in TDDFT. To answer this question we recall the Helmholtz decomposition [16] which states that an arbitrary vector field $\mathbf{F}(\mathbf{r}, t)$ can be written as the sum of a longitudinal (curl-free) and transverse (divergence-free) component as

$$\mathbf{F}(\mathbf{r}, t) = \mathbf{F}_L(\mathbf{r}, t) + \mathbf{F}_T(\mathbf{r}, t) \quad (104)$$

where

$$\begin{aligned} \mathbf{F}_L(\mathbf{r}, t) &= -\frac{1}{4\pi} \nabla \int d\mathbf{r}' \frac{\nabla' \cdot \mathbf{F}(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|}, \\ \mathbf{F}_T(\mathbf{r}, t) &= \frac{1}{4\pi} \nabla \times \int d\mathbf{r}' \frac{\nabla' \times \mathbf{F}(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|}. \end{aligned} \quad (105)$$

Similarly, any current density can be expressed as $\mathbf{j}(\mathbf{r}, t) = \mathbf{j}_L(\mathbf{r}, t) + \mathbf{j}_T(\mathbf{r}, t)$. Yet with only the scalar potential we have the EOM of Eq. (59) for the non-interacting system and we can only control the density. The density, however, only determines the longitudinal part of the current as can be seen by the continuity equation

$$\partial_t n(\mathbf{r}, t) = -\nabla \cdot \mathbf{j}_L(\mathbf{r}, t). \quad (106)$$

Hence, the density $n(\mathbf{r}, t)$ gives no information about the transverse part of the current density and we would not be able to reproduce the full gauge-invariant current. Of course, this was not a problem in the proof of the RG theorem but shows an obvious issue in the relation between current densities and scalar potentials. It is in general impossible to find a scalar potential $v(\mathbf{r}, t)$ that yields a previously specified current density $\mathbf{j}(\mathbf{r}, t)$, except for some special cases [123]. This issue (recast as transversal contributions to the xc forces) will become important again in Secs. 3.2.3 and 3.4.

There are only a few dedicated approximations to the xc scalar and vector potentials available in TDCDFT. An approximation for the xc vector potential was first derived through linear response theory by Vignale and Kohn [124]. This was a spatially local but frequency dependent approximation which has certain pathologies [16]. Later, this functional was re-derived in a hydrodynamic fashion [125–127]. Yet in most cases the xc vector potential is discarded and merely an adiabatic functional for the scalar part from DFT is employed [74]. However, there are several known exact constraints that the xc potentials should obey and thus could be useful for functional construction as for the ground state case [128].

Exact constraints

According to Newton’s third law, the rate of change of the total momentum $\mathbf{P}(t)$ of a many-body system is equal to the external force acting on it and internal forces of the system should have no contribution to the net force. Given that the net force due to the interaction potential is zero, the net force arising from the set of xc potentials $(v_{xc}(\mathbf{r}, t), \mathbf{A}_{xc}(\mathbf{r}, t))$ should also equal zero [16]. This exact property of the xc potential is the zero-force theorem. It holds also in TDDFT where the external forces are purely longitudinal (see also Sec. 3.2.1). Similarly, the rate of change of the total angular momentum $\mathbf{L}(t)$ of a many-body system depends solely on the net torque due to external forces while the net torque due to internal forces vanishes. In TDDFT this is not always the case, since we saw that the current densities of the interacting and the KS system are in general not the same given that their transverse contributions could be different. Hence the net torque due to the xc potentials could be non-vanishing.

However, for TDCDFT this problem does not arise. It is suitable to define the force terms in the KS system, $\mathbf{F}_s(\mathbf{r}, t) = \mathbf{F}(\mathbf{r}, t) + \mathbf{F}_H(\mathbf{r}, t) + \mathbf{F}_{xc}(\mathbf{r}, t)$, with the external, Hartree and xc-forces expressed as (see also Sec. 3.2.3)

$$\mathbf{F}(\mathbf{r}, t) = -\nabla v(\mathbf{r}, t) - \partial_t \mathbf{A}(\mathbf{r}, t) + \boldsymbol{\nu} \times [\nabla \times \mathbf{A}(\mathbf{r}, t)], \quad (107)$$

$$\mathbf{F}_H(\mathbf{r}, t) = -\nabla v_H(\mathbf{r}, t), \quad (108)$$

$$\mathbf{F}_{xc}(\mathbf{r}, t) = -\nabla v_{xc}(\mathbf{r}, t) - \partial_t \mathbf{A}_{xc}(\mathbf{r}, t) + \boldsymbol{\nu} \times [\nabla \times \mathbf{A}_{xc}(\mathbf{r}, t)] \quad (109)$$

where the velocity $\boldsymbol{\nu}$ is defined as $\boldsymbol{\nu}(\mathbf{r}, t) = \mathbf{j}(\mathbf{r}, t)/n(\mathbf{r}, t)$. We recall that in TDCDFT the density and current density are exactly reproduced by the KS system unlike in TDDFT. The zero-force theorem in TDCDFT can thus be generalized to

$$\int d\mathbf{r} n(\mathbf{r}, t) \mathbf{F}_{xc}(\mathbf{r}, t) = 0. \quad (110)$$

Given that the current densities of the interacting and the KS system match, the total angular momentum of both systems are equal and one has that

$$\begin{aligned} 0 &= \partial_t \mathbf{L}(t) - \partial_t \mathbf{L}_s(t) = \int d\mathbf{r} n(\mathbf{r}, t) \mathbf{r} \times [\mathbf{F}(\mathbf{r}, t) - \mathbf{F}_s(\mathbf{r}, t)] \\ &= - \int d\mathbf{r} n(\mathbf{r}, t) \mathbf{r} \times [\mathbf{F}_H(\mathbf{r}, t) + \mathbf{F}_{xc}(\mathbf{r}, t)]. \end{aligned} \quad (111)$$

Because the net torque that comes from the Hartree force vanishes, we are left with the zero-torque theorem for TDCDFT [77]

$$\int d\mathbf{r} n(\mathbf{r}, t) \mathbf{r} \times \mathbf{F}_{xc}(\mathbf{r}, t) = 0. \quad (112)$$

The zero-force and zero-torque theorems intuitively make sense since they come from the fact that the xc force can be expressed as the divergence of a stress tensor $nF_{xc,\mu} = \sum_j \nabla_j P_{xc,\mu j}$ [129]. Thus any accurate approximation to the xc scalar and vector potentials should fulfill these exact constraints. One also sees from Eqs. (107) and (109) that both functionals should be designed together to be consistent. An approximation that fulfills these constraints is discussed in Sec. 3.2.3.

UNIFYING PERSPECTIVE: FORCE-BASED APPROACH TO DENSITY FUNCTIONAL THEORIES

As we have seen, the different versions of DFTs, namely, ground state DFT (Sec. 2.1.2), TDDFT (Sec. 2.2.1), CDFT (Sec. 2.3.1) and TDCDFT (Sec. 2.4.1), have quite distinct foundations and consider different physical situations. In the case of DFT and CDFT, the minimum energy principle was used for different Hamiltonians while for TDDFT and TDCDFT the EOMs of the respective time-dependent Hamiltonians were employed. What they all share is that they employ the KS construction to find approximations to the unknown xc potentials. They do not necessarily have to be based on the KS formalism, as an orbital-free formulation is possible, however it is not very accurate so far [130, 131]. From this perspective it seems relatively straightforward to use approximations from one theory in the other ones. Due to the abundance of approximate xc functionals in ground state DFT (and the lack of approximate functionals in the other DFTs) it is common practice to also employ these functionals in the other settings. However, employing these ground state functional approximations in the other situations makes them less reliable [132]. Since each of the discussed DFTs is based on different mappings, there is a priori no reason to assume that the same approximations can be used in different theories. For instance, using an adiabatic DFT approximation in TDCDFT can lead to violations of the zero-torque theorem or even the zero-force theorem [133] and many other exact relations.

The simplest way to rectify this situation is to develop dedicated functionals and xc potentials for each of the different DFTs and to not use them in other settings. A different yet more efficient way would be to find a unifying approach that uniquely determines the xc potentials in all these different DFTs. Then one can develop approximations within such a unifying framework, which makes these approximations automatically applicable to all the discussed DFTs. The latter approach is the one that we will pursue in this chapter. Of course the question is which unifying framework to use. Here a look at classical physics can help. If we consider classical mechanics, there are several equivalent ways of representing the same physics. Originally Newton developed a force-based approach that considers EOMs, later the Lagrangian perspective based on the action principle and the Hamiltonian formulation based on the energy principle were introduced [134]. This equivalence indicates that we should be able to do the same and represent, for instance, the minimum energy (ground state) problem of the static Schrödinger equation as a force balance problem. An idea that was already highlighted by Tokatly [77] and Runge and Gross [14]. If we are able to recast the static problem also as an EOM problem of forces, then naturally we have all the four different

DFTs captured within the same framework and this is exactly what we will do. The minimum energy principle of DFT and CDFT will only be the basis from which we can deduce that there is an equivalent force balance that determines the xc potentials. This will allow us to seamlessly connect all the different DFTs via their xc potentials and derive an orbital dependent approximation for the exchange part of the xc potentials. We then show how these approximations relate to the most common ground state DFT approximation, namely the LDA.

This chapter is divided into four sections. In Sec. 3.1 we derive the EOMs of the one-body reduced density matrix (1-RDM) which contains all the necessary EOMs of the different DFTs as limiting cases. From the EOMs we establish in Sec. 3.2 exact expressions for the xc potentials of the different DFTs based on the idea of a local force balance and subsequent functional approximations of exact-exchange type. Further in Sec. 3.3 we show how in the homogeneous case these EOM-based approximations lead to the usual exchange LDA potential that we saw in Sec. 2.1.2. In Sec. 3.4 we then investigate whether we can use more complex xc potentials to increase the accuracy of lower-lying DFTs, e.g., use TDCDFT vector potentials in the TDDFT setting.

3.1 EQUATIONS OF MOTION: FROM THE REDUCED DENSITY MATRIX TO THE DENSITY

In the TDDFT and TDCDFT case we saw that time-dependent quantum many-body systems can be described by local force equations, since they allow to establish the corresponding one-to-one correspondences. Such a force based perspective is not new but was already introduced by Runge and Gross [14] and later on by Vignale [121, 125, 135] and Tokatly [75, 77, 136, 137]. The authors also nicely connected this perspective to quantum hydrodynamics, where the density and density currents are interpreted as a fluid and the different force terms are interpreted as compressabilities, shear and torque modules of the quantum fluid. In this way they deduced certain approximations to the respective xc potentials [77, 125, 129]. In this section, we present the fundamental EOM of the 1-RDM from which we can deduce all the other necessary EOMs. The basic quantities we intend to focus on later are the particle and current densities, which are all one-body quantities. Thus their EOMs can be deduced from the EOM of the 1-RDM. This allows us to establish a direct relation between the basic functional variables (density, paramagnetic or physical current) and their corresponding potentials (scalar and/or vector potential). To cover all situations discussed in the first chapter we consider the magnetic Hamiltonian of Eq. (90) which we simply re-write as

$$\hat{H} = \underbrace{\sum_{i=1}^N h(\mathbf{r}_i, t)}_{=\hat{T}+\hat{V}} + \hat{W}, \quad (113)$$

to easily understand some derivations which will be done later. Naturally, we recover the usual Schrödinger Hamiltonian when we set $\mathbf{A} \equiv 0$ and the static case for time-independent Hamiltonians. Given that the Hamiltonian of Eq. (90) contains only one- and two-body operators, a reduced form of the wavefunction that still provides exact results for the expectation values of the Hamiltonian would need to include at least two different particle coordinates. If we introduce the spin-summed p^{th} -order reduced density matrix (p -RDM), $p \in (1, \dots, N)$,

$$\begin{aligned} \rho_{(p)}(\mathbf{r}_1, \dots, \mathbf{r}_p, \mathbf{r}'_1, \dots, \mathbf{r}'_p, t) \\ = \frac{N!}{p!(N-p)!} \sum_{\substack{\sigma_1 \dots \sigma_p \\ \sigma'_1 \dots \sigma'_p}} \int \Psi(\mathbf{x}_1, \dots, \mathbf{x}_p, \mathbf{x}_{p+1}, \dots, \mathbf{x}_N, t) \\ \Psi^*(\mathbf{x}'_1, \dots, \mathbf{x}'_p, \mathbf{x}_{p+1}, \dots, \mathbf{x}_N, t) d\mathbf{x}_{p+1} \dots d\mathbf{x}_N, \end{aligned} \quad (114)$$

then we need at least the (diagonal of the) 2-RDM to calculate the expectation value of some two-body operator $\hat{B} = \sum_{i < j} b(\mathbf{r}_i, \mathbf{r}_j)$. That is, the interaction energy is given by [27]

$$\begin{aligned} \langle \Psi(t) | \hat{W} | \Psi(t) \rangle &= \sum_{i=1}^N \sum_{j>i}^N \int \Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N, t) w(|\mathbf{r}_i - \mathbf{r}_j|) \Psi^*(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N, t) d\mathbf{x}_1 \dots d\mathbf{x}_N \\ &= \int \rho_{(2)}(\mathbf{r}, \mathbf{r}_2, \mathbf{r}_2, \mathbf{r}, t) w(|\mathbf{r} - \mathbf{r}_2|) d\mathbf{r} d\mathbf{r}_2, \end{aligned}$$

where we use the notation $\mathbf{x}_1 = \mathbf{r}_1 \sigma_1$ as in Chap. 2. For any one-body operator, such as, the kinetic energy, the 1-RDM

$$\rho_{(1)}(\mathbf{r}, \mathbf{r}', t) = N \sum_{\sigma_1, \sigma'_1} \int \Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N, t) \Psi^*(\mathbf{x}'_1, \mathbf{x}_2, \dots, \mathbf{x}_N, t) d\mathbf{x}_2 \dots d\mathbf{x}_N \quad (115)$$

suffices. The expectation value of the kinetic energy then becomes

$$\begin{aligned} \langle \Psi(t) | \hat{T} | \Psi(t) \rangle &= \frac{N}{2} \int \Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N, t) (-i\nabla_1 + \mathbf{A}(\mathbf{r}_1, t))^2 \Psi^*(\mathbf{x}'_1, \mathbf{x}_2, \dots, \mathbf{x}_N, t) d\mathbf{x}_1 \dots d\mathbf{x}_N \\ &= \frac{1}{2} \int (-i\nabla + \mathbf{A}(\mathbf{r}, t))^2 \rho_{(1)}(\mathbf{r}', \mathbf{r}, t) \Big|_{\mathbf{r}=\mathbf{r}'} d\mathbf{r} \end{aligned}$$

where we indicate that we set $\mathbf{r} = \mathbf{r}'$ after acting with the gradient operators. For the external potential energy we find

$$\begin{aligned} \langle \Psi(t) | \hat{V}(t) | \Psi(t) \rangle &= N \int \Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N, t) v(\mathbf{r}_1, t) \Psi^*(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N, t) d\mathbf{x}_1 \dots d\mathbf{x}_N \\ &= \int v(\mathbf{r}, t) \underbrace{\rho_{(1)}(\mathbf{r}, \mathbf{r}, t)}_{=n(\mathbf{r}, t)} d\mathbf{r}. \end{aligned} \quad (116)$$

The 1- and the 2-RDMs are connected via

$$\rho_{(1)}(\mathbf{r}, \mathbf{r}') = \frac{2}{N-1} \int \rho_{(2)}(\mathbf{r}, \mathbf{r}_2, \mathbf{r}', \mathbf{r}_2) d\mathbf{r}_2 \quad (117)$$

and the one-particle density is written as

$$n(\mathbf{r}, t) = \rho_{(1)}(\mathbf{r}, \mathbf{r}). \quad (118)$$

This led to the idea that since we only need to know the 2-RDM of the many-electron system to determine the energy, we can find the minimum by only varying the 2-RDM (the 1-RDM and the density are trivially connected to the 2-RDM as can be seen above) instead of the whole wavefunction. However, a minimization by varying over the set of all possible 2-RDMs is a very difficult problem [138] since all the constraints the 2-RDM have to fulfill to correspond to a physical wavefunction, scale exponentially with the number of particles [139]. So the exponential wall we discussed in Sec. 2.1 reappears here again. This also applies to the 1-RDM [139], but lifting the restriction of only pure states makes the N -representability conditions for the 1-RDM much simpler.

Aside from the static case, the 1-RDM can be used also in the time-dependent situations

$$\begin{aligned} i\partial_t \rho_{(1)}(\mathbf{r}, \mathbf{r}', t) &= \left[h(\mathbf{r}, t) - \bar{h}(\mathbf{r}', t) \right] \rho_{(1)}(\mathbf{r}, \mathbf{r}', t) \\ &+ 2 \int [w(\mathbf{r}_2 - \mathbf{r}) - w(\mathbf{r}_2 - \mathbf{r}')] \rho_{(2)}(\mathbf{r}, \mathbf{r}_2, \mathbf{r}', \mathbf{r}_2, t) d\mathbf{r}_2. \end{aligned} \quad (119)$$

Here the overline is to indicate that we take the complex conjugate of the operator. We see from Eq. (119) that to propagate the 1-RDM one needs the time-dependent 2-RDM. Note that sometimes a different normalization convention for the 2-RDM is used, for example, in Ref. [140]. It is not hard to realize that due to the two-body interaction $w(|\mathbf{r} - \mathbf{r}'|)$, the EOM of the 2-RDM will contain the 3-RDM. So too, the EOM of the 3-RDM will include the 4-RDM and so on till one reaches the complete N -RDM. This chain of EOMs is known as the Bogoliubov–Born–Green–Kirkwood–Yvon (BBGKY) hierarchy. The usual way to use this hierarchy is to truncate the chain at a suitable level. This is usually done after the EOM of the 2-RDM. However, if we have mapping theorems as in the different DFTs, then we know that we can express the higher order RDMs as functionals of the corresponding densities. In this way we can stop at any order and we can close the BBGKY hierarchy by employing the basic mapping theorems. What is then left is to find an approximation for the unknown p -RDM terms. The KS construction does so by using the respective terms from an auxiliary non-interacting system.

Let us next connect the basic quantities of the different DFTs to the 1-RDM and its EOMs. The continuity equation can then be derived from the EOM of the 1-RDM by associating

$$i\partial_t n(\mathbf{r}, t) = i\partial_t \rho_{(1)}(\mathbf{r}, \mathbf{r}', t) \Big|_{\mathbf{r}'=\mathbf{r}}. \quad (120)$$

After acting with the operators on the right hand side of Eq. (119), we set $\mathbf{r}' = \mathbf{r}$. Hence the whole interaction part drops out as well as the terms including the

external potential v . We are then left with the terms involving the kinetic operator

$$i\partial_t n(\mathbf{r}, t) = \frac{1}{2} \left[(i\nabla + \mathbf{A}(\mathbf{r}, t))^2 - (i\nabla' - \mathbf{A}(\mathbf{r}', t))^2 \right] \rho_{(1)}(\mathbf{r}, \mathbf{r}', t) \Big|_{\mathbf{r}'=\mathbf{r}}, \quad (121)$$

where ∇ acts on the coordinate \mathbf{r} and ∇' on \mathbf{r}' . To evaluate the remaining terms we note that the ∇ and ∇' in the kinetic term both act on the vector potentials and the wavefunction such that we have

$$(\pm i\nabla - \mathbf{A})^2 = -\nabla^2 \mp i(\nabla \cdot \mathbf{A}) \mp 2i\mathbf{A} \cdot \nabla + \mathbf{A}^2. \quad (122)$$

Therefore the terms proportional to \mathbf{A}^2 also cancel out. As a result we obtain the continuity equation (92) where the one-particle (physical) current as in the previous chapter can be split into a paramagnetic and a diamagnetic contribution and written in terms of the 1-RDM as

$$\begin{aligned} \mathbf{j}(\mathbf{r}_1, t) &= \frac{1}{2i} \left[(\nabla - i\mathbf{A}(\mathbf{r}_1, t)) - (\nabla' + i\mathbf{A}(\mathbf{r}'_1, t)) \right] \rho_{(1)}(\mathbf{r}_1, \mathbf{r}'_1, t) \Big|_{\mathbf{r}'_1=\mathbf{r}_1} \\ &= N\mathfrak{S} \sum_{\sigma_1} \int \Psi^* \nabla \Psi \, dx_2 \dots dx_N - \mathbf{A}(\mathbf{r}_1, t) n(\mathbf{r}_1, t) \\ &= \mathbf{j}_{\text{para}}(\mathbf{r}_1, t) + \mathbf{j}_{\text{dia}}(\mathbf{r}_1, t). \end{aligned} \quad (123)$$

If we take $\mathbf{A} = 0$ we recover the continuity equation of the usual Schrödinger equation, that is, Eq. (44).

We derive the EOM for the current densities by taking the time derivative of Eq. (123) and by using the EOM of the 1-RDM (119). For notational clarity we introduce some relations regarding the application of the gradient operator which occur in the derivation of the EOM of the current density

$$\begin{aligned} \nabla(\nabla \cdot \mathbf{A}) &= ((\nabla \otimes \nabla)\mathbf{A}) + (\nabla \cdot \mathbf{A})\nabla \\ \nabla(\mathbf{A} \cdot \nabla) &= (\nabla \otimes \mathbf{A})\nabla + (\mathbf{A} \cdot \nabla)\nabla \\ \nabla\mathbf{A}^2 &= 2(\nabla \otimes \mathbf{A})\mathbf{A} + \mathbf{A}^2\nabla \end{aligned} \quad (124)$$

where \otimes denotes the dyadic(outer) product of two vectors. By setting $\mathbf{r}' = \mathbf{r}$ in the EOM of the current density, a few terms get cancelled and by making use of the continuity equation (92) we get

$$\begin{aligned}
\partial_t \mathbf{j}(\mathbf{r}, t) &= -n(\mathbf{r}, t) \partial_t \mathbf{A}(\mathbf{r}, t) + \frac{1}{2i} [(\nabla - i\mathbf{A}(\mathbf{r}, t)) \\
&\quad - (\nabla' + i\mathbf{A}(\mathbf{r}', t))] \partial_t \rho_{(1)}(\mathbf{r}, \mathbf{r}', t) \Big|_{\mathbf{r}'=\mathbf{r}} \\
&= -\frac{1}{4} (\nabla - \nabla') [(\mathbf{i}\nabla + \mathbf{A}(\mathbf{r}, t))^2 \\
&\quad - (\mathbf{i}\nabla' - \mathbf{A}(\mathbf{r}', t))^2] \rho_{(1)}(\mathbf{r}, \mathbf{r}', t) \Big|_{\mathbf{r}'=\mathbf{r}} \\
&\quad + \mathbf{A}(\mathbf{r}, t) (\nabla \cdot \mathbf{j}(\mathbf{r}, t)) \\
&\quad - (\nabla v(\mathbf{r}, t) + \partial_t \mathbf{A}(\mathbf{r}, t)) n(\mathbf{r}, t) \\
&\quad - 2 \int (\nabla w(\mathbf{r}' - \mathbf{r})) \rho_{(2)}(\mathbf{r}, \mathbf{r}', \mathbf{r}, \mathbf{r}', t) d\mathbf{r}'.
\end{aligned} \tag{125}$$

We can already identify different force terms, like the interaction force

$$\mathbf{F}_W[\Psi](\mathbf{r}, t) = -2 \int (\nabla w(\mathbf{r}' - \mathbf{r})) \rho_{(2)}(\mathbf{r}, \mathbf{r}', \mathbf{r}, \mathbf{r}', t) d\mathbf{r}', \tag{126}$$

and the (gauge-independent) force contribution from the electric field $\mathbf{E} = -(\nabla v + \partial_t \mathbf{A})$ that couples exclusively to the density. In the first term involving the 1-RDM in Eq. (125), we separate the parts including the vector potential \mathbf{A} and the terms that remain give rise to the kinetic force term,

$$\begin{aligned}
\mathbf{F}_T[\Psi](\mathbf{r}, t) &= \frac{1}{4} (\nabla - \nabla') (\nabla^2 - \nabla'^2) \rho_{(1)}(\mathbf{r}, \mathbf{r}', t) \Big|_{\mathbf{r}'=\mathbf{r}} \\
&= \frac{N}{2} \Re \sum_{\sigma} \int ((-\nabla^2 \Psi^*) \nabla \Psi + \Psi^* \nabla \nabla^2 \Psi) d\mathbf{x}_2 \dots d\mathbf{x}_N.
\end{aligned} \tag{127}$$

Putting all the remaining terms together yields the contribution from the Lorentz force and further internal forces involving the vector potential as

$$\begin{aligned}
\partial_t \mathbf{j} &= -n \overbrace{(\nabla v + \partial_t \mathbf{A})}^{-\mathbf{E}} + \mathbf{j} \times \overbrace{(\nabla \times \mathbf{A})}^{\mathbf{B}} + (\mathbf{A} \otimes \mathbf{j}) \overleftarrow{\nabla} \\
&\quad + ((\mathbf{j} + n\mathbf{A}) \otimes \mathbf{A}) \overleftarrow{\nabla} + \mathbf{F}_T[\Psi] + \mathbf{F}_W[\Psi].
\end{aligned} \tag{128}$$

We have obtained the EOM for the current, the *force balance equation*. This EOM can also be found in index notation and second quantization form in, e.g., Ref. [27]. It is easy to get the standard textbook expression of the Lorentz force by introducing the velocity $\mathbf{v} = \mathbf{j}/n$. To get to the compact form of the force balance equation above we used the vector identities

$$(\mathbf{A} \otimes \mathbf{j}) \overleftarrow{\nabla} = (\nabla \cdot \mathbf{j}) \mathbf{A} + (\mathbf{j} \cdot \nabla) \mathbf{A}, \tag{129}$$

$$\mathbf{j} \times (\nabla \times \mathbf{A}) = (\nabla \otimes \mathbf{A}) \mathbf{j} - (\mathbf{j} \cdot \nabla) \mathbf{A}. \tag{130}$$

where

$$\left((\mathbf{a} \otimes \mathbf{b}) \overleftarrow{\nabla} \right)_i = \sum_j \frac{\partial}{\partial r_j} \mathbf{a}_i \mathbf{b}_j. \quad (131)$$

By some non-trivial manipulation the forces due to kinetic and interaction effects can be represented in a form of divergence of a stress tensor, which describes the internal stresses in a fluid moving with velocity \mathbf{v} [75]. Therefore the integrals of these forces automatically vanish $\int \mathbf{F}_T \, d\mathbf{r} = \int \mathbf{F}_W \, d\mathbf{r} = 0$ in accordance with Newton's third law. A different way is to consider that for \mathbf{F}_W the interaction potential $w(\mathbf{r} - \mathbf{r}')$ is symmetric under the exchange of $\mathbf{r} \leftrightarrow \mathbf{r}'$, and therefore the full space integral has to vanish. Further, we see that the integrated forms of the first two terms on the right hand side of the force balance equation (128) give the Lorentz force [27, Eq. (3.38)]. The remaining two terms are explicitly expressed in divergence form. This implies that by integrating the force balance equation over the entire space, one gets the classical force expression and all quantum mechanical contributions cancel out as purely internal effects in accordance with the correspondence principle [16].

To fully cover the various settings which were discussed in the previous chapter, we also determine the corresponding EOM for the paramagnetic current

$$\begin{aligned} \partial_t \mathbf{j}_{\text{para}} = & -n \nabla v + (\nabla \otimes \mathbf{A})(\mathbf{j}_{\text{para}} - n\mathbf{A}) \\ & + (\mathbf{j}_{\text{para}} \otimes \mathbf{A}) \overleftarrow{\nabla} + \mathbf{F}_T[\Psi] + \mathbf{F}_W[\Psi]. \end{aligned} \quad (132)$$

While the paramagnetic current only appears explicitly as a basic quantity in ground state CDFT, and that here we consider a general time-dependent setting, we will see in the following that we can employ this gauge-dependent expression to find a definition for the xc potentials also in this case. Also for the other static DFTs we will see that we can use the respective EOMs to establish an exact expression of the corresponding xc potentials, even for a (hypothetical) ground state CDFT with the physical current.

3.2 EXACT XC POTENTIALS FROM THE FORCE BALANCE EQUATION

In the following we now do two things. Firstly, given that the basic one-to-one correspondences have been established (Chap. 2), we employ the EOM of the 1-RDM for an interacting and an auxiliary non-interacting (KS) system to establish defining relations for the different xc potentials. This does not only work for the time-dependent setting but also for the static setting, where the one-to-one correspondence based on the energy formulation guarantees the existence of a unique xc potential. Besides, we will recover several of the previously discussed exact constraints. Secondly, because all of these defining relations are given in terms of the EOM of the 1-RDM, we can easily connect them and show how approximations from one DFT setting have to be adopted to be applicable to the others. We will do so specifically for the local exchange approximation [141].

3.2.1 (Time-dependent) Density functional theory exchange-correlation potentials

We start with the ground state DFT case where only static, scalar external potentials are considered. In this setting we rely on the Hohenberg-Kohn theorem discussed in Sec. 2.1.2 which guarantees the existence of a well-defined density-potential mapping, in order to match the densities $n[\Psi] = n[\Phi] = n$ of the interacting and the non-interacting systems, respectively. In the ground state case the time derivative of any observable is zero. This applies also to the force balance equation (128) of the individual systems

$$\partial_{tj}[\Psi] = -n\nabla v + \mathbf{F}_T[\Psi] + \mathbf{F}_W[\Psi] = 0, \quad (133)$$

$$\partial_{tj_s}[\Phi] = -n\nabla v_s + \mathbf{F}_T[\Phi] = 0. \quad (134)$$

One will usually not make use of an equation for the current in this setting, given that a scalar potential enables us to control only the particle density and not the current density. However, the only current terms that appear are the time-derivatives, which by construction are zero. This only becomes an issue in the time-dependent setting where the time-derivative of the current is no longer zero. We now subtract Eq. (133) from Eq. (134) to gain access to the Hxc potential which is defined as $v_{\text{Hxc}} = v_s - v$ (see also Sec. 2.2.1),

$$n\nabla v_{\text{Hxc}} = -\mathbf{F}_{\text{Hxc}}[\Phi, \Psi] = \mathbf{F}_T[\Phi] - \mathbf{F}_T[\Psi] - \mathbf{F}_W[\Psi]. \quad (135)$$

Since the many-body wavefunctions Ψ and Φ of the interacting and auxiliary non-interacting system, respectively, are uniquely determined by the density, the interaction and stress tensors are functionals of the density as well, i.e., $\mathbf{F}_{\text{Hxc}}[\Phi, \Psi] = \mathbf{F}_{\text{Hxc}}[n]$. Thus Eq. (135) is an exact density functional definition of the Hxc potential in ground state DFT. At this point we highlight the main difference to the standard energy-based approach to DFT. In that approach the Hxc potential is obtained by making a functional derivative of the energy functional. However, the exact ground state energy functional is non-differentiable with respect to the density [142], so regularization techniques have to be employed to circumvent this issue [118, 143]. In our present approach, we do not have to deal with these differentiability issues as v_{Hxc} is expressed directly in terms of the internal stress tensors. The form of Eq. (135) as a means of obtaining v_{Hxc} has been used before in [77] and [141] where the internal stress tensors of both the interacting and non-interacting systems were involved. Eq. (135) holds *exactly* and we also realize that if Φ and Ψ are ground state wavefunctions satisfying the Schrödinger equation without vector potential, then $\mathbf{F}_{\text{Hxc}}[\Phi, \Psi]/n$ is purely a gradient field, so it has only longitudinal contributions (see also discussion about the Helmholtz decomposition in Sec. 2.4.1). This becomes important again in Sec. 3.4 where we investigate whether we can get more accurate approximations for (TD)DFT by using a non-interacting auxiliary system with a vector potential in combination with the usual KS scalar potential. We have seen that the xc potentials can usually be separated into an

exchange and correlation part. This is also the case here and from Eq. (135) v_{Hxc} can be expanded into a Hartree-exchange and a remaining correlation part as

$$n\nabla v_{\text{Hxc}} = \underbrace{-\mathbf{F}_W[\Phi]}_{\rightarrow v_{\text{Hx}}} + \underbrace{\mathbf{F}_T[\Phi] - \mathbf{F}_T[\Psi] + \mathbf{F}_W[\Phi] - \mathbf{F}_W[\Psi]}_{\rightarrow v_c}, \quad (136)$$

$$n\nabla v_{\text{Hx}} = -\mathbf{F}_W[\Phi], \quad (137)$$

$$n\nabla v_c = \mathbf{F}_T[\Phi] - \mathbf{F}_T[\Psi] + \mathbf{F}_W[\Phi] - \mathbf{F}_W[\Psi]. \quad (138)$$

Here $\mathbf{F}_W[\Phi]$ means that we calculate the interaction-stress tensor defined in Eq. (126) not with the exact interacting wavefunction but with the exact non-interacting wavefunction. The Hartree-exchange potential v_{Hx} from Eq. (137) is a functional of the non-interacting wavefunction Φ which is usually assumed to be a Slater-determinant. Therefore v_{Hx} already counts as a full-fledged orbital-dependent approximation to the xc potential, called the *local-exchange* approximation [141]. One thing that is not a priori clear is whether the functional derivative of the well-known exchange approximation of the exchange energy functional [144] actually yields this local-exchange potential. The EOM-based local-exchange approximation has only been shown to coincide with the energy-based exchange approximation in the case of a spin-singlet two-particle system [141].

Let us now consider the time-dependent situation and assume a time-dependent scalar potential in the interacting and auxiliary non-interacting systems. This is the usual setting of TDDFT. To derive a defining relation like Eq. (135) that works in this setting, we consider the second-time derivative of the density instead of the force balance equation as already done by Runge and Gross (see also Sec. 2.2.1). What we then need to match are the time-dependent densities of both the interacting and the non-interacting systems. Using the RG theorem [14] of TDDFT and its extensions [15, 90, 145] we know that we can match the densities of these different systems. Starting from the continuity Eq. (44) we make a further derivative to get $\partial_t^2 n = -\nabla \cdot \partial_t \mathbf{j}$, where the EOM of the current appears again. Using this EOM that we already considered in Sec. 2.2.1 to establish the extended form of the RG theorem, we have for both systems

$$\partial_t^2 n = \nabla(n\nabla v) - \nabla(\mathbf{F}_T[\Psi] + \mathbf{F}_W[\Psi]), \quad (139)$$

$$\partial_t^2 n = \nabla(n\nabla v_s) - \nabla\mathbf{F}_T[\Phi]. \quad (140)$$

Assuming that both have the same time-dependent density throughout time and subtracting the two equations above leads to Eq. (135), which we restate here again:

$$\nabla(n\nabla v_{\text{Hxc}}) = -\nabla\mathbf{F}_{\text{Hxc}}[\Phi, \Psi]. \quad (141)$$

Again, due to the RG theorem and its extensions we can express the states by the density (and the respective initial states), which implies that $\nabla\mathbf{F}_{\text{Hxc}}[\Phi, \Psi] = \nabla\mathbf{F}_{\text{Hxc}}[\Phi_0, \Psi_0, n]$. Such an equation can be solved efficiently and a numerical construction that gives exact results of v_{xc} for two- and three-dimensional many-electron systems has been demonstrated by Nielsen et al. [146].

We see that for the static case we could also have used the divergence of the local-force-equation (135) since $\mathbf{F}_{\text{Hxc}}/n$ is purely longitudinal. In a static setting, the two defining relations (135) and (141) contain exactly the same information and so they will both lead to the same approximations. Yet in a time-dependent setting, Eq. (135) cannot be used given that the scalar potential cannot control the full current density, but only its longitudinal part. In that case the EOMs of the interacting and the non-interacting systems cannot be made to match at all times. That is why we need to work with Eq. (141) in TDDFT.

Eq. (141) can be expanded into its different Hxc parts as we did before and the local-exchange approximation becomes [141, Eq. (24)]

$$\nabla(n\nabla v_{\text{Hxc}}) = -\nabla\mathbf{F}_W[\Phi]. \quad (142)$$

Since we no longer have that $\mathbf{F}_{\text{Hxc}}/n$ is purely longitudinal, we see that we cannot a priori use an approximation based on Eq. (135) in the time-dependent setting. This again highlights possible problems that arise when using ground state DFT approximations in TDDFT. On the other hand, using a TDDFT approximation based on Eq. (141), such as the local-exchange approximation of Eq. (142) in the ground state case is perfectly valid. We will see that we find such nice consistencies throughout by going from more general DFTs to more specialized DFTs.

3.2.2 Paramagnetic current density functional theory exchange-correlation potentials

We have established defining relations for the xc potential in (TD)DFT including static and time-dependent external scalar potentials. Let us now look at CDFT which we know is a natural generalization of DFT to cases including magnetic fields. The density quantity corresponding to the external potential \mathbf{A} that appears in the Hamiltonian of Eq. (90) is then the current density for which different forms could be chosen to get determining equations for the exact xc potentials depending on the setting. In principle, the xc potentials are obtained as the functional derivatives of the energy expression with respect to the density and current, while keeping the potentials fixed [107, 116]. However, given that the vector potential explicitly appears in the expression for the physical current (73), the functional derivative is no longer viable and as we saw in CDFT (Sec. 2.3.1), it is rather the paramagnetic current that must be taken as a corresponding density quantity. Therefore in this section we match the paramagnetic current of the interacting and the non-interacting systems to get a defining equation for the xc potentials. That this is indeed possible relies on a weaker version of the Hohenberg-Kohn theorem based on the work of Vignale and Rasolt [107, 116] (see also Sec. 2.3.1).

From Eq. (132) the EOM for both the interacting and the non-interacting reference system are given as,

$$\begin{aligned} \partial_t \mathbf{j}_{\text{para}} &= -n \nabla v + (\nabla \otimes \mathbf{A})(\mathbf{j}_{\text{para}} - n\mathbf{A}) \\ &\quad + (\mathbf{j}_{\text{para}} \otimes \mathbf{A}) \overleftarrow{\nabla} + \mathbf{F}_T[\Psi] + \mathbf{F}_W[\Psi], \end{aligned} \quad (143)$$

$$\begin{aligned} \partial_t \mathbf{j}_{\text{para}} &= -n \nabla v_s + (\nabla \otimes \mathbf{A}_s)(\mathbf{j}_{\text{para}} - n\mathbf{A}_s) \\ &\quad + (\mathbf{j}_{\text{para}} \otimes \mathbf{A}_s) \overleftarrow{\nabla} + \mathbf{F}_T[\Phi]. \end{aligned} \quad (144)$$

By subtracting the two EOMs above and defining $v_{\text{Hxc}} = v_s - v$ and $\mathbf{A}_{\text{xc}} = \mathbf{A}_s - \mathbf{A}$

$$\begin{aligned} n \nabla v_{\text{Hxc}} &= (\nabla \otimes \mathbf{A}_{\text{xc}})(\mathbf{j}_{\text{para}} - n\mathbf{A} - n\mathbf{A}_{\text{xc}}) \\ &\quad - (\nabla \otimes \mathbf{A})n\mathbf{A}_{\text{xc}} + (\mathbf{j}_{\text{para}} \otimes \mathbf{A}_{\text{xc}}) \overleftarrow{\nabla} - \mathbf{F}_{\text{Hxc}}[\Phi, \Psi]. \end{aligned} \quad (145)$$

we get a defining equation for v_{Hxc} and \mathbf{A}_{xc} for matched densities and paramagnetic currents. Again we can express everything in terms of the basic quantities of CDFT due to Vignale's results, that is $\mathbf{F}_{\text{Hxc}}[\Phi, \Psi] = \mathbf{F}_{\text{Hxc}}[\mathbf{j}_{\text{para}}, n]$. It is now possible to determine v_{Hxc} and \mathbf{A}_{xc} separately by using the Helmholtz decomposition that splits a vector field uniquely into a curl-free (longitudinal) and a divergence-free (transverse) component. This same decomposition was recently suggested in Ref. [147] so as to make magnetic-field functionals, source-free. The internal-force terms are decomposed as $\mathbf{F}_{\text{Hxc}}/n = -\nabla\varphi + \nabla \times \boldsymbol{\alpha}$ with the curl-free component $-\nabla\varphi$ and the divergence-free component $\nabla \times \boldsymbol{\alpha}$. If we now attribute $v_{\text{Hxc}} = \varphi$, then the vector potential has to satisfy the following equation

$$\begin{aligned} (\nabla \otimes \mathbf{A}_{\text{xc}})(\mathbf{j}_{\text{para}} - n\mathbf{A} - n\mathbf{A}_{\text{xc}}) - (\nabla \otimes \mathbf{A})n\mathbf{A}_{\text{xc}} \\ + (\mathbf{j}_{\text{para}} \otimes \mathbf{A}_{\text{xc}}) \overleftarrow{\nabla} = n \nabla \times \boldsymbol{\alpha}[\Phi, \Psi]. \end{aligned} \quad (146)$$

From these, the corresponding local-exchange approximation to the potentials are obtained as $v_{\text{Hxc}} = \varphi_x[\Phi]$ and

$$\begin{aligned} (\nabla \otimes \mathbf{A}_x)(\mathbf{j}_{\text{para}} - n\mathbf{A} - n\mathbf{A}_x) - (\nabla \otimes \mathbf{A})n\mathbf{A}_x \\ + (\mathbf{j}_{\text{para}} \otimes \mathbf{A}_x) \overleftarrow{\nabla} = n \nabla \times \boldsymbol{\alpha}_x[\Phi]. \end{aligned} \quad (147)$$

We notice that if we consider the limit of no external vector potentials we get back the local-exchange approximation of Eqs. (137) and (142).

When the densities and the paramagnetic densities are made to match via the continuity equation, this gives rise to a condition for \mathbf{A}_{xc} , which in Ref. [148] was termed a "remarkable identity". Given that the densities $n[\Phi] = n[\Psi]$ are made to match, hence their time-derivatives also match. This implies that $\nabla \cdot \mathbf{j}[\Phi] = \nabla \cdot \mathbf{j}[\Psi]$ from the continuity equation (92). If we now assume that the paramagnetic currents are the same, this gives $\nabla \cdot (n\mathbf{A}_s) = \nabla \cdot (n\mathbf{A})$ and consequently

$$\nabla \cdot (n\mathbf{A}_{\text{xc}}) = 0. \quad (148)$$

As such we get a further condition for \mathbf{A}_{xc} that is valid in the paramagnetic CDFT setting. This new condition (148) can be considered as a further form of gauge fixing that comes together with a loss of gauge freedom for \mathbf{A}_{xc} . This gauge freedom was lost from the start by considering \mathbf{j}_{para} which is not a gauge invariant quantity. This reduced freedom in the choice of \mathbf{A}_{xc} when matching paramagnetic currents might also be the reason why we obtain a rigid balance equation like Eq. (145) rather than an evolution equation that we get for \mathbf{A}_{xc} in the time-dependent case of Sec. 3.2.3. Note that once we match the paramagnetic currents and the densities, the "remarkable identity" Eq. (148) is valid both for the ground-state and the time-dependent setting. In the ground-state case, $\nabla \cdot \mathbf{j}[\Phi] = \nabla \cdot \mathbf{j}[\Psi] = 0$ is additionally valid. For a time-dependent setting, Eq. (148) can be fulfilled at every time by treating it as a gauge condition and by choosing a corresponding time-dependent gauge. However, such a time-dependent gauge field $\Lambda(\mathbf{r}, t)$ also influences the scalar potential as we saw in Eq. (85), thus it would no longer be possible to simultaneously fulfill $v_{\text{Hxc}} = \varphi$, where φ is determined by the longitudinal xc force. All these indications support the fact that the relevant current density quantities to be used are the physical current for a time-dependent setting and the paramagnetic current for ground-state CDFT.

By considering a new scalar potential $u = v + \frac{1}{2}|\mathbf{A}|^2$ [114] it was noted that this provides a concave ground state energy functional that fits into Lieb's convex conjugate formulation [43] that was adopted to static CDFT. This is also beneficial in the present EOM-based approach as it simplifies the expression for the xc potentials (145). By using this new scalar potential we get a term $\frac{1}{2}\nabla|\mathbf{A}|^2 = (\mathbf{A} \cdot \nabla)\mathbf{A} + \mathbf{A} \times (\nabla \times \mathbf{A}) = (\nabla \otimes \mathbf{A})\mathbf{A}$ causing the terms quadratic in \mathbf{A} , \mathbf{A}_s from Eqs. (143) and (144) to drop out. This gives us a simplified form of (145) with the new scalar xc potential $u_{\text{Hxc}} = u_s - u$

$$n\nabla u_{\text{Hxc}} = (\nabla \otimes \mathbf{A}_{\text{xc}})\mathbf{j}_{\text{para}} + (\mathbf{j}_{\text{para}} \otimes \mathbf{A}_{\text{xc}})\overleftarrow{\nabla} - \mathbf{F}_{\text{Hxc}}[\Phi, \Psi]. \quad (149)$$

We recall that the vorticity (82) was considered as a basic variable in static CDFT [107]. Therefore, when considering an xc potential that matches the paramagnetic current and the density like before, then the vorticities of the systems also agree by definition.

3.2.3 (Time-dependent) current density functional theory exchange-correlation potentials

In the case of general time-dependent electromagnetic fields we consider the physical current (204) in order to match the systems and derive the respective deter-

mining equations for the xc potentials. We start by repeating Eq. (128) for both, the interacting and the non-interacting systems,

$$\begin{aligned} \partial_t \mathbf{j} = & -n(\nabla v + \partial_t \mathbf{A}) + \mathbf{j} \times (\nabla \times \mathbf{A}) + (\mathbf{A} \otimes \mathbf{j}) \overleftarrow{\nabla} \\ & + ((\mathbf{j} + n\mathbf{A}) \otimes \mathbf{A}) \overleftarrow{\nabla} + \mathbf{F}_T[\Psi] + \mathbf{F}_W[\Psi], \end{aligned} \quad (150)$$

$$\begin{aligned} \partial_t \mathbf{j} = & -n(\nabla v_s + \partial_t \mathbf{A}_s) + \mathbf{j} \times (\nabla \times \mathbf{A}_s) + (\mathbf{A}_s \otimes \mathbf{j}) \overleftarrow{\nabla} \\ & + ((\mathbf{j} + n\mathbf{A}_s) \otimes \mathbf{A}_s) \overleftarrow{\nabla} + \mathbf{F}_T[\Phi]. \end{aligned} \quad (151)$$

To match the currents of both systems in the time-dependent case we rely on Vignale's extension of the RG theorem to TDCDFT [121] (see also Sec. 2.4.1). In the ground state case, such an extension for the Hohenberg-Kohn theorem that includes the physical current is not available to date [114, 115, 149]. Apart from the physical current \mathbf{j} , the density n of the interacting and non-interacting system will also be matched. For the time-dependent setting, due to the continuity equation, we see that it suffices to match the physical currents since the matching of the densities follows straightforwardly. This is not possible in the ground state case, since the time-derivative of the density that appears in the continuity equation will be zero naturally, thus the current and the density have to be controlled independently.

Subtracting Eq. (150) from Eq. (151) gives the determining equation for the xc potentials $v_{\text{Hxc}} = v_s - v$ and $\mathbf{A}_{\text{xc}} = \mathbf{A}_s - \mathbf{A}$

$$\begin{aligned} n(\partial_t \mathbf{A}_{\text{xc}} + \nabla v_{\text{Hxc}}) = & \mathbf{j} \times (\nabla \times \mathbf{A}_{\text{xc}}) + (\mathbf{A}_{\text{xc}} \otimes (\mathbf{j} + n\mathbf{A})) \overleftarrow{\nabla} \\ & + ((\mathbf{j} + n\mathbf{A} + n\mathbf{A}_{\text{xc}}) \otimes \mathbf{A}_{\text{xc}}) \overleftarrow{\nabla} - \mathbf{F}_{\text{Hxc}}[\Phi, \Psi], \end{aligned} \quad (152)$$

where \mathbf{F}_{Hxc} is defined as in Eq. (135) and we have $\mathbf{F}_{\text{Hxc}}[\Phi, \Psi] = \mathbf{F}_{\text{Hxc}}[\Phi_0, \Psi_0, \mathbf{j}, n]$. This equation was considered before in [77, Eq. (21)] but the dependence of the internal-force terms on the xc vector potential was not expressed explicitly. Further, making use of the same Helmholtz decomposition for $\mathbf{F}_{\text{Hxc}}/n$ as before, this gives $v_{\text{Hxc}} = \varphi$ and the vector potential has to fulfill the evolution equation,

$$\begin{aligned} n\partial_t \mathbf{A}_{\text{xc}} = & \mathbf{j} \times (\nabla \times \mathbf{A}_{\text{xc}}) + (\mathbf{A}_{\text{xc}} \otimes (\mathbf{j} + n\mathbf{A})) \overleftarrow{\nabla} \\ & + ((\mathbf{j} + n\mathbf{A} + n\mathbf{A}_{\text{xc}}) \otimes \mathbf{A}_{\text{xc}}) \overleftarrow{\nabla} - n\nabla \times \boldsymbol{\alpha}[\Phi, \Psi]. \end{aligned} \quad (153)$$

By neglecting all correlation contributions from \mathbf{F}_{Hxc} as in Eq. (136), meaning we set $\mathbf{F}_{\text{Hxc}}[\Phi, \Psi] \approx \mathbf{F}_W[\Phi]$, we get a corresponding version of Eq. (153), where the exchange part of the vector potential depends solely on the Slater-determinant wavefunction of the KS system,

$$\mathbf{F}_W[\Phi]/n = -\nabla\varphi_x[\Phi] + \nabla \times \boldsymbol{\alpha}_x[\Phi], \quad (154)$$

$$v_{\text{Hxc}} = \varphi_x[\Phi], \quad (155)$$

$$\begin{aligned} n\partial_t\mathbf{A}_x &= \mathbf{j} \times (\nabla \times \mathbf{A}_x) + (\mathbf{A}_x \otimes (\mathbf{j} + n\mathbf{A})) \overleftarrow{\nabla} \\ &+ ((\mathbf{j} + n\mathbf{A} + n\mathbf{A}_x) \otimes \mathbf{A}_x) \overleftarrow{\nabla} - n\nabla \times \boldsymbol{\alpha}_x[\Phi]. \end{aligned} \quad (156)$$

This gives us the local-exchange approximation for the scalar and the vector potential.

We note that the separation of scalar potential $v_{\text{Hxc}} = \varphi$ from the vector potential is simply a specific choice of gauge at this point. Actually, up until Eq. (152) there was still complete gauge freedom for the choices of $(v_{\text{Hxc}}, \mathbf{A}_{\text{xc}})$. What still remains from the original gauge freedom is the possibility to add a time-independent gradient field to the vector potential. Furthermore, the vector potential \mathbf{A}_{xc} which is a solution to the evolution equation Eq. (156), depends on previous instances of time and so it already includes memory effects. The xc potential captures the transverse contributions $\nabla \times \boldsymbol{\alpha}$ to the Hxc force $\mathbf{F}_{\text{Hxc}}/n$ that are lost in the case where one considers only the exchange potential from the longitudinal part of $\mathbf{F}_{\text{Hxc}}/n$ as in Eq. (141). We note that it is advantageous that the determining relation for \mathbf{A}_{xc} has the form of an evolution equation. For instance, if any part of the forces on the right hand side of Eq. (153) is not balanced, this can just be absorbed into the time-derivative $\partial_t\mathbf{A}_{\text{xc}}$.

We get an additional condition for \mathbf{A}_{xc} in terms of \mathbf{j}_{para} due to the requirement that the current densities should match $\mathbf{j}[\Phi] = \mathbf{j}[\Psi]$. Hence, by definition of the physical current density (204), we get the condition

$$\mathbf{j}_{\text{para}}[\Phi] - \mathbf{j}_{\text{para}}[\Psi] = n\mathbf{A}_{\text{xc}}. \quad (157)$$

Furthermore, we know that the initial states (Φ_0, Ψ_0) and the initial density fix v_{Hxc} (by fixing \mathbf{F}_{Hxc}) and \mathbf{A}_{xc} (by Eq. (157)) up to a gauge at the initial time. Therefore, this allows us to determine \mathbf{A}_{xc} and approximations like \mathbf{A}_x at the next time step uniquely via the evolution equation (152). If we now integrate Eq. (152) over the whole space and apply Gauss' theorem like in Sec. 2.4.1 we arrive at the zero-force and zero-torque conditions [77, Eq. (22)] that are always fulfilled by the exact pair $(v_{\text{Hxc}}, \mathbf{A}_{\text{xc}})$ and are used as consistency checks for approximate potentials,

$$\int n(\partial_t\mathbf{A}_{\text{xc}} + \nabla v_{\text{Hxc}}) \, \text{d}\mathbf{r} = \int \mathbf{j} \times (\nabla \times \mathbf{A}_{\text{xc}}) \, \text{d}\mathbf{r}, \quad (158)$$

$$\int n\mathbf{r} \times (\partial_t\mathbf{A}_{\text{xc}} + \nabla v_{\text{Hxc}}) \, \text{d}\mathbf{r} = \int \mathbf{r} \times (\mathbf{j} \times (\nabla \times \mathbf{A}_{\text{xc}})) \, \text{d}\mathbf{r}. \quad (159)$$

Let us now discuss about some peculiarity of the continuity equation in the different settings. Contrary to the stationary case, it is possible in the time-dependent case to get the density n at every time from the fixed initial state and the physical current \mathbf{j} by just integrating the continuity equation over time. This fits to the

insight that the complementary variable of the density, v , can be removed from the force balance equation (128) by making use of the gauge freedom of \mathbf{A} (see Sec. 2.4.1). Thereby making the physical current \mathbf{j} the quantity to be naturally matched between the interacting and the non-interacting system. This leads to another gauge which sets $v_{\text{Hx}} = 0$ such that, now the whole Hxc force \mathbf{F}_{Hxc} , instead of just its transverse part, is contained in Eq. (153). This is different from the gauge choice we implicitly had by doing the Helmholtz decomposition. However, given that the relation between the density and the current via the continuity equation does not hold in the same way for the ground state setting, one must keep in mind that a vector field \mathbf{A}_{xc} alone cannot control both quantities, hence a scalar potential v_{Hxc} is needed in this case.

Let us briefly also come back to the static case. In Sec. 3.2.3 we have given the defining relation for CDFT using the paramagnetic current and the density having an appropriate mapping. Now, if we assume that we also had a mapping for the static case that connects the physical current of the interacting system and of the non-interacting auxiliary system, then we can indeed provide a defining equation by Eq. (152), where we merely have to set $\partial_t \mathbf{A}_{\text{xc}} = 0$. This makes the inversion for the corresponding xc vector potential more involved, yet is valid nevertheless. We also notice that in the case where the vector potentials are zero, this approximation reduces the local-exchange approximation of Eq. (137). Keeping in mind that even with a mapping that would establish CDFT for physical currents the usual way of performing functional derivatives to obtain the xc potentials and vector potentials becomes problematic, we see a further nice advantage of the EOM approach. We will use this advantage also in Chap. 4.

3.3 LOCAL DENSITY APPROXIMATION FROM EXCHANGE FORCES

Having established defining equations for xc potentials in the different DFTs we realize that all the different EOM-based local-exchange approximations reduce to the local-exchange approximations of Eqs. (137) and (142) in the limit of zero external vector potential. However, how these local-exchange approximations correspond to the well-established energy-based approximations is what we do not know. It is only for the special case of two particles in a singlet configuration that the EOM-based exchange approximation is known to be equivalent to the usual energy-based exchange approximation [141]. In this section we want to give more insight into how the EOM-based approximations are related to the energy-based approximations. We do this by demonstrating that in the homogeneous case, the local-exchange approximation reduces to the well-known exchange-only LDA of ground-state DFT [9]. The way the derivation is presented here actually involves a direct connection to the $X\alpha$ method that we previously mentioned in Sec. 2.1.2, which was introduced by Slater [54] as a simplification to the Hartree-Fock method. In our derivation we see that the parameter α can be interpreted as the position-choice of a *reference point* \mathbf{r}_λ .

Single Slater Expression

As we recall, the wavefunction of the ground state for a non-interacting system is usually a single Slater determinant of the form of Eq. (10). Hence we can express the force terms for the non-interacting system in terms of this Slater determinant wavefunction. Here we are particularly interested in the interaction force term $\mathbf{F}_W[\Phi]$ which has the form of Eq. (126). This is the term that needs to be determined to get an expression for v_{Hx} . For this we need to get the expression of the 2-RDM in terms of the orbitals that make up the Slater determinant (10). We start with the definition of the 1-RDM for such a single Slater determinant wavefunction obtained after summing up all spin degrees of freedom and integrating out all orbitals with particle positions $\mathbf{r}_2 \dots \mathbf{r}_N$,

$$\rho_{(1)}(\mathbf{r}, \mathbf{r}') = \sum_{i=1}^N \sum_{\sigma} \phi_i(\mathbf{r}, \sigma) \phi_i^*(\mathbf{r}', \sigma). \quad (160)$$

The 2-RDM can be expressed in as similar form as a determinant of the 1-RDM

$$\rho_{(2)}(\mathbf{r}, \mathbf{r}_2, \mathbf{r}', \mathbf{r}'_2) = \frac{1}{2} \left(\rho_{(1)}(\mathbf{r}, \mathbf{r}') \rho_{(1)}(\mathbf{r}_2, \mathbf{r}'_2) - \frac{1}{2} \rho_{(1)}(\mathbf{r}, \mathbf{r}'_2) \rho_{(1)}(\mathbf{r}_2, \mathbf{r}') \right). \quad (161)$$

We note that an extra $\frac{1}{2}$ shows up in the second term due to the mixing of spin coordinates between the particles with coordinates $\mathbf{r}\sigma_1$ and $\mathbf{r}_2\sigma_1$ for which only half of them are not perpendicular because of their spin coordinates. Substituting this into the interaction force term \mathbf{F}_W , only the diagonal term remains

$$\rho_{(2)}(\mathbf{r}, \mathbf{r}_2, \mathbf{r}, \mathbf{r}_2) = \frac{1}{2} \left(n(\mathbf{r})n(\mathbf{r}_2) - \frac{1}{2} \left| \rho_{(1)}(\mathbf{r}, \mathbf{r}_2) \right|^2 \right) \quad (162)$$

and we get interaction force term of Eq. (126) as

$$\begin{aligned} \mathbf{F}_W[\Phi] &= - \int (\nabla w(\mathbf{r} - \mathbf{r}_2)) \left(n(\mathbf{r})n(\mathbf{r}_2) - \frac{1}{2} \left| \rho_{(1)}(\mathbf{r}, \mathbf{r}_2) \right|^2 \right) d\mathbf{r}_2 \\ &= -n(\mathbf{r}) \nabla \int w(\mathbf{r} - \mathbf{r}_2) n(\mathbf{r}_2) d\mathbf{r}_2 + \frac{1}{2} \int (\nabla w(\mathbf{r} - \mathbf{r}_2)) \left| \rho_{(1)}(\mathbf{r}, \mathbf{r}_2) \right|^2 d\mathbf{r}_2 \quad (163) \\ &= \mathbf{F}_H[\Phi] + \mathbf{F}_x[\Phi]. \end{aligned}$$

We see that the first term is simply the Hartree mean-field contribution to the force. Let us now look into the second term which contains the pure exchange effects from which we can define an effective exchange potential functional v_x ,

$$n \nabla v_H = -\mathbf{F}_H[\Phi] \quad (164)$$

$$\Rightarrow v_H[n](\mathbf{r}) = \int w(\mathbf{r} - \mathbf{r}_2) n(\mathbf{r}_2) d\mathbf{r}_2,$$

$$n \nabla v_x = -\mathbf{F}_x[\Phi]. \quad (165)$$

Following, we look into the exchange force term by considering the special case of the homogeneous electron gas.

Local Density Approximation derivation

Following the standard references [3, 9], we consider the homogeneous limit, i.e. the 3D uniform-electron-gas case in a volume $V = L^3$ with periodic boundary conditions. This leads to spatial orbitals of the form

$$\varphi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{V}} e^{i\mathbf{k}\cdot\mathbf{r}} \quad (166)$$

with $\mathbf{k} = (n_x, n_y, n_z)2\pi/L$. Each one of these orbitals is doubly occupied starting with the lowest energy $n_x, n_y, n_z = 0, \pm 1, \pm 2, \dots$ up to the Fermi surface $|p| = p_f = \hbar k_f$ with $k_f = (3\pi^2 n)^{1/3}$ (this is the "closed shell" assumption which requires an even number of electrons). The energy levels are given as $E(n_x, n_y, n_z) = \hbar^2/8ml^2[(2n_x)^2 + (2n_y)^2 + (2n_z)^2]$ which for large quantum numbers corresponds to just the number per unit energy range. The 1RDM in this setting is defined as

$$\rho_{(1)}(\mathbf{r}, \mathbf{r}') = 2 \sum_{\mathbf{k}} \varphi_{\mathbf{k}}(\mathbf{r}) \varphi_{\mathbf{k}}^*(\mathbf{r}') = \frac{2}{V} \sum_{\mathbf{k}} e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')} \quad (167)$$

where the sum is considered over all occupied orbitals \mathbf{k} . If the volume is large enough such that the spacing between consecutive energy eigenstates becomes very small, the sum can be replaced by an integral

$$\sum_{\mathbf{k}} \rightarrow \int_0^{k_f} dn; \quad dn = \frac{V}{(2\pi)^3} d\mathbf{k} = \frac{V}{8\pi^3} k^2 dk \sin\theta d\theta d\phi$$

such that the 1-RDM becomes

$$\begin{aligned} \rho_{(1)}(\mathbf{r}, \mathbf{r}') &= \frac{1}{4\pi^3} \int_{|\mathbf{k}| < k_f} e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')} d\mathbf{k} \\ &= \frac{1}{4\pi^3} \int_0^{k_f} k^2 dk \int_0^\pi \sin\theta e^{ik|\mathbf{r}-\mathbf{r}'|\cos\theta} d\theta \int_0^{2\pi} d\phi \\ &= \frac{1}{2\pi^2} \int_0^{k_f} k^2 dk \int_0^\pi \sin\theta e^{ik|\mathbf{r}-\mathbf{r}'|\cos\theta} d\theta \\ &= \frac{1}{2\pi^2} \int_0^{k_f} k^2 \left(\frac{2 \sin(k|\mathbf{r}-\mathbf{r}'|)}{k|\mathbf{r}-\mathbf{r}'|} \right) dk \\ &= \frac{1}{\pi^2 |\mathbf{r}-\mathbf{r}'|} \int_0^{k_f} k \sin(k|\mathbf{r}-\mathbf{r}'|) dk \\ &= \frac{1}{\pi^2} \frac{\sin(k_f |\mathbf{r}-\mathbf{r}'|) - k_f |\mathbf{r}-\mathbf{r}'| \cos(k_f |\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|^3} \end{aligned} \quad (168)$$

The integral over the sphere of radius $k_f = p_f/\hbar$ has been transformed to spherical coordinates (r, θ, ϕ) , with the z-axis pointing to the direction $\mathbf{r} - \mathbf{r}'$ and θ being the angle between $\mathbf{r} - \mathbf{r}'$ and the \mathbf{k} -vector. For an arbitrary density $n(\mathbf{r})$, k_f will depend on the position \mathbf{r}

$$k_f(\mathbf{r}) = (3\pi^2 n(\mathbf{r}))^{1/3}, \quad (169)$$

which raises the question of which point \mathbf{r}_p we should consider in the integral for $\rho_{(1)}(\mathbf{r}, \mathbf{r}')$ above, since it depends on two positions, \mathbf{r} and \mathbf{r}' . The standard choice of the argument of k_f is usually the mid-point between \mathbf{r} and \mathbf{r}' [9]. However, we make this choice variable by choosing an linear combination of \mathbf{r} and \mathbf{r}' , that is, $\mathbf{r}_\lambda = \mathbf{r} + \lambda(\mathbf{r}' - \mathbf{r}) = \mathbf{r} + \lambda\delta\mathbf{r}$. At the end we will show the connection between our parameter λ and the standard derivation. We would now like to express the 1-RDM in terms of $(\mathbf{r}_\lambda, |\delta\mathbf{r}|)$. By substituting $t = k_f(\mathbf{r}_\lambda)|\mathbf{r} - \mathbf{r}'| = k_f(\mathbf{r}_\lambda)|\delta\mathbf{r}|$ and putting (169) into Eq. (168) we get

$$\rho_{(1)}(\mathbf{r}, \mathbf{r}') = 3n(\mathbf{r}_\lambda) \frac{\sin t - t \cos t}{t^3}. \quad (170)$$

We then make use of this expression to evaluate the exchange term in Eq. (126) for the usual Coulomb interaction potential $w(\mathbf{r} - \mathbf{r}') = |\mathbf{r} - \mathbf{r}'|^{-1}$,

$$\begin{aligned} \mathbf{F}_x &= \frac{1}{2} \int \left(\nabla \frac{1}{|\mathbf{r} - \mathbf{r}'|} \right) \left| \rho_{(1)}(\mathbf{r}, \mathbf{r}') \right|^2 d\mathbf{r}' \\ &= -\frac{9}{2} \int \frac{\mathbf{r} - \mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|^3} n(\mathbf{r}_\lambda)^2 \left(\frac{\sin t - t \cos t}{t^3} \right)^2 d\mathbf{r}' \\ &= \frac{9}{2} \int \frac{\delta\mathbf{r}}{|\delta\mathbf{r}|^3} n(\mathbf{r}_\lambda)^2 \left(\frac{\sin t - t \cos t}{t^3} \right)^2 d\delta\mathbf{r}. \end{aligned} \quad (171)$$

We do a transformation of this integral to spherical coordinates again, $d\delta\mathbf{r} = |\delta\mathbf{r}|^2 d|\delta\mathbf{r}| d\Omega = |\delta\mathbf{r}|^2 \frac{dt}{k_f} d\Omega$ and $d\Omega = \sin\vartheta d\vartheta d\varphi$, and get

$$\begin{aligned} \mathbf{F}_x &= \frac{9}{2} \int \frac{\delta\mathbf{r}}{|\delta\mathbf{r}|^3} \frac{|\delta\mathbf{r}|^2}{k_f} n(\mathbf{r}_\lambda)^2 \left(\frac{\sin t - t \cos t}{t^3} \right)^2 dt d\Omega \\ &= \frac{9}{2} \int \frac{\delta\mathbf{r}}{|\delta\mathbf{r}|^2} \frac{n(\mathbf{r}_\lambda)^2}{(3\pi^2 n(\mathbf{r}_\lambda))^{\frac{2}{3}}} \frac{(\sin t - t \cos t)^2}{t^5} dt d\Omega \\ &= \frac{9}{2(3\pi^2)^{\frac{2}{3}}} \int \frac{\delta\mathbf{r}}{|\delta\mathbf{r}|^2} n(\mathbf{r}_\lambda)^{\frac{4}{3}} \frac{(\sin t - t \cos t)^2}{t^5} dt d\Omega \end{aligned} \quad (172)$$

Given that the LDA exchange energy depends on the local density, which is assumed to be slowly varying, it seems natural to relate the exchange force to the local gradient of the density term. Hence we make a Taylor expansion of $n(\mathbf{r}_\lambda)^{\frac{4}{3}}$ at \mathbf{r} ,

$$n(\mathbf{r}_\lambda)^{\frac{4}{3}} = n(\mathbf{r})^{\frac{4}{3}} + \frac{4}{3} \lambda \delta\mathbf{r} (\nabla n(\mathbf{r})) n(\mathbf{r})^{\frac{1}{3}} + \dots \quad (173)$$

Due to the symmetry in the integral over $\delta\mathbf{r}$ all even terms of the Taylor expansion vanish in Eq. (172). We further consider only the first-order approximation in Eq. (173). Recalling also the relation (165) we get the exchange force term as

$$\begin{aligned}
\mathbf{F}_x(\mathbf{r}) &= -n(\mathbf{r})\nabla v_x[n](\mathbf{r}) \\
&\approx \frac{9}{2(3\pi^2)^{\frac{2}{3}}} \int \frac{\delta\mathbf{r}}{|\delta\mathbf{r}|^2} \frac{4}{3} \lambda \delta\mathbf{r} (\nabla n(\mathbf{r})) n(\mathbf{r})^{\frac{1}{3}} \frac{(\sin t - t \cos t)^2}{t^5} dt d\Omega \\
&= \frac{9}{2} \frac{4\lambda n(\mathbf{r})^{\frac{1}{3}}}{3(3\pi^2)^{\frac{2}{3}}} \underbrace{\int \frac{\delta\mathbf{r}}{|\delta\mathbf{r}|} \left(\frac{\delta\mathbf{r}}{|\delta\mathbf{r}|} \cdot \nabla n(\mathbf{r}) \right) d\Omega}_{\frac{4\pi}{3} \nabla n(\mathbf{r})} \underbrace{\int \frac{(\sin t - t \cos t)^2}{t^5} dt}_{\frac{1}{4}} \\
&= \frac{2}{3} \lambda \left(\frac{3}{\pi} \right)^{\frac{1}{3}} n(\mathbf{r})^{\frac{1}{3}} \nabla n(\mathbf{r}) = 2\lambda \left(\frac{3}{\pi} \right)^{\frac{1}{3}} n(\mathbf{r}) \nabla n(\mathbf{r})^{\frac{1}{3}} \tag{174}
\end{aligned}$$

where the vector projection of an arbitrary vector \mathbf{a} yields

$$\int \frac{\delta\mathbf{r}}{|\delta\mathbf{r}|} \frac{\delta\mathbf{r} \cdot \mathbf{a}}{|\delta\mathbf{r}|} d\Omega = \frac{4\pi}{3} \mathbf{a}. \tag{175}$$

The first order term of the local-exchange potential is simply the local-density approximation from Eq. (174) and then comparing it to the usual LDA expression v_x^{LDA} Eq. (36),

$$v_x^{\text{LDA}}[n](\mathbf{r}) = -2\lambda \left(\frac{3}{\pi} \right)^{\frac{1}{3}} n(\mathbf{r})^{\frac{1}{3}} = 2\lambda v_x^{\text{LDA}}[n](\mathbf{r}). \tag{176}$$

If one chooses $\lambda = 1/2$, meaning the density is taken at the middle point between \mathbf{r} and \mathbf{r}' , this is exactly like in the usual energy-based derivation [9], and we recover the usual LDA exchange-only potential. The competing values, $\alpha = 1$ and $\alpha = 2/3$ for the usual LDA in the $X\alpha$ method, come from applying the uniform-electron-gas approximation at different stages of the derivation. This ambiguity has led to an attitude where α was taken as an adjustable parameter that can be fitted to empirical evidence [55]. In our derivation we have denoted such variable parameter as λ which is related to α by $\lambda = 3\alpha/4$. In our derivation this parameter has a clear conceptual meaning which is the point around which the Taylor expansion (173) is made.

3.4 TRANSVERSAL EXCHANGE FORCES

We have derived local-exchange approximations for different DFTs based on the corresponding EOMs. We have further seen that all of these approximations are connected to each other and reduce, for the case of a homogeneous electron gas with no external scalar or vector potential, to the usual exchange-only LDA. This in turn also shows that the common practice of applying ground state DFT approximations like the LDA to other DFT settings introduces further, often uncontrolled

approximations. On the other hand, the more complex DFT settings usually include the simpler ones as special cases. For instance, TDCDFT has in general (v, \mathbf{A}) that control (n, \mathbf{j}) and thus the cases where we only vary the scalar potentials $(v, 0)$ are also included. The local-exchange approximation of TDCDFT then approximates the pair (n, \mathbf{j}) while in the corresponding TDDFT setting the local-exchange approximation only approximates n . In other words, since we saw in Sec. 2.4.1 that TDDFT is a special case of TDCDFT in the limit of no magnetic fields and the same holds for the respective defining equations in Sec. 3.2, we can use the local-exchange approximation of TDCDFT also in TDDFT. It seems plausible that such a higher-lying approximation is more accurate when applied to a lower-lying DFT setting. Specifically, the local-exchange approximation of TDCDFT takes into account also the transverse part of the exchange forces. It therefore becomes interesting to investigate whether there are any transverse contributions present in the exchange forces. We note that due to Eq. (135) for the static case, the total \mathbf{F}_{Hxc} is purely longitudinal. This is, however, not necessarily the case for the exchange part. Further, in the time-dependent setting, even the full \mathbf{F}_{Hxc} has a transversal part for the case with only scalar external potentials.

We note that in the KS construction, nothing prevents us from using different auxiliary systems as long as they allow to control the same objects as in the interacting theory. That is, even if in the interacting theory there is no external vector potential we can still use a vector potential in the auxiliary system to have the same density and (paramagnetic) current density. For instance, for a non-zero \mathbf{A}_x as defined in Eq. (156), in this case all the transversal contributions need to come from $\mathbf{F}_W[\Phi]$.

To get an idea about under which conditions such transversal exchange forces would appear, we in the following consider a general two-electron system. Since the structure of the Slater determinant wavefunction is quite simple for this case, it is easy to analyze. Two-electron systems are a common playground to analyze properties in electronic structure theory as they provide a relevant connection between the relatively simple one-electron systems and many-electron systems. In a two-electron system, the spins of the electrons may be configured to form either a singlet state or a triplet state [150]. We investigate the interaction force term $\mathbf{F}_W[\Phi]$ for these two cases. We conclude with an outlook to the general N particle case.

Singlet state

We consider two electrons and the wavefunction is simply obtained from Eq. (10) as

$$\begin{aligned}\Phi(\mathbf{r}, \mathbf{r}_2) &= \frac{1}{\sqrt{2}} \det \begin{pmatrix} \phi_1(\mathbf{r}\sigma) & \phi_2(\mathbf{r}\sigma) \\ \phi_1(\mathbf{r}_2\sigma_2) & \phi_2(\mathbf{r}_2\sigma_2) \end{pmatrix} \\ &= \frac{1}{\sqrt{2}} (\phi_1(\mathbf{r}\sigma)\phi_2(\mathbf{r}_2\sigma_2) - \phi_1(\mathbf{r}_2\sigma_2)\phi_2(\mathbf{r}\sigma))\end{aligned}\quad (177)$$

and as we recall $\phi_i(\mathbf{x}) = \phi_i(\mathbf{r})\chi(\sigma)$ where $\sigma \in \{\uparrow, \downarrow\}$. There are in total four possible arrangements of the spin wavefunctions so that two-electron wavefunction $\Phi(\mathbf{r}_1, \mathbf{r}_2)$ remains antisymmetric [8]. One of these is the spin singlet $S = (|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)/\sqrt{2}$ which combines with a symmetric spatial wavefunction to give

$$\Phi(\mathbf{r}, \mathbf{r}_2) = \frac{1}{\sqrt{2}} (\phi_1(\mathbf{r})\phi_2(\mathbf{r}_2) + \phi_2(\mathbf{r})\phi_1(\mathbf{r}_2)) \otimes S. \quad (178)$$

The remaining three spin wavefunctions are called spin triplet and combine with an antisymmetric spatial wavefunction to form the triplet states which we will look at in the next section. Since the wavefunction we consider can also be time-dependent, the wave functions can in general be complex. We will, however, not indicate the time-dependence explicitly but consider $\Phi = \Phi(t)$ and some arbitrary time t . The particle and the current density for a singlet state are defined as

$$n(\mathbf{r}) = 2|\phi(\mathbf{r})|^2 \quad (179)$$

$$\mathbf{j}(\mathbf{r}) = 2\Im\{\phi^*(\mathbf{r})\nabla\phi(\mathbf{r})\} \quad (180)$$

In polar representation the orbitals can be expressed as

$$\phi(\mathbf{r}) = \sqrt{n(\mathbf{r})/2}e^{iu(\mathbf{r})} \quad (181)$$

and the 1-RDM for the doubly-filled orbital is then expressed

$$\rho_{(1)}(\mathbf{r}, \mathbf{r}') = 2\phi(\mathbf{r})\phi^*(\mathbf{r}') = \sqrt{n(\mathbf{r})n(\mathbf{r}')}e^{i(\mathbf{u}(\mathbf{r})-\mathbf{u}(\mathbf{r}'))} \quad (182)$$

with $\mathbf{u}(\mathbf{r}) = \mathbf{j}(\mathbf{r})/n(\mathbf{r})$. Substituting this 1-RDM in the expression for the exchange force of Eq. (163) we get

$$\begin{aligned}\mathbf{F}_W[\Phi] &= \mathbf{F}_x = \mathbf{F}_H + \frac{1}{2} \int (\nabla w(\mathbf{r} - \mathbf{r}'))n(\mathbf{r})n(\mathbf{r}') \, d\mathbf{r}' \\ &= \mathbf{F}_H - \frac{1}{2}\mathbf{F}_H \\ &= \frac{1}{2}\mathbf{F}_H\end{aligned}\quad (183)$$

We see that the interaction force has only Hartree mean-field contributions and so is purely longitudinal. This implies from Eq. (156) that at all times $\mathbf{A}_x = 0$ and

that all exchange effects are accounted for by only v_x . In this case, we gain no extra information from making use of the xc potentials for TDCDFT in a time-dependent setting where no vector potential is considered.

To make this observation more concrete we make use the Helmholtz decomposition and see if the conditions for a vector field to be transverse are fulfilled. We saw previously (154) that the interaction force could be decomposed into a curl-free and divergence-free part $\mathbf{F}_x/n = -\nabla\varphi_x[\Phi] + \nabla \times \boldsymbol{\alpha}_x[\Phi]$ where

$$\varphi_x = \frac{1}{4\pi} \int \frac{\nabla' \cdot (\mathbf{F}'_x/n)}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}', \quad (184)$$

$$\boldsymbol{\alpha}_x = \frac{1}{4\pi} \int \frac{\nabla' \times (\mathbf{F}'_x/n)}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \quad (185)$$

are valid when (\mathbf{F}'_x/n) vanishes faster than $1/r$ at the boundaries as $r \rightarrow \infty$. Hence to see whether the interaction force has non-vanishing longitudinal and transverse contributions, we check for $\nabla \cdot (\mathbf{F}_x/n)$ and $\nabla \times (\mathbf{F}_x/n)$ respectively. Let us start with

$$\nabla \cdot \frac{\mathbf{F}_x}{n} = \nabla \cdot \left(-\nabla \int w(\mathbf{r} - \mathbf{r}')n(\mathbf{r}') d\mathbf{r}' + \frac{1}{2n(\mathbf{r})} \int (\nabla w(\mathbf{r} - \mathbf{r}'))|\rho_{(1)}(\mathbf{r}, \mathbf{r}')|^2 d\mathbf{r}' \right) \quad (186)$$

where for the case of a singlet state we recall the 1RDM from (182) and make use of the relation $4\pi\delta^3(\mathbf{r} - \mathbf{r}') = -\nabla^2|\mathbf{r} - \mathbf{r}'|^{-1}$ to get

$$\begin{aligned} \nabla \cdot \frac{\mathbf{F}_x}{n} &= - \int (\nabla^2 w(\mathbf{r} - \mathbf{r}'))n(\mathbf{r}') d\mathbf{r}' - \frac{\nabla n(\mathbf{r}, t)}{2n^2(\mathbf{r})} \int (\nabla w(\mathbf{r} - \mathbf{r}'))n(\mathbf{r})n(\mathbf{r}') d\mathbf{r}' \\ &+ \frac{1}{2n(\mathbf{r})} \int (\nabla^2 w(\mathbf{r} - \mathbf{r}'))n(\mathbf{r})n(\mathbf{r}') d\mathbf{r}' + \frac{1}{2n(\mathbf{r})} \int \nabla w(\mathbf{r} - \mathbf{r}')(\nabla n(\mathbf{r}))n(\mathbf{r}') d\mathbf{r}' \\ &= \int 4\pi\delta^3(\mathbf{r} - \mathbf{r}')n(\mathbf{r}') d\mathbf{r}' - \frac{1}{2n(\mathbf{r})} \int 4\pi\delta^3(\mathbf{r} - \mathbf{r}')n(\mathbf{r})n(\mathbf{r}') d\mathbf{r}' \\ &= 2\pi n(\mathbf{r}). \end{aligned}$$

By substituting this result in Eq. (184) we see that the longitudinal part of the force indeed has only Hartree contributions. We now check for $\nabla \times (\mathbf{F}_x/n)$:

$$\nabla \times \frac{\mathbf{F}_x}{n} = \nabla \times \left(-\nabla \int w(\mathbf{r} - \mathbf{r}')n(\mathbf{r}') d\mathbf{r}' + \frac{1}{2n(\mathbf{r})} \int (\nabla w(\mathbf{r} - \mathbf{r}'))|\rho_{(1)}(\mathbf{r}, \mathbf{r}')|^2 d\mathbf{r}' \right) \quad (187)$$

The first term in the equation above is always zero as it is a curl of a gradient. We again substitute the 1-RDM for a singlet (182) to get

$$\begin{aligned}\nabla \times \frac{\mathbf{F}_x}{n} &= \nabla \times \left(\frac{1}{2n(\mathbf{r})} \int (\nabla w(\mathbf{r} - \mathbf{r}')) n(\mathbf{r}) n(\mathbf{r}') d\mathbf{r}' \right) \\ &= \nabla \times \left(\nabla \frac{1}{2} \int w(\mathbf{r} - \mathbf{r}') n(\mathbf{r}') d\mathbf{r}' \right) \\ &= 0\end{aligned}\tag{188}$$

We see that for a two-particle singlet $\nabla \cdot (\mathbf{F}_x/n) \neq 0$ and $\nabla \times (\mathbf{F}_x/n) = 0$. The latter is what was expected, since from Eq. (183) it was clear that the interaction force is 1/2 the Hartree-term which is a pure gradient term.

Triplet state

Let us next consider the spin triplet case. The wavefunction is given as

$$\Phi(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} (\phi_1(\mathbf{r})\phi_2(\mathbf{r}_2) - \phi_2(\mathbf{r})\phi_1(\mathbf{r}_2)) \otimes S.\tag{189}$$

where the spin triplet is $S \in \{|\uparrow\uparrow\rangle, \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle), |\downarrow\downarrow\rangle\}$. The particle density is given as

$$n(\mathbf{r}, t) = |\phi_1(\mathbf{r})|^2 + |\phi_2(\mathbf{r})|^2.\tag{190}$$

The 1-RDM from (160) in this case is given as

$$\rho_{(1)}(\mathbf{r}, \mathbf{r}') = \phi_1(\mathbf{r})\phi_1^*(\mathbf{r}') + \phi_2(\mathbf{r})\phi_2^*(\mathbf{r}').\tag{191}$$

We now evaluate $|\rho_{(1)}(\mathbf{r}, \mathbf{r}')|^2$ that will be replaced in the exchange force in Eq. (163)

$$\begin{aligned}|\rho_{(1)}(\mathbf{r}, \mathbf{r}')|^2 &= (\phi_1^*(\mathbf{r})\phi_1(\mathbf{r}') + \phi_2^*(\mathbf{r})\phi_2(\mathbf{r}'))(\phi_1(\mathbf{r})\phi_1^*(\mathbf{r}') + \phi_2(\mathbf{r})\phi_2^*(\mathbf{r}')) \\ &= |\phi_1(\mathbf{r})|^2|\phi_1(\mathbf{r}')|^2 + |\phi_2(\mathbf{r})|^2|\phi_2(\mathbf{r}')|^2 \\ &\quad + \phi_1(\mathbf{r})\phi_1^*(\mathbf{r}')\phi_2^*(\mathbf{r})\phi_2(\mathbf{r}') + \phi_2(\mathbf{r})\phi_2^*(\mathbf{r}')\phi_1^*(\mathbf{r})\phi_1(\mathbf{r}')\end{aligned}$$

The interaction force in this case is then given as

$$\begin{aligned}\mathbf{F}_W[\Phi]/n &= \mathbf{F}_x/n - \nabla \int w(\mathbf{r} - \mathbf{r}') n(\mathbf{r}') d\mathbf{r}' \\ &\quad + \frac{1}{2n(\mathbf{r})} \int (\nabla w(\mathbf{r} - \mathbf{r}')) \cdot \\ &\quad \quad (|\phi_1(\mathbf{r})|^2|\phi_1(\mathbf{r}')|^2 + |\phi_2(\mathbf{r})|^2|\phi_2(\mathbf{r}')|^2 \\ &\quad \quad + \phi_1(\mathbf{r})\phi_1^*(\mathbf{r}')\phi_2^*(\mathbf{r})\phi_2(\mathbf{r}') + \phi_2(\mathbf{r})\phi_2^*(\mathbf{r}')\phi_1^*(\mathbf{r})\phi_1(\mathbf{r}')) d\mathbf{r}'\end{aligned}\tag{192}$$

which is again the sum of the Hartree contribution to the force and the other part is the exchange force.

We now evaluate the curl of \mathbf{F}_x to check for transverse contribution of the interaction force. We already see that the first term in (192) will vanish since this is the Hartree contribution which is purely longitudinal. Using vector identities we are left with

$$\begin{aligned}
\nabla \times \frac{\mathbf{F}_x}{n} &= \frac{1}{2n(\mathbf{r})} \int \nabla \times (\nabla w(\mathbf{r} - \mathbf{r}')) \\
&\quad (|\phi_1(\mathbf{r})|^2 |\phi_1(\mathbf{r}')|^2 + |\phi_2(\mathbf{r})|^2 |\phi_2(\mathbf{r}')|^2 + \phi_1(\mathbf{r}) \phi_1^*(\mathbf{r}') \phi_2^*(\mathbf{r}) \phi_2(\mathbf{r}') \\
&\quad + \phi_2(\mathbf{r}) \phi_2^*(\mathbf{r}') \phi_1^*(\mathbf{r}) \phi_1(\mathbf{r}')) \, d\mathbf{r}' \\
&+ \frac{1}{2} \int \nabla \left[\frac{1}{n(\mathbf{r})} (\phi_1(\mathbf{r}) \phi_1^*(\mathbf{r}) \phi_2^*(\mathbf{r}) \phi_2(\mathbf{r}) + \phi_2(\mathbf{r}) \phi_2^*(\mathbf{r}) \phi_1^*(\mathbf{r}) \phi_1(\mathbf{r}) \right. \\
&\quad \left. + |\phi_1(\mathbf{r})|^2 |\phi_1(\mathbf{r})|^2 + |\phi_2(\mathbf{r})|^2 |\phi_2(\mathbf{r})|^2) \right] \times (\nabla w(\mathbf{r} - \mathbf{r}')) \, d\mathbf{r}' \\
&= \frac{1}{2} \int |\phi_1(\mathbf{r}')|^2 \nabla \left(\frac{|\phi_1(\mathbf{r})|^2}{n(\mathbf{r})} \right) \times (\nabla w(\mathbf{r} - \mathbf{r}')) \, d\mathbf{r}' \\
&+ \frac{1}{2} \int |\phi_2(\mathbf{r}')|^2 \nabla \left(\frac{|\phi_2(\mathbf{r})|^2}{n(\mathbf{r})} \right) \times (\nabla w(\mathbf{r} - \mathbf{r}')) \, d\mathbf{r}' \\
&+ \frac{1}{2} \int \phi_1^*(\mathbf{r}') \phi_2(\mathbf{r}') \nabla \left(\frac{\phi_1(\mathbf{r}) \phi_2^*(\mathbf{r})}{n(\mathbf{r})} \right) \times (\nabla w(\mathbf{r} - \mathbf{r}')) \, d\mathbf{r}' \\
&+ \frac{1}{2} \int \phi_2^*(\mathbf{r}') \phi_1(\mathbf{r}') \nabla \left(\frac{\phi_2(\mathbf{r}) \phi_1^*(\mathbf{r})}{n(\mathbf{r})} \right) \times (\nabla w(\mathbf{r} - \mathbf{r}')) \, d\mathbf{r}' \\
&= \frac{1}{2} \int |\phi_1(\mathbf{r}')|^2 \left(\frac{((\nabla \phi_1^*(\mathbf{r})) \phi_1(\mathbf{r}) + \phi_1^*(\mathbf{r}) \nabla \phi_1(\mathbf{r})) n(\mathbf{r}) - |\phi_1(\mathbf{r})|^2 \nabla n(\mathbf{r})}{n^2(\mathbf{r})} \right) \times \nabla w \, d\mathbf{r}' \\
&+ \frac{1}{2} \int |\phi_2(\mathbf{r}')|^2 \left(\frac{((\nabla \phi_2^*(\mathbf{r})) \phi_2(\mathbf{r}) + \phi_2^*(\mathbf{r}) \nabla \phi_2(\mathbf{r})) n(\mathbf{r}) - |\phi_2(\mathbf{r})|^2 \nabla n(\mathbf{r})}{n^2(\mathbf{r})} \right) \times \nabla w \, d\mathbf{r}' \\
&+ \frac{1}{2} \int \phi_1^*(\mathbf{r}') \phi_2(\mathbf{r}') \left(\frac{((\nabla \phi_1(\mathbf{r})) \phi_2^*(\mathbf{r}) + \phi_1(\mathbf{r}) \nabla \phi_2^*(\mathbf{r})) n(\mathbf{r}) - \phi_1(\mathbf{r}) \phi_2^*(\mathbf{r}) \nabla n(\mathbf{r})}{n^2(\mathbf{r})} \right) \times \nabla w \, d\mathbf{r}' \\
&+ \frac{1}{2} \int \phi_2^*(\mathbf{r}') \phi_1(\mathbf{r}') \left(\frac{((\nabla \phi_2(\mathbf{r})) \phi_1^*(\mathbf{r}) + \phi_2(\mathbf{r}) \nabla \phi_1^*(\mathbf{r})) n(\mathbf{r}) - \phi_2(\mathbf{r}) \phi_1^*(\mathbf{r}) \nabla n(\mathbf{r})}{n^2(\mathbf{r})} \right) \times \nabla w \, d\mathbf{r}'.
\end{aligned}$$

In general this part is non-vanishing. For instance, if we choose, the instantaneous orbitals as Gaussians

$$\phi_1(\mathbf{r}) = \sin(2x) \sin(2y) \sin(2z) e^{-|\mathbf{r}|^2/2} \quad (193)$$

$$\phi_2(\mathbf{r}) = \cos(2x) \cos(2y) \cos(2z) e^{-|\mathbf{r}|^2/2}, \quad (194)$$

the forces \mathbf{F}_x/n and the curl of the forces are shown in Figs. 1 and 2, respectively. We therefore see that indeed already for a triplet state we get transversal exchange forces.

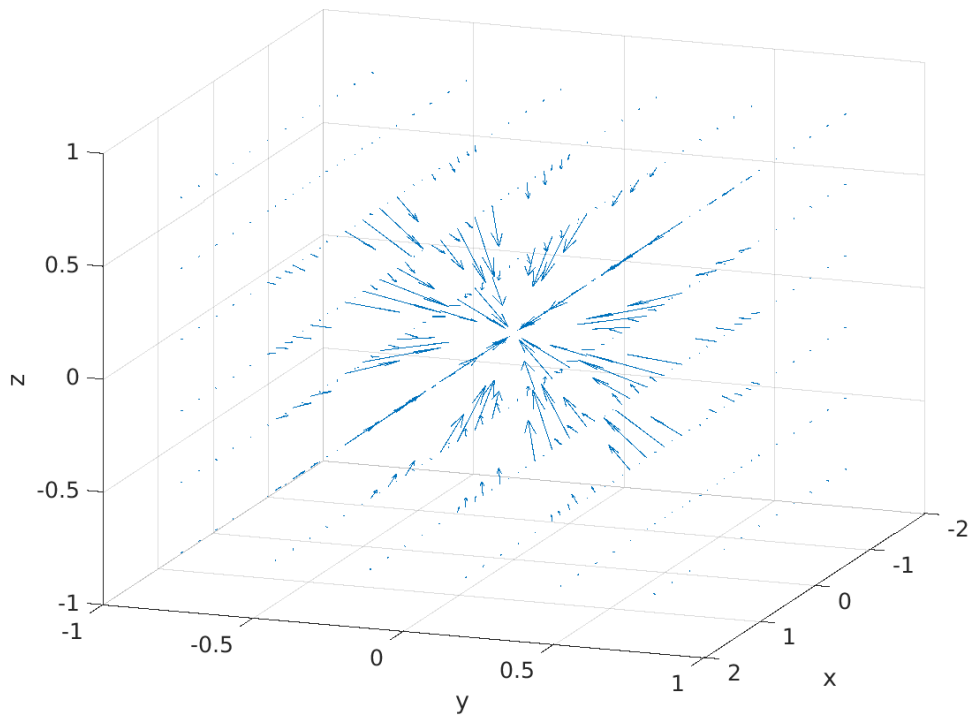


Figure 1: The exchange-force field \mathbf{F}_x/n for two particles in two Gaussian orbitals ϕ_1, ϕ_2 (triplet state).

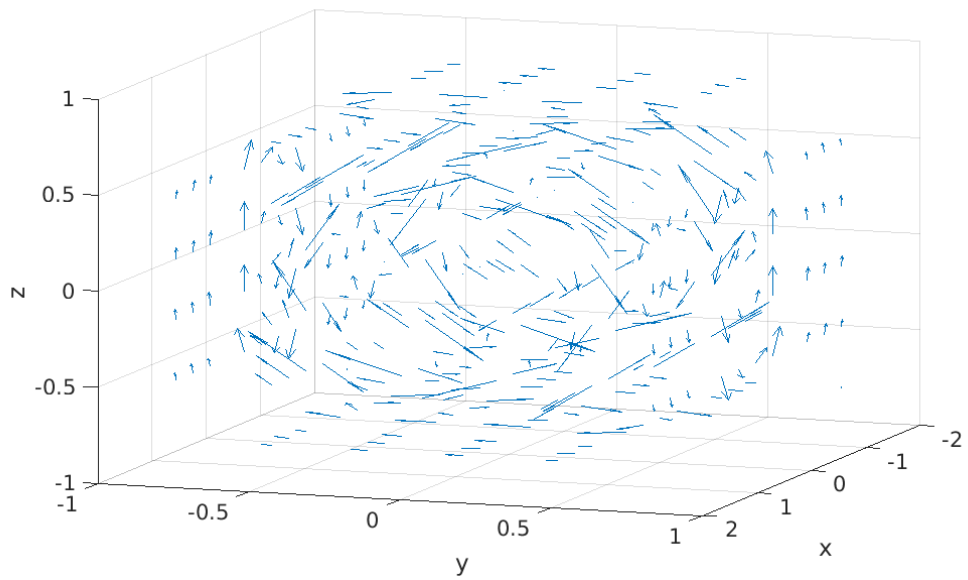


Figure 2: The curl of the exchange-force field \mathbf{F}_x/n for two particles in two Gaussian orbitals ϕ_1, ϕ_2 (triplet state).

Thus if we use a (TD)CDFT formulation, that is, a KS system including a scalar and vector xc potential, for the case of an interacting system without a vector potential, we find new contributions. The transversal part then adapts the current of the KS system to resemble the one from the interacting system. In the ground state case this has some subtle consequences. The exact interacting system without external vector potential has zero (paramagnetic) current and thus the KS system including the xc vector potential should have so as well. Clearly, if the self-consistent solution including the \mathbf{A}_x does not have zero paramagnetic contribution, then it is a violation of an exact constraint. In other words, for the ground state case with only external scalar potential, one should enforce

$$\nabla \times \mathbf{F}_x/n \equiv \nabla \times \mathbf{F}_c/n. \quad (195)$$

So we have a consistency condition for the correlation term. This is a new constraint in order to improve upon the local-exchange approximation. In the absence of a correlation part it seems possible to enforce as a side condition, e.g., via Lagrange multipliers or as a penalty term, that $\nabla \times \mathbf{F}_x/n \equiv 0$. Such a constraint would include beyond the spin singlet case correlation contributions.

From the observation that already for a spin-triplet situation we will find non-zero transversal contributions to the exchange forces, we can conclude that this also holds for the general N -particle case. It therefore becomes interesting to consider to what extent an inclusion of the transversal exchange forces by using TDCDFT instead of TDDFT for the same problem imply. It is to be expected that a TDCDFT calculation should lead to a better description than a normal TDDFT simulation in exchange approximation. For the static case, it is to be expected that the transversality of the exchange forces for situations with no external magnetic field give us a good way to judge the quality of correlation approximations.

FORCE-BASED APPROACH TO NUMERICALLY CONSTRUCT DENSITY-POTENTIAL MAPPINGS

So far we have shown that the force-based approach to DFTs is able to connect different settings and provides a straightforward orbital-dependent local-exchange approximation. To do so we used EOMs and connected the external fields to their internal control objectives. For instance, the scalar external potential to the density. Since the various xc potentials are defined as the difference between density-potential mappings, the EOM-based approach also allows us access to the different mappings. This is well known for TDDFT, where the inversion of the EOM of Eq. (59) allows to find the exact potential for a given initial state and time-dependent density [146]. However, as demonstrated in Ref. [15], the EOMs can also be used to numerically construct density-potential mappings in equilibrium. This becomes specifically interesting in the case where there are no mapping theorems available. So one can test numerically whether a possible mapping exists. Such a question arose in the case of CDFT, where it is so far unclear whether a Hohenberg–Kohn mapping between the physical current density and the external vector potential exists. The problem has been circumvented by using the paramagnetic current instead.

A similar problem arises once we change the setting and consider instead of continuous real space, a discretized lattice system. Already for the ground state density, rigorous results are, so far, only available for problems involving temperature [151]. Going beyond the static density, further quantities have been proposed to be in a one-to-one relation with an external control field, such as the kinetic energy density to a generalized hopping or the link current to the Peierls phase [152]. So in this chapter we highlight the potential that the EOM approach has to numerically investigate some of these mappings. For simplicity we will focus on the lattice case, but nothing prevents us fundamentally from using this approach for the continuum setting as well. The main reason is that numerical investigations even for simple continuum situations can already be very intricate [146]. Among others, subtle issues with boundary conditions and numerical representation of continuum operators arise that often need highly specialized treatment [15]. Thus here we will investigate the mappings between the lattice density and the scalar lattice potential and between the lattice kinetic energy density and the hopping, respectively, in a setting where the Peierls phase is involved. This distinguishes the following investigations from previous studies [153]. We will also focus on the static case, since for the time-dependent situation on a lattice, the respective mapping have already been established by Tokatly [152] and Farzanehpour&Tokatly [154].

In Sec. 4.1 we introduce the formulation of many-body systems on a lattice and define the observables of interest that we want to control with some external field. Then we briefly discuss what different DFTs there are for the lattice setting and the physical quantities that are involved. In Sec. 4.2 we show how we make use of the EOMs to numerically investigate the mappings in question and give an example for each case and provide some outlook.

4.1 MANY ELECTRONS ON A LATTICE

We consider for simplicity a one-dimensional lattice with L sites. To make the description and the following derivations a little bit more efficient we do not consider specifically only N electrons but we consider the full problem in Fock space. That is, we work with indefinite number of particles. This avoids to carry along the particle number explicitly and we can perform very efficient manipulations of the EOMs. The reason being that we can use the Fermionic creation and annihilation operators that obey anticommutation relations $\{\hat{c}_m^{\sigma\dagger}, \hat{c}_n^{\sigma'}\} = \hat{c}_m^{\sigma\dagger}\hat{c}_n^{\sigma'} - \hat{c}_n^{\sigma'}\hat{c}_m^{\sigma\dagger} = \delta_{mn}\delta_{\sigma\sigma'}$, where σ is again the spin degrees of freedom of the particles. The lattice Hamiltonian in this case reads

$$\hat{H} = \sum_{m,n=1}^L \sum_{\sigma=\uparrow,\downarrow} T_{m,n} e^{i\phi_{m,n}} \hat{c}_m^{\sigma\dagger} \hat{c}_n^{\sigma} + \sum_{m=1}^L \underbrace{\sum_{\sigma=\uparrow,\downarrow} \hat{c}_m^{\sigma\dagger} \hat{c}_m^{\sigma}}_{=\hat{n}_m} v_m + \frac{1}{2} \sum_{m,n=1}^L \sum_{\sigma,\sigma'=\uparrow,\downarrow} W_{mnmn} \hat{c}_m^{\sigma\dagger} \hat{c}_n^{\sigma'\dagger} \hat{c}_n^{\sigma'} \hat{c}_m^{\sigma}. \quad (196)$$

The first term can be connected to a finite-difference representation of the Laplacian and describes how the particles can move between sites. The hopping matrix $T_{m,n}$ can be interpreted as how easy it is for the electrons to hop from one site to another. The phase $\phi_{m,n}$ is called the Peierls phase and describes the influence of an external vector potential on the lattice electrons. It is connected to the minimal-coupling prescription by

$$\phi_{m,n} = \int_m^n \boldsymbol{\lambda}_{m,n} \cdot \mathbf{A}(\mathbf{r}) d\mathbf{r}, \quad (197)$$

where $\boldsymbol{\lambda}_{m,n}$ is the orientation of the connection between site m and n in real space (could be, for instance, along the z direction) and $\mathbf{A}(\mathbf{r})$ the external vector potential. The phase hence measures how the vector potential changes when going from site n to site m . Since $T_{m,n}$ is symmetric and naturally we have that Peierls phase is skew-symmetric $\phi_{m,n} = -\phi_{n,m}$ the whole expression is Hermitean. Perturbatively the first term is the equivalent of the kinetic energy for the general case including magnetic fields (see Sec. 2.3). The second term is the external scalar potential energy and captures the effect of the scalar potential v_m acting on the electrons at site m . The last term corresponds to the Coulomb interaction W between the electrons. Often it is reduced to just a simple on-site interaction, that is,

$W_{mmmm}\hat{c}_m^{\sigma\dagger}\hat{c}_n^{\sigma'\dagger}\hat{c}_n^{\sigma'}\hat{c}_m^{\sigma} \rightarrow U\hat{c}_m^{\uparrow\dagger}\hat{c}_m^{\uparrow}\hat{c}_m^{\downarrow\dagger}\hat{c}_m^{\downarrow}$. This, together with just a next-neighbor hopping matrix $T_{m,n}$ gives rise to the Hubbard Hamiltonian.

Similar to the previous chapter, we will consider different settings where different external terms control different observables. The form of these observables, however, depends on the specific choices we make for $T_{m,n}$ and $\phi_{m,n}$. In order to be specific we therefore choose only next neighbor hopping $T_{m,m+1} = -t_m = T_{m+1,m}$ and zero else. We will, however, not assume just one t throughout the lattice but allow for a site dependent hopping. Because it does not make sense (unless we would have somehow a change in the topology of our space like in general relativity) that we have a different form of derivative that changes throughout space, it only leaves a local change in mass, since the $T_{m,n}$ depend on the mass. We will come back to what we can control with this locally dependent mass in the next section. Furthermore we choose a periodic setting such that $L + 1 = 1$ and the first term in Eq. (196) becomes

$$\sum_{\sigma=\uparrow,\downarrow} \sum_{m,n=1}^L T_{m,n} e^{i\phi_{m,n}} \hat{c}_m^{\sigma\dagger} \hat{c}_n^{\sigma} \rightarrow \sum_{m,\sigma} \left(T_{m,m+1} e^{i\phi_{m,m+1}} \hat{c}_m^{\sigma\dagger} \hat{c}_{m+1}^{\sigma} + T_{m+1,m} e^{i\phi_{m+1,m}} \hat{c}_{m+1}^{\sigma\dagger} \hat{c}_m^{\sigma} \right).$$

As will become more clear below (see Sec. 4.2 for more details) for this one-dimensional setting we do not need to have locally changing phases. Indeed, for an alleged mappings it will turn out to be even detrimental. Hence in the following we will only consider a constant magnetic field $\phi_{m,m+1} = \phi/L$. Furthermore, since we merely want to see the possibility of having a density-potential mapping for different quantities, we set $W \equiv 0$ in the following. It will only add further terms in the EOMs but will not change our conclusions. The final form of the Hamiltonian for which we will investigate different mappings is therefore

$$\hat{H} = - \sum_{m,\sigma} t_m \left(e^{i\phi/L} \hat{c}_m^{\sigma\dagger} \hat{c}_{m+1}^{\sigma} + e^{-i\phi/L} \hat{c}_{m+1}^{\sigma\dagger} \hat{c}_m^{\sigma} \right) + \sum_m v_m \hat{n}_m. \quad (198)$$

We therefore have the following external parameters in our Hamiltonian that we want to use to control different quantities: The on-site potential v_m and the site dependent hopping amplitude t_m and the overall phase ϕ .

Let us next identify the quantities we want to control via the different external parameters. The obvious choice is the (spin-summed) density $n_m = \langle \Phi | \hat{n}_m | \Phi \rangle$, which is defined by the density operator at site m as

$$\hat{n}_m = \sum_{\sigma} \hat{c}_m^{\sigma\dagger} \hat{c}_m^{\sigma}. \quad (199)$$

In analogy to the continuum case we want to control n_m via the potential v_m . Taking the time derivative of the density (see App. A for the derivation) leads to the lattice version of the continuity equation (92) given as

$$\partial_t n_m = i(Q_{m,m+1} + Q_{m,m-1} - c.c). \quad (200)$$

The quantity $Q_{m,m+1}$ defined on each link is called complex link current density [152]

$$Q_{m,m+1} = \tilde{T}_{m,m+1} \gamma_{m,m+1}. \quad (201)$$

It is given in terms of a link density $\gamma_{m,m+1}$ that is the first off-diagonal of the spin-summed 1-RDM and is defined by

$$\begin{aligned} \gamma_{m,n} &= \sum_{\sigma} \langle \Phi | \hat{\gamma}_{m,n}^{\sigma} | \Phi \rangle \\ \hat{\gamma}_{m,n}^{\sigma} &= \hat{c}_m^{\sigma\dagger} \hat{c}_n^{\sigma}. \end{aligned} \quad (202)$$

The complex hopping is defined as

$$\tilde{T}_{m,m+1} = t_m e^{i\phi/L} \quad (203)$$

The continuity equation can be obtained, similarly to the continuous case, by taking the diagonal of the EOM of the 1-RDM (see Eq. (229) in the Appendix). The EOM of other quantities such as the complex link current can simply be obtained by the product of the EOM of the 1-RDM with the phase and the hopping. We see from Eq. (200) that it is the imaginary part of $Q_{m,m+1}$ that enters the continuity equation and is equal to the physical link current density $J_{m,m+1}$

$$J_{m,m+1} = 2\Im Q_{m,m+1}, \quad (204)$$

which describes the flow of particles from the site m to the site $m+1$. The real part of $Q_{m,m+1}$ determines the kinetic energy density $K_{m,m+1}$ on a link

$$K_{m,m+1} = 2\Re Q_{m,m+1}. \quad (205)$$

The physical link current density is antisymmetric, $J_{m,n} = -J_{n,m}$, the link kinetic energy density is symmetric, $K_{m,n} = K_{n,m}$ and the complex current is Hermitean, $Q_{m,n} = Q_{n,m}^*$. The continuity equation (200) then takes the form

$$\partial_t n_m = -(J_{m,m+1} + J_{m,m-1}). \quad (206)$$

We will in the following try to control n_m via the scalar potential v_m and $K_{m,m+1}$ via the hopping amplitude t_m . A further quantity that we potentially can control is $J_{m,m+1}$ via the phase ϕ . The latter point seems counter-intuitive at first sight. We note that Eq. (206) for the static case implies that at each link the current density is the same. We therefore have a constant link current density throughout the one-dimensional system. We can thus only control the strength of the homogeneous current through the periodic system. Dimensionally this value J can then be connected to the phase ϕ . Indeed, varying the phase locally will not modify the current strength as long as the total phase difference accumulated when going through the lattice stays the same. This point we will discuss in a little more detail in Sec. 4.2. Hence we choose to consider a global phase ϕ which is distributed

equally over all sites as ϕ/L as in Eq. (203) such that summing up all the phases on the ring yields back the total flux ϕ .

Now that we have identified the different quantities that we can potentially control, let us define the EOMs that relate these quantities and the external potentials. As we will see in Sec. 4.2 we will make use of these EOMs to check the density-potential mappings. We have already introduced one of the EOMs, the continuity equation (206), which is the first order EOM of the density. However we do not get further information on how to control the density with the scalar potential from this EOM, because the potential does not appear explicitly. Taking another time-derivative of the continuity equation, we get the second order EOM of the density as

$$\partial_t^2 n_m = -(\partial_t J_{m,m+1} - \partial_t J_{m-1,m}) \quad (207)$$

This involves the EOM of the current $J_{m,m+1}$, which is the imaginary part of $Q_{m,m+1}$. Therefore we choose to first derive the EOM of the complex link current $Q_{m,m+1}$ and from that we can get the EOM for the physical link current. Knowing from Eq. (201) how the complex link current relates to the 1-RDM, we make use of the EOM of the 1-RDM (see Eq. (229) in Appendix A) and get the EOM of $Q_{m,m+1}$ simply as

$$\begin{aligned} \partial_t Q_{m,m+1} &= -it_m e^{i\phi/L} \partial_t \gamma_{m,m+1} \\ &= i \left((-t_m t_{m-1} \gamma_{m-1,m+1} + t_m t_{m+1} \gamma_{m,m+2}) e^{2i\phi/L} - t_m^2 D_+ n_m - Q_{m,m+1} D_+ v_m \right). \end{aligned} \quad (208)$$

Here we have introduced the forward (backward) difference operators D_+ (D_-) that act on one-index objects as $D_+ f_i = f_{i+1} - f_i$, $D_- f_i = f_i - f_{i-1}$. We do a similar derivation for $Q_{m-1,m}$ (see Eq. (232) in Appendix A) and by taking the imaginary parts for both EOMs and substituting in Eq. (207) we get the second order EOM for the density as

$$\partial_t^2 n_m = -D_- (D_+ Y_m - 2t_m^2 D_+ n_m - (D_+ v_m) K_{m,m+1}), \quad (209)$$

where the term Y_m is defined as

$$Y_m = 2\Re(t_m t_{m-1} \gamma_{m-1,m+1} e^{2i\frac{\phi}{L}}). \quad (210)$$

This term can be connected to the kinetic stress tensor of Eq. (127) that shows up in the force balance equation in the previous chapter [152].

The other quantity of interest is the kinetic energy density K . To control K with the hopping t we need an EOM that gives a relation between these two. An intuitive choice is of course the EOM of the kinetic energy density which is the real part of the EOM of Q (208) and is given as

$$\partial_t K_{m,m+1} = -D_+ \Xi_m + (D_+ v_m) J_{m,m+1} \quad (211)$$

with

$$\Xi_m = 2\Im(t_m t_{m-1} \gamma_{m-1, m+1} e^{2i\frac{\phi}{L}}). \quad (212)$$

For ground states the left hand side of Eq. (211) is always zero. Hence this EOM does not provide a relation between t and K . The EOM of the link current on the other hand gives us this relation

$$\partial_t J_{m, m+1} = D_+ Y_m - 2t_m^2 D_+ n_m - (D_+ v_m) K_{m, m+1}. \quad (213)$$

We will therefore use this EOM to control the kinetic energy density $K_{m, m+1}$ with the hopping t_m . We could also make use of the 2nd order EOM of the density given in Eq. (209) since both t and K appear. However, we can see from Eq. (207) that this is just the forward difference of the EOMs of the link current of Eq. (213). We see how to determine t_m by inverting Eq. (213) for a specific case in Sec. 4.2 We discuss in Sec. 4.2 how we make use of these EOMs to control the density n and the kinetic energy density $K_{m, m+1}$ with the scalar potential v and the hopping t , respectively.

Density functional theories on a lattice

The main difference between the lattice and the continuum case becomes already evident from the respective continuity equations, i.e., Eqs. (44) and (206). Where in the continuum case we have a local current density, in the lattice case we have a non-local link current. The same holds true for the force densities, that have been local in the continuum setting but now become non-local and connect different sites. This discreteness has certain consequences. Firstly, while in the continuum by just increasing the flow of particles, we can in principle reach arbitrarily high local currents, the fact that we have a fixed hopping (at least for the physical interacting reference Hamiltonian that we want to solve approximately with some lattice DFT) also limits the maximal value a link current can attain [152]. The same holds true for the kinetic energy density. We therefore have quite strong v -representability conditions for $J_{m, m+1}$ and $K_{m, m+1}$ and with this also on the possible changes of density per site. Again, we can use the 1-RDM to find these constraints on the link current density and the kinetic energy density. Following Ref. [155] we first highlight that for every state and for any $\lambda \in \mathbb{C}$ it holds that

$$\begin{aligned} 0 \leq \|(\hat{c}_m^\sigma - \lambda \hat{c}_n^\sigma) \Phi\|^2 &= \langle \Phi | (\hat{c}_m^{\sigma\dagger} - \lambda^* \hat{c}_n^{\sigma\dagger})(\hat{c}_m^\sigma - \lambda \hat{c}_n^\sigma) | \Phi \rangle \\ &= \gamma_{m, m}^\sigma + |\lambda|^2 \gamma_{n, n}^\sigma - \lambda^* \gamma_{m, n}^\sigma - \lambda \gamma_{n, m}^\sigma. \end{aligned} \quad (214)$$

If we the set $\lambda = \gamma_{m, n}^\sigma / \gamma_{n, n}^\sigma$ we can rearrange the above inequality and find

$$|\gamma_{m, n}^\sigma|^2 \leq \gamma_{m, m}^\sigma \gamma_{n, n}^\sigma = n_m^\sigma n_n^\sigma. \quad (215)$$

We note that the choice of λ is problematic if $\gamma_{n, n}^\sigma = 0$. This is easily circumvented by interchanging the role of m and n if $\gamma_{m, m}^\sigma \neq 0$. If both $\gamma_{m, m}^\sigma$ and $\gamma_{n, n}^\sigma$ are zero, we

immediately see that $\gamma_{m,n}^\sigma = 0$. From this condition on the 1-RDM we get a bound for the absolute value of the current $J_{m,m+1}$ in Eq. (204) in terms of the densities as

$$\begin{aligned} |J_{m,m+1}| &= 2t |\text{Im}\{e^{i\phi/L}\gamma_{m,m+1}\}| \\ &\leq 2t_m |\gamma_{m,m+1}| \\ &\leq 2t_m \sqrt{n_m n_{m+1}} \end{aligned} \quad (216)$$

In a similar way, the bound for the kinetic energy density $K_{m,m+1}$ is

$$\begin{aligned} |K_{m,m+1}| &= 2t |\text{Re}\{e^{i\phi/L}\gamma_{m,m+1}\}| \\ &\leq 2t_m |\gamma_{m,m+1}| \\ &\leq 2t_m \sqrt{n_m n_{m+1}} \end{aligned} \quad (217)$$

As we have pointed out before, the link current for an eigenstate is homogeneous throughout the lattice (even when the density is not), and we see from Eq. (216) that this current is restricted by the minimum over all m of the right hand side of the inequality. We therefore have for the (homogeneous) current of the ground state that

$$J \leq \min_m 2t_m \sqrt{n_m n_{m+1}}. \quad (218)$$

For the kinetic energy density, which is in general inhomogeneous, we just have the above local bounds. These results therefore provide representability constraints and tell us which possible values $K_{m,m+1}$, n_m and J can take. Put differently, these constraints restrict the set of representable densities for which a one-to-one correspondence can exist. For instance, if we consider 4 electrons then no external potential exists that allows for some site m that $n_m > 4$.

However, even with these restrictions in mind it is challenging to establish the fundamental mappings. For instance, already for ground state DFT on a lattice, the only rigorous mapping established to date is for systems with finite temperature [151]. The reason being that for zero temperature one does not know under which conditions a ground state has non-zero density on every site. If the density is zero on a site, then the potential there does not influence the density and we have many potentials that lead to the same density. For the continuum case one can rely on results from functional analysis that guarantee that the density is non-zero everywhere [146]. This makes an investigation of the mapping even for simple lattice systems interesting. For more complex observables such as the kinetic energy density the situation is even more involved. Since the kinetic energy density $K_{m,m+1}$ contains the control potential, in this case the site-dependent hopping t_m , we can no longer use the simple proof strategy of Hohenberg and Kohn. This relies on a linear relation between the functional variable and the control potential [153]. We have, however, indication that a mapping between $K_{m,m+1}$ and t_m exists. This is based on the EOMs and their use in the time-dependent lattice settings. For instance in lattice TDDFT, Farzanehpour and Tokatly [154] have proven

that regardless of the geometry or size of the lattice there exist a unique mapping $v_m(t) \rightarrow n_m(t)$. Similarly a "generalized TDCDFT" for the lattice is presented in [152] where the basic variable is the complex link current $Q_{m,m+1}(t)$ and it is proven that the mapping ($Q_{m,m+1}(t) \rightarrow \tilde{T}_{m,m+1}(t)$) is unique. In this same work, the usual TDCDFT is also established between the physical link current and the Peierls phase under certain conditions. One of which is related to the bound of the link current which we discussed above. Assuming that such mappings exist also for the static case, we can of course still make use of the EOMs to define approximations to the xc potentials as we did in the previous chapter. However, here we instead make use of the EOMs in a different capacity to investigate whether such mappings exist also in the static case. This approach has been used in Ref. [153] to numerically investigate the mapping between the set of densities ($n_m, K_{m,m+1}$) and the potentials (v_m, t_m). In our case we make use of the EOMs for the Hamiltonian of Eq. (198), which also includes a Peierls phase in contrast to Ref. [153], and check numerically whether the density and the kinetic energy density are controlled by their conjugate external potentials. In other terms, we investigate whether one-to-one correspondences between n_m and v_m and $K_{m,m+1}$ and t_m , respectively, exist. We also comment on the controllability of the link current or all these objects together at once.

4.2 CONSTRUCTION OF DENSITY-TO-POTENTIAL MAPPINGS

As we stated above the EOMs give an exact relation between possible sets of densities and potentials. In this section we investigate the one-to-one correspondence between the particle density n_m and the scalar potential v_m for the lattice configuration described by Eq. (198) by employing the second order EOM of the density. Furthermore we investigate the mapping between the kinetic energy density $K_{m,m+1}$ and the hopping t_m by making use of the EOM of the link current to establish the relation between these two quantities.

It is clear that the forward mappings $v_m \mapsto n_m$ and $t_m \mapsto K_{m,m+1}$ exist by solving the ground state problem. What we want to investigate is whether also the inverse mappings $n_m \mapsto v_m$ and $K_{m,m+1} \mapsto t_m$ exist. This would imply that the $v_m \mapsto n_m$ and $t_m \mapsto K_{m,m+1}$ mappings are invertible and hence one-to-one. In order to investigate this we choose some arbitrary values for n_m and $K_{m,m+1}$ that fulfill basic representability conditions and then try to construct the correspond v_m and t_m numerically. We will do so by an iterative procedure. To start the iterative procedure we make an initial guess $v_m^{(0)}$ or $t_m^{(0)}$, respectively. It is helpful to adhere the above representability conditions for the initial guess for $t_m^{(0)}$.

1. We then solve the ground state problem with one of the corresponding guess put into Eq. (198). From this we get a ground state $\Phi^{(0)}$ and the corresponding quantities $n_m^{(0)}$ or $K_{m,m+1}^{(0)}$, respectively

2. We then use the EOMs (see details below) to update to a new potential $v_m^{(1)}$ or hopping $t_m^{(1)}$, respectively.
3. We then solve the ground state problem with the new control fields $v_m^{(1)}$ or $t_m^{(1)}$, respectively.

We repeat these steps until the control fields $v_m^{(i)} \rightarrow v_m^{(i+1)}$ or $t_m^{(i)} \rightarrow t_m^{(i+1)}$, respectively no longer change. We will discuss further details and the results below. Furthermore we comment on inverting the phase-to-current mapping and controlling all objectives at once.

Iteration procedure for $n_m \mapsto v_m$ mapping

To have a density that is potentially v representable we have to obey certain minimal conditions. Firstly, if we consider only N particles, then $\sum_m n_m = N$ has to hold. Further, we only consider densities that obey $n_m > 0$ on the whole lattice. To avoid any problems we can just generate some densities n_m by some arbitrary potential and see whether we get back the same potential we started with. This also indicates a one-to-one relation. Given such a density we then use Eq. (209) to find the corresponding potential for a fixed $\tilde{T}_{m,m+1} = t_m e^{i\phi/L}$. We do so by making an initial guess for the potential $v_m^{(0)}$ on all sites and proceed as discussed above. We note that we have a gauge freedom here and fix only $L - 1$ of all L sites, since we can just add a constant to the potential without changing the physics. This is exactly the same gauge freedom as discussed in Sec. 2.1.2.

Given that the number of particles is fixed by the sum of occupations at every site, the statement $\sum_m \dot{n}_m = 0$ is valid. Therefore there are only $L - 1$ EOMs for the density that are non-trivial and from which we get an update for the potentials. However, with the above gauge condition the number of non-trivial potentials is also $L - 1$ such that everything fits and the potential on the L th site can be fixed to a constant, for instance the initial guess $v_L^{(0)}$. To be explicit, let us take as an example for the inversion scheme the four site case (other explicit cases are given in App. A.1). We use three of the EOMs to get an update for the potentials at three sites while the potential v_1 is fixed to our initial guess $v_1^{(0)}$ (we use $K_m = K_{m,m+1}$ to not overload notation),

$$\begin{aligned}
v_2^{(i+1)} &= \frac{-(B+D)^{(i)} K_2^{(i)} K_4^{(i)} - B^{(i)} K_3^{(i)} K_4^{(i)} + A^{(i)} K_2^{(i)} K_3^{(i)} + v_1 C^{(i)}}{C^{(i)}} \\
v_3^{(i+1)} &= \frac{-(A+B)^{(i)} K_1^{(i)} K_3^{(i)} + A^{(i)} K_2^{(i)} K_3^{(i)} - D^{(i)} K_1^{(i)} K_4^{(i)} - (B+D)^{(i)} K_2^{(i)} K_4^{(i)} + v_1 C^{(i)}}{C^{(i)}} \\
v_4^{(i+1)} &= \frac{(A+B+D)^{(i)} K_1^{(i)} K_2^{(i)} + (A+B)^{(i)} K_1^{(i)} K_3^{(i)} + A^{(i)} K_2^{(i)} K_3^{(i)} + v_1 C^{(i)}}{C^{(i)}}.
\end{aligned} \tag{219}$$

We solve the three EOMs and obtain the update formulae (219) where A, B, C and D are

$$\begin{aligned} A^{(i)} &= (Y_2 - Y_1)^{(i)} - 2t_1^2(n_2 - n_1) - (Y_1 - Y_4)^{(i)} + 2t_4^2(n_1 - n_4) \\ &= (Y_2 - 2Y_1 + Y_4)^{(i)} - 2t_1^2(n_2 - n_1) + 2t_4^2(n_1 - n_4) \end{aligned} \quad (220)$$

$$\begin{aligned} B^{(i)} &= (Y_3 - Y_2)^{(i)} - 2t_2^2(n_3 - n_2) - (Y_2 - Y_1)^{(i)} + 2t_1^2(n_2 - n_1) \\ &= (Y_3 - 2Y_2 + Y_1)^{(i)} - 2t_2^2(n_3 - n_2) + 2t_1^2(n_2 - n_1) \end{aligned} \quad (221)$$

$$\begin{aligned} D^{(i)} &= (Y_4 - Y_3)^{(i)} - 2t_3^2(n_4 - n_3) - (Y_3 - Y_2)^{(i)} + 2t_2^2(n_3 - n_2) \\ &= (Y_4 - 2Y_3 + Y_2)^{(i)} - 2t_3^2(n_4 - n_3) + 2t_2^2(n_3 - n_2) \end{aligned} \quad (222)$$

$$C^{(i)} = ((K_1K_2 + K_1K_3 + K_2K_3)K_4 + K_1K_2K_3)^{(i)} \quad (223)$$

and

$$Y_m^{(i)} = 2\Re(t_m t_{m-1} \gamma_{m-1, m+1}^{(i)} e^{2i\frac{\phi}{L}}). \quad (224)$$

In every step of the iteration scheme, the density n_m is fixed to that of the target system while the other quantities K, Y are updated by solving the ground state problem with the scalar potentials v_m^i from the previous iteration. This is repeated until the calculated densities converge to those of the target system (see App. A for details)

As an example we show the numerical results for this inversion scheme for four sites in Figure 3 (see details of the reference system in the caption) which we compare to the target system. The densities and the control field v_m of the target system are plotted in blue while the red plots correspond to the converged potential and densities. As an initial guess for the potential we take $v_m^0 = 0.1$. We see in Figure 3 that the target potential and the converged potential differ purely by a constant shift. This is simply because the potential at site 1 is fixed to our initial guess $v_1^{(0)} = 0.1$. The density we get upon convergence agrees with the target density. To highlight that we indeed got back the same wave function we also plot the kinetic energy density and the current density, which are not determined by the density. As we see all converged quantities are indistinguishable on the displayed scale from the reference quantities.

This result is representative for the different situations (changing N, L and the target densities as well as the hoppings and phases or initial guess) that we investigated. For two sites with $N = 2$, $v_m = \sin(\frac{2\pi m}{L})$, $t_m = \sin(\frac{2\pi m}{L})$ and $\phi/L = \pi/4$ and also for three sites with $N = 4$, $v_m = \sin(\frac{2\pi m}{L}) + 0.1$, $t_m = \cos(\frac{2\pi m}{L})$ and $\phi/L = \pi/4$. Numerically we find that as long as the density is non-zero at every site we can uniquely reconstruct the corresponding potential and with this also the exact wavefunction. It is, however, unclear whether for all reasonable lattice Hamiltonians the reverse holds. That is, that under which conditions the ground state of a Hamiltonian on a lattice has non-zero density everywhere. To guarantee a one-to-one relation a characterization of these conditions will become important.

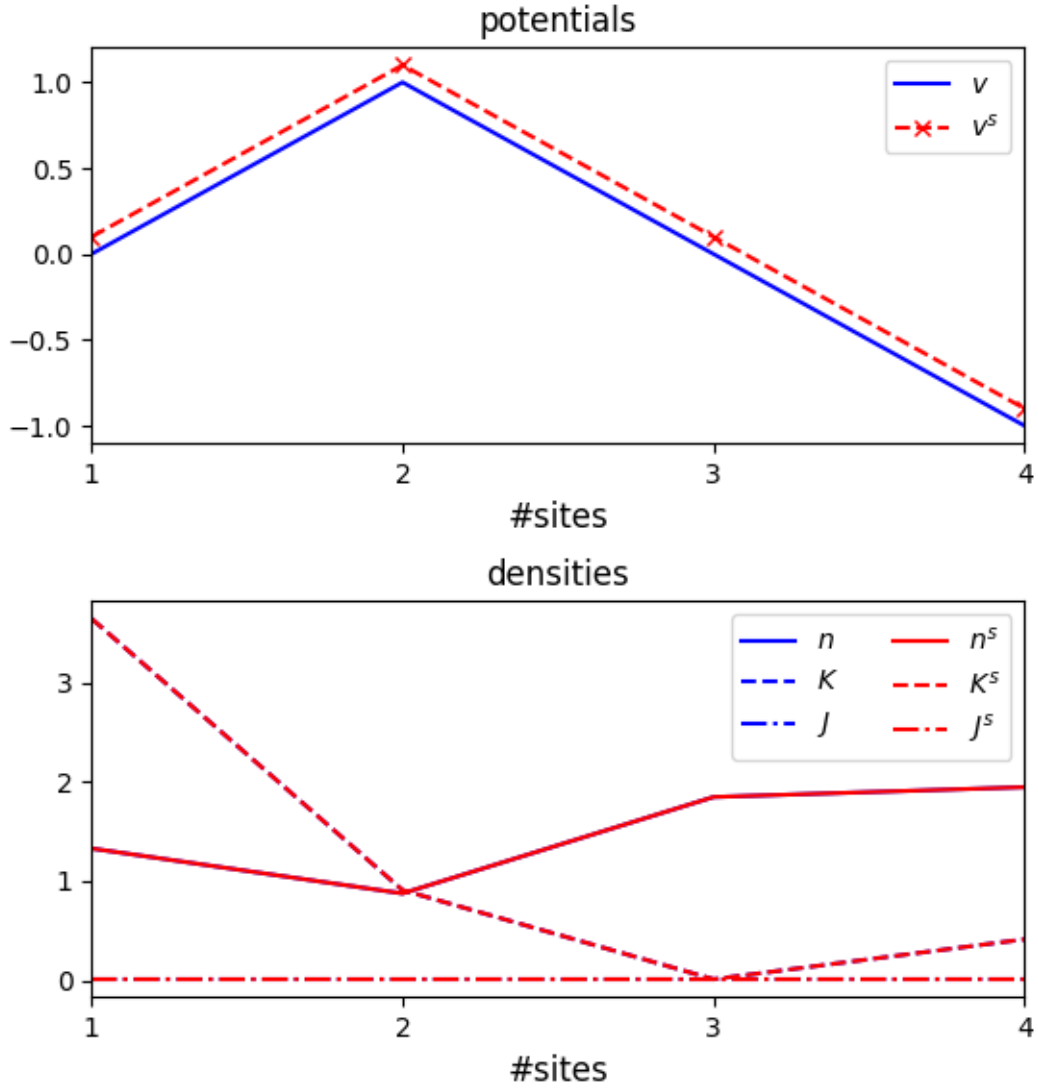


Figure 3: Inversion of the density n for $N = 6$ particles on $L = 4$ sites. The reference systems potential is $v = \sin(\frac{2\pi m}{L})$, the hopping is $t = \cos(\frac{2\pi m}{L}) + 1.1$ and the phase is $\phi/L = \pi/3$. The upper plot shows the target scalar potential (solid blue line) and the updated (converged) scalar potential v^s (dashed red) against sites m . Up to an inconsequential shift they are the same. The lower plot shows the target density n (solid blue line), the densities K (dashed blue line), J (dashed dotted blue line) and the corresponding densities n^s, K^s, J^s at convergence (in red).

Iteration procedure for $K_{m,m+1} \mapsto t_m$ mapping

Next we fix v_m and ϕ and adopt t_m to generate a prescribed kinetic energy density. Knowing that the EOM (213) is equal to zero we get indeed a simple update scheme for the hopping t_m as

$$t_m^{(i+1)} = \frac{-\beta^{(i)} \pm \sqrt{\beta^{(i)2} - 8D_+n_m^{(i)}K_{m,m+1}D_+v_m}}{4D_+n_m^{(i)}} \quad (225)$$

$$\beta^{(i)} = 2\Re \left((t_{m-1}\gamma_{m-1,m+1} - t_{m+1}\gamma_{m,m+2})^{(i)} e^{2i\frac{\phi}{L}} \right). \quad (226)$$

We choose the hopping positive to avoid potential gauge ambiguities [153] and in every iteration we compare the $K_m^{(i+1)}$ that we obtain with both $t_m^{(i+1)}$ of the \pm solutions in (226) and choose the hopping that gives $K_m^{(i+1)}$ closer to that of the target system. In every step of the iteration scheme to update the hopping $t_m^{(i+1)}$, the kinetic energy density is fixed to that of the target system while the density $n^{(i)}$ and reduced density matrix $\gamma_{m,n}^{(i)}$ are updated by solving the ground state problem with the hopping $t_m^{(i)}$ evaluated in the previous iteration. From the denominator of Eq. (226) we see that our update scheme is restricted to systems with inhomogeneous densities. For homogeneous systems we would need to use a different relation between K and t .

Again we give an explicit example for $L = 4$ (see details of the reference system in the caption). The initial guess for the hoppings are $t_m^{(0)} = 1$. In the upper plot of Figure 4 we see that the converged hopping (dashed red) agrees nicely with the reference hopping (solid blue). In the lower plot we display besides the kinetic energy density (dashed blue and red lines) also the density (solid blue and red) and the current density (dashed dotted blue and red) of the target system (blue) and the converged quantities (red). We find that the EOM inversion recovers the exact quantities.

Again the presented result is representative for the different situations that we investigated. With the current update scheme we can uniquely reconstruct the reference wave function and the corresponding quantities as long as the system is inhomogeneous. If the density becomes the same on two consecutive sites our method becomes unstable. Yet we do think that by either using different EOMs to find a relation between t and K or by even ad-hoc methods like in the case of density-potential inversions [156] that increase the hopping where the $K^{(i)}$ is too small, might overcome this problem. We do not think that for these cases there is not a one-to-one correspondence in general. As an example see the explicit inversion for the fully homogeneous system in Ref. [153].

These two examples highlight that the EOM approach is also interesting to establish or investigate basic facts of DFTs. Even for lattice DFT at zero temperature basic questions about the existence and the properties of the density-potential mapping are unanswered [151]. We can think of investigating not only the individual mappings $n_m \mapsto v_m$ and $K_{m,m+1} \mapsto t_m$ but also to the combined mapping

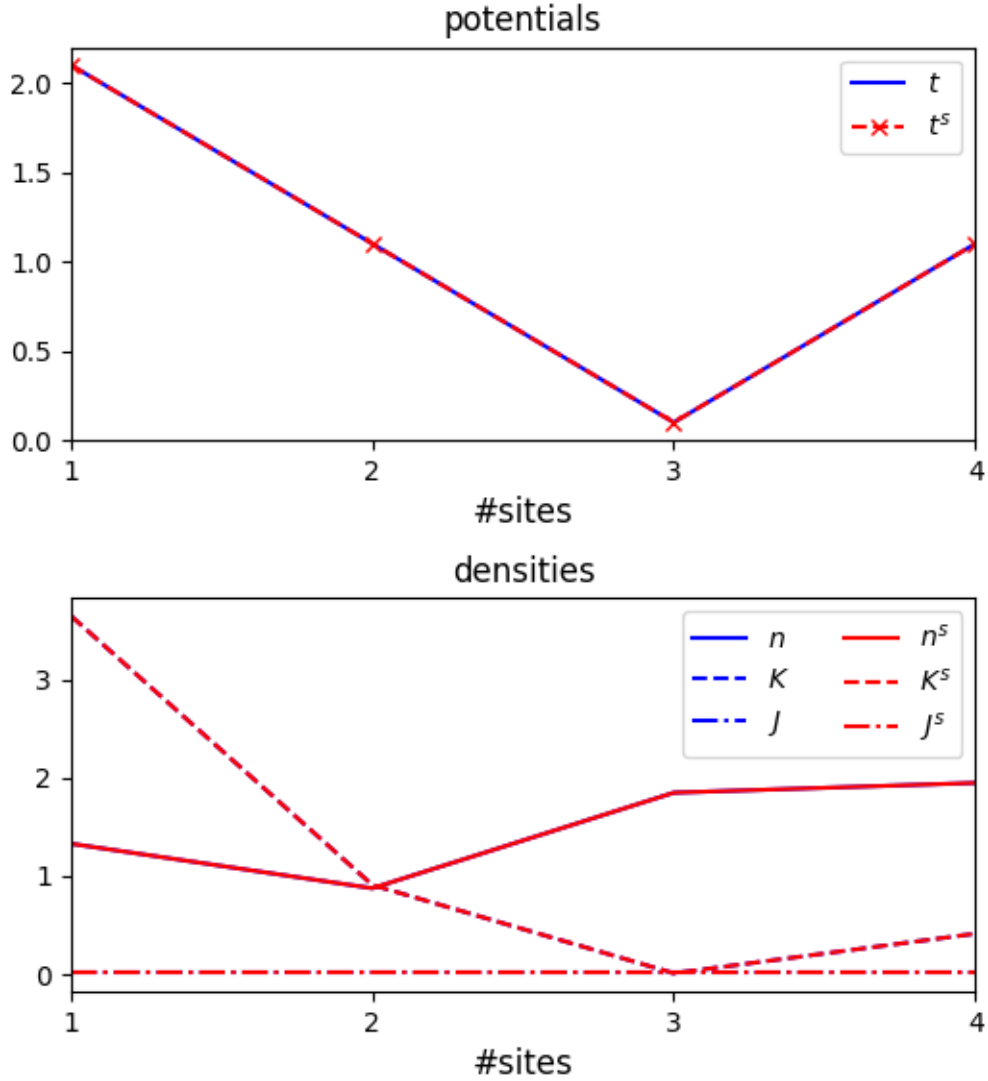


Figure 4: Inversion of the kinetic energy density K for $N = 6$ particles on $L = 4$ sites. The reference system is given by the hopping $t = \cos(\frac{2\pi m}{L}) + 1.1$, the scalar potential $v = \sin(\frac{2\pi m}{L})$ and the phase $\phi/L = \pi/3$. In the upper plot we show the reference hopping (solid blue) and the updated (converged) hopping t^s (dashed red). In the lower plot we show the target kinetic energy density K (dashed blue line), density n (solid blue line), the current J (dashed-dotted blue line) and the corresponding densities n^s, K^s, J^s at convergence (in red).

$(n_m, K_{m,m+1}) \mapsto (v_m, t_m)$ as done for the case without the Peierls phase in Ref. [153]. Especially interesting in our setting is if we can even control $(n_m, K_{m,m+1}, J)$ at the same time and with this basically fix all parts of the Hamiltonian uniquely. The control of the current and its connection to the Peierls phase has also implications for the continuum setting and CDFT with the physical current. Firstly, even in the continuum case we will have only a homogeneous current if we are in only one-dimension. This becomes obvious from the continuity equation (44) for one dimension, where having a static density implies that the current is constant. So also in the continuum, for one spatial dimension we have many inhomogeneous fields $A(x)$ that will generate all the same static current. So we have also in this case restrict the possible control fields to just a number to establish a possible one-to-one relation. For two and three-dimensional lattices we expect to find a mapping between all possible ring currents (we still have the rule that everything that flows in also flows out due to the continuity equation) and corresponding phases. Similar to the continuum, where the continuity equation only allows transversal currents for static states. Investigating this sofar elusive setting numerically and see whether we can control the transversal part of the full physical current is a very interesting opportunity to employ the EOM-based approach and to construct potentials for a given density and transversal current.

CONCLUSION AND OUTLOOK

In this thesis we have reviewed some challenges that arise in the *ab-initio* description of many-electron systems and to address this we have proposed a novel promising approximation scheme for density functional theories.

In the first chapter, we addressed four important settings commonly considered in many-body quantum mechanics to study the structure and dynamics of matter. We discussed some density functional methods that have been developed to solve many-body systems in these various settings, namely, (TD)DFT and (TD)CDFT and their respective approximations. Despite being successful methods some limitations arise for instance due to the standard energy-based approach to determine xc potentials and the possible deficiencies that arise from using ground state functional approximations in other settings.

In chapter 3, we presented a way to treat these issues by introducing an approach to determine xc potentials of these different DFTs based on the EOMs of specific current densities rather than resorting to the usual minimum energy principle or energy expressions. These EOMs describe many-body systems in a hydrodynamic manner as a balance of forces in the systems. From this we were able to show that by employing the usual KS formulation, instead of approximating the energy functionals what we need to approximate are these forces. In this way we have established exact determining relations for xc potentials that give way to orbital-dependent approximations. This approach has some advantages as it avoids not only functional differentiability issues but also the numerically costly optimized-effective-potential procedure to determine xc potentials. As such the EOMs provide approximations directly on the level of the potentials. The novelty of this approximation scheme is that it unifies various DFT settings via the EOMs. As such we need not only follow the standard way of using ground state approximations for time-dependent settings but we actually show that the reverse is possible and in general one can indeed connect different DFT settings (with or without (time-dependent) magnetic fields) to improve on the xc potentials. We have highlighted this connection for local-exchange approximations for (TD)DFT and (TD)CDFT by showing, for instance, differences between ground-state DFT and TDDFT arising from the transversal contribution to the local forces as well as the gauge-fixing due to the Helmholtz decomposition that separates the scalar and the vector xc potential. To further highlight this connection and its benefits, we made use of the (TD)CDFT formulation to treat an interacting system without magnetic field and found that transversal contributions to the exchange force arise even for the simple case of a triplet state. This led to a new condition to improve on the local-exchange approximation in the static case. Although by avoiding the

usual energy expressions, the connection between the presented local-exchange approximations and the standard energy-based approximations is not clear a priori, we however showed that for a homogeneous system, these approximations reduce to the usual exchange LDA and even pointed out how it intuitively connects to the $X\alpha$ method.

In Chapter 4 we showed the capacity that this EOM-based approach has to numerically investigate fundamental mapping theorems in DFTs. For the simple case of a one dimensional lattice system in a ground state setting with Peierls phase, we were able to establish numerically that there is a one-to-one correspondence between densities and scalar potentials given that the density is non-zero at every site. Similarly, we also showed numerically that there is a one-to-one mapping between kinetic energy densities and hoppings as long as the system is inhomogeneous, but other tactics can be used to make this true in general. This shows that the EOM-based approach to DFTs are of a great advantage in numerically constructing potentials for given sets of densities, particularly for cases where the mapping theorems are non-existent. Following the inversion schemes established for the one-dimensional lattice system, an interesting next step will be to investigate the mapping of all three quantities n_m, K_m, J simultaneously. It will also be useful to follow this EOM-based approach to numerically investigate the possibility to construct potentials for a given density and the transversal part of the full physical current in the cases of two and three-dimensional lattices.

The insights presented in this thesis is a good starting point for further investigations and provides a pathway to future interesting applications. A next interesting step is trying to find approximations also to the correlation part of the xc potentials. One possible route is to get expressions for the force terms $\mathbf{F}_T[\Psi]$ and $\mathbf{F}_W[\Psi]$ in terms of explicit approximations of the involved reduced quantities, 1-RDM and diagonal of the 2-RDM, and make use of auxiliary equations that determine these quantities [157]. Furthermore, since we have seen how using TDCDFT for a static problem with no magnetic field has led to transversal contributions in the exchange force, it will be beneficial to explicitly investigate and compare how this differs if we instead used TDDFT. In that sense, one can compare the quality of the correlation approximations. While we have now presented the EOM-based approach only for purely fermionic systems, this could be straightforwardly extended to other settings such as coupled electron-photon systems to establish defining relations for xc potentials in the framework of quantum electro-dynamical DFT (QEDFT) [158–161].

We have thus presented here an approximation scheme which, on the same level of accuracy, allows one to switch between various situations in a consistent manner and capture significant features that are often missed out in the standard approach to DFTs. This unifying framework will therefore be a great tool to study the qualitative change in the properties of the same system, such as a molecule or solid state system, when exposed to different external perturbations or situations and in general this will provide a better understanding of material properties.

EQUATIONS OF MOTION ON THE LATTICE

Here we show the derivation of the EOMs that we used in the lattice setting to do the numerical inversion schemes of the density and the kinetic energy density. We start with the EOM of the 1-RDM and show how from this we derive other EOMs that will be used to numerically investigate one-to-one mappings between densities and potentials. We further show two more examples for the inversion of the the density. We later on discuss some technical details about the implementation of the inversion scheme.

A.1 EOM OF THE DENSITY

We start with the EOM of the 1-RDM (202) and obtain further the EOMs for the density and the link current. For a non-interacting Hamiltonian of the form (198) the EOM of an arbitrary time-independent operator \hat{O} is given by

$$\partial_t \hat{O} = i \langle \Phi | [\hat{H}, \hat{O}] | \Phi \rangle \quad (227)$$

where Φ is again the Slater determinant wavefunction for the ground state. Based on the usual commutation relations we use

$$\left[\hat{c}_k^{\sigma\dagger} \hat{c}_{k+a}^\sigma, \hat{c}_l^{\sigma'\dagger} \hat{c}_{l+b}^{\sigma'} \right] = \delta_{\sigma\sigma'} \delta_{k+a,l} \hat{c}_k^{\sigma\dagger} \hat{c}_{l+b}^{\sigma'} - \delta_{\sigma\sigma'} \delta_{k,l+b} \hat{c}_l^{\sigma'\dagger} \hat{c}_{k+a}^\sigma. \quad (228)$$

in our derivations of the EOMs. For the 1-RDM (202) we then obtain the EOM as

$$\begin{aligned}
-i\partial_t \gamma_{m,n} &= \langle \Phi | \hat{H}, \hat{\gamma}_{m,n} | \Phi \rangle \\
&= \langle \Phi | \left[\sum_{k=1,\sigma}^L \left(T_{k,k+1} e^{i\phi_{k,k+1}} \hat{c}_k^{\sigma\dagger} \hat{c}_{k+1}^\sigma + T_{k+1,k} e^{i\phi_{k+1,k}} \hat{c}_{k+1}^{\sigma\dagger} \hat{c}_k^\sigma + v_k \hat{n}_{k,\sigma} \right), \sum_{\sigma'} \hat{c}_m^{\sigma'\dagger} \hat{c}_n^{\sigma'} \right] | \Phi \rangle \\
&= \langle \Phi | \sum_{k=1,\sigma\sigma'}^L T_{k,k+1} e^{i\phi_{k,k+1}} \left[\hat{c}_k^{\sigma\dagger} \hat{c}_{k+1}^\sigma, \hat{c}_m^{\sigma'\dagger} \hat{c}_n^{\sigma'} \right] | \Phi \rangle \\
&\quad + \langle \Phi | \sum_{k=1,\sigma\sigma'}^L T_{k+1,k} e^{i\phi_{k+1,k}} \left[\hat{c}_{k+1}^{\sigma\dagger} \hat{c}_k^\sigma, \hat{c}_m^{\sigma'\dagger} \hat{c}_n^{\sigma'} \right] | \Phi \rangle \\
&\quad + \langle \Phi | \sum_{k\sigma\sigma'} \left[v_k \hat{n}_{k,\sigma}, \hat{c}_m^{\sigma'\dagger} \hat{c}_n^{\sigma'} \right] | \Phi \rangle \\
&= \langle \Phi | \sum_{k=1,\sigma\sigma'}^L T_{k,k+1} e^{i\phi_{k,k+1}} \left(\delta_{\sigma\sigma'} \delta_{k+1,m} \hat{c}_k^{\sigma\dagger} \hat{c}_n^{\sigma'} - \delta_{\sigma\sigma'} \delta_{k,n} \hat{c}_m^{\sigma'\dagger} \hat{c}_{k+1}^\sigma \right) \\
&\quad + \sum_{k=1,\sigma\sigma'}^L T_{k+1,k} e^{i\phi_{k+1,k}} \left(\delta_{\sigma\sigma'} \delta_{k,m} \hat{c}_{k+1}^{\sigma\dagger} \hat{c}_n^{\sigma'} - \delta_{\sigma\sigma'} \delta_{k+1,n} \hat{c}_m^{\sigma'\dagger} \hat{c}_k^\sigma \right) \\
&\quad + \sum_{k\sigma\sigma'} v_k \left(-\delta_{\sigma\sigma'} \delta_{n,k} \hat{c}_m^{\sigma\dagger} \hat{c}_k^{\sigma'} + \delta_{\sigma\sigma'} \delta_{k,m} \hat{c}_k^{\sigma\dagger} \hat{c}_n^{\sigma'} \right) | \Phi \rangle \\
&= \langle \Phi | \sum_{\sigma} \left(T_{m-1,m} e^{i\phi_{m-1,m}} \hat{c}_{m-1}^{\sigma\dagger} \hat{c}_n^\sigma - T_{n,n+1} e^{i\phi_{n,n+1}} \hat{c}_m^{\sigma\dagger} \hat{c}_{n+1}^\sigma \right. \\
&\quad \left. + T_{m+1,m} e^{i\phi_{m+1,m}} \hat{c}_{m+1}^{\sigma\dagger} \hat{c}_n^\sigma - T_{n,n-1} e^{i\phi_{n,n-1}} \hat{c}_m^{\sigma\dagger} \hat{c}_{n-1}^\sigma + \hat{c}_m^{\sigma\dagger} \hat{c}_n^\sigma (v_m - v_n) \right) | \Phi \rangle \\
&= -t_{m-1} e^{i\phi/L} \gamma_{m-1,n} + t_n e^{i\phi/L} \gamma_{m,n+1} \\
&\quad - t_m e^{-i\phi/L} \gamma_{m+1,n} + t_{n-1} e^{-i\phi/L} \gamma_{m,n-1} - \gamma_{m,n} (v_m - v_n) \tag{229}
\end{aligned}$$

To get the first order EOM of the density which is the continuity equation (200), we use the diagonal of the EOM for the 1-RDM since $n_m = \gamma_{m,m}$ and we get

$$\begin{aligned}
\partial_t n_m &= i \left(t_m e^{i\phi_{m,m+1}} \gamma_{m,m+1} + t_m e^{i\phi_{m,m-1}} \gamma_{m,m-1} - c.c \right) \\
&= i (Q_{m,m+1} + Q_{m,m-1} - c.c) \\
&= -(J_{m,m+1} + J_{m,m-1}). \tag{230}
\end{aligned}$$

We further derive the second order time derivative of the density as this will be of use in our inversion scheme to update the potentials. Thus from (230) we have

$$\begin{aligned}
\partial_t^2 n_m &= -(\partial_t J_{m,m+1} + \partial_t J_{m,m-1}) \\
&= -(\partial_t J_{m,m+1} - \partial_t J_{m-1,m}) \tag{231}
\end{aligned}$$

which we can write as $\partial_t^2 n_m = -D_- \partial_t J_m$. We have derived $\partial_t J_m$ from the EOM of $Q_{m,m+1}$ in (252). What we need to get is $\partial_t J_{m-1}$ which we obtain as $2\Im \partial_t Q_{m-1,m} = 2\Im(\tilde{T}_{m-1,m} \partial_t \gamma_{m-1,m})$. Making use of Eq. (229) we first get $\partial_t Q_{m-1,m}$

$$\begin{aligned}
 & -i\partial_t(\tilde{T}_{m-1,m} \gamma_{m-1,m}) \\
 &= (-t_{m-1} t_{m-2} \gamma_{m-2,m} + t_{m-1} t_m \gamma_{m-1,m+1}) e^{2i\phi/L} \\
 &\quad - t_m^2 (n_m - n_{m-1}) - Q_{m-1,m} D_- v_m \\
 &= (t_m t_{m-1} \gamma_{m-1,m-1} - t_{m-1} t_{m-2} \gamma_{m-2,m}) e^{2i\phi/L} \\
 &\quad - t_m^2 D_+ n_{m-1} + Q_{m,m-1} D_+ v_{m-1}
 \end{aligned} \tag{232}$$

From this we obtain the EOM of $\partial_t J_{m-1,m}$ as

$$\partial_t J_{m-1,m} = D_+ Y_{m-1} - 2t_m^2 D_+ n_{m-1} - K_{m-1,m} D_+ v_{m-1} \tag{233}$$

where Y_i has been defined in (253). Thus the second order time derivative of the density $\partial_t^2 n_m$ from (231) is given as

$$\partial_t^2 n_m = -D_- (D_+ Y_m - 2t_m^2 D_+ n_m - (D_+ v_m) K_m) \tag{234}$$

As we discussed in Sec. 4.2 only $L - 1$ EOMs are non-trivial. Hence to update the potentials we make use of $L - 1$ of the equations and one of the potentials is fixed to our initial guess. We make use of Mathematica to solve these EOMS. Then we update every term except t, n and ϕ . Following we derive the update formulae of the potentials for two, three and four sites.

For 2 sites

From the EOM (234) we can do inversion of the density for two sites by obtaining first the update formula for the potential. Knowing that (234) must yield zero in the ground state case, we have for two sites

$$\begin{aligned}
 \partial_t^2 n_0 &= -D_- (D_+ Y_0 - 2t_0^2 D_+ n_0 - (D_+ v_0) K_0) = 0 \\
 D_+ Y_0 - 2t_0^2 D_+ n_0 - (D_+ v_0) K_0 - D_+ Y_1 + 2t_1^2 D_+ n_1 + (D_+ v_1) K_1 &= 0 \\
 (Y_1 - Y_0) - 2t_0^2 (n_1 - n_0) - (v_1 - v_0) K_0 - (Y_0 - Y_1) + 2t_1^2 (n_0 - n_1) + (v_0 - v_1) K_1 \\
 2(Y_1 - Y_0) - 2(t_0^2 + t_1^2) (n_1 - n_0) - (v_1 - v_0) (K_0 + K_1) &= 0 \\
 v_1^{(i+1)} &= \frac{2(Y_0 - Y_1)^{(i)} + 2(t_0^2 + t_1^2) (n_1 - n_0) + (K_0 + K_1)^{(i)} v_0}{K_0 + K_1}. \tag{235}
 \end{aligned}$$

For 3 sites

We now construct the same scheme for $L = 3$ sites. From the 2nd order EOM of the density we have

$$\begin{aligned}
 \partial_t^2 n_0 &= (Y_1 - Y_0) - 2t_0^2 (n_1 - n_0) - (v_1 - v_0) K_0 - ((Y_0 - Y_2) - 2t_2^2 (n_0 - n_2) - (v_0 - v_2) K_2) \\
 \partial_t^2 n_1 &= (Y_2 - Y_1) - 2t_1^2 (n_2 - n_1) - (v_2 - v_1) K_1 - ((Y_1 - Y_0) - 2t_0^2 (n_1 - n_0) - (v_1 - v_0) K_0) \\
 \partial_t^2 n_2 &= (Y_0 - Y_2) - 2t_2^2 (n_0 - n_2) - (v_0 - v_2) K_2 - ((Y_2 - Y_1) - 2t_1^2 (n_2 - n_1) - (v_2 - v_1) K_1)
 \end{aligned}$$

(236)

We get the update for v_1 and v_2 in terms of v_0 as

$$v_1^{(i+1)} = \frac{A^{(i)}K_1^{(i)} - B^{(i)}K_2^{(i)} + C^{(i)}v_0}{C^{(i)}} \quad (237)$$

$$v_2^{(i+1)} = \frac{(A+B)^{(i)}K_0^{(i)} + A^{(i)}K_1^{(i)} + C^{(i)}v_0}{C^{(i)}} \quad (238)$$

where A, B, C are simply

$$\begin{aligned} A^{(i)} &= (Y_1 - Y_0) - 2t_0^2(n_1 - n_0) - (Y_0 - Y_2) + 2t_2^2(n_0 - n_2) \\ &= (Y_1 - 2Y_0 + Y_2)^{(i)} - 2t_0^2(n_1 - n_0) + 2t_2^2(n_0 - n_2) \end{aligned} \quad (239)$$

$$\begin{aligned} B^{(i)} &= (Y_2 - Y_1) - 2t_1^2(n_2 - n_1) - (Y_1 - Y_0) + 2t_0^2(n_1 - n_0) \\ &= (Y_2 - 2Y_1 + Y_0)^{(i)} - 2t_1^2(n_2 - n_1) + 2t_0^2(n_1 - n_0) \end{aligned} \quad (240)$$

$$C^{(i)} = (K_0K_1 + K_0K_2 + K_1K_2)^{(i)} \quad (241)$$

For 4 sites

From the 2nd order EOM of the density we get for 4 sites

$$\begin{aligned} \partial_t^2 n_0 &= (Y_1 - Y_0) - 2t_0^2(n_1 - n_0) - (v_1 - v_0)K_0 - ((Y_0 - Y_3) - 2t_3^2(n_0 - n_3) - (v_0 - v_3)K_3) \\ \partial_t^2 n_1 &= (Y_2 - Y_1) - 2t_1^2(n_2 - n_1) - (v_2 - v_1)K_1 - ((Y_1 - Y_0) - 2t_0^2(n_1 - n_0) - (v_1 - v_0)K_0) \\ \partial_t^2 n_2 &= (Y_3 - Y_2) - 2t_2^2(n_3 - n_2) - (v_3 - v_2)K_2 - ((Y_2 - Y_1) - 2t_1^2(n_2 - n_1) - (v_2 - v_1)K_1) \\ \partial_t^2 n_3 &= (Y_0 - Y_3) - 2t_3^2(n_0 - n_3) - (v_0 - v_3)K_3 - ((Y_3 - Y_2) - 2t_2^2(n_3 - n_2) - (v_3 - v_2)K_2) \end{aligned} \quad (242)$$

Making use of 3 of the above EOMs and Mathematica we get the potentials as

$$v_1^{(i+1)} = \frac{-(B+D)^{(i)}K_1^{(i)}K_3^{(i)} - B^{(i)}K_2^{(i)}K_3^{(i)} + A^{(i)}K_1^{(i)}K_2^{(i)} + v_0C^{(i)}}{C^{(i)}} \quad (243)$$

$$v_2^{(i+1)} = \frac{-(A+B)^{(i)}K_0^{(i)}K_2^{(i)} + A^{(i)}K_1^{(i)}K_2^{(i)} - D^{(i)}K_0^{(i)}K_3^{(i)} - (B+D)^{(i)}K_1^{(i)}K_3^{(i)} + v_0C^{(i)}}{C^{(i)}} \quad (244)$$

$$v_3^{(i+1)} = \frac{(A+B+D)^{(i)}K_0^{(i)}K_1^{(i)} + (A+B)^{(i)}K_0^{(i)}K_2^{(i)} + A^{(i)}K_1^{(i)}K_2^{(i)} + v_0C^{(i)}}{C^{(i)}} \quad (245)$$

where A, B, C and D are

$$\begin{aligned} A^{(i)} &= (Y_1 - Y_0) - 2t_0^2(n_1 - n_0) - (Y_0 - Y_3) + 2t_3^2(n_0 - n_3) \\ &= (Y_1 - 2Y_0 + Y_3)^{(i)} - 2t_0^2(n_1 - n_0) + 2t_3^2(n_0 - n_3) \end{aligned} \quad (246)$$

$$\begin{aligned} B^{(i)} &= (Y_2 - Y_1) - 2t_1^2(n_2 - n_1) - (Y_1 - Y_0) + 2t_0^2(n_1 - n_0) \\ &= (Y_2 - 2Y_1 + Y_0)^{(i)} - 2t_1^2(n_2 - n_1) + 2t_0^2(n_1 - n_0) \end{aligned} \quad (247)$$

$$\begin{aligned} D^{(i)} &= (Y_3 - Y_2) - 2t_2^2(n_3 - n_2) - (Y_2 - Y_1) + 2t_1^2(n_2 - n_1) \\ &= (Y_3 - 2Y_2 + Y_1)^{(i)} - 2t_2^2(n_3 - n_2) + 2t_1^2(n_2 - n_1) \end{aligned} \quad (248)$$

$$C^{(i)} = ((K_0K_1 + K_0K_2 + K_1K_2)K_3 + K_0K_1K_2)^{(i)} \quad (249)$$

A.2 EOM OF THE CURRENT

We now derive the EOM of the link current $Q_{m,m+1}$, as we will need it to show the mapping between the kinetic energy density and the hopping in Sec. 4.2. We start with the EOM of the complex link current since its imaginary part gives us the link current. Knowing how the complex link current relates to the 1-RDM (250) we make use of the EOM of the 1-RDM to get that for the complex link current

$$\begin{aligned} -i\partial_t Q_{m,m+1} &= -i\tilde{T}_{m,m+1}\partial_t \gamma_{m,m+1} \\ &= t_m e^{i\phi_{m,m+1}} \left(-t_{m-1} e^{i\phi_{m-1,m}} \gamma_{m-1,m+1} + t_{m+1} e^{i\phi_{m+1,m+2}} \gamma_{m,m+2} \right. \\ &\quad \left. - t_m e^{i\phi_{m+1,m}} D_+ n_m - \gamma_{m,m+1} D_+ v_m \right) \\ &= (-t_m t_{m-1} \gamma_{m-1,m+1} + t_m t_{m+1} \gamma_{m,m+2}) e^{2i\frac{\phi}{L}} - t_m^2 D_+ n_m - Q_{m,m+1} D_+ v_m. \end{aligned} \quad (250)$$

We get the EOM of link current knowing the relation (204)

$$\begin{aligned} \partial_t J_{m,m+1} &= 2\Im \partial_t Q_{m,m+1} \\ &= 2\Re (-i\partial_t Q_{m,m+1}) \end{aligned} \quad (251)$$

which from (250) becomes

$$\partial_t J_{m,m+1} = D_+ Y_m - 2t_m^2 D_+ n_m - (D_+ v_m) K_{m,m+1} \quad (252)$$

and Y_m reads

$$Y_m = 2\Re(t_m t_{m-1} \gamma_{m-1,m+1} e^{2i\frac{\phi}{L}}). \quad (253)$$

In a similar manner we get the EOM for the kinetic energy density knowing the relation (205)

$$\begin{aligned} \partial_t K_{m,m+1} &= 2\Re \partial_t Q_{m,m+1} \\ &= -2\Im (-i\partial_t Q_{m,m+1}) \end{aligned} \quad (254)$$

which from (250) becomes

$$\partial_t K_{m,m+1} = -D_+ \Xi_m + (D_+ v_m) J_{m,m+1} \quad (255)$$

where

$$\Xi_m = 2\Im(t_m t_{m-1} \gamma_{m-1,m+1} e^{2i\frac{\phi}{L}}). \quad (256)$$

A.3 FURTHER DETAILS OF THE INVERSION SCHEME IMPLEMENTATION

In Sec. 4.2 we discussed how to numerically investigate the one-to-one mapping between densities and potentials by making use of suitable EOMs. Here we give some details about the numerical implementation of these inversion schemes. We make use of the eigensolver "linalg.eigh" in Python 3.5 to diagonalize the Hamiltonian (198) and solve the ground state problem.

Initial value of control fields v and t

To do the inversion of n and K respectively, we follow the self-consistent iteration scheme discussed in Chap. 4. For this we need an initial value for the control fields in each case. For the inversion of the density n discussed in the main text we choose as initial potential $v_m^{(0)} = 0.1$. For the the inversion of the kinetic energy density K the initial hopping is set to $t_m^{(0)} = 1$.

Convergence criteria

To determine that the self-consistent scheme has converged we check that the norm of the difference between the target density and the updated density in each case is less than a very small number ϵ . In our algorithm we have chosen $\epsilon = 10^{-8}$. For this convergence criterion the inversion of the density n and that of the kinetic energy density K converges after about 50 iterations.

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ACRONYMS

1 -RDM	one-body Reduced Density Matrix
2 -RDM	two-body Reduced Density Matrix
ALDA	Adiabatic Local Density Approximation
CDFT	Current Density Functional Theory
DFT	Density Functional Theory
EOM	Equation Of Motion
GGA	Generalized Gradient Approximation
Hxc	Hartree-exchange-correlation
KS	Kohn-Sham
LDA	Local Density Approximation
RG	Runge-Gross
TDCDFT	Time-dependent Current Density Functional Theory
TDDFT	Time-dependent Density Functional Theory
xc	Exchange Correlation

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