Density functional study of
Wigner crystallization in quantum rings

(Dichtefunktionaluntersuchung der
Wignerkrystallisation in Quantenringen)

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Abstract

A system as simple as a few electrons confined in a quasi one-dimensional quantum ring shows a surprisingly rich variety of ground states depending on the system parameters. Fermi liquid states with different total spin and angular momentum can be observed as the ring circumference or the magnetic flux are varied. The latter gives rise to a persistent current which is a remarkable manifestation of the Aharonov-Bohm effect. An even more interesting situation is encountered when the strength of the electron-electron interaction is increased. As the latter becomes dominant over the kinetic energy a correlated ground state, known as a Wigner molecule (or a Wigner crystal in an extended system), supersedes the Fermi liquid state. Indeed, quantum Monte Carlo calculations show that in the strongly interacting quantum ring pronounced oscillations are visible in the pair correlation function, indicating a strong spatial correlation of the electrons.

In this thesis we pursue the possibility to describe the evolution of the ground state of the quantum ring from a Fermi liquid state to a strongly correlated Wigner molecule using density functional theory (DFT). In contrast to wave function-based methods—such as the quantum Monte Carlo method—DFT is not limited to small particle numbers. The basic idea which underlies this decisive advantage is to express the complicated many-body problem in terms of much simpler collective variables, such as the (spin-) density or the paramagnetic current density. A consequence thereof is the possibility to define an auxiliary non-interacting system, known as the Kohn-Sham system, providing direct access to the ground state energy and density of the interacting system. While being exact in principle, the practical application of DFT requires an adequate approximation for the exchange-correlation functional. The latter accounts for all quantum many-body effects. Promising candidates for the description of strongly correlated ground states are orbital-dependent functionals which depend explicitly on the Kohn-Sham orbitals and only implicitly on the collective variables. In this work we employ the exact-exchange functional which is the Fock exchange energy evaluated with the Kohn-Sham orbitals. From an orbital-dependent functional the local effective Kohn-Sham potential is determined as the solution of the very complicated optimized effective potential (OEP) integral equation. This makes tempting the use of the simplifying Krieger-Li-Iafrate (KLI) approximation which is so far believed to be quite accurate.

To discern the formation of the correlated ground state we resort exclusively to collective variables which are directly accessible within DFT. We place a very weak impurity potential—with a strength much less than the Coulomb interaction energy per particle—in the quantum ring. Such a “vanishing” impurity will not influence the uncorrelated electrons in the Fermi liquid state and the persistent current will retain its non-interacting value. In contrast, in a correlated state the Wigner molecule has to tunnel as a whole through the impurity potential which will drastically reduce the persistent current. Indeed, we find that the current is independent of the electron-electron interaction in the Fermi liquid state and drops exponentially with increasingly strong electron-electron interaction after the Wigner molecule is formed. The decrease of the current is accompanied by the emergence of pronounced charge- and spin-density waves. The resulting antiferromagnetic order is in perfect agreement with exact diagonalization calculations. By taking the amplitude of the density oscillations as the order parameter we confirm that in the DFT calculation the formation of the Wigner molecule is a second order quantum phase transition. Comparing the results computed using the KLI approximation with the results obtained from a numerical solution of the full OEP equation we find that the KLI approximation may predict a Fermi liquid ground state where the OEP finds a Wigner molecule.

Using the persistent current as the localization criterion, we should in principle resort to current-density functional theory which yields directly both the ground state density and the paramagnetic current density of the interacting system. The corresponding Kohn-Sham system contains not only the effective scalar potential but also an effective vector potential. Both effective potentials can be determined using an extension of the OEP method which expresses the effective potentials as the solutions of two coupled integral equations. The latter can be considerably simplified using a KLI-type approximation. We will show, however, that this approximation cannot be employed in the pinned Wigner crystal state with its broken angular symmetry, since it predicts a current of the interacting system which violates the continuity equation. We show that in contrast a solution of the OEP equations does not suffer from this shortcoming.
Zusammenfassung


1 Introduction

Almost thirty years ago Büttiker et al. [1983] proposed that the ground state of small normal (i.e. not superconducting) rings might support a finite orbital magnetic moment if a magnetic flux is applied through the center of the ring. This peculiar feature, known as the persistent current, is a manifestation of the Aharonov-Bohm effect [Aharonov and Bohm, 1959]. Considerable effort was undertaken to detect the persistent currents experimentally. First conclusive results were obtained in mesoscopic rings where the magnetic response revealed the existence of an orbital magnetic moment [Webb et al., 1985; Timp et al., 1987; Lévy et al., 1990; Chandrasekhar et al., 1991; Ihn et al., 2003]. Unfortunately, the physical situation in mesoscopic quantum rings is rather complicated due to the simultaneous presence of scatterers and a magnetic field in an interacting many-electron system. This makes it difficult to provide a full explanation of the observed unexpectedly large magnitude of the persistent current.

In the following time much effort was spent on further decreasing the size of the rings with the goal to reach eventually the nanoscopic regime. This, however, proved to be a challenge and the experimental realization of truly nano-sized quantum rings containing a small number of electrons became possible only about ten years ago [Lorke et al., 2000]. The first evidence of the Aharonov-Bohm effect in nanoscopic rings was not acquired from magnetic response, i.e. the persistent current. Instead a closely related phenomenon was observed in addition energy spectra. Namely, it was found that the total angular momentum of the ground-state changes to a higher integer value as the magnetic flux penetrating the ring is increased. In a non-interacting system such a change in the ground-state angular momentum should occur as the flux is increased by a flux quantum $\hbar/e$ (in a system with an even number of electrons) or by half a flux quantum (in a system with an odd number of electrons) whereas in a system of $N$ interacting electrons this period is found to be $\hbar/N_e$ because of simultaneous changes of the total spin and the total angular momentum. A direct measurement of the persistent current in nanoscopic rings was reported by Keyser et al. [2002] and more recently by Kleemans et al. [2007]. Its magnitude proved to be in better agreement with the theoretically calculated values than in the mesoscopic case [Fomin et al., 2008].

Much longer than their experimental history, nanoscopic quantum rings served as a prototypical system for theoretical studies of interacting electrons in the presence of impurities and magnetic fields. Most of the quantum rings discussed to date are one-dimensional or quasi one-dimensional, i.e. their width is considered to be finite but so small compared to the circumference that the transverse electron motion is restricted to the lowest subband. At first glance, such a system may seem rather simple, yet it shows a surprisingly rich variety of possible ground states. Besides the aforementioned dependence of the ground-state angular momentum on the magnetic flux, the total spin changes with the flux or with the strength of the electron-electron interaction, the latter effect being a clear manifestation of the exchange interaction.

A very interesting physical situation can be encountered at low electron densities when the Coulomb interaction between the electrons dominates over the kinetic energy. A correlated ground state, distinctly different from the Fermi liquid state may then be formed. While the kinetic energy attains minimum in a delocalized Fermi liquid ground state, the Coulomb interaction keeps the electrons separated at maximal relative distances favouring a correlated ordered state. Indeed, using the quantum Monte Carlo method, Pederiva et al. [2002] and Emperador et al. [2003] found that the pair correlation function shows pronounced oscillations in the strongly correlated system which are not present in the Fermi liquid state. This signifies a strong spatial correlation of the electrons, a state which is known as Wigner crystal or, in a finite system, as Wigner molecule. Configuration-interaction studies also show that the ground state of a one-dimensional or quasi one-dimensional quantum ring can often be understood as a rotating Wigner molecule [Koskinen et al., 2001].
Computational techniques like the configuration-interaction method or quantum Monte Carlo methods used so far to describe Wigner crystallization in quantum rings can be considered “exact” because they sample the full many-body wavefunction. The price for this high accuracy is that they scale exponentially with the number of particles\(^1\) and thus cannot be applied to inhomogeneous systems with more than a few electrons. Density functional theory provides a highly appealing way to circumvent this limitation. Its exceptional computational efficiency is based on the idea to cast the complicated many-body problem in terms of simple collective variables such as the density (in density functional theory, DFT), the spin density (in spin-density functional theory, SDFT) or the current density (in current-density functional theory, CDFT). The formal justification for this simplification is provided by the Hohenberg-Kohn theorem [Hohenberg and Kohn, 1964] which establishes a one-to-one correspondence between the ground-state density and the external potential and thus allows to understand all observables—in particular the ground-state energy—as functionals of the density. An important consequence of the Hohenberg-Kohn theorem with far-reaching practical implications has first been pointed out by Kohn and Sham [1965] who noticed that the Hohenberg-Kohn theorem can equally well be applied to a non-interacting electron gas. This allows to define the auxiliary Kohn-Sham system of non-interacting particles moving in an effective potential with a ground-state density that equals the ground-state density of the interacting system in the given external potential. The vast majority of practical applications of DFT employ this Kohn-Sham scheme because the solution of a single-particle Schrödinger-type equation (the Kohn-Sham equation) can be done in a very simple and efficient way providing direct access to the ground-state density and energy of the interacting many-body system.

Thanks to its efficiency and accuracy, DFT provides a basis for ab-initio studies of realistic many-particle systems [Dreizler and Gross, 1990]. It has been successfully applied to systems as different as solids, atoms, molecules and nanostructures like quantum dots or rings. DFT has also been used to study Wigner crystals in extended one-dimensional [Tanatar et al., 1998], two-dimensional [Choudhury and Ghosh, 1995] and three-dimensional systems [Das and Mahanty, 1988] where the symmetry-breaking periodic density modulation of the pinned Wigner crystal has been introduced by hand. These calculations show that at low electron densities the Wigner crystal supersedes the Fermi liquid state. Similarly, Räsänen et al. [2003] found that in a rectangular quantum dot density oscillations build up when the electron density is lowered—a result which has been interpreted as a formation of a pinned Wigner molecule.

In the present work we study the formation of a pinned Wigner molecule in a quasi one-dimensional quantum ring. To detect the emergence of the correlated state we trace a dependence of the persistent current on the electron interaction parameter. This dependence provides a more conclusive criterion of collective electron localization due to the Wigner molecule formation than the density alone can do. In contrast to the microscopic pair correlation function, the persistent current density is directly accessible within CDFT—and to usually a very good approximation within DFT. However, in a perfect quantum ring the Wigner molecule can glide freely along the ring and the persistent current of the correlated ground state will be exactly equal to the current of the non-interacting system [Krive et al., 1995]. To stop the rotation of the Wigner molecule we introduce a very weak impurity potential with a strength negligible compared to the Coulomb energy per particle in the quantum ring. Clearly, such a potential will neither influence the uncorrelated electrons in the Fermi liquid state nor the formation of the Wigner crystal. Yet, the Wigner molecule now has to tunnel as a whole through the impurity potential and we expect that the persistent current will be drastically reduced once a correlated ground state is formed.

In principle, DFT is an exact theory. Its practical application, however, requires a suitable approximation for the exchange-correlation energy functional \(E_{xc}\). The latter is the part of the total energy which, by definition, accounts for the quantum many-body effects. The simplest, yet successfully used approxi-

\(^1\)For the quantum Monte Carlo method applied to a fermionic system without any further approximations this is true at least for systems which are not strictly one-dimensional [Troyer and Wiese, 2005].
mation for $E_{xc}$ is the local density approximation (LDA). It expresses $E_{xc}$ of an inhomogeneous system as

$$E_{xc}^{LDA}[n(r)] = \int d^3r \varepsilon_h^{xc}(n(r)) n(r)$$

(1.1)

where $\varepsilon_h^{xc}(n)$ is the exchange-correlation energy per particle in the homogeneous system with the density $n$. Provided that Wigner crystal-type correlations are accounted for in the homogeneous reference system, the LDA is in principle capable of describing a Wigner molecule. Yet, it still suffers from the self-interaction error which destabilizes the Wigner crystal state [Yannouleas and Landman, 1999]. More promising candidates are functionals which depend directly on the Kohn-Sham orbitals and thus only implicitly on the collective variables. The most prominent such orbital dependent functional is probably the exact-exchange functional which is the Fock exchange energy evaluated with the Kohn-Sham orbitals. In general, employing orbital-dependent functionals requires application of the optimized effective potential (OEP) method which allows to determine the local effective potential in which the fictitious Kohn-Sham particles move. The OEP equation is, however, a complicated integral equation which urges for simplifying approximations. A very popular one is the Krieger-Li-Iafrate (KLI) approximation which is so far believed to yield ground state energies and densities close to those obtained from an exact OEP calculation [Kümmel and Perdew, 2003a; Kümmel and Kronik, 2008]. Yet, there is also evidence that the KLI approximation may fail in some situations. Kümmel et al. [2004] showed that it largely overestimates the polarizabilities in a chain of hydrogen atoms and dimers while the exact-exchange OEP method produces results which are in a far better agreement with the experimental data. The reason for this failure are the potential barriers between the electron density maxima which are too low in the KLI approximation. It deserves to be investigated whether a similar tendency of the KLI approximation to favour a delocalized state can be also observed in the context of the Wigner crystallization.

Employing the persistent current makes it in principle necessary to use the current-density functional theory (CDFT) [Vignale and Rasolt, 1988] which—in addition to the ground state density—provides a direct access to the paramagnetic current density of the interacting system. As in DFT, a practical application of CDFT employs the auxiliary Kohn-Sham system where fictitious non-interacting particles move in an effective scalar and vector potential. An adequate approximation of the exchange-correlation functional must fulfill certain exact properties. In the context of CDFT one of such requirements is that the current of the interacting system must satisfy the continuity equation. This is guaranteed if the effective vector potential is computed from a gauge-invariant exchange-correlation energy functional [Vignale and Rasolt, 1988]. The exact-exchange functional clearly is such a gauge-invariant functional and the effective vector potential calculated using a generalization of the OEP method [Pittalis et al., 2006] thus has to have this property. Yet, it is not clear a priori whether an approximate solution of the CDFT-OEP equations—such as the KLI approximation [Pittalis et al., 2006]—preserves this property. All calculations employing the CDFT-KLI approximation reported so far [Pittalis et al., 2006; Hellbig et al., 2008] study rotationally symmetric systems. Regardless of the employed approximation, in such a system the current always satisfies the continuity equation. If this is also true in a system with an explicitly broken angular symmetry has not been discussed to date and is addressed in the present work.

**Outline of the present work**

This thesis is structured as follows. The first part is devoted to the study of Wigner crystallization in quantum rings in the framework of density functional theory. We introduce the Wigner crystal in chapter 2 and the quantum ring in chapter 3. The related experimental and theoretical work is reviewed. In chapters 4 and 5 we present density functional theory and spin-density functional theory and describe the OEP formalism as well as the simplifying KLI approximation. To conclude this technical part we give
a motivation for choosing the persistent current as the localization criterion and introduce the electron localization function. The results of the calculations are reported and discussed in chapter 7. We first introduce the model for the quantum ring which is used in the numerical calculations. We then study in detail the Wigner transition in the quasi one-dimensional quantum ring both for spinless (i.e. fully spin-polarized) electrons and for the spin-dependent case. For the former case we consider the Wigner transition under the influence of a very weak and a strong impurity potential. Finally the influence of the KLI approximation is investigated by computing for comparison the Wigner transition using an exact numerical solution of the OEP equations.

In the second part of the thesis we address the question of gauge invariance and its relation to the continuity equation in OEP and KLI calculations in the framework of current-density functional theory (CDFT). In chapters 8 and 9 we first introduce CDFT and provide an inherently gauge-invariant derivation of the CDFT-OEP equations. Chapter 9 contains also a short presentation of the CDFT-KLI approximation followed by a detailed discussion of the gauge invariance of the CDFT-OEP and CDFT-KLI equations. After a short discussion of gauge invariance in the one-dimensional model system we show in chapter 10 numerically that the solution of the CDFT-KLI equations may result in a current of the interacting system which violates the continuity equation. We show that the exact solution of the CDFT-OEP equations does not suffer from this shortcoming. We finally address briefly the description of the Wigner transition within current-density functional theory.

A summary and the conclusions are given in chapter 11. The numerical method is presented in the appendix. This chapter also serves as a documentation for the developed software program.

The results presented in this thesis are the subjects of the following publications (status at the time of submission of this thesis):


Part I.

Wigner crystallization in quantum rings: a density functional study
2 The Wigner crystal in three-, two- and one-dimensional systems

It was pointed out by Wigner [1934] that the ground state of an interacting many-electron system can differ qualitatively from the homogeneous electron gas. If the kinetic energy is completely neglected—which corresponds to infinitely heavy electrons—the particles would occupy the absolute minima of the potential energy surface. Such a many electron state, where the electrons are localized at discrete lattice sites, is called a Wigner crystal.

An opposite extreme is the non-interacting electron gas, where the kinetic energy is minimized by evenly distributing each electron throughout the system. The corresponding single-electron states are plane waves.

In a real interacting system, the Coulomb interaction tends to localize the electrons and the kinetic energy favours their delocalization. It thus seems very natural that the ratio of the kinetic and the Coulomb energy is the decisive quantity which determines whether the ground state is gas-like or Wigner crystal-like. It is easy to give a rough estimate of this ratio. In a non-interacting homogeneous three-dimensional electron gas, the kinetic energy per electron $T_{3D}$ is sixty percent of the Fermi energy. The latter provides the relevant (and in fact the only) energy scale and is proportional to $n^{2/3}$, where $n$ is the electron density.

Similarly, we can estimate the respective ratio in a two-dimensional system to be

$$\frac{V_{2D}}{T_{2D}} \sim n^{-1/2} \quad (2.2)$$

and in a one-dimensional system it is

$$\frac{V_{1D}}{T_{1D}} \sim n^{-1} \quad (2.3)$$

In all three cases the kinetic energy dominates for high densities as a consequence of the Pauli principle, whereas for low densities the Coulomb interaction which favours the Wigner crystal becomes more important. An estimate of the ratio between $T$ and $V$ is conveniently expressed by the dimensionless interaction parameter $r_S$, which expresses the radius of the sphere that contains on average exactly one electron in units of the (effective) Bohr radius. The latter is given by

$$a_B^* = \frac{4\pi\epsilon\epsilon_0}{m_0^*e^2} \quad (2.4)$$

where $m_0^*$ and $\epsilon$ are the effective electron mass and the dielectric constant in the host material, which can be GaAs for example, and $\epsilon_0$ is the vacuum dielectric constant. In a three-dimensional system, the interaction parameter is related to the density as

$$r_S^{3D} = \left( \frac{3}{4\pi n} \right)^{1/3} \frac{1}{a_B^*} \quad (2.5)$$
whereas in two and one spatial dimensions, the respective relations are

\[ r_{2D}^{S} = \left( \frac{1}{\pi n} \right)^{1/2} \frac{1}{a_B^*} \]

and

\[ r_{1D}^{S} = \frac{1}{2n} \frac{1}{a_B^*} . \]

Of course, the above considerations by themselves do not provide any estimate for the critical density of a transition from the Fermi liquid to the Wigner crystal. In two and three dimensions, quantum Monte Carlo simulations indicate that a Wigner crystal forms at a critical value of \( r_{2D}^{S,c} = 37 \pm 5 \) [Tanatar and Ceperley, 1989] and \( r_{3D}^{S,c} = 100 \pm 20 \) [Ceperley and Alder, 1980], respectively.\(^1\)

The one-dimensional system is somewhat peculiar and has to be treated differently. In contrast to many-electron systems in two and three dimensions, which are known to be Fermi liquids, the ground state of a one-dimensional many-electron system is a so-called Luttinger liquid [Giamarchi, 2004; Voit, 1995]. In a Luttinger liquid, the energetically low-lying excitations are not individual particle-hole excitations as in the Fermi liquid, but are of a collective bosonic nature. The Luttinger model is exactly solvable by the bosonization technique which expresses the Hamiltonian in terms of the displacement fields corresponding to the elementary plasmonic excitations [Giamarchi, 2004]. Using this technique, Schulz [1993] showed that for a long-range electron-electron interaction, irrespective of its strength, the density-density correlation function contains a slowly decaying oscillatory contribution with the wave vector \( 4k_F \) which signifies a tendency to form a periodic structure with a lattice constant that equals exactly the average interparticle spacing. Although there is no true long-range order in a one-dimensional system, the \( 4k_F \) component of the density-density correlation function may be interpreted (due to its extremely slow decay) as an emergence of a one-dimensional Wigner crystal. Interestingly, in the case of a short-range electron-electron interaction—which can occur due to the presence of conducting gate electrodes that screen the long-range Coulomb interaction—the \( 4k_F \) component decays much faster [Schulz, 1993]. The bosonization method does not provide a numerical value for the critical \( r_{1D}^{S,c} \) at which the Wigner crystal forms. As in the two- and three-dimensional system this value has to be obtained from a many-body calculation, for instance by using the quantum Monte Carlo method. Using the latter Shulenburg et al. [2008] estimated from the emergence of the \( 4k_F \) component in the pair correlation function that Wigner crystallization happens in a quasi one-dimensional quantum wire at \( r_{1D}^{S,c} \sim 1 \). The precise value, however, was found to depend strongly on the width of the wire and is in general larger for wider wires.

In addition to the continuum description of the one-dimensional Wigner crystal, the latter has also been studied in lattice-type models. Valenzuela et al. [2003] found that electrons arrange at the lattice sites of a so-called generalized Wigner lattice if the Coulomb interaction is much stronger than the kinetic energy described by the hopping matrix element. In a generalized Wigner lattice the electrons arrange like classical particles distributed over the lattice sites such that the Coulomb energy is minimized. As the strength of the Coulomb interaction is reduced, the classical generalized Wigner lattice is replaced by a quantum mechanical Wigner crystal where the electrons extend over several lattice sites. Still, the density distribution is sharply peaked at the lattice sites of the generalized Wigner lattice. By further reducing the Coulomb interaction strength, the Wigner crystal is replaced by a weakly modulated charge-density wave. However, no sharp value of the interaction strength at which the Wigner transition takes place was given. Concurrent with the charge ordering, an anti-ferromagnetic spin ordering has been found.

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\(^1\)Slightly different critical values of \( r_S \) — which are nevertheless of the same order of magnitude — have been calculated earlier by Ceperley [1978] who obtained \( r_{2D}^{S,c} = 33 \pm 2 \) and \( r_{3D}^{S,c} = 67 \pm 5 \).
although its characteristic energy scale is much smaller than the typical Coulomb interaction energy of the charge-ordered phase.

In a semiclassical model the one-dimensional Wigner crystal with a screened, short-range electron-electron interaction is frequently described as an elastic chain which can be completely characterized by three independent quantities: the electron mass, the lattice parameter and the sound velocity. Using this semiclassical model, Glazman et al. [1992] showed that the one-dimensional Wigner crystal is stabilized by an arbitrarily weak pinning potential in spite of the strong quantum fluctuations which lead to the absence of long-range order. While the quantum fluctuations effectively compensate the action of the pinning potential compared to the classical case, it nevertheless retains its stabilizing effect because this potential itself suppresses the quantum fluctuations. In the absence of a metallic gate which screens the electron-electron interaction, the long-rangeness of the Coulomb interaction enhances the pinning [Glazman et al., 1992].

Wigner crystallization has been also addressed in finite one-dimensional systems like one-dimensional quantum dots and quantum rings. Using the elastic chain-model, Krive et al. [1995] studied the persistent current in a one-dimensional Wigner crystal ring. While the persistent current of the Wigner crystal in a rotationally perfect quantum ring is exactly the same as the persistent current of non-interacting electrons, an impurity pins the Wigner crystal and thus reduces the persistent current. The amount by which the persistent current of the pinned Wigner crystal is reduced compared to the non-interacting value depends on the strength of the pinning potential relative to the typical energy scale of the Wigner crystal ring. For a screened electron-electron interaction the latter is given by $T_s^2 = \frac{\hbar}{s^2 L}$, where $s$ is the sound velocity and $L$ is the circumference of the ring. If the pinning potential is weak, the suppression depends exponentially on its strength. In contrast, for a strong pinning potential $V_p$ the persistent current is suppressed according to a power law $(T_s/\alpha V_p)^{1/\alpha}$, where $\alpha = \frac{\pi a}{m s a} \ll 1$ ($a$ is the lattice spacing of the Wigner crystal) determines the magnitude of the quantum fluctuations which are small for a stiff crystal. However, if the pinning potential is very weak ($V_p \ll T_s$) the persistent current of the non-interacting system is recovered irrespective of the stiffness of the Wigner crystal. If the short-range screened interaction is replaced by the long-range Coulomb potential the suppression of the persistent current is enhanced.

The elastic chain model assumes the existence of the Wigner crystal and studies its properties. Yet, it does not address the formation of the Wigner crystal. In contrast, evidence for Wigner crystallization in a quasi one-dimensional ring has been found by Emperador et al. [2003] using the quantum Monte Carlo method. As is frequently done in many-body studies of the Wigner crystal, the pair correlation function was employed to detect the formation of the correlated state. Emperador et al. found that in the quantum ring with a high electron density the pair correlation function merely shows the usual Fermi liquid oscillations indicating an uncorrelated state. When the density was lowered, pronounced oscillations were observed in the pair correlation function exactly at the positions the electrons would occupy to minimize the Coulomb energy. This strong spatial correlation signifies the formation of the correlated Wigner molecule. Since the ring—and thus the many-body Hamiltonian—were chosen to have a perfect rotational symmetry, the density remained homogeneous even in the strongly correlated ground state.

Szafran et al. [2004] studied the ground state as well as the first few excited states of up to five electrons in a rectangular one-dimensional potential well using the configuration-interaction (CI) method. In the CI approach, the many-body wavefunction is expanded in a series of Slater determinants which consist of occupied and unoccupied single-particle orbitals. It provides a reliable but computationally very expensive method which is suitable only for a small number of particles. It was found that at low electron densities—corresponding to a long quantum dot—the ground state density of the $N$-electron system always shows $N$ distinct maxima which is characteristic for a Wigner molecule (as the Wigner crystal in a finite system is usually called). Irrespective of the number of particles and the size of the system the total spin in the
2. The Wigner crystal in three-, two- and one-dimensional systems

ground state was always the lowest possible one, i.e. $\frac{1}{2}$ for an odd and 0 for an even number of electrons, although in the largest quantum dots studied a degeneracy between the states with the lowest total spin and states with a higher total spin has been observed. Considering additionally the influence of a short-ranged attractive impurity potential located in the center of the potential well, Szafran et al. [2004] showed that the impurity can significantly perturb Wigner crystallization by trapping one of the electrons. The resulting density profile shows a sharp peak at the location of the impurity potential and the remaining electrons are distributed symmetrically on both sides of the central peak.

In the context of density functional theory, the three-dimensional Wigner crystal has been investigated by Das and Mahanty [1988], albeit not employing the frequently used Kohn-Sham system (see chapter 4). Instead, a local density approximation—which locally approximates the inhomogeneous system by a homogeneous one with the respective density—was applied both to the exchange-correlation functional and to the kinetic energy. The resulting expression for the kinetic energy is equivalent to the Thomas-Fermi-von Weizsäcker functional and the exchange-correlation energy has been extracted from the ground state energy of the three-dimensional homogeneous electron gas. Within this local approximation, the total energy of the system is a functional that depends explicitly on the density profile. For the latter, a uniform distribution was superimposed with a periodic modulation that corresponds either to a fcc or to a bcc lattice. For values of the interaction parameter that exceed $r_S \simeq 30$ the fcc lattice was found to be lower in energy than the uniform electron liquid. The latter is energetically lower than the bcc lattice for interaction parameters smaller than $r_S \simeq 38$. Still, in the Wigner crystal phase, the fcc lattice was found to be favourable over the bcc lattice which can be explained as a purely electrostatic effect.

Using the local approximation for the kinetic energy functional and an appropriate local density approximation for the exchange-correlation functional, the Wigner crystallization in the two-dimensional electron gas has been studied by Choudhury and Ghosh [1995] and in the quasi one-dimensional system by Tanatar et al. [1998]. In both calculations, the periodic density oscillations were imposed by hand as in the three-dimensional case discussed above. For high electron densities, the energy functional assumes its minimum value for the uniform electron gas, whereas for low densities the ground state was found to possess the periodically modulated electron density. The transition from a two-dimensional Fermi liquid to the Wigner crystal was found to occur at $r_{2D,c}^{2D} = 32$. In the quasi one-dimensional model the Wigner crystal was found to form at $r_{1D,c}^{1D} \sim 5$, where the precise value depends on the width of the lateral confining potential which defines the quasi one-dimensional quantum wire.

Spin-density functional theory in the local spin-density approximation has also been used to study the formation of Wigner molecules in finite systems. Räsänen et al. [2003] investigated the electronic structure of polygonal two-dimensional quantum dots confined by a hard-wall potential. It has been shown that spin-density functional theory predicts the formation of Wigner molecules as the electron density is lowered by increasing the area of the quantum dots. The transition has been estimated to occur at the critical value $r_S^{2D} \simeq 4$, only weakly influenced by the number of electrons in the dot or the shape of the quantum dot. It has been found that spin-density functional theory always leads to an antiferromagnetic ordering of the electrons in the Wigner molecule. The ground state energy of this solution was found to be always lower than the ground state energy obtained from a density functional theory calculation imposing the constraint that both spin densities coincide. This observation, in fact, reflects the general trend that in density functional theory the ground state energy of a solution with some broken symmetry (i.e. spin or spatial symmetry) is lower than the ground state energy of the solution with the preserved symmetry. This symmetry breaking may be interpreted as a mapping of the internal structure of the many-body wavefunction to the laboratory system [Koskinen et al., 2001]. Spontaneous symmetry breaking in density functional theory is not restricted to Wigner crystallization. An interesting example in a very different physical situation has been studied by Pankratov and Scheffler [1995] who considered the formation of an exciton in a surface band of GaAs(110). After the exciton is created it gets localized by locally deforming the lattice which spontaneously breaks the translational symmetry.
In all density functional approaches that employ a local density approximation (LDA) the expression for the exchange-correlation functional is based on the exchange-correlation energy per electron in the homogeneous electron gas. Such an approximation can be suitable to describe the Wigner crystal if the low-density homogeneous system with appropriate Wigner crystal-type correlations is properly taken into account. An example is the Wigner interpolation [Wigner, 1934] but also the modern LDA functional based on the Ceperley-Alder exchange-correlation energy [Ceperley and Alder, 1980] incorporates the Wigner crystal as the low-density limit. Yet, the LDA suffers from the self-interaction error, i.e. a spurious electrostatic interaction of each electron with itself which destabilizes the Wigner crystal phase. A possible remedy to this problem is the application of functionals that depend explicitly on the Kohn-Sham orbitals (see chapter 5).

Experimental detection of the Wigner crystal is difficult. First, one needs a very low charge-carrier density so that Coulomb effects play the dominant role. Second, a very clean system is required, otherwise Anderson localization might obscure the effects related to Wigner crystallization. However, it has also been argued for the two-dimensional system that disorder might stabilize the Wigner crystal down to values of $r_{S}^{2D,c} \approx 7.5$ [Chui and Tanatar, 1995]. Still the nature of the ground state of the strongly interacting many electron system in the presence of disorder remains a difficult problem.

The first experimental evidence for “classical” Wigner crystallization (at a temperature sufficiently high for electrons to obey Boltzmann statistics) was found by Grimes and Adams [1979] and Gallet et al. [1982] in a two-dimensional monolayer of electrons on the surface of liquid Helium which provides a very smooth surface. The formation of the Wigner crystal below a critical temperature of 0.457 K (at an electron surface density of $n_{S} = (4.4\pm0.4)\cdot10^{8}$ cm$^{-2}$) has been detected by the appearance of a resonance that could be attributed to a coupled plasmon-ripplon mode that can only form after the electron liquid has undergone the Wigner crystallization. Rippions are standing capillary waves on the surface of liquid Helium which can couple to the plasmon oscillations of the Wigner crystal.

The first evidence for the formation of a pinned two-dimensional quantum Wigner crystal has been found in magneto-transport experiments by Willett et al. [1988]. The key result of this measurement is that the longitudinal transport becomes thermally activated when the filling factor (which, for a given strength of the magnetic field, is simply proportional to the density) falls below a certain threshold value. One possible interpretation is the formation of a two-dimensional Wigner crystal which is subsequently pinned by defects. However, this system is considerably more complicated since the electrons are subjected to a strong magnetic field and consequently the non-interacting states are Landau-levels rather than the plane waves in a free electron gas.

More recently, Yoon et al. [1999] reported the observation of a metal-insulator transition in a two-dimensional hole system formed in a GaAs/AlGaAs heterostructure at $r_{S}^{c} = 35.1 \pm 0.9$. A value which is consistent with the critical $r_{S}^{2D,c} = 37 \pm 5$ obtained by Tanatar and Ceperley [1989] for the ideal two-dimensional electron-gas using a quantum Monte Carlo simulation. Apart from the good agreement between the measured and the theoretically obtained critical values of the interaction parameter, Yoon et al. provide two more arguments why they believe that this metal-insulator transition is related to the formation of a pinned Wigner crystal. First, they infer from the comparison between their $r_{S}^{c}$ and the degree of disorder in their sample with previously published data that their sample is in the clean limit. The degree of disorder can be expressed by the scattering time which is related to the mobility of the charge carriers. Second, in the insulating phase, the system shows an activation behaviour: once the applied voltage exceeds a certain threshold value, the resistance of the sample drops rapidly. This can be interpreted as a depinning of the Wigner crystal.

Electron localization in a two-dimensional quantum dot was investigated by Zhitenev et al. [1999] using single-electron capacitance spectroscopy. The quantum dot was fabricated using the two-dimensional electron gas that forms in a GaAs/AlGaAs heterostructure and the number of electrons in the dot can be

---

2Anderson localization is a single-particle effect. Individual electrons can be localized in a random potential due to an increased back scattering probability. The origin of the latter are quantum interferences. [Anderson, 1958]

11
controlled by a metallic top gate situated above the quantum dot. By applying a larger and larger negative bias to the top gate, the electrons get depleted from the dot. In addition to the top gate, a metallic side gate which surrounds the dot was created. The idea behind the experiment is the following. At fixed side gate bias, a small ac voltage is added to the fixed dc bias of the top gate. If the bias of the top gate is such that an electron can be added to the dot, the ac voltage will cause an electron to oscillate between the dot and the contact which is formed by the underlying GaAs layer. Thus, whenever one measures a response of the dot (the oscillating electron) to the ac voltage, the dc bias of the top gate corresponds to an energy level of the many-electron system in the dot to which the additional electron can be added. By sweeping from a large negative bias of the top gate towards more positive values, one can thus probe how the addition energy spectrum evolves with increasing particle number in the dot. Applying an additional negative bias to the side gate predominantly affects the states in which the electron has a finite probability to reside at the periphery of the dot. Zhitenev et. al found that, for a large negative bias of the top gate, the ac response is only weakly dependent on the bias of the side gate while the spacing of the responses as a function of the top gate bias fluctuates strongly. On adding more and more electrons to the dot, the dependence on the side gate bias becomes stronger. Simultaneously, the spacing of the ac responses on varying the top gate bias decreases and eventually becomes periodic. This signals the transition from localized states, which are only weakly affected by a change in the exterior parts of the system, to extended states as the electron number is increased.

In quasi one-dimensional systems, signatures of Wigner crystallization were first observed by Auslaender et al. [2005]. They studied the dependence of the elementary excitations in quasi one-dimensional quantum wires fabricated in a GaAs/AlGaAs heterostructure on the strength of the Coulomb interaction. The latter was varied by depleting the electron density using a negatively biased gate electrode. When the electron density in any of the occupied subbands is lower than some threshold value, the character of the collective excitations changes abruptly. This change can be attributed to the transition from an extended to a localized many-body state. Simultaneously, the conductance drops in step-like fashion at a finite electron density which also indicates the localization of electrons in the respective subband.

Finally, we should mention that a very indirect indication of Wigner crystallization has been found from crystal structure analysis. Horsch et al. [2005] reported charge ordering in Na$_3$Cu$_2$O$_4$ and Na$_8$Cu$_5$O$_10$ compounds. In these materials, the copper and the oxygen ions form chains where the copper ions are arranged along a straight line between two parallel lines formed by the oxygen ions. Each copper ion has bonds to the four neighboring oxygen ions. From the crystal structure analysis data different Cu–O bond lengths have been inferred which were interpreted as an ordering of the copper ions in the different oxidation states Cu$^{2+}$ and Cu$^{3+}$. This corresponds to a charge ordering that cannot be explained as a charge density wave related to an instability of the Fermi surface because for the present system electronic structure calculations rule out the existence of a charge density wave with the observed periodicity. Consequently, the charge ordering has been explained as a Wigner crystal which is controlled by the long-rangeness of the Coulomb interaction and its emergence has been promoted by a suppression of the kinetic energy due to the narrow bandwidth.

Similarly, Kakiuchi et al. [2007] studied the crystal structure of the low-temperature phase of (DI-DCNQI)$_2$Ag. DI-DCNQI is a planar organic molecule that contains a benzene ring with a delocalized $\pi$-electron system. The DI-DCNQI molecules are piled up on top of each other and the resulting columns are linked by the silver ions. In the low-temperature phase the positions of the silver ions are shifted with respect to their positions in the high-temperature phase. The origin of this shift has been explained as an accumulation of negative charge which attracts the silver cations. From the shifted positions of the latter one can infer that the electron-rich areas form a body-centered tetragonal lattice which has been interpreted as a Wigner crystal. The central argument in favour of a Wigner crystal rather than a charge density wave is that the narrow bandwidth emphasizes the role of the electron-electron interaction. Yet, in this system the discrimination between a Wigner crystal and a charge density wave is less conclusive than in the Na$_3$Cu$_2$O$_4$ and Na$_8$Cu$_5$O$_10$ compounds discussed above.
3 Quantum rings and persistent currents

The quantum nature of electrons confined in a ring geometry manifests itself most clearly as an oscillatory dependence of their ground state properties on an applied magnetic flux [Aharonov and Bohm, 1959]. The prototypical example thereof is the existence of a persistent current which was first proposed to occur in small normal rings by Büttiker et al. [1983]. Ever since then, much work—experimental as well as theoretical—has been devoted to the study of electrons in quantum rings. While a special focus has always been put on the detection of persistent currents also other interesting physical quantities have been studied. Popular among these are the addition energy spectrum or transport properties through open quantum rings attached to conducting leads. In the latter case the quantum ring serves as an Aharonov-Bohm interferometer (see below). The addition energy spectrum, which measures the energy required to add another electron to the system, reveals in particular in quantum dots a periodic structure reminiscent of atomic shells. Quantum dots are therefore frequently referred to as artificial atoms [Reimann and Manninen, 2002].

In this chapter we discuss the experimental work primarily focused on the detection of persistent currents. To commence the theoretical discussion we first introduce a non-interacting one-dimensional model and subsequently present some calculations for interacting electrons in nanoscopic quantum rings.

3.1 Experimental situation

One of the most studied physical phenomena in quantum rings is the Aharonov-Bohm effect [Aharonov and Bohm, 1959]. It manifests itself, for instance, in a persistent current but in general it also affects other physical quantities which become periodic functions of the magnetic field strength. The first successful experimental observation of the Aharonov-Bohm effect in quantum rings was based on a measurement of the resistance of a gold ring versus magnetic field strength [Webb et al., 1985]. The ring connected to metallic leads acts as an Aharonov-Bohm interferometer because the phase picked up by an electron depends on whether it propagates through the left or through the right arm. The diameter and the width of the gold ring were estimated from scanning transmission electron microscopy to be 784 nm and 41 nm, respectively. It was found that the magneto-resistance oscillates as the magnetic field strength is varied. The oscillation period of 0.00759 T corresponds to within 10% to the addition of one flux quantum through the center of a ring with a diameter of roughly 790 nm.

Similar measurements were carried out by Timp et al. [1987] on rings formed in a GaAs/AlGaAs heterostructure with a high electron mobility. The samples were prepared by electron-beam lithography yielding rings with diameters of 1 µm, 2 µm and 2.5 µm. The magneto-resistance showed Aharonov-Bohm oscillations with periods of 0.95 mT, 1.4 mT and 5.8 mT for the ring with a diameter of 1 µm, 2 µm and 2.5 µm, respectively. These oscillation periods are consistent with the addition of one flux quantum through the center of the respective ring.

These rings are in the mesoscopic regime where the large number of electrons and the presence of scatterers considerably complicate the situation. An important step towards the observation of Aharonov-Bohm oscillations in truly nano-scaled systems was the fabrication of quantum rings on AlGaAs/GaAs heterostructures by local oxidation of the surface using the tip of an atomic force microscope. Keyser et al. [2002] used this technique to create a two-dimensional quantum ring with an inner diameter of
approximately 190 nm and an outer diameter of around 450 nm. Using gate electrodes situated in the plane of the ring, adjacent to the contacts with the surrounding two-dimensional electron gas, the device can be tuned from an open ring—forming an Aharonov-Bohm interferometer—into the Coulomb blockade regime. Keyser et al. found that the conductance through the open ring is an oscillatory function of the magnetic field applied perpendicular to the plane of the ring. The oscillation period was estimated such that every 62 mT a flux quantum enters the ring. The corresponding diameter of an electron orbit is 300 nm, a value which agrees well with the dimensions of the ring structure. If the ring is operated in the Coulomb blockade regime, the electron number can be increased (or decreased) stepwise by tuning the gate voltage. The latter influences the Fermi level in the ring and consequently determines whether or not an electron can tunnel into the device. It was found that the height of the conductance peaks that are observed when an electron tunnels into the ring depends on the strength of the magnetic field. The measured oscillation period allows to estimate that every 36 mT a flux quantum enters the area surrounded by the tunneling electrons. This corresponds to a diameter of 380 nm of the electron orbit which is also in good agreement with the size of the ring device.

Using essentially the same technique to prepare a quantum ring structure on top of a two-dimensional electron gas, Ihn et al. [2003] prepared a similarly sized quantum ring that was estimated to contain approximately 200 electrons. Operating the ring in the Coulomb-Blockade regime, Aharonov-Bohm oscillations were detected that correspond to a flux quantum entering the ring every 75 mT. The corresponding radius of the electron orbit coincides with the device geometry.

While these rings are considerably smaller than the mesoscopic rings studied earlier e.g. by Webb et al. [1985] and Timp et al. [1987] they still contain a large number of electrons. The first results of rings containing only one or two electrons were obtained by Lorke et al. [2000] in self-assembled InAs quantum rings. Since these structures—with a ring radius of merely about 14 nm—are much smaller than the previously mentioned rings, considerably stronger magnetic fields are required to observe Aharonov-Bohm oscillations. Lorke et al. studied the quantum rings in a perpendicular magnetic field with strengths up to 12 T which corresponds to 1.5 flux quanta threading the ring. Using far infrared spectroscopy, a change in the ground state (from which the excitations are detected) was found to occur at a magnetic field strength of 8 T. Embedding the rings in a field-effect transistor allows to measure the capacitance as a function of the gate voltage. It was found that the gate voltage at which the lowest capacitance maximum is observed—which corresponds to the addition of one electron to the ring—shifts as a function of the magnetic field. This comes as no surprise since the single-electron energies in the quantum ring depend on the flux threading the ring. Yet, a change in the slope of the gate voltage shift was found to occur at around 8 T. This can be interpreted as a transition of the lowest single-electron state from angular momentum $m = 0$ to $m = 1$. The value of 8 T was found to agree very well with the theoretically calculated level crossing point in a quantum ring with the geometry estimated for the sample.

In a similar system of self-assembled InAs quantum rings containing on average between one and two electrons, Kleemans et al. [2007] measured directly the magnetic response due to the persistent current. Placing a sample containing approximately $1.5 \cdot 10^{11}$ rings in a magnetic field with a strength of up to 15 T an oscillation of the magnetization was observed at approximately 14 T. The amplitude of the oscillation was found to be $17 \mu_B$ ($\mu_B$ is the Bohr magneton). In a perfect ring of the same diameter (approximately 11.5 nm) the respective transition leading to the oscillation should be observed at a magnetic field strength of 5 T. Yet, the large value of 14 T was attributed to the shape of the sample. Using cross-section tunneling microscopy, it was found that the repulsive potential in the center of the ring is not particularly strong and the potential forming the ring-like structure shows a strong anisotropy. In such a potential the first level-crossing was found to appear at the experimentally observed value of 14 T. Still, the calculated amplitude of the oscillation is only $4 \mu_B$, considerably smaller than the measured value.
3.2. Theory of the one-dimensional and quasi one-dimensional quantum ring

Besides being an interesting nanoscopic system that can nowadays be studied experimentally, quantum rings provide an ideal test-ground for many-body calculations as they allow to study the simultaneous effects of electron confinement, impurities and magnetic fields in an interacting system. In this section we will discuss what is known so far about the ground state of electrons in one-dimensional and quasi one-dimensional quantum rings starting from the simple case of non-interacting spinless (i.e. fully spin-polarized) electrons and subsequently include the electrons’ spin and interaction effects.

Non-interacting electrons in a one-dimensional ring

The simplest model of a quantum ring is a one-dimensional wire of length $L = 2 \pi R$ with periodic boundary conditions which is—in the non-interacting case—characterized by the Hamiltonian

$$\hat{H} = -\frac{\hbar^2}{2m^*_0 R^2} \frac{d^2}{d\varphi^2}$$  \hspace{1cm} (3.1)

where $\varphi$ denotes the polar angle and $m^*_0$ is the effective electron mass. The normalized eigenfunctions of the Hamiltonian (3.1) are the angular-momentum eigenstates

$$\phi_m(\varphi) = \frac{1}{\sqrt{L}} e^{im\varphi} \quad (m \in \mathbb{Z})$$  \hspace{1cm} (3.2)

and the corresponding single-particle energies are

$$\varepsilon_m = \frac{\hbar^2 m^2}{2m^*_0 R^2}.$$  \hspace{1cm} (3.3)

Note that states with angular momentum $m$ and $-m$ are degenerate.

From the single particle states (3.2) and energies (3.3) we can easily construct the non-interacting $N$-particle ground state by subsequently occupying the $N$ lowest single-particle states. If the particle number $N$ is odd, it is easily seen that the total angular momentum of the ground state is zero since for every occupied angular momentum eigenstate $\phi_m$ there exists also an occupied state $\phi_{-m}$. Since the highest occupied states will have angular momenta $\pm \frac{N}{2} - \frac{1}{2}$, the resulting ground state energy is given by

$$E = \frac{\hbar^2}{2m^*_0 R^2} \sum_{m=1}^{\frac{N-1}{2}} 2m^2.$$  \hspace{1cm} (3.4)

In contrast, if the particle number is even, the non-interacting ground state is twofold degenerate since the states with total angular momenta $\pm \frac{N}{2}$ have the same ground state energy

$$E = \frac{\hbar^2}{2m^*_0 R^2} \left( \left( \frac{N}{2} \right)^2 + \sum_{m=1}^{\frac{N}{2}-1} 2m^2 \right).$$  \hspace{1cm} (3.5)

Persistent current in the non-interacting system

What happens if we place the quantum ring in a magnetic field such that a flux $\Phi$ penetrates the ring but the electrons move in a field-free region? The effect of the magnetic flux-tube, which is accounted for by a tangential vector potential

$$A = \frac{\Phi}{L} e^{i\varphi},$$  \hspace{1cm} (3.6)
3. Quantum rings and persistent currents

is to tilt the spectrum by changing the single-particle energies according to

$$
\varepsilon_m^\Phi = \frac{\hbar^2}{2m_0^* R^2} \left( m - \frac{\Phi}{\Phi_0} \right)^2
$$

(3.7)

($\Phi_0 = \frac{\hbar}{e}$ is the magnetic flux quantum). As a consequence, the magnetic flux lifts the degeneracy between the states with angular momenta $m$ and $-m$. The ten lowest single-particle energies for a flux $\Phi = 0.3\Phi_0$ are depicted in figure 3.1.

A state with angular momentum $m$ carries a paramagnetic current density

$$
j_{m,p} = \frac{1}{L m_0^*} \frac{\hbar}{m} m
$$

(3.8)

but the full current density contains now also a diamagnetic term and is given by

$$
j_m = \frac{1}{L m_0^*} \frac{\hbar}{m} \left( m - \frac{\Phi}{\Phi_0} \right).
$$

(3.9)

Now consider the non-interacting ground state of $N$ electrons (for simplicity, we consider the spinless or fully spin-polarized case). If the number of flux quanta is between zero and one half (for odd particle number) or between zero and one (for even particle number), the states with angular momentum between $-\frac{N-1}{2}$ and $\frac{N-1}{2}$ (for odd particle number) or between $-\frac{N}{2}$ and $\frac{N}{2}$ (for even particle number) are occupied.

To be more specific, we first consider as an example three non-interacting fully spin-polarized electrons. The ground state energy and the angular momentum are shown as functions of the magnetic flux in the top panel of figure 3.2. At half-integer values of the flux the ground state changes from a state with total angular momentum $M$ to a state with total angular momentum $M + 3$ (in units of $\hbar$). The corresponding persistent current density is plotted in the bottom panel of figure 3.2. At the ground state transitions from angular momentum $M$ to angular momentum $M + 3$ the current jumps discontinuously. It changes sign
3.2. Theory of the one-dimensional and quasi one-dimensional quantum ring

\[ E \left( \frac{\hbar^2}{m_0^*} R^2 \right) \]

\[ j \left( \frac{\hbar}{m_0^*} R_L \right) \]

\[ \Phi \left[ \Phi_0 \right] \]

**Figure 3.2.** Ground state energy and persistent current density of three non-interacting fully spin-polarized electrons as a function of the magnetic flux. Top panel: ground state energy (green curve) and the energies of the states with total angular momenta (in units of \( \hbar \)) \( M = -6 \), \( M = -3 \), \( M = 0 \), \( M = 3 \) and \( M = 6 \). At half-integer values of the flux the ground state changes from one of the angular momenta to the next. Bottom panel: The persistent current density changes sign at the minima of the ground state energy. At the ground state transitions it jumps discontinuously.

at the local minima of the ground state energy. A very similar behaviour can be observed for even particle number. To illustrate this we plot in figure 3.3 the ground state energy (top panel) and the persistent current density (bottom panel) of four non-interacting electrons as functions of the magnetic flux. There is, however, one qualitative difference between the system containing an even number and the system containing an odd number of particles. While in the latter the ground state transitions occur at half-integer values of the magnetic flux, the respective transitions occur at integer numbers of flux quanta in the system containing an even number of particles (see figure 3.3).

It can already be seen in figures 3.2 and 3.3 that the persistent current \( j \) can be expressed as the derivative of the ground state energy with respect to the flux

\[ e j(\Phi) = -\frac{dE(\Phi)}{d\Phi} . \]  

This expression is known as the Byers-Yang relation [Byers and Yang, 1961] which also holds in higher dimensions. We will present a simple proof for the non-interacting one-dimensional case in chapter 6.

So far we have discussed the simplest system of non-interacting spinless (i.e. fully spin-polarized) electrons. Including the spin but still neglecting the electron-electron interaction has a qualitative effect on the Aharonov-Bohm oscillations only if the particle number is odd [Loss and Goldbart, 1991]. In this case one of the two spin subsystems contains an even number and the other one an odd number of electrons. Consequently, the total ground state angular momentum changes twice as the magnetic flux is increased by one flux quantum and the periodicity of the Aharonov-Bohm oscillations becomes \( \Phi_0/2 \). Note that this does not happen in a system containing an even number of electrons because in the ground state both of its spin subsystems contain the same number of electrons and hence the angular momentum changes happen either at half-integer values or at integer values of the magnetic flux.
3. Quantum rings and persistent currents

\[ \Phi \]

\[ \Phi_0 \]

\[ m \]

\[ R \]

\[ E \]

\[ m_0 \]

\[ M = -6, M = -2, M = 2, M = 6 \]

\[ 5 \]

\[ 6 \]

\[ 7 \]

\[ 8 \]

\[ -2 \]

\[ -1.5 \]

\[ -1 \]

\[ -0.5 \]

\[ 0 \]

\[ 0.5 \]

\[ 1 \]

\[ 1.5 \]

\[ 2 \]

\[ -2 \]

\[ -1.5 \]

\[ -1 \]

\[ -0.5 \]

\[ 0 \]

\[ 0.5 \]

\[ 1 \]

\[ 1.5 \]

\[ 2 \]

Figure 3.3.: Ground state energy and persistent current density of four non-interacting fully spin-polarized electrons as a function of the magnetic flux. Top panel: ground state energy (green curve) and the energies of the states with total angular momenta (in units of \( \hbar \)) \( M = -6, M = -2, M = 2 \) and \( M = 6 \). At integer values of the flux the ground state changes from one of the angular momenta to the next. Bottom panel: The persistent current density changes sign at the minima of the ground state energy. At the ground state transitions it jumps discontinuously.

Interaction effects

The one-dimensional clean ring containing non-interacting electrons described so far is of course the simplest possible model. A more realistic description requires to account for a finite width of the quantum ring, the presence of impurities and of course for interactions. Numerous theoretical studies have been devoted to the investigation of interacting electrons in quantum rings using for instance the configuration-interaction (CI) method, Monte Carlo simulations and employing density functional theory in the local spin-density approximation. A comprehensive review of the physics of one-dimensional and quasi one-dimensional quantum rings has been given by Viefers et al. [2003], including results obtained for lattice models like the Hubbard model which we will not discuss further here. For the ground state quantities of interest in the present work the lattice models provide the same physical picture as the continuum models to be outlined in this section. To a large extend the following summary will be based on the review by Viefers et al. and the cited original articles.

As discussed above, including the electrons’ spin in a one-dimensional ring containing an odd number of non-interacting electrons merely reduces the periodicity of the Aharonov-Bohm oscillations to \( \Phi_0 / 2 \). Yet, in the interacting system a number of ground states with different spin and total angular momentum can be observed as the magnetic flux or the strength of the electron-electron interaction are varied. To be more specific, consider a quasi one-dimensional ring containing two electrons [Viefers et al., 2000]. For a vanishing magnetic flux, the ground state is a singlet state (a state with total spin \( S = 0 \)) with total angular momentum \( M = 0 \). As the flux is increased, the ground state becomes a triplet state \( (S = 1) \) with \( M = -1 \). Finally, for values of the flux close to one flux quantum the ground state is again a singlet state \( (S = 0) \) with \( M = -2 \). The same results were obtained in an exact diagonalization study by Niemelä et al. [1996]. Using the CI method, similar changes of the ground state angular momentum and total spin...
were observed in two and three electron quantum rings [Liu et al., 2006] and in quantum rings containing up to six electrons [Liu et al., 2008]. Quantum rings containing four and ten electrons were studied by Emperador et al. [2003] employing the quantum Monte Carlo method. In good qualitative agreement with the previously discussed results these calculations also show a variety of ground states with different \( M \) and \( S \) as the magnetic flux is changed. In all cases, additional ground states were found that are not present in the non-interacting case. This provides a clear manifestation of the importance of interactions to fully explain the periodicity of the Aharonov-Bohm oscillations in quasi one-dimensional quantum rings.

Changes in the ground state spin and angular momentum have also been observed as the strength of the electron-electron interaction is increased at a fixed value of the magnetic flux. A Hartree-Fock calculation shows that with increasingly strong Coulomb interaction the total spin increases accompanied by changes of the ground state angular momentum [Bellucci and Onorato, 2009]. Since Hartree-Fock theory emphasizes the exchange contribution, it comes as no surprise that in the strongly interacting system the ground state will finally be a fully spin-polarized state. Yet, an inclusion of first order correlations does not alter this picture and has only a qualitative influence at those values of the interaction strength and the magnetic flux where the ground state spin and angular momentum change. This is consistent with many-body calculations which show that in the strongly interacting quantum ring states with different total spin—including the fully polarized state—become almost degenerate with the ground state [Pederiva et al., 2002; Saiga et al., 2007].

It is interesting to note that in the ground state of the quasi one-dimensional ring \( M \) and \( S \) assume those values for which the pair correlation function indicates that the electrons form an equilateral polygon [Liu et al., 2006, 2008]. This notion agrees with the results obtained by Koskinen et al. [2001] who studied up to seven electrons in the quasi one-dimensional ring using the CI method. Koskinen et al. found that the many-body spectrum accurately resembles that of a rigidly rotating molecule with vibrational excitations and antiferromagnetic spin-ordering. This result even holds if the interaction between the electrons is not particularly strong or for a system which is not strictly one-dimensional, i.e. for a ring with a finite width approaching the two-dimensional case.

Mean-field calculations like spin-density functional theory often map out the internal structure of the many-body wavefunction to the laboratory frame. Indeed, it has been confirmed by Reimann et al. [1999] that spin-density functional theory in the local spin-density approximation predicts a spin-density wave in a narrow quantum ring containing twelve or thirteen electrons. Additionally, a weak charge-density wave was found, the amplitude of which increases when the density is reduced: In a ring containing four electrons a pronounced separation of the electrons with antiferromagnetic order was observed which was interpreted as the formation of a Wigner molecule.

Evidence for Wigner crystallization in a quasi one-dimensional quantum ring has also been found by Pederiva et al. [2002] employing the variational Monte Carlo method. The internal structure of the many-body wavefunction can be monitored by the pair-correlation function which yields the probability to find another electron at distance \( r' \) from an electron situated at position \( r \). In the high-density quantum ring the pair-correlation function showed essentially no oscillatory structure beyond that usually found in a Fermi liquid. As the density was lowered, oscillations started to build up in the pair-correlation function which correspond to electrons localized around those positions in the quasi one-dimensional ring that would be occupied by classical point charges. Interestingly, in the narrow, quasi one-dimensional quantum ring the oscillations were found to build up quickly on increasing the interaction strength (i.e. lowering the density) and did not increase further for interaction parameter larger than \( r_S = 6 \). In contrast, in a wide quantum ring pronounced oscillations were found to build up essentially at the same value of the interaction parameter as in the narrow ring but the amplitude of the oscillation continued to grow on further increasing \( r_S \). This was explained by the fact that in the narrow ring the strong confinement potential already determines the geometrical structure of the charge distribution. In the wide ring the localization (monitored by the pair-correlation function) is first similar to the quasi one-dimensional case
but further increasing the Coulomb interaction results in a more two-dimensional localization. It should be emphasized that in all cases the charged density in the laboratory frame retained its circular symmetry corresponding to the symmetry of the many-body Hamiltonian. Note that this is again in contrast to the results of mean-field calculations which tend to break the rotational symmetry in the laboratory frame.

Two-dimensional and quasi one-dimensional quantum rings threaded by a magnetic flux have been studied using current-spin density functional theory employing a local approximation for the exchange-correlation functional. In addition to the spin-density, current-spin density functional theory (in principle) allows to determine the exact current of the interacting system directly from the Kohn-Sham orbitals (see chapter 8). Viefers et al. [2000] confirmed that the energy (and hence the persistent current) in a two-dimensional quantum ring with two, four or six electrons is essentially a periodic function of the flux penetrating the ring (the deviation was attributed to a small but non-zero probability to find the electrons in a region with a magnetic field present). The addition of a Gaussian impurity potential to the ring was found to suppress the persistent current. The electrons are gradually localized forming a spin-density wave as well as a charge-density wave. A similar effect—a decreasing persistent current concurrent with the emergence of a spin-density and charge-density wave—was observed when the width of the ring is decreased. Note that this is in qualitative agreement with the picture of a rigidly rotating electron molecule in the quasi one-dimensional quantum ring mapped out to the laboratory frame by the mean-field method.

We finally mention an interesting result obtained by Chwiej and Szafran [2009], who studied a two-dimensional quantum ring in a uniform magnetic field containing up to three electrons by exact diagonalization. It was found that a Wigner molecule is pinned—corresponding to an inhomogeneous density—at those values of the magnetic field strength where the ground state energy shows a maximum. Remember that precisely at those values the magnetic flux the angular momentum of the ground state changes. Yet, in the presence of an impurity potential the cusps in the energy are replaced by smooth maxima. A similar situation was encountered in an exact diagonalization study by Szafran and Peeters [2004] who found that a Wigner molecule formed in a quantum dot may be pinned by an arbitrarily weak impurity potential at those values of the magnetic field strength where the angular momentum of the ground state changes. Placing one or two symmetrically arranged attractive impurity potentials in the ring, Chwiej and Szafran found that the many-body state was pinned by the impurities only when its internal symmetry coincided with the symmetry of the impurity arrangement. In the case of a single impurity potential this may always happen, only depending on the magnetic field strength as discussed above. In contrast, if two defects are placed symmetrically in the quantum ring, a state with three electrons never gets pinned because its internal symmetry does not coincide with the symmetry of the impurity configuration. Contrary to the one-dimensional situation discussed in this thesis, the persistent current is not stopped when the Wigner molecule is pinned. It is replaced by current vortices circulating around the density maxima. Clearly, this vortex formation cannot be observed in our quasi one-dimensional calculation.
A long-standing challenge in many areas of physics and chemistry is the solution of the interacting, inhomogeneous many-electron problem. In its “simplest” form—including only an external electrostatic potential but no magnetic fields—it is characterized by the Hamiltonian

\[
\hat{H} = -\frac{\hbar^2}{2m_0} \int d^3r \hat{\Psi}(r) \nabla^2 \hat{\Psi}(r) + \frac{1}{2} \frac{e^2}{4\pi\varepsilon\varepsilon_0} \int \int d^3rd^3r' \hat{\Psi}(r') \hat{\Psi}(r) \frac{1}{|r-r'|} \hat{\Psi}(r) \hat{\Psi}(r') + \int d^3r V_{\text{ext}}(r) \hat{\Psi}(r) \hat{\Psi}(r),
\]

where \( \hat{\Psi}(r) \) and \( \hat{\Psi}(r) \) are field operators. One way to attack this problem is to find approximations for the many-particle wave function. One of the earliest and most prominent examples is Hartree-Fock theory, where the energy is minimized assuming that the wave function is a single Slater determinant. The wave function-based approach can be further refined by expanding the true many-particle wave function as a series of Slater determinants (and in practice truncating the expansion at some point), a scheme known as the configuration-interaction method. While the wave function-based methods can be very accurate, they are computationally very expensive and hence only feasible for small particle numbers.

A different approach is to consider the density as the basic variable which is a function of only three spatial variables, in contrast to the \( N \)-body wave function depending on \( 3N \) variables. An early attempt in this spirit was undertaken by Thomas and Fermi (see e.g. [Landau and Lifschitz, 1962]) who approximated the kinetic energy of an inhomogeneous electron gas locally by the energy of the free electron gas with the respective density. The self-consistently determined electron-electron interaction was considered as a purely electrostatic one. At the time of Thomas and Fermi however, such a density functional approach was considered as a rather crude approximation (which the Thomas-Fermi model clearly is). After the invention of the Thomas-Fermi model in 1934, it took thirty years, until Hohenberg and Kohn [1964] and Kohn and Sham [1965] provided the formulation of a modern density functional approach which is (at least in principle) an exact theory. In this chapter we review the Hohenberg-Kohn theorem which states a one-to-one correspondence between the external single-particle potential and the density and present the Kohn-Sham equations which cast the solution of the many-body problem in terms of an effective single-particle problem. The second half of this chapter is devoted to the discussion of some subtle difficulties that arise from the original formulation of density functional theory and their remedy. We finally introduce briefly spin-density functional theory for later reference.

### 4.1. The Hohenberg-Kohn theorem

The basic theorem which underlies density functional theory was proved by Hohenberg and Kohn [1964]. In its original formulation it states that i) the density of a many-electron system with a given type of electron-electron interaction uniquely determines the external potential (up to an additive constant), and ii) the energy is a functional of the density which assumes its minimum at the true ground state density. The minimum value of the energy functional equals the ground state energy.
It is easy to see that an external potential determines the density since it fixes the Hamiltonian and hence the many-body wave function $\Psi(r_1, \ldots, r_N)$. The density

$$n(r) = N \int d^3r_2 \cdots d^3r_N |\Psi(r, r_2, \ldots, r_N)|^2$$

(4.2)

is therefore a functional of the external potential $V_{\text{ext}}(r)$. The reverse statement, i.e. that the density determines the external potential, can be shown by reductio ad absurdum. Consider two external potentials $V_{\text{ext}}(r)$ and $V'_{\text{ext}}(r)$, which differ by more than a constant, i.e.

$$V_{\text{ext}}(r) - V'_{\text{ext}}(r) \neq \text{const}$$

(4.3)

but lead to the same density $n(r)$. Since $V_{\text{ext}}$ and $V'_{\text{ext}}$ correspond to two different Hamiltonians $\hat{H}$ and $\hat{H}'$, the associated ground state wave functions $\Psi$ and $\Psi'$ will not be equal. From the variational principle we can now deduce the inequality

$$E' = \langle \Psi' | \hat{H}' | \Psi' \rangle < \langle \Psi | \hat{H} | \Psi \rangle + \int d^3r [V'_{\text{ext}}(r) - V_{\text{ext}}(r)] n(r)$$

(4.4)

i.e.

$$E' < E + \int d^3r [V'_{\text{ext}}(r) - V_{\text{ext}}(r)] n(r)$$

(4.5)

By interchanging the primed and unprimed variables (and requiring that both densities coincide) the same reasoning leads to

$$E < E' + \int d^3r [V_{\text{ext}}(r) - V'_{\text{ext}}(r)] n(r)$$

(4.6)

Adding both inequalities one finally obtains the contradiction

$$E + E' < E + E'$$

(4.7)

It has thus been proven that if the two external potentials $V_{\text{ext}}$ and $V'_{\text{ext}}$ differ by more than a constant, the corresponding ground state densities must not be equal. Together with the observation that the potential determines the density which has been stated above, a one-to-one correspondence between the density and the external potential has been established

$$n(r) \leftrightarrow V_{\text{ext}}(r)$$

(4.8)

The one-to-one correspondence between the external potential and the density implies that the ground state wave function $\Psi$ is a density functional. We can therefore define the energy functional

$$E[n(r)] = F[n(r)] + \int d^3r n(r)V_{\text{ext}}(r)$$

(4.9)

where the universal functional

$$F[n(r)] = \langle \Psi | \hat{T} + \hat{V}_{\text{ee}} | \Psi \rangle$$

(4.10)

has been introduced. The operators

$$\hat{T} = -\frac{\hbar^2}{2m^*_0} \int d^3r \hat{\Psi}^\dagger(r) \nabla^2 \hat{\Psi}(r)$$

(4.11)

and

$$\hat{V}_{\text{ee}} = \frac{1}{2} \frac{e^2}{4\pi\varepsilon_0} \int d^3r d^3r' \hat{\Psi}^\dagger(r')\hat{\Psi}^\dagger(r) \frac{1}{|r-r'|} \hat{\Psi}(r)\hat{\Psi}(r')$$

(4.12)
4.2. The Kohn-Sham equation

denote the kinetic energy and the electron-electron interaction, respectively. The functional $F[n]$ does not contain any reference to the external potential and is thus (for a fixed type of interaction) determined solely by the density. Resorting to the variational principle, one can show that $E[n]$ in fact assumes its minimum value, which is the ground state energy $E_0$, at the true ground state density $n_0(r)$ if the admissible densities are restricted to those yielding the correct particle number

$$N = \int d^3r n(r).$$  \hspace{1cm} (4.13)

The key point for the proof of this statement is the well-known fact that the energy of an $N$-particle system

$$E = \langle \Psi | \hat{H} | \Psi \rangle = F[n] + \int d^3r n(r) V_{\text{ext}}(r)$$  \hspace{1cm} (4.14)

has its minimum (with respect to arbitrary variations of the wave function $\Psi$ keeping the number of particles constant) at the true ground state wave function $\Psi_0$. If the trial wave function $\Psi$ is the ground state wave function associated with a different external potential $V'_{\text{ext}}$, then one finds the inequality

$$E = F[n] + \int d^3r n(r) V_{\text{ext}}(r) > F[n_0] + \int d^3r n_0(r) V_{\text{ext}}(r) = E_0,$$  \hspace{1cm} (4.15)

which completes the proof.

4.2. The Kohn-Sham equation

An important aspect of the Hohenberg-Kohn theorem is that it allows one in principle to determine the ground state density and energy as the minimum of the energy functional $E[n]$. However, the exact form of the universal functional $F[n]$ is unknown. Although there exist some approximations depending explicitly on the density like the Thomas-Fermi-Kirzhnitz-von Weizsäcker functional the direct minimization of the energy functional has not become a popular computational technique. Fortunately, Kohn and Sham [1965] came up with the idea to reformulate the minimization of the energy functional in terms of a single-particle equation with an effective local potential. In this section we will discuss the derivation of this single-particle equation called the Kohn-Sham equation.

The starting point for the derivation of the Kohn-Sham equation is the partitioning of the universal functional

$$F[n] = T_S[n] + E_H[n] + E_{\text{xc}}[n]$$  \hspace{1cm} (4.16)

into the kinetic energy $T_S[n]$ of a system of non-interacting electrons with the density $n(r)$, the classical electrostatic Hartree energy

$$E_H[n] = \frac{e^2}{2 4\pi\epsilon\epsilon_0} \int \int d^3r d^3r' n(r)n(r') \frac{1}{|r - r'|},$$  \hspace{1cm} (4.17)

and the so-called exchange-correlation energy $E_{\text{xc}}[n]$ which is formally defined to account for all the remaining terms. In particular, $E_{\text{xc}}$ contains all quantum many-body effects. With this partitioning of $F[n]$, the Hohenberg-Kohn energy functional can be expressed as

$$E[n] = T_S[n] + E_H[n] + E_{\text{xc}}[n] + \int d^3r n(r) V_{\text{ext}}(r).$$  \hspace{1cm} (4.18)

The minimization of the energy functional with respect to the density yields the expression

$$\frac{\delta E[n]}{\delta n(r)} = \frac{\delta T_S[n]}{\delta n(r)} + V_{\text{ext}}(r) + V_H[n](r) + V_{\text{xc}}[n](r) = \mu,$$  \hspace{1cm} (4.19)
where
\[ V_H[n](r) = \frac{\delta E_H[n]}{\delta n(r)} = \frac{e^2}{4\pi\epsilon\epsilon_0} \int d^3r' \frac{n(r')}{|r-r'|} \] (4.20)
is the Hartree potential and the exchange-correlation potential is defined as
\[ V_{xc}[n](r) = \frac{\delta E_{xc}[n]}{\delta n(r)}. \] (4.21)
The parameter \( \mu \) has been introduced as a Lagrangian multiplier to ensure constant particle number. Comparing this expression with the respective expression for the non-interacting system with the external potential
\[ \frac{\delta E[n]}{\delta n(r)} = \frac{\delta T_S[n]}{\delta n(r)} + V(r) = \mu, \] (4.22)
it is clear, that both expressions are formally equivalent if one identifies the external potential of the non-interacting system with the sum of the external potential, the Hartree potential and the exchange-correlation potential of the interacting system [Jones and Gunnarsson, 1989]. We will denote this effective potential
\[ V_S[n](r) = V_{ext}(r) + V_H[n](r) + V_{xc}[n](r) \] (4.23)
as the Kohn-Sham potential.

The density that satisfies equation (4.22) can be found by solving a single-particle Schrödinger equation and the same density is a solution of equation (4.19): simply solve the effective single-particle equation
\[ \left[ -\frac{\hbar^2}{2m_0} \nabla^2 + V_S[n](r) \right] \phi_k(r) = \varepsilon_k \phi_k(r) \] (4.24)
which we will refer to as the Kohn-Sham equation and determine the density from the Kohn-Sham orbitals \( \phi_k \) via
\[ n(r) = \sum_{k=1}^{N} |\phi_k(r)|^2 \] (4.25)
\( (N \) is the number of electrons).

Since the Hartree and the exchange-correlation potential are functionals of the density, equations (4.23), (4.24) and (4.25) have to be solved self-consistently. First one solves the Kohn-Sham equation (4.24) for a given trial potential. Then one computes the density (4.25) from the solutions of the Kohn-Sham equation and uses this density to determine a new Kohn-Sham potential (4.23).

It is not only the density that can be thus obtained directly from the solution of the single-particle Kohn-Sham equation. Also the ground state energy can be computed directly from the Kohn-Sham eigenvalues \( \varepsilon_k \) and is given by
\[ E_0 = E[n_0] = \sum_{k=1}^{N} \varepsilon_k - \int d^3r \ n_0(r) \left[ V_{xc}[n_0](r) + \frac{1}{2} V_H[n_0](r) + E_{xc}[n_0] \right]. \] (4.26)

We finally note that, for any practical calculation, the exchange-correlation energy and the exchange-correlation potential—which are not known exactly—have to be approximated. We will discuss this further in chapter 5.
4.3. DFT on rigorous grounds

While the original formulation and proof of the Hohenberg-Kohn theorem and the associated minimum principle for the energy functional are simple and elegant, they contain some subtle difficulties. The first one is that Hohenberg and Kohn assume $V$-representable densities—that is densities which can be created by some external, local and multiplicative potential $V_{\text{ext}}$ [Levy, 1979]. Yet, it was shown by Lieb [1983] that it is not true that every density (even the “nice” ones) can be obtained as the ground state density of a system with such a local external potential. Consequently, the functional $F[n]$ from the original formulation given by Hohenberg and Kohn [1964] is not defined for all densities. A remedy to this problem was given by Levy [1979] and Lieb [1983], an approach which is known as the constrained search formalism.

The second issue that requires a careful investigation is the question whether the universal functional $F[n]$ (or $Q[n]$, as it will be denoted in the context of the constrained search formalism) is differentiable at all. A comprehensive review of these more formal aspects, which are nevertheless at the heart of DFT, has been given by van Leeuwen [2003]. Our discussion will closely follow this review.

The constrained search formulation

It is possible to extend the proof of the Hohenberg-Kohn theorem to $N$-representable densities, i.e. densities which can be obtained from some antisymmetric $N$-particle wave function [Coleman, 1963], a generalization which also allows one to extend the Hohenberg-Kohn theorem to degenerate ground states.

Following Levy [1979], we consider the functional

$$Q[n] = \min_{\Psi \rightarrow n} \left\langle \Psi \left| \hat{T} + \hat{V}_{\text{ee}} \right| \Psi \right\rangle,$$  \hspace{1cm} (4.27)

which is minimized over all $N$-particle wave functions $\Psi$ yielding the fixed trial density $n(r)$.\footnote{If the density is $V$-representable, then the functional $Q[n]$ equals the functional $F[n]$.} Such a density is called $N$-representable. With the aid of the functional $Q[n]$ one can define the energy functional

$$E[n] = Q[n] + \int d^3r n(r)V_{\text{ext}}(r)$$  \hspace{1cm} (4.28)

and show that—for a given external potential $V_{\text{ext}}—E[n]$ evaluated with an arbitrary density is always greater than or equal to the ground state energy $E_0$ of an $N$-particle system with the external potential $V_{\text{ext}}$, i.e.

$$Q[n] + \int d^3r n(r)V_{\text{ext}}(r) \geq E_0.$$  \hspace{1cm} (4.29)

Furthermore, one can show that if the trial density $n(r)$ is the true ground state density $n_0(r)$, then the value of the functional $E[n]$ equals the ground state energy

$$Q[n_0] + \int d^3r n_0(r)V_{\text{ext}}(r) = E_0.$$  \hspace{1cm} (4.30)

To prove these two statements we first introduce the abbreviation $\Psi_n^{\text{min}}$ for the wave function yielding the density $n(r)$ that minimizes the expectation value $\left\langle \hat{T} + \hat{V}_{\text{ee}} \right\rangle$. With this short-hand notation, the functional $Q[n]$ is then expressed as

$$Q[n] = \left\langle \Psi_n^{\text{min}} \left| \hat{T} + \hat{V}_{\text{ee}} \right| \Psi_n^{\text{min}} \right\rangle,$$  \hspace{1cm} (4.31)
and the energy functional becomes
\[ E[n] = \left\langle \Psi_n^\text{min} \left| T + V_{ee} \right| \Psi_n^\text{min} \right\rangle + \int d^3r n(r)V_{\text{ext}}(r) \]
\[ = \left\langle \Psi_n^\text{min} \left| \hat{T} + V_{ee} + \hat{V} \right| \Psi_n^\text{min} \right\rangle , \]  
(4.32)

where the potential operator \( \hat{V} = \sum_i^N V_{\text{ext}}(r_i) \) represents the external single-particle potential. It follows from the variational principle, that
\[ \left\langle \Psi_n^\text{min} \left| \hat{T} + V_{ee} + \hat{V} \right| \Psi_n^\text{min} \right\rangle \geq E_0 , \]
(4.33)

which proves the first of the above statements.

Since the true ground state energy is the expectation value of the Hamilton operator \( \hat{H} = \hat{T} + V_{ee} + \hat{V} \) evaluated with the true ground state wave function \( \Psi_0 \), we can infer from the minimum principle that
\[ \left\langle \Psi_{n_0}^\text{min} \left| \hat{T} + V_{ee} + \hat{V} \right| \Psi_{n_0}^\text{min} \right\rangle \geq \left\langle \Psi_0 \left| \hat{T} + V_{ee} + \hat{V} \right| \Psi_0 \right\rangle , \]
(4.34)

where \( \Psi_{n_0}^\text{min} \) is that wave function that minimizes \( \left\langle \hat{T} + V_{ee} \right\rangle \) and yields the ground state density. Since the ground state wave function \( \Psi_0 \) also leads to the ground state density, we can subtract the potential energy \( \int d^3r n_0(r)V_{\text{ext}}(r) \) and obtain
\[ \left\langle \Psi_{n_0}^\text{min} \left| \hat{T} + V_{ee} \right| \Psi_{n_0}^\text{min} \right\rangle \geq \left\langle \Psi_0 \left| \hat{T} + V_{ee} \right| \Psi_0 \right\rangle . \]
(4.35)

But remember that \( \Psi_{n_0}^\text{min} \) is defined such that exactly the reverse relation
\[ \left\langle \Psi_{n_0}^\text{min} \left| \hat{T} + V_{ee} \right| \Psi_{n_0}^\text{min} \right\rangle \leq \left\langle \Psi_0 \left| \hat{T} + V_{ee} \right| \Psi_0 \right\rangle \]
(4.36)

holds. Both expression can be true only if the left- and right-hand sides are equal. Hence we find
\[ E_0 = E[n_0] = Q[n_0] + \int d^3r n_0(r)V_{\text{ext}}(r) . \]
(4.37)

**A brief note on the differentiability of the universal functional \( Q[n] \)**

Trying to minimize the energy functional requires the calculation of functional derivatives. However, an unpleasant feature of the functional \( Q[n] \) is that its differentiability cannot be established.\(^2\)

A possible remedy was suggested by Lieb [1983], who introduced yet another functional
\[ F_L[n] = \inf_{\hat{D} \rightarrow n} \text{Tr} \hat{D} \left( \hat{T} + V_{ee} \right) , \]
(4.38)

\(^2\)The Gâteaux-differentiability of a functional \( G : \mathcal{B} \rightarrow \mathbb{R} \), which maps a function \( f \in \mathcal{B} \) from some function space \( \mathcal{B} \) to the real numbers means that the linear functional
\[ \frac{\delta G}{\delta f}[h] = \lim_{\epsilon \to 0} \frac{G[f + \epsilon h] - G[f]}{\epsilon} \]

\((h \in \mathcal{B}) \) exists. The proof that a particular functional is Gâteaux-differentiable requires that the functional is convex, i.e. that for any two \( f_0, f_1 \in \mathcal{B} \) and \( 0 \leq \lambda \leq 1 \) the relation
\[ G[f_0 + \lambda(f_1 - f_0)] \leq \lambda G[f_1] + (1 - \lambda)G[f_0] . \]

holds. This is not true for the Levy-Lieb functional \( Q[n] \).
where $\text{Tr} \hat{D} \left( \hat{T} + \hat{V}_{ee} \right)$ denotes the trace of the operator $\hat{D} \left( \hat{T} + \hat{V}_{ee} \right)$. The search runs over all $N$-particle density matrices

$$\hat{D} = \sum_{k} \lambda_{k} |\Psi_{k}\rangle \langle \Psi_{k}| \quad \left( \sum_{k} \lambda_{k} = 1 \right)$$

(4.39)

which yield the density

$$n(r) = \text{Tr} \hat{n} \hat{D}(r)$$

(4.40)

and $\{ |\Psi_{k}\rangle \}$ is an orthonormal set of antisymmetric $N$-particle wave functions. If the density $n(r)$ can be obtained from one single antisymmetric $N$-particle wave function the functionals $F_{L}[n]$ and $Q[n]$ coincide and if this density is $V$-representable all three functionals $F_{L}[n]$, $Q[n]$ and $F[n]$ are equivalent.

An important property of the Lieb functional $F_{L}[n]$ is that it is differentiable on all ensemble-$V$-representable densities, but nowhere else [van Leeuwen, 2003]. An ensemble-$V$-representable density is a density of the form of equation (4.40), where the $N$-particle states $|\Psi_{k}\rangle$ that are used to construct the density matrix stem from some external potential $V_{\text{ext}}$. The key point is now that every “sensible” density (i.e. a density which is non-negative everywhere and corresponds to a finite kinetic energy) can be approximated to arbitrary precision by an ensemble-$V$-representable one [van Leeuwen, 2003].

The differentiability of the Lieb functional carries over to its non-interacting version

$$T_{L}[n] = \inf_{\hat{D} \rightarrow n} \text{Tr} \hat{D} \hat{T}$$

(4.41)

which means that we can also minimize the non-interacting energy functional with respect to the density, a construction which eventually leads to the Kohn-Sham equation.

To conclude our formal considerations, we finally note a consequence from the statement that every “sensible” density can be approximated by an ensemble-$V$-representable density as closely as desired. Let $n_{\text{int}}(r)$ be the ground state density of an interacting system. Then we can find an ensemble-$V$-representable density that “almost” equals $n_{\text{int}}$. On the other hand, we require that the non-interacting Kohn-Sham system has the same density as the interacting one. Yet, the Kohn-Sham equation can rigorously be established for an ensemble-$V$-representable density (since for such a density the non-interacting Lieb functional is differentiable). If we require that the ensemble-$V$-representable density which approximates the $V$-representable density of the interacting system \(^3\) coincides with the ensemble-$V$-representable which we have in mind when differentiating the non-interacting Lieb functional, then we obtain from the above statement that there is also a non-interacting $V$-representable density that approximates to arbitrary precision the interacting $V$-representable one. This notion finally puts the derivation of the Kohn-Sham scheme on a rigorous ground, at least for all presently known practical applications.

4.4. Collinear spin-density functional theory

One of the first and still most important extensions of density functional theory is spin-density functional theory, which has been introduced by von Barth and Hedin [1972] and Rajagopal and Callaway [1973]. Without proof, we present here their results.

Consider a system of $N$ interacting electrons subject to the external scalar potential $V_{\text{ext}}(r)$ and an external magnetic field $B_{\text{ext}}(r)$. In the most general case, but without taking an orbital interaction with the magnetic field into account, the many-body Hamiltonian is given by

$$\hat{H} = \hat{H}_{0} + \int d^{3}r \hat{n}(r)V_{\text{ext}}(r) - \int d^{3}r \hat{m}(r) \cdot B_{\text{ext}}(r),$$

(4.42)

\(^3\)The density of the interacting system can surely be considered as interacting-$V$-representable, since we simply deal with some interacting system in some local external potential.
exchange-correlation potential is defined as
\[ \hat{V}_{xc}(\mathbf{r}) = -\epsilon_{xc}(n_{\uparrow}, n_{\downarrow}) + \epsilon_{xc}(n_{\uparrow} + n_{\downarrow}) \]
where \( \hat{n}(\mathbf{r}) \) is the density operator and
\[ \hat{m}(\mathbf{r}) = -\mu_B \hat{\Psi}^{\dagger}(\mathbf{r}) \sigma \hat{\Psi}(\mathbf{r}) \]
is the operator of the magnetization density. In the latter expression, \( \mu_B \) is the Bohr magneton, \( \sigma \) is the vector of Pauli spin matrices and \( \hat{\Psi} = (\hat{\Psi}_{\uparrow}, \hat{\Psi}_{\downarrow}) \) is the two-component spinor of fermionic field operators.

It was shown by von Barth and Hedin [1972] that one cannot prove a one-to-one correspondence between the external fields and the densities in spin-density functional theory. Instead, von Barth and Hedin [1972] proved a one-to-one correspondence between the ground state many-body wave function \( \Psi \) and the densities, which can in turn be exploited to define the energy functional
\[ E[n, m] = Q[n, m] + \int d^3 r \, n(\mathbf{r}) V_{\text{ext}}(\mathbf{r}) - \int d^3 r \, m(\mathbf{r}) \cdot \mathbf{B}_{\text{ext}}(\mathbf{r}), \]
where \( n(\mathbf{r}) \) and \( m(\mathbf{r}) \) are understood as the expectation values of the density and magnetization density, respectively. In a more modern formalism than the one originally used by von Barth and Hedin [1972], the universal functional \( Q[n, m] \) can be defined in the spirit of the constrained search formalism as
\[ Q[n, m] = \min_{\Psi \to n, m} \left\{ \left\langle \Psi \left| \hat{T} + V_{\text{ee}} \right| \Psi \right\rangle \right. . \]

In practice, many calculations—including the ones presented in this thesis—apply spin-density functional theory to the collinear case, where the external magnetic field and the magnetization density are assumed to be oriented along the \( z \)-direction everywhere, i.e. \( \mathbf{B}_{\text{ext}}(\mathbf{r}) = B_{\text{ext}}(\mathbf{r}) \mathbf{e}_z \) and \( m(\mathbf{r}) = m_z(\mathbf{r}) \mathbf{e}_z \) (\( \mathbf{e}_z \) is a unit vector pointing in the direction of the \( z \)-axis). The \( z \)-component of the magnetization density can be expressed by the spin-densities \( n_{\uparrow}(\mathbf{r}) \) and \( n_{\downarrow}(\mathbf{r}) \) as
\[ m_z(\mathbf{r}) = -\mu_B (n_{\uparrow}(\mathbf{r}) - n_{\downarrow}(\mathbf{r})) \]
where the indices \( \uparrow \) and \( \downarrow \) denote the spin-projection parallel or antiparallel to the \( z \)-axis. In the collinear approximation, the coupling between the spins and the external magnetic field corresponds to a Zeeman term, which can be absorbed into the external potential. We denote this spin-dependent external potential by
\[ V_{\text{ext}, \sigma}(\mathbf{r}) = V_{\text{ext}}(\mathbf{r}) \pm \mu_B B_z(\mathbf{r}) \quad (\sigma = \uparrow, \downarrow). \]

Using the same reasoning as Hohenberg and Kohn (see section 4.2), minimization of this energy functional leads to the spin-dependent Kohn-Sham equation
\[ \left[ -\frac{\hbar^2}{2m_0^2} \nabla^2 + V_{S,\sigma}(\mathbf{r}) \right] \phi_{k,\sigma}(\mathbf{r}) = \varepsilon_{k,\sigma} \phi_{k,\sigma}(\mathbf{r}). \]
The spin-dependent Kohn-Sham potential \( V_{S,\sigma} \), which is a functional of both spin-densities \( n_{\uparrow} \) and \( n_{\downarrow} \) reads
\[ V_{S,\sigma}[n_{\uparrow}, n_{\downarrow}](\mathbf{r}) = V_{\text{ext},\sigma}(\mathbf{r}) + V_{\text{H}}[n](\mathbf{r}) + V_{\text{xc},\sigma}[n_{\uparrow}, n_{\downarrow}](\mathbf{r}), \]
where the Hartree potential depends only on the total density \( n = n_{\uparrow} + n_{\downarrow} \) and the spin-dependent exchange-correlation potential is defined as
\[ V_{\text{xc},\sigma}[n_{\uparrow}, n_{\downarrow}](\mathbf{r}) = \frac{\delta E_{\text{xc}}[n_{\uparrow}, n_{\downarrow}]}{\delta n_{\sigma}(\mathbf{r})}. \]

\[ \text{This difficulty is known as the non-uniqueness problem which was later analyzed in detail by Eschrig and Pickett [2001] and Capelle and Vignale [2001].} \]
From the Kohn-Sham orbitals $\phi_{k,\sigma}$ one can calculate the spin-density

$$n_\sigma(r) = \sum_{k=1}^{N_\sigma} |\phi_{k,\sigma}|^2$$  \hspace{1cm} (4.51)

and thus the total electron density $n(r)$. The ground state energy is given by the following expression very similar to equation (4.26):

$$E_0 = E[n_{\uparrow,0}, n_{\downarrow,0}] = \sum_{\sigma=\uparrow,\downarrow} \left[ \sum_{k=1}^{N_\sigma} \varepsilon_{k,\sigma} - \int d^3r n_{\sigma,0}(r) V_{xc,\sigma}[n_{\uparrow,0}, n_{\downarrow,0}](r) \right]$$

$$- \frac{1}{2} \int d^3r n_0(r) V_{\text{H}}[n_0](r) + E_{xc}[n_{\uparrow,0}, n_{\downarrow,0}]$$  \hspace{1cm} (4.52)

where $n_0(r) = n_{\uparrow,0}(r) + n_{\downarrow,0}(r)$. 
5 The optimized effective potential method in density functional theory

A key point for the practical usability of any density functional theory scheme is a suitable approximation for the exchange-correlation energy functional. The simplest, yet very successfully used approximation is the so-called local density approximation (LDA) [Kohn and Sham, 1965], where the exchange-correlation energy of the inhomogeneous system is locally approximated by the exchange-correlation energy of a homogeneous system with the respective density, i.e.

$$E_{xc}^{LDA}[n(r)] = \int d^3r \ n(r) \epsilon_{xc}(n(r)) . \quad (5.1)$$

The exchange-correlation energy per electron $\epsilon_{xc}(n)$ in the homogeneous electron gas with the density $n$ can be calculated to very high accuracy using Monte-Carlo techniques [Ceperley and Alder, 1980]. Although the LDA takes the homogeneous electron gas as a reference system, it works surprisingly well even for strongly inhomogeneous systems [Dreizler and Gross, 1990]. It has been successfully applied to a variety of systems with very prominent examples in solid-state physics like the calculation of band structures or lattice constants. However, the LDA is not free from problems and one of its most prominent failures, which is particularly related to the Wigner crystal transition discussed in this work, is the self-interaction error. The origin of the self-interaction error is the partitioning of the electron-electron interaction into the classical electrostatic Hartree term and the exchange-correlation energy containing everything else, in particular all quantum many-body effects. In the classical Hartree energy, the electrons are described as continuous charge-density distributions interacting electrostatically. Consequently, the Hartree energy contains an interaction of each electron with itself. This self-interaction is fully canceled by the exact exchange-correlation energy but not by approximate expressions such as the LDA. The self-interaction error manifests itself as a tendency to delocalize the electrons. In a system with both localized and delocalized electrons, the self-interaction error affects the localized electrons stronger and thus results in a distortion of the Kohn-Sham eigenvalue spectrum.

The second fundamental problem of the LDA, which we briefly describe for completeness, is the lack of derivative discontinuities. Extending DFT to non-integer particle numbers, Perdew et al. [1982] showed that the exact exchange-correlation potential consists of straight lines as a function of the particle number. These lines change slope whenever the particle number reaches an integer value. The resulting exchange-correlation potential—which is the derivative of the exchange-correlation energy—therefore shows discontinuous jumps at integer particle numbers. This so-called derivative discontinuity is an important part of the fundamental band gap, which is usually underestimated in the LDA. Furthermore, neglect of the derivative discontinuity can lead to non-integer particle numbers. A prominent example is the dissociation of LiH, for which the LDA incorrectly predicts that it dissociates into Li$^{+0.25}$H$^{-0.25}$ [Perdew et al., 1982].

Both problems of the LDA can be cured in a systematic way by the exact-exchange functional

$$E_{exx} = -\frac{1}{2} \frac{\epsilon^2}{4\pi \epsilon_0} \sum_{\sigma=1,1} \sum_{j,k} N^\sigma \int d^3r \ \int d^3r' \ \phi^*_{j,\sigma}(r) \phi_{k,\sigma}(r') \phi_{k,\sigma}(r') \phi_{j,\sigma}(r') \frac{|r - r'|}{|r - r'|} . \quad (5.2)$$

The exact exchange functional expresses the exchange-energy as the Fock exchange energy evaluated with the Kohn-Sham orbitals $\{\phi_{j,\sigma}\}$ providing one more exact ingredient to the DFT energy functional.
To be honest we should not forget to mention that, while employing the exact-exchange functional does improve upon the LDA by removing the self-interaction error and providing derivative discontinuities, in many practical applications of DFT the LDA functional actually performs better, mostly due to a subtle error cancellation between its exchange and correlation parts.

Traditional functionals like the LDA are explicit functionals of the density, making it easy to calculate the exchange-correlation potential \( V_{xc} \) which is defined as a functional derivative of the exchange-correlation energy \( E_{xc} \) with respect to the density \( n \)

\[
V_{xc,\sigma} = \frac{\delta E_{xc}}{\delta n_{\sigma}}. 
\]  

(5.3)

In contrast, the exact-exchange functional depends explicitly on the orbitals but only implicitly on the density. The calculation of the exchange-correlation potential is therefore not as straightforward as e.g. for the LDA functional. Instead, \( V_{xc,\sigma} \) is given as the solution of the optimized effective potential (OEP) integral equation [Sharp and Horton, 1953; Talman and Shadwick, 1976]. The derivation of this integral equation will be outlined in the following section 5.1.

**5.1. The optimized effective potential equation in density functional theory**

To calculate the exchange-correlation potential from an implicit functional like the exact-exchange functional we start by writing the derivative of the exchange-correlation energy with respect to the Kohn-Sham potential \( V_S,\sigma \) using the chain rule of functional derivation as

\[
\frac{\delta E_{xc}}{\delta V_{S,\sigma}(r)} = \sum_{\sigma'=\uparrow,\downarrow} \int d^3r' \frac{\delta E_{xc}}{\delta n_{\sigma'}(r')} \frac{\delta n_{\sigma'}(r')}{\delta V_{S,\sigma}(r')}.
\]  

(5.4)

On the other hand, since \( E_{xc} \) is an explicit functional of the Kohn-Sham orbitals, we can write

\[
\frac{\delta E_{xc}}{\delta V_{S,\sigma}(r)} = \sum_{\sigma'=\uparrow,\downarrow} \sum_{k=1}^{N_{\sigma'}} \int d^3r' \frac{\delta E_{xc}}{\delta \phi_{k,\sigma'}(r')} \frac{\delta \phi_{k,\sigma'}(r')}{\delta V_{S,\sigma}(r)} + \text{c.c.},
\]  

(5.5)

where the sum runs over all occupied Kohn-Sham levels and c.c. denotes complex conjugation. The functional derivatives \( \frac{\delta E_{xc}}{\delta \phi_{k,\sigma'}(r')} \) can then be calculated explicitly. Combining both equations and using the definition of the exchange-correlation potential given in equation (5.3) we obtain

\[
\sum_{\sigma'=\uparrow,\downarrow} \int d^3r' V_{xc,\sigma'}(r') \frac{\delta n_{\sigma'}(r')}{\delta V_{S,\sigma}(r)} = \sum_{\sigma'=\uparrow,\downarrow} \sum_{k=1}^{N_{\sigma'}} \int d^3r' \frac{\delta E_{xc}}{\delta \phi_{k,\sigma'}(r')} \frac{\delta \phi_{k,\sigma'}(r')}{\delta V_{S,\sigma}(r)} + \text{c.c.}
\]  

(5.6)

The functional derivatives of the Kohn-Sham orbitals with respect to the effective potential can be calculated using first order perturbation theory

\[
\delta \phi_{k,\sigma}(r) = \sum_{j\neq k} \frac{\phi_{j,\sigma}(r)}{\varepsilon_k,\sigma - \varepsilon_j,\sigma} \int d^3r' \phi_{j,\sigma}^*(r') V_{S,\sigma}(r') \phi_{k,\sigma}(r'),
\]  

(5.7)

where the \( \varepsilon_{k,\sigma} \) are the Kohn-Sham eigenvalues. We thus find

\[
\frac{\delta \phi_{k,\sigma}(r)}{\delta V_{S,\sigma}(r')} = \delta_{\sigma,\sigma'} \sum_{j\neq k} \frac{\phi_{j,\sigma}(r)}{\varepsilon_k,\sigma - \varepsilon_j,\sigma} \phi_{j,\sigma}^*(r') \phi_{k,\sigma}(r').
\]  

(5.8)
5.2. DFT-KLI approximation

The OEP equation (5.12) is an integral equation for which a direct solution is not known in general. Yet there exists a widely used approximation—thought to be quite accurate—which allows the transformation of the OEP equation into a Fredholm integral equation of the second kind with a separable kernel which is readily solved. This approximation is named the KLI approximation after its inventors Krieger, Li, and Iafrate [Krieger et al., 1992a,b]. Before we actually step into the discussion of the KLI approximation we should mention that Kümmel and Perdew [2003b,a] have invented an iterative solution of the full OEP equation which we will present in section 5.3. The computational cost of this iterative method is in many cases only slightly higher than the cost of the solution of the KLI equation. Considering the popularity of the KLI approximation it nevertheless deserves to be discussed. In the following we will first present two alternative derivations of the KLI approximation and then show how the KLI equation can be solved.

and

\[
\frac{\delta n_\sigma(r)}{\delta V_{\epsilon_{k,\sigma}}(r')} = \sum_{k=1}^{N_e} \phi^*_{k,\sigma}(r) \frac{\delta \phi_{k,\sigma}(r)}{\delta V_{\epsilon_{k,\sigma}}(r')} + \text{c.c.} = \sum_{k=1}^{N_e} \frac{\delta_{\epsilon_{k,\sigma}}}{\epsilon_{k,\sigma} - \epsilon_{j,\sigma}} \sum_{j \neq k} \phi^*_{j,\sigma}(r) \phi_{j,\sigma}(r) \phi_{k,\sigma}(r') + \text{c.c.} \quad (5.9)
\]

Inserting the variation of the Kohn-Sham orbitals (5.8) and the variation of the density (5.9) into equation (5.6) we obtain the DFT-OEP equation

\[
\sum_{k=1}^{N_e} \sum_{j \neq k} \frac{\phi^*_{j,\sigma}(r) \phi_{k,\sigma}(r)}{\epsilon_{k,\sigma} - \epsilon_{j,\sigma}} \int d^3r' \left( V_{xc,\sigma}(r') - u_{k,\sigma}(r') \right) \phi_{k,\sigma}(r') \phi_{j,\sigma}(r') + \text{c.c.} = 0. \quad (5.10)
\]

Defining the orbital potentials

\[
u_{k,\sigma}(r) = \frac{1}{\phi^*_{k,\sigma}(r)} \frac{\delta E_{xc}}{\delta \phi_{k,\sigma}(r)} \quad (5.11)
\]

finally yields the DFT-OEP equation in the form

\[
\sum_{k=1}^{N_e} \phi_{k,\sigma}(r) \sum_{j \neq k} \frac{\phi^*_{j,\sigma}(r)}{\epsilon_{k,\sigma} - \epsilon_{j,\sigma}} \int d^3r' \left( V_{xc,\sigma}(r') - u_{k,\sigma}(r') \right) \phi_{k,\sigma}(r') \phi_{j,\sigma}(r') + \text{c.c.} = 0. \quad (5.12)
\]

The DFT-OEP equation (5.12) can be cast into a physically transparent form if we define the orbital shifts

\[
\psi_{k,\sigma}(r) = \sum_{j \neq k} \frac{\phi_{j,\sigma}(r)}{\epsilon_{k,\sigma} - \epsilon_{j,\sigma}} \int d^3r' \left( V_{xc,\sigma}(r') - u_{k,\sigma}(r') \right) \phi_{k,\sigma}(r') \phi_{j,\sigma}(r'), \quad (5.13)
\]

which are the first order corrections to the Kohn-Sham wavefunctions subjected to the perturbation \( V_{xc} - u_{k,\sigma} \), i.e. replacing the orbital potentials by the Kohn-Sham exchange-correlation potential. Using this definition, the OEP equation simply reads

\[
\sum_{k=1}^{N_e} \phi_{k,\sigma}(r) \psi^*_{k,\sigma}(r) + \text{c.c.} = 0 , \quad (5.14)
\]

which means that the first order shift in the density vanishes when replacing the orbital potentials by the Kohn-Sham exchange-correlation potential.

5.2. The KLI approximation to the DFT-OEP integral equation

The OEP equation (5.12) is an integral equation for which a direct solution is not known in general. Yet there exists a widely used approximation—thought to be quite accurate—which allows the transformation of the OEP equation into a Fredholm integral equation of the second kind with a separable kernel which is readily solved. This approximation is named the KLI approximation after its inventors Krieger, Li, and Iafrate [Krieger et al., 1992a,b]. Before we actually step into the discussion of the KLI approximation we should mention that Kümmel and Perdew [2003b,a] have invented an iterative solution of the full OEP equation which we will present in section 5.3. The computational cost of this iterative method is in many cases only slightly higher than the cost of the solution of the KLI equation. Considering the popularity of the KLI approximation it nevertheless deserves to be discussed. In the following we will first present two alternative derivations of the KLI approximation and then show how the KLI equation can be solved.
Approximation of the energy denominator

The simplest, yet not very transparent and controllable method to derive the KLI approximation is to replace the energy denominator $\varepsilon_{k,\sigma} - \varepsilon_{j,\sigma}$ by a constant $\Delta \varepsilon_\sigma$ [Krieger et al., 1990]. The orbital shift then becomes

$$
\psi_{k,\sigma}(r) \approx \frac{1}{\Delta \varepsilon_\sigma} \sum_{j \neq k} \phi_{j,\sigma}(r) \int d^3r' \left( V_{\text{xc},\sigma}(r') - u_{k,\sigma}^*(r') \right) \phi_{k,\sigma}(r') \phi_{j,\sigma}^*(r')
$$

$$
= \frac{1}{\Delta \varepsilon_\sigma} \left( \sum_j \phi_{j,\sigma}(r) \int d^3r' \left( V_{\text{xc},\sigma}(r') - u_{k,\sigma}^*(r') \right) \phi_{k,\sigma}(r') \phi_{j,\sigma}^*(r')
\right.

\left. - \phi_{k,\sigma}(r) \int d^3r' \left( V_{\text{xc},\sigma}(r') - u_{k,\sigma}^*(r') \right) \phi_{k,\sigma}(r') \phi_{k,\sigma}^*(r') \right)

= \frac{1}{\Delta \varepsilon_\sigma} \left( (V_{\text{xc},\sigma}(r) - u_{k,\sigma}^*(r)) \phi_{k,\sigma}(r) - \left( V_{\text{xc},\sigma}^k - \bar{u}_{k,\sigma} \right) \phi_{k,\sigma}(r) \right),
$$

(5.15)

where the completeness relation

$$
\sum_j \phi_{j,\sigma}^*(r') \phi_{j,\sigma}(r) = \delta(r - r')
$$

(5.16)

has been used and the orbital averages

$$
\bar{V}_{\text{xc},\sigma}^k = \int d^3r \, V_{\text{xc},\sigma}(r) \phi_{k,\sigma}^*(r) \phi_{k,\sigma}(r) \quad \text{and} \quad \bar{u}_{k,\sigma} = \int d^3r \, u_{k,\sigma}^*(r) \phi_{k,\sigma}^*(r) \phi_{k,\sigma}(r)
$$

(5.17a)

(5.17b)

have been defined. Inserting the approximated orbital shift (5.15) into the OEP equation (5.14) yields the KLI equation

$$
n_{\sigma}(r) V_{\text{xc},\sigma}(r) = \sum_k N_{\sigma} n_{k,\sigma}(r) \left( \Re u_{k,\sigma}(r) + \bar{V}_{\text{xc},\sigma}^k - \Re \bar{u}_{k,\sigma} \right).
$$

(5.18)

Here we should point out that the KLI equation uniquely determines the exchange-correlation potential only up to an additive constant. This can easily be seen replacing $V_{\text{xc},\sigma}(r')$ in equation (5.18) by $V_{\text{xc},\sigma}(r) + C$ and using the normalization of the Kohn-Sham orbitals, i.e. $\int d^3r \, n_{k,\sigma}(r) = 1$. This constant is usually fixed by requiring that in a finite system the exchange-correlation potential asymptotically approaches zero for $r \rightarrow \infty$. Since this condition is fulfilled by the so-called Slater potential

$$
V_{\text{Slater},\sigma}(r) = \frac{1}{n_{\sigma}(r)} \sum_k N_{\sigma} n_{k,\sigma}(r) \Re u_{k,\sigma}(r),
$$

(5.19)

requiring the same asymptotics for the exchange-correlation potential amounts to setting $V_{\text{xc},\sigma}^{N_{\sigma}} = \Re \bar{u}_{N_{\sigma},\sigma}$ ($N_{\sigma}$ denotes the highest occupied Kohn-Sham orbital with spin $\sigma$) [Krieger et al., 1992a]. The reason for this choice is that sufficiently far away from the system the density is dominated by the highest occupied Kohn-Sham orbital and consequently the corresponding coefficient given by $V_{\text{xc},\sigma} - \Re \bar{u}_{N_{\sigma},\sigma}$ should be zero to ensure the desired asymptotic behaviour of the exchange-correlation potential.
KLI as a mean-field approximation

Following Krieger et al. [1990], we used a hard-to-motivate replacement of the energy denominator by some constant to derive the KLI approximation. To argue why it nevertheless often yields reasonable results, an alternative derivation of the same equation (5.18) was given by Krieger et al. [1992b]. Here we slightly generalize the work of Krieger et al. [1992b] to DFT in the presence of an external vector potential. As the starting point we note that as a straightforward consequence of first order perturbation theory the orbital shift defined by equation (5.13) satisfies

\[
\left( \hat{H}_{KS,\sigma} - \varepsilon_{k,\sigma} \right) \psi_{k,\sigma}(r) = \sum_{j \neq k} \frac{(\varepsilon_{j,\sigma} - \varepsilon_{k,\sigma})\phi_{j,\sigma}(r)}{\varepsilon_{k,\sigma} - \varepsilon_{j,\sigma}} \int d^3r' \left( V_{xc,\sigma}(r') - u_{k,\sigma}^*(r') \right) \phi_{k,\sigma}(r') \phi_{j,\sigma}(r')
\]

\[
= - \sum_{j \neq k} \phi_{j,\sigma}(r) \int d^3r' \left( V_{xc,\sigma}(r') - u_{k,\sigma}^*(r') \right) \phi_{k,\sigma}(r') \phi_{j,\sigma}^*(r')
\]

\[
= - \left[ V_{xc,\sigma}(r) - u_{k,\sigma}^*(r) - \left( \bar{V}_{xc,\sigma} - \bar{u}_{k,\sigma}^* \right) \right] \phi_{k,\sigma}(r).
\]  

(5.20)

If we write the Kohn-Sham Hamiltonian as \( \hat{H}_{KS,\sigma} = \hat{T}_S + V_{S,\sigma}(r) \) (where \( \hat{T}_S \) is the single-particle kinetic energy operator that may or may not contain an external vector potential), solve equation (5.20) for \( V_{S,\sigma}(r) \phi_{k,\sigma}(r) \) and multiply by the complex-conjugate Kohn-Sham orbital \( \phi_{k,\sigma}^*(r) \) from the left we find

\[
V_{S,\sigma}(r) \phi_{k,\sigma}^*(r) \psi_{k,\sigma}(r) = - \left[ V_{xc,\sigma}(r) - u_{k,\sigma}^*(r) - \left( \bar{V}_{xc,\sigma} - \bar{u}_{k,\sigma}^* \right) \right] \phi_{k,\sigma}(r) \phi_{k,\sigma}(r)
\]

\[
- \phi_{k,\sigma}(r) \hat{T}_S \psi_{k,\sigma}(r) + \varepsilon_{k,\sigma} \phi_{k,\sigma}^*(r) \psi_{k,\sigma}(r).
\]  

(5.21)

Next we add the complex conjugate of this expression and sum over all occupied states. Using the OEP equation (5.14) then yields

\[
V_{xc,\sigma}(r) n_{\sigma}(r) = \sum_k n_{k,\sigma}(r) \left( \Re u_{k,\sigma}(r) + \bar{V}_{xc,\sigma} - \Re \bar{u}_{k,\sigma} \right)
\]

\[
- \frac{1}{2} \sum_k \left( \phi_{k,\sigma}^*(r) \hat{T}_S \psi_{k,\sigma}(r) + \phi_{k,\sigma}(r) \hat{T}_S^* \psi_{k,\sigma}^*(r) - \varepsilon_{k,\sigma} \phi_{k,\sigma}^*(r) \psi_{k,\sigma}(r) - \varepsilon_{k,\sigma} \phi_{k,\sigma}(r) \psi_{k,\sigma}^*(r) \right).
\]  

(5.22)

By invoking once again the Kohn-Sham equation (4.24) and the OEP equation (5.14), the last two terms in this expression can be transformed into

\[
\sum_k \left( \varepsilon_{k,\sigma} \phi_{k,\sigma}(r) \psi_{k,\sigma}^*(r) + \varepsilon_{k,\sigma} \phi_{k,\sigma}^*(r) \psi_{k,\sigma}(r) \right) = \sum_k \left( \psi_{k,\sigma}^*(r) \hat{T}_S \phi_{k,\sigma}(r) + \psi_{k,\sigma}(r) \hat{T}_S^* \phi_{k,\sigma}^*(r) \right)
\]

(5.23)

and hence we find

\[
V_{xc,\sigma}(r) n_{\sigma}(r) = \sum_k n_{k,\sigma}(r) \left( \Re u_{k,\sigma}(r) + \bar{V}_{xc,\sigma} - \Re \bar{u}_{k,\sigma} \right)
\]

\[
- \frac{1}{2} \sum_k \left( \phi_{k,\sigma}^*(r) \hat{T}_S \psi_{k,\sigma}(r) + \phi_{k,\sigma}(r) \hat{T}_S^* \psi_{k,\sigma}^*(r) - \psi_{k,\sigma}(r) \hat{T}_S \phi_{k,\sigma}(r) - \psi_{k,\sigma}^*(r) \hat{T}_S^* \phi_{k,\sigma}^*(r) \right).
\]  

(5.24)
In the presence of an external vector potential $\mathbf{A}_{\text{ext}}(\mathbf{r})$, the kinetic energy operator is given by

$$
\hat{T}_S = -\frac{\hbar^2}{2m_0} \nabla^2 - \frac{i\hbar e}{m_0} \mathbf{A}_{\text{ext}}(\mathbf{r}) \cdot \nabla - \frac{i\hbar e}{m_0} \left( \nabla \cdot \mathbf{A}_{\text{ext}}(\mathbf{r}) \right) + \frac{e^2}{2m_0^*} A_{\text{ext}}^2(\mathbf{r}) \tag{5.25}
$$

and its complex conjugate reads

$$
\hat{T}_S^* = -\frac{\hbar^2}{2m_0} \nabla^2 + \frac{i\hbar e}{m_0} \mathbf{A}_{\text{ext}}(\mathbf{r}) \cdot \nabla + \frac{i\hbar e}{m_0} \left( \nabla \cdot \mathbf{A}_{\text{ext}}(\mathbf{r}) \right) + \frac{e^2}{2m_0^*} A_{\text{ext}}^2(\mathbf{r}) \tag{5.26}.
$$

Inserting these expressions into equation (5.24) we finally obtain after some simple manipulations

$$
V_{xc,\sigma}(\mathbf{r}) n_{\sigma}(\mathbf{r}) = \sum_k n_{k,\sigma}(\mathbf{r}) \left( \Re u_{k,\sigma}(\mathbf{r}) + V_{xc}^k - \Re \bar{u}_{k,\sigma} \right) \\
- \frac{\hbar}{2m_0} \sum_k \nabla \cdot \left( \hbar \psi_{k,\sigma}(\mathbf{r}) \nabla \phi_{k,\sigma}^*(\mathbf{r}) + i e \mathbf{A}_{\text{ext}}(\mathbf{r}) \phi_{k,\sigma}^*(\mathbf{r}) \psi_{k,\sigma}(\mathbf{r}) \right) + \text{c.c.} \tag{5.27}
$$

Note that this is an exact transformation of the OEP equation and still a complicated to solve integral equation. Its benefit lies in the fact that it may serve as a starting point for simplifying approximations to the OEP equation. The most simple one is to neglect completely all terms containing the orbital shifts, which leads exactly to the KLI equation (5.18). While this approximation may seem rather crude, it can nevertheless be motivated as a mean field approximation since the neglected terms vanish when averaged with the density $n(\mathbf{r})$. To show this we slightly generalize the proof given by Grabo et al. [2000] to the case of a non-vanishing external vector potential. Consider the integral

$$
I = \int d^3 r \sum_{k=1}^{N_{\sigma}} \nabla \cdot \left( \hbar \psi_{k,\sigma}(\mathbf{r}) \nabla \phi_{k,\sigma}^*(\mathbf{r}) + i e \mathbf{A}_{\text{ext}}(\mathbf{r}) \phi_{k,\sigma}^*(\mathbf{r}) \psi_{k,\sigma}(\mathbf{r}) \right) + \text{c.c.} \tag{5.28}
$$

which amounts to precisely the difference between the exact OEP equation and the KLI approximation averaged with the density $n_{\sigma}(\mathbf{r})$. From the definition of the orbital shift we immediately derive the equation

$$
\hat{T}_S \psi_{k,\sigma}(\mathbf{r}) = \sum_{j \neq k}^{N_{\sigma}} \frac{\varepsilon_{j,\sigma} \phi_{k,\sigma}^*(\mathbf{r}) \phi_{j,\sigma}(\mathbf{r})}{\varepsilon_{k,\sigma} - \varepsilon_{j,\sigma}} D_{k,j,\sigma} - V_{\bar{S},\sigma}(\mathbf{r}) \phi_{k,\sigma}(\mathbf{r}) \psi_{k,\sigma}(\mathbf{r}) \tag{5.29},
$$

where we have defined the matrix elements

$$
D_{k,j,\sigma} = \int d^3 r' \left( V_{xc}(\mathbf{r}') - u_{k,\sigma}(\mathbf{r}') \right) \phi_{j,\sigma}^*(\mathbf{r}') \phi_{k,\sigma}(\mathbf{r}') \tag{5.30}.
$$

Inserting it, together with

$$
\hat{T}_S^* \phi_{k,\sigma}(\mathbf{r}) = \left( \hat{H}_{KS,\sigma} - V_{\bar{S},\sigma}(\mathbf{r}) \right) \phi_{k,\sigma}(\mathbf{r}) = \varepsilon_{k,\sigma} \phi_{k,\sigma}(\mathbf{r}) - V_{\bar{S},\sigma}(\mathbf{r}) \phi_{k,\sigma}(\mathbf{r}) \tag{5.31},
$$

into equation (5.28), we find

$$
I = \int d^3 r \sum_{k=1}^{N_{\sigma}} \sum_{j \neq k}^{N_{\sigma}} D_{k,j,\sigma} \phi_{k,\sigma}^*(\mathbf{r}) \phi_{j,\sigma}(\mathbf{r}) + \text{c.c.} = 0 \tag{5.32}.
$$

The integral vanishes by virtue of the orthogonality of the Kohn-Sham orbitals.
Solution of the KLI equation

Technically speaking, the KLI equation is a Fredholm integral equation of the second kind with a separable kernel. As already shown by Krieger et al. [1992b], it can be solved using a standard technique which we will outline in the following.

We first divide the KLI equation by the density and subsequently average it with the density of the \( j \)-th Kohn-Sham level to obtain

\[
\bar{V}_{xc,\sigma}^j = \bar{V}_{Slater,\sigma}^j + \sum_{k} M_{j,k,\sigma} \left( \bar{V}_{xc,\sigma}^k - \Re \bar{u}_{k,\sigma} \right).
\]

(5.33)

In this expression we have defined the \( N_\sigma \times N_\sigma \)-matrix

\[
M_{j,k,\sigma} = \int d^3 r \frac{n_{j,\sigma}(r)n_{k,\sigma}(r)}{n_\sigma(r)}
\]

(5.34)

and \( \bar{V}_{Slater,\sigma}^j \) is defined to be

\[
\bar{V}_{Slater,\sigma}^j = \int d^3 r V_{Slater,\sigma}(r)n_{j,\sigma}(r).
\]

(5.35)

At this point we should note that we have already fixed the average \( \bar{V}_{xc,\sigma}^N_\sigma \) by requiring that the KLI potential vanishes asymptotically. For the matrix \( \hat{M}_\sigma \) this means that we can omit the last column and the last row and only have to deal with a matrix equation that determines the remaining \( N_\sigma - 1 \) unknowns \( \bar{V}_{xc,\sigma}^j \) (\( j = 1, \ldots, N_\sigma - 1 \)).

After rearranging equation (5.33) we see that a solution of the matrix equation

\[
\sum_{k} \left( \delta_{j,k} - M_{j,k,\sigma} \right) \left( \bar{V}_{xc,\sigma}^k - \Re \bar{u}_{k,\sigma} \right) = \bar{V}_{Slater,\sigma}^j - \Re \bar{u}_{j,\sigma} \quad (j = 1, \ldots, N_\sigma - 1)
\]

(5.36)

determines the averages \( \bar{V}_{xc,\sigma}^k \) which in turn can be plugged into the KLI equation (5.18) to calculate the exchange-correlation potential \( V_{xc,\sigma}(r) \).

If we would not have pre-determined \( \bar{V}_{xc,\sigma}^N_\sigma \) by fixing the boundary condition, we would have run into trouble solving equation (5.36) since the rank of the full \( N_\sigma \times N_\sigma \)-matrix \( \hat{1} - \hat{M}_\sigma \) is \( N_\sigma - 1 \) rather than \( N_\sigma \) and hence this matrix is not invertible in contrast to the truncated matrix used in equation (5.36).

5.3. Iterative construction of the exact-exchange potential

So far, we have presented the KLI approximation to the OEP equation and discussed a straightforward and numerically inexpensive scheme to solve the KLI equation. While the KLI approximation often yields reasonable ground state energies and Kohn-Sham eigenvalues (see for instance [Krieger et al., 1992a,b; Kümmel and Perdew, 2003b]), it is still an approximation that is not well controlled in the sense that its range of applicability is not predictable. On the other hand, for many years a solution of the full OEP equation was only possible for highly symmetric systems (e.g. with spherical symmetry), where the solution of the OEP equation could be reduced to a one-dimensional problem [Talman and Shadwick, 1976].

The first three-dimensional calculations involving the solution of the full OEP equation were presented by Görling and Levy [1994, 1995] who used a basis set expansion and a numerical inversion of the Kohn-Sham response function to solve the OEP equation for the exact-exchange potential. Since a constant shift
of the potential does not alter the density, one has, however, to ensure that such variations of the potential are excluded when evaluating the inverse of the Kohn-Sham response function given by
\[
\left( \frac{\delta n_\sigma(r)}{\delta V_{S,\sigma}(r')} \right)^{-1}.
\]
In addition to this difficulty, the explicit evaluation of the Kohn-Sham response function and its inverse involves not only the occupied states but in principle all unoccupied Kohn-Sham orbitals and eigenvalues which makes this scheme computationally costly.

A different scheme for the solution of the OEP equation based on an iteration of equation (5.27) without the external vector potential, together with the definition of the orbital shift (5.13), has been proposed by Kümmel and Perdew [2003b,a]. Once an approximate \( V_{xc,\sigma} \) is known—which can, for instance, be obtained from a solution of the KLI equation—it can be used to calculate the orbital shifts. Then a new \( V_{xc,\sigma} \) is found by inserting these orbital shifts into the OEP equation (5.27). This scheme can in principle be iterated to determine the OEP potential. However, a numerical problem can arise for finite systems since the solution of equation (5.27) for the exchange-correlation potential requires a division by the density which approaches zero far away from the system.

To circumvent this possible numerical difficulty, Kümmel and Perdew [2003b,a] suggested yet another iterative solution based on the OEP equation in the form given by equation (5.14):
\[
\sum_k N_\sigma \phi_{k,\sigma}(r) \psi_{k,\sigma}^*(r) + c.c. = 0.
\] (5.37)
The key point is that this sum only vanishes if the correct exchange-correlation potential is used to construct the orbital shift. If, however, we use an approximate \( V_{xc,\sigma} \), then this sum will yield a non-vanishing residual function
\[
S_\sigma(r) = \sum_k N_\sigma \phi_{k,\sigma}(r) \psi_{k,\sigma}^*(r) + c.c.
\] (5.38)
The residual \( S_\sigma(r) \) can be interpreted as a measure for the deviation between the approximate \( V_{xc,\sigma} \) and the exact solution of the OEP equation (corresponding to \( S_\sigma(r) = 0 \)). It can thus be used to construct a new approximation for the exchange-correlation potential
\[
V_{xc,\sigma}^{\text{new}}(r) = V_{xc,\sigma}(r) + \gamma S_\sigma(r).
\] (5.39)
The positive number \( \gamma \) (with dimension energy times volume) expresses the fact that \( S_\sigma(r) \) is only an estimate for the deviation between the exact and the approximate exchange-correlation potential and not the deviation itself. The value of \( \gamma \) is determined empirically for a specific calculation and in some sense parallels the mixing parameter employed in the linear mixing used to stabilize the self-consistent solution of the Kohn-Sham equation (see section A.3).

A further interpretation of \( \gamma \) as being related to the average of the exchange-correlation potential from the present step divided by the density has been given by Kümmel and Perdew [2003a]. First, solve the differential equation (5.20), which determines the orbital shift from the occupied Kohn-Sham orbitals for \( \left( \hat{T}_S - \varepsilon_{k,\sigma} \right) \psi_{k,\sigma} \). Inserting this expression into the OEP equation in the form of equation (5.22) then yields
\[
V_{xc,\sigma}(r) = V_{xc,\sigma}(r) + \frac{V_{S,\sigma}(r)}{2n_\sigma(r)} S_\sigma(r).
\] (5.40)
If \( V_{xc,\sigma} \) is already the true exchange-correlation potential, then \( S_\sigma(r) \) vanishes and the above identity is a trivial one. If, however, \( V_{xc,\sigma} \) is only an approximation to the solution of the OEP equations, then the
resulting orbital shifts will lead to a non-vanishing $S_\sigma(r)$. In that case the second term on the right-hand side represents an error term and one can expect to improve the approximation by subtracting this error term. Yet, Kümmel and Perdew [2003a] pointed out that a subtraction of the entire term $\frac{V_{xc,\sigma}(r)}{2n_\sigma(r)} S_\sigma(r)$ can lead to instabilities due to a drastic change of the potential from one iteration to the next. Instead, only that part of the error that is proportional to the exchange-correlation potential should be subtracted resulting in a new approximation to $V_{xc,\sigma}$ given by

$$V_{xc,\sigma}^{\text{new}}(r) = V_{xc,\sigma}(r) - \frac{V_{xc,\sigma}(r)}{2n_\sigma(r)} S_\sigma(r).$$

(5.41)

Since this expression again requires a division by the density, it may suffer from the same numerical problems in the outer region of a finite system as mentioned above. It can thus be beneficial to deal with an approximate error term that involves the average $\int r n_{xc,\sigma}(r)$ instead of the position-dependent term $\frac{V_{xc,\sigma}(r)}{2n_\sigma(r)}$. The constant value $\gamma$ actually plays the role of (the negative) of this average.

Once the new exchange-correlation potential has been found by calculating the residue $S_\sigma(r)$ from equation (5.38) and updating $V_{xc,\sigma}$ via equation (5.39), the correct asymptotic behaviour, i.e.

$$\bar{V}_{N\sigma}^{\text{new}}(r) = \text{Re} \bar{u}_{N\sigma,\sigma}$$

(5.42)

has to be ensured by subtracting $\int r n_{xc,\sigma}(r) \left( V_{xc,\sigma}^{\text{new}}(r) - \text{Re} u_{N\sigma,\sigma}(r) \right)$ from the new exchange-correlation potential. With this new $V_{xc,\sigma}$ one can now calculate new orbital shifts which in turn yield a new correction to the exchange-correlation potential. Using the exact-exchange functional (5.2), Kümmel and Perdew [2003b,a] have shown that this scheme can be iterated to find the exchange-correlation potential that solves the OEP equation.
6 Measure of electron localization

In this chapter we pose the question of how to distinguish between a localized and a delocalized state of the many-body system. In principle, all the information about a state is contained in its wavefunction. The many-body wavefunction, however, is a complicated object which is not even accessible by density functional theory. Using directly the Kohn-Sham orbitals on the other hand is neither justified nor helpful: we simply do not know how the Kohn-Sham orbitals of the localized state should differ from the ones of the delocalized state. But what quantity can then be used to measure electron localization? There have been several localization criteria suggested in the literature, two of which we will discuss in this chapter.

We first introduce the persistent current as a natural localization criterion and discuss its relation to the static limit of the conductivity. Afterwards we present the electron localization function, which is based on a local expansion of the pair-correlation function and provides a real-space picture of electron localization.

6.1. Persistent current and the curvature of the ground state energy

An intuitively appealing criterion to distinguish a localized state from a delocalized one is whether the state is able to carry a current or not. Being able to induce a persistent current in a quantum ring simply by penetrating it with a magnetic flux makes the current criterion especially well suited for our purposes. Yet, it is not restricted to the study of quantum rings—although the ring geometry is often used as a formal tool—and has been extensively applied to the study of metal-insulator transitions in more general situations [Scalapino et al., 1993; Stafford and Millis, 1993; Kotlyar and Das Sarma, 2001]. In fact, in a seminal paper Kohn [1964] first discussed the relation between the localization and the conductivity of a state employing the ring geometry and the persistent current merely as a formal device. To illustrate the persistent current criterion we will briefly review Kohn’s arguments, in particular the application to a delocalized and a localized state.

We have already shown in chapter 3 that a magnetic flux $\Phi$ penetrating a quantum ring gives rise to a persistent current. A closely related phenomenon is the flux dependence of the ground state energy and the link between the latter and the persistent current is established by the Byers-Yang relation [Byers and Yang, 1961]

$$\frac{dE(\Phi)}{d\Phi} = -ej(\Phi).$$

(6.1)

Employing the Hellmann-Feynman theorem, it is easy to show the Byers-Yang relation for a one-dimensional system of interacting electrons (for simplicity we omit the spin). To this end we write the flux-dependent ground state energy $E(\Phi)$ as the expectation value

$$E(\Phi) = \left\langle \Psi \left| \hat{H} \right| \Psi \right\rangle.$$

(6.2)

Since the flux enters only the kinetic part $\hat{T}$ of the Hamiltonian $\hat{H}$ the derivative of the ground state energy

$$\frac{dE(\Phi)}{d\Phi} = -ej(\Phi).$$

(6.1)
6. Measure of electron localization

with respect to the flux is given by
\[
\frac{dE(\Phi)}{d\Phi} = \left< \Psi \left| \frac{d\hat{H}}{d\Phi} \right| \Psi \right> = \left< \Psi \left| \frac{d\hat{T}}{d\Phi} \right| \Psi \right>.
\] (6.3)

Expressing \( \hat{T} \) via the fermionic field operators \( \hat{\Psi}(x) \) and \( \hat{\Psi}^\dagger(x) \) (where \( x = R\varphi \) denotes the coordinate along the ring with radius \( R = 2\pi L \)) as
\[
\hat{T} = -\frac{\hbar^2}{2m^*_0} \int dx \hat{\Psi}^\dagger(x) \frac{d^2}{dx^2} \hat{\Psi}(x) - e \int dx \hat{j}_p(x) \frac{\Phi}{L}
+ \frac{e^2}{2m^*_0} \int dx \hat{n}(x) \frac{\Phi^2}{L^2}
\] (6.4)

immediately yields
\[
\frac{d\hat{T}}{d\Phi} = -\frac{e}{L} \int dx \left\{ \hat{j}_p(x) - \frac{e}{m^*_0} \frac{\Phi}{L} \hat{n}(x) \right\}.
\] (6.5)

In the above equations we have defined the operator of the paramagnetic current density as
\[
\hat{j}_p(x) = \frac{\hbar}{2m^*_0} \left[ \hat{\Psi}^\dagger(x) \frac{d}{dx} \hat{\Psi}(x) - \left( \frac{d}{dx} \hat{\Psi}^\dagger(x) \right) \hat{\Psi}(x) \right]
\] (6.6)

and \( \hat{n}(x) = \hat{\Psi}^\dagger(x) \hat{\Psi}(x) \) is the density operator. The derivative of the ground state energy is then given by the expectation value of the total current density operator \( \hat{j}_p(x) - \frac{e}{m^*_0} \frac{\Phi}{L} \hat{n}(x) \) as
\[
\frac{dE(\Phi)}{d\Phi} = -\frac{e}{L} \int dx \left< \Psi \left| \hat{j}_p(x) - \frac{e}{m^*_0} \frac{\Phi}{L} \hat{n}(x) \right| \Psi \right> = -\frac{e}{L} \int dx j(\Phi) = -ej(\Phi),
\] (6.7)

where \( j(\Phi) \) denotes the expectation value of the current density, which in one dimension is independent of \( x \) by virtue of the continuity equation.

An interesting link between the flux-dependence of the ground state energy and the conductivity \( \sigma \) (which allows to calculate the current induced by an electric field) has been pointed out by Kohn [1964]. The key argument is the formal equivalence between a Hamiltonian containing the vector potential \( \Phi \) and the Hamiltonian of a charged particle in a time-dependent electric field (oriented along the \( x \)-direction)
\[
E(t) = E_0 e^{i\omega t}.
\] (6.8)

The formal equivalence allows to express the static limit of the imaginary part \( \sigma'' \) of the conductivity as the curvature of the ground state energy, i.e.
\[
\lim_{\omega \to 0} \omega \sigma''(\omega) = -\frac{1}{L} \frac{d^2 E(\Phi)}{d\Phi^2} \bigg|_{\Phi=0} = \frac{e}{L} \frac{dj(\Phi)}{d\Phi} \bigg|_{\Phi=0}.
\] (6.9)

Since a change of the flux amounts to a change in the boundary conditions, it is clear that—in the limit of a very large system—the energy of a localized state will not be affected by changing the flux, thus yielding a vanishing static limit of the conductivity. In contrast, the energy of a delocalized state is susceptible to the change of the boundary conditions which will be reflected by a finite value of \( \lim_{\omega \to 0} \omega \sigma''(\omega) \).

To illustrate the relation between the localization of a state, its persistent current and the static conductivity the following example of a delocalized and a localized particle has been given by Kohn [1964].
Consider a single free particle on a ring with circumference $L = 2\pi R$ with wave function and energy given by
\[
\phi(\varphi) = \frac{1}{\sqrt{L}} e^{im\varphi} \quad \text{and} \quad E(\Phi) = \frac{\hbar^2}{2m_0^* R^2} \left( m - \frac{\Phi}{\Phi_0} \right)^2. \tag{6.10}
\]
We then find
\[
j(\Phi) = \frac{\hbar}{L m_0^* R} \left( m - \frac{\Phi}{\Phi_0} \right) \tag{6.11}
\]
and
\[
\lim_{\omega \to 0} \omega \sigma''(\omega) = -\frac{1}{L} \frac{ne^2}{m^*} = -\frac{2}{L} D \tag{6.12}
\]
where $D = \frac{ne^2}{2m_0^*}$ is the Drude weight and $n = \frac{1}{L}$ is the density. This familiar result clearly indicates conducting behaviour. If, however, the wave function of the particle is localized in some area $d \ll L$ it cannot carry a current because otherwise the static continuity equation would be violated. Consequently, the energy is unaffected by the flux and hence
\[
\lim_{\omega \to 0} \omega \sigma''(\omega) = 0, \tag{6.13}
\]
reflecting the non-conducting nature of the localized state.

### 6.2. The electron localization function

A second, independent criterion to measure electron localization is provided by the electron localization function (ELF). Originally introduced in quantum chemistry by Becke and Edgecombe [1990] to provide an intuitive picture for atomic shell structure, lone electron pairs and chemical bonding, the ELF is based on the simple idea, that the more localized an electron is, the more it repels other like-spin electrons due to the Pauli repulsion. Stated in a different way, that is better suited to give a quantitative answer, the question underlying the definition of the ELF is: What is the probability to find a second like-spin electron anywhere in the vicinity of a reference electron with a given spin?

To answer this question, we first introduce the parallel-spin pair-correlation function which is defined as
\[
g(r_\sigma, r'_\sigma) = \frac{1}{N_\sigma(N_\sigma - 1)} \left\langle \Psi \left| \hat{\Psi}_\sigma(\mathbf{r}) \hat{\Psi}_\sigma(\mathbf{r}') \psi(\mathbf{r}) \psi(\mathbf{r}') \right| \Psi \right\rangle, \tag{6.14}
\]
where $\hat{\Psi}_\sigma$ and $\hat{\Psi}_\sigma^\dagger$ are fermionic field operators and $\Psi$ is some antisymmetric $N$-particle wavefunction ($N_\sigma$ is the number of particles with spin-projection $\sigma = \uparrow, \downarrow$). The parallel-spin pair-correlation function tells us the probability (for the given many-body state $\Psi$), to find one electron with spin $\sigma$ at position $r$ and a second electron with parallel spin at position $r'$. Now suppose we want to know the probability to find the second electron at $r'$ if we know for sure that the reference electron is located at $r$. This probability is given by dividing the pair-correlation function by the probability to find an electron with spin $\sigma$ at position $r$. The latter is simply the spin-density divided by $N_\sigma$. We can thus define the conditional pair probability
\[
P(r_\sigma, r'_\sigma) = N_\sigma \frac{g(r_\sigma, r'_\sigma)}{n_\sigma(r)}. \tag{6.15}
\]

---

1. We still assume periodic boundary conditions, i.e. a ring-like system but take $x = R\varphi$ to be limited to the interval $-\frac{L}{2} \leq x \leq \frac{L}{2}$. Localization near the origin of the wavefunction then means $\phi(x = \pm \frac{L}{2}) = 0$ apart from terms that vanish exponentially with increasing $L$. 

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This function, depending on two coordinates, is still too complicated for our purpose. Following Becke and Edgecombe [1990], we expand the function \( P(r_\sigma, r'_\sigma) \) as a power series in the distance \( s = r' - r \) (around \( s = 0 \)) and subsequently calculate the spherical average over \( s \).

As a consequence of the Pauli principle, the zeroth-order term in the expansion (which is the probability to find the second electron at exactly the same place as the first one) vanishes, as well as the first-order term since the expansion is carried out around a minimum. The first non-vanishing term is the term which is of second order in \( s \):

\[
P(r_\sigma, s_\sigma) = \frac{N_\sigma}{2n_\sigma(r)} \sum_{i,j} s_i s_j \frac{\partial^2 g(r_\sigma, s_\sigma)}{\partial s_i \partial s_j} \bigg|_{s=0} + \mathcal{O}(s^3),
\]

and, after spherical averaging, reads

\[
\langle P(r_\sigma, s_\sigma) \rangle_s \propto s^2 \frac{N_\sigma}{2n_\sigma(r)} \left( \frac{\partial^2 g(r_\sigma, s_\sigma)}{\partial s_i \partial s_j} \bigg|_{s=0} \right) + \mathcal{O}(s^3).
\]

This expression tells us the probability to find an electron with spin \( \sigma \) anywhere close to a reference electron at position \( r \) with the same spin. Note that this probability is closely related to the curvature of the exchange-hole [Dobson, 1991].

Using the coefficient \( \frac{1}{n_\sigma(r)} \frac{\partial^2 g(r_\sigma, s_\sigma)}{\partial s_i \partial s_j} \bigg|_{s=0} \) of the term quadratic in \( s \), Becke and Edgecombe [1990] defined the electron localization function

\[
\eta_\sigma(r) = \frac{1}{1 + \chi^2_\sigma(r)},
\]

where

\[
\chi_\sigma(r) = \frac{\partial^2 g(r_\sigma, s_\sigma)}{\partial s_i \partial s_j} \bigg|_{s=0}
\]

and \( g_{\text{hom}}(r_\sigma, s_\sigma) \) is the same-spin pair-correlation function in the homogeneous electron gas with a spin-density that equals the local value \( n_\sigma(r) \). This definition restricts the values of the ELF to the interval \( 0 \leq \eta_\sigma(r) \leq 1 \), where a value of \( \eta_\sigma = 1 \) corresponds to perfect localization and a value of \( \eta_\sigma = \frac{1}{2} \) corresponds to electron-gas like delocalization.

\[\text{The ELF in a single-particle picture}\]

The electron localization function was originally introduced for Hartree-Fock theory, where the many-body wave function \( \Psi \) is a Slater-determinant of Hartree-Fock orbitals. It has also been used in the context of density functional theory, although a rigorous justification that the ELF evaluated with the Kohn-Sham orbitals yields a meaningful picture of electron localization in the interacting system is lacking.\(^3\) Nevertheless, previous applications of the ELF within density functional theory indicate that the ELF provides

\[2\] With this interpretation it is difficult to assign a physical meaning in terms of localization or delocalization to ELF values less than one half since it is unclear what “more delocalized than the homogeneous electron gas” should mean.

\[3\] A motivation to use the ELF within DFT has been given by Savin et al. [1992], who noticed that the ELF can be expressed in terms of the Pauli kinetic energy. The Pauli kinetic energy has been defined as the difference between the kinetic energy density of the system under consideration and a bosonic system with the respective density. The kinetic energy density of a bosonic system with density \( n(r) \)—which represents the lower bound for the kinetic energy density—is simply \( \frac{1}{2} |\nabla n(r)|^2 \) and thus strictly accessible within DFT. The other part of the Pauli kinetic energy, the kinetic energy density of the actual system is, however, only accessible for the Kohn-Sham system but not for the interacting one.
a useful tool, too, when evaluated with the Kohn-Sham orbitals [Savin et al., 1992; Räsänen et al., 2008; Burnus et al., 2005]. We will thus proceed to express the electron localization function in terms of the Kohn-Sham orbitals. In contrast to the original formulation of the ELF we will not restrict ourselves to real-valued orbitals. Complex-valued single-particle orbitals have previously been used by Burnus et al. [2005] to derive a time-dependent generalization of the ELF.

If the many-body wave function $\Psi$ is understood as a Slater-determinant of the occupied Kohn-Sham orbitals, one can—after a lengthy but straightforward calculation—express the same-spin pair-correlation function as

$$g(r_\sigma, s_\sigma) = \frac{1}{N_\sigma (N_\sigma - 1)} \left[ n_\sigma(r)n_\sigma(s) - \sum_{j,k=1}^{N_\sigma} \phi_{j,\sigma}^*(r)\phi_{k,\sigma}^*(s)\phi_{k,\sigma}(r)\phi_{j,\sigma}(s) \right].$$

(6.20)

The second derivative of $g(r_\sigma, s_\sigma)$ with respect to $s$ evaluated at $s = 0$ is then found to be

$$\nabla_s g(r_\sigma, s_\sigma)_{s=0} = \frac{2n_\sigma(r)}{N_\sigma (N_\sigma - 1)} \left[ \tau_\sigma(r) - \frac{j_{p,\sigma}^2(r)}{n_\sigma(r)} - \frac{(\nabla n_\sigma(r))^2}{4n_\sigma(r)} \right],$$

(6.21)

where

$$\tau_\sigma(r) = \sum_{k=1}^{N_\sigma} |\nabla \phi_{k,\sigma}(r)|^2 = \sum_{k=1}^{N_\sigma} \left( \nabla \phi_{k,\sigma}^*(r) \cdot \nabla \phi_{k,\sigma}(r) \right)$$

(6.22)

is the kinetic energy density of the system of $N_\sigma$ particles with the orbitals $\phi_{k,\sigma}$. The term in brackets in equation (6.21) equals the respective expression in the time-dependent ELF [Burnus et al., 2005] and differs from the original expression for real-valued orbitals given by Becke and Edgecombe [1990b] by the term $\frac{j_{p,\sigma}^2(r)}{n_\sigma(r)}$ which can be understood as a kinetic energy density associated with the currents in the system.

To define the ELF, $\nabla_s g(r_\sigma, s_\sigma)_{s=0}$ is divided by the respective quantity in a homogeneous electron gas with the density $n_\sigma$ which equals the local value of the density in the inhomogeneous system:

$$\nabla_s g_{\text{hom}}(r_\sigma, s_\sigma)_{s=0} = \frac{2n_\sigma(r)}{N_\sigma (N_\sigma - 1)} \tau_\sigma(n_\sigma(r)).$$

(6.23)

The kinetic energy density $\tau_{\text{hom}}(n_\sigma)$ of the homogeneous electron gas with the density $n_\sigma$ depends on the spatial dimension of the system. In three dimensions it is given by $\tau_{\text{hom}}^{3D}(n_\sigma) = \frac{3}{5} (6\pi^2)^{2/3} n_\sigma^{5/3}$ [Becke and Edgecombe, 1990], in two dimensions by $\tau_{\text{hom}}^{2D}(n_\sigma) = \frac{2}{3} \pi n_\sigma^2$ [Räsänen et al., 2008] and in one dimension by $\tau_{\text{hom}}^{1D}(n_\sigma) = \frac{1}{6} n_\sigma^{3/2}$. Using equations (6.21) and (6.23), the ELF is then found to be

$$\eta_\sigma(r) = \frac{1}{1 + \chi_\sigma^2(r)}$$

(6.24)

with

$$\chi_\sigma(r) = \frac{\tau_\sigma(r) - \frac{j_{p,\sigma}^2(r)}{n_\sigma(r)} - \frac{(\nabla n_\sigma(r))^2}{4n_\sigma(r)}}{\tau_{\text{hom}}(n_\sigma(r))}.$$
7 Exact-exchange study of the Wigner crystal transition

In this chapter we study the dependence of the ground state on the strength of the electron-electron interaction. The first and easiest way to do so is to use spinless—or fully spin polarized—electrons and calculate the ground state for different values of the interaction parameter using density functional theory. We always employ the exact exchange functional and solve the optimized effective potential equation in the KLI approximation.

Next, we generalize the study to the spin-dependent case. Important new features that arise from the inclusion of the spin degree of freedom can be understood from the dependence of the transition on the impurity potential strength previously considered in the fully spin-polarized case. Again, in all calculations we use the exact-exchange functional and solve the OEP equation using the KLI approximation.

We finally discuss the fully spin-polarized problem solving the OEP equation exactly without resorting to the KLI approximation. It is thus possible to estimate the influence of the latter on the Wigner crystallization.

In all calculations we use GaAs material parameters, i.e. an effective electron mass \( m^*_0 = 0.0665m_e \) (\( m_e \) is the mass of an electron) and the dielectric constant is \( \epsilon = 12.5 \).

7.1. The quasi one-dimensional quantum ring model

Most of the quantum rings discussed are one-dimensional or quasi one-dimensional. Yet, matrix elements of the one-dimensional Coulomb interaction have the unpleasant feature that they diverge. To avoid this divergence one usually introduces a cut-off length \( a \) and replaces the Coulomb potential at distances short than \( a \) by some constant. While this construction seems rather artificial, it can nevertheless be motivated physically [Friesen and Bergersen, 1980]. To this end we first consider a three-dimensional quantum ring which shall be lying in the \( xy \)-plane and is usually described by a harmonic potential

\[
V_{\text{ext}}(r) = V_R (r - R)^2 + V_z(z) \tag{7.1}
\]

centered at some radius \( R \). The height of the ring, which is given by the confinement potential \( V_z(z) \) in the perpendicular \( z \)-direction, is usually assumed to be small compared to the width and the circumference, so that in the \( z \)-direction, only the lowest subband is occupied. Consequently, the exact form of \( V_z \) is unimportant. Any single-particle wavefunction in this confining potential will thus be of the form

\[
\phi_{n,m}(r) = \chi_{n,m}(r, \varphi)\xi(z) , \tag{7.2}
\]

where the quantum numbers \( n \) and \( m \) label the transverse subband and the angular motion. In a rotationally symmetric ring, \( m \) will simply be the \( z \)-component of the angular momentum.

Similarly, if we increase the strength of the radial confining potential \( V_R \), all electrons will eventually be in the lowest transverse subband, i.e. \( n = 0 \) and a typical single-particle wave function reads

\[
\phi_{m}(r) = \psi_m(\varphi)\chi(r)\xi(z) , \tag{7.3}
\]
where all expectation values are understood as averages over the transverse and the $z$-direction. Such a quantum ring, where the single-particle orbitals differ only by their angular part, will be called a quasi one-dimensional quantum ring.

Using the adiabatic approximation of the wave function in the quasi one-dimensional ring given by equation (7.3) allows to introduce an effective quasi one-dimensional Coulomb interaction. In the usual three-dimensional case, two electrons interact via the Coulomb repulsion

$$V_C(r, r') = \frac{e^2}{4\pi \epsilon \epsilon_0} \frac{1}{|r - r'|}.$$  

Following Friesen and Bergersen [1980], we find the effective one-dimensional Coulomb interaction by averaging the three-dimensional Coulomb interaction over the radial and the $z$-direction:

$$\langle V_C \rangle_{r,r',z,z'}(\phi, \phi') = \int r dr r' dr' \int dz dz' \frac{|\chi(r)|^2|\chi(r')|^2|\xi(z)|^2|\xi(z')|^2}{|r - r'|}.$$  

We will, however, not evaluate this integral analytically (what can be done, for instance if one assumes Gaussian wave functions $\chi(r)$ and $\xi(z)$ [Friesen and Bergersen, 1980]). Instead, we choose the reasonable approximation

$$V_{1D}^C(x, x') = \frac{e^2}{4\pi \epsilon \epsilon_0} \min \left( \frac{|x - x'|^{-1}}{\epsilon a}, a^{-1} \right)$$  

which, for large distances, shows the usual $1/x$-behaviour, but is replaced by some finite value for distances shorter than $a$. Here and in the following $x = R\phi$ will denote the coordinate along the ring and we will understand the distance between $x$ and $x'$ as the shorter of the two arcs between both points. As in the often used conceptionally similar model potential

$$\tilde{V}_{1D}^C(x, x') = \frac{e^2}{4\pi \epsilon \epsilon_0} \frac{1}{\sqrt{(x - x')^2 + a^2}},$$  

the parameter $a$ corresponds to the transverse extension of the quantum ring and can be interpreted as a minimal distance between the electrons [Bednarek et al., 2003].

In order to induce the persistent current, our quasi one-dimensional ring will be penetrated by a magnetic flux $\Phi$ through its center, such that the electrons (which are confined to the ring) move in a field-free region. In symmetric gauge, the corresponding vector potential is given by

$$\mathbf{A}_{\text{ext}}(\mathbf{r}) = \frac{\Phi}{2\pi R} \mathbf{e}_\phi,$$  

where $\mathbf{e}_\phi$ is a unit vector that always points in the direction tangential to the ring [Viefers et al., 2003]. Apart from inducing the persistent current, the related lifting of the degeneracy between left- and right-moving states has an important technical consequence since it facilitates convergence.

Finally we place a repulsive Gaussian impurity potential

$$V_{\text{imp}}(x) = V_0 e^{-\frac{(x-x_0)^2}{b^2}}$$  

centered at $x_0$ with the width $b$ and a strength $V_0 > 0$ in the ring, that will serve to break the rotational invariance. An impurity with a finite strength leads to a non-uniform density, even in the non-interacting case, whereas a “vanishing” impurity potential merely pins the Wigner molecule but leaves individual electrons unaffected. Of course, a “vanishing” impurity potential should not be understood as $V_0 = 0$, but
7.1. The quasi one-dimensional quantum ring model

Figure 7.1.: Schematic sketch of the quasi one-dimensional quantum ring model penetrated by a magnetic flux $\Phi$. Depending on its strength, the repulsive Gaussian impurity potential $V_{\text{imp}}$ can be used i) to create an inhomogeneous electron density if it is sufficiently strong or ii) if it is very weak pins the Wigner molecule but leaves individual electrons unaffected.

rather means that its strength is much smaller than the Coulomb energy per electron. All reported calculations were performed with a width of $b = 0.025L$ ($L$ is the ring circumference). For the “vanishing” impurity potential increasing $b$ makes the convergence more difficult (because the potential becomes less effective in pinning the Wigner molecule) but otherwise the choice of $b$ does not qualitatively influence the results.

Putting together the vector potential, the impurity potential and the quasi one-dimensional Coulomb interaction, we obtain the many-body Hamiltonian that describes our quantum ring model sketched in figure 7.1:

$$
\hat{H} = \frac{1}{2m_0} \sum_{\sigma = \uparrow, \downarrow} \int dx \hat{\Psi}_\sigma^\dagger(x) \left( -i \hbar \frac{d}{dx} + e \frac{\Phi}{L} \right)^2 \hat{\Psi}_\sigma(x) \\
+ \frac{1}{2} \sum_{\sigma, \sigma' = \uparrow, \downarrow} \int dx \int dx' \hat{\Psi}_\sigma^\dagger(x) \hat{\Psi}_\sigma^\dagger(x') V_{1D}^{\text{C}}(x, x') \hat{\Psi}_{\sigma'}(x') \hat{\Psi}_\sigma(x) \\
+ \sum_{\sigma = \uparrow, \downarrow} \int dx \hat{\Psi}_\sigma^\dagger(x) V_{\text{imp}}(x) \hat{\Psi}_\sigma(x).
$$

(7.10)

To solve this problem, we use DFT and SDFT.

**How to tune the electron-electron interaction**

In order to investigate the transition from a Fermi liquid state to a Wigner molecule, one has to be able to tune the ratio between the kinetic energy and the potential energy arising from the electron-electron interaction. We have already discussed in chapter 2, that this ratio depends on the electron density. A rough estimate is given by the observation that the Coulomb energy per particle scales as the inverse distance between the particles, i.e. as $n$, $n^{1/2}$ and $n^{1/3}$ in one, two and three dimensions, respectively. In contrast, the kinetic energy per particle of a one-dimensional non-interacting homogeneous electron gas scales as $n^2$ and of the three dimensional one as $n^{2/3}$. In the two-dimensional case, the kinetic energy per particle is independent of the density. Consequently, the ratio between the kinetic energy (of the non-interacting electron gas) and the Coulomb energy scales as $n$, $n^{1/2}$ and $n^{1/3}$, in one, two and three
dimensions, respectively. Experimentally, it would thus be most feasible to change the strength of the electron-electron interaction relative to the kinetic energy by varying the electron density.

In this work, we use the persistent current as a criterion to distinguish between a Fermi liquid and a Wigner crystal. Changing the density via changing the electron number, however, alters the persistent current even in the non-interacting system which conceals the interaction effect. For our purpose it is favourable to exclude this trivial single-particle contribution and to retain only the influence of many-body effects. This can be done by using a different (but somewhat artificial) way to control the ratio of the kinetic to the Coulomb energy. Namely, let us introduce a parameter $\xi$ into the Hamiltonian

$$\hat{H}_\xi = \xi \left( \hat{T} + \hat{V}_{\text{imp}} \right) + \hat{V}_{\text{ee}}$$

(7.11)

that allows to scale the single-electron part (consisting of the kinetic energy operator $\hat{T}$ and the interaction with the Gaussian impurity potential $\hat{V}_{\text{imp}}$) relative to the electron-electron interaction $\hat{V}_{\text{ee}}$. Of course, this scaling affects also the energy eigenvalues but we will merely be interested in the Kohn-Sham orbitals which will be used to determine the density and current density. We can formally identify the scaling parameter $\xi$ with the ratio between the “true” effective electron mass $m_0^*$ and some fictitious electron mass $m^*$

$$\xi = \frac{m_0^*}{m^*}$$

(7.12)

which makes it easy to establish a relation between the one-dimensional interaction parameter

$$r_S = \frac{1}{2N} \frac{L}{a_B^*}$$

(7.13)

and the scaling parameter. The interaction parameter simply measures the “radius” of the region in space which each electron occupies in units of the effective Bohr radius

$$a_B^* = 4\pi\epsilon\epsilon_0 \frac{\hbar^2}{m_0^* e^2}.$$  

(7.14)

The latter is defined with the “true” effective electron mass $m_0^*$ and the dielectric constant $\epsilon$ of the host material. The scaling is then done replacing the true effective electron mass by the fictitious one which amounts to multiply $r_S$ with $\xi^{-1}$. The interaction parameter corresponding to the electron mass $m^*$ is thus given by

$$r_S = \frac{1}{2N} \frac{L}{a_B^* m_0^*}.$$  

(7.15)

Obviously, this scaling also affects the impurity potential the strength of which is renormalized according to

$$V_0 \rightarrow V_0^* = V_0 \xi = V_0 \frac{m_0^*}{m^*}.$$  

(7.16)

Finally, to ensure that the results for the non-interacting system are unaffected by the scaling all observables, in particular the persistent current, have to be calculated with the true effective electron mass $m_0^*$. It can thus be guaranteed that any dependence of the observables on the scaling parameter (and thus on $r_S$) is purely an interaction effect.
7.2. Wigner crystallization of fully spin-polarized electrons

In this section, we study the Wigner crystallization of ten spinless (i.e. fully spin-polarized) electrons in the quasi one-dimensional quantum ring using density functional theory. We account for the exchange-correlation energy using the exact-exchange functional and solve the OEP equation using the KLI approximation. The persistent current is induced by a magnetic flux of \( \Phi = 0.3 \Phi_0 \) (unless otherwise stated), where \( \Phi_0 = \frac{h}{2e} \) is the flux quantum. The results of these calculations have been published in [Siegmund et al., 2009].

“Vanishing” impurity potential

We first consider an impurity potential with a strength \( V_0 = 0.001 \text{ meV} \). Since the Kohn-Sham eigenvalues are of the order of several milli electron volts, this impurity potential will not influence the motion of the individual electrons. In fact, this can be assured by computing the persistent current of non-interacting electrons without any impurity potential and with the present one. In both cases we find the same value for the current density.

Starting with an almost non-interacting system (\( r_S = 0.1 \)), we perform self-consistent calculations for various values of the interaction parameter between \( r_S = 0.1 \) and \( r_S = 5.0 \). The resulting values of the persistent current are shown as a function of \( r_S \) in figure 7.2. In the almost non-interacting case, the persistent current density coincides with the persistent current density of the non-interacting system (represented by the dashed line in figure 7.2). As we increase the interaction strength, which is done by varying the effective electron mass, we find that the persistent current stays constant up to a critical value \( r_S^c \) of the interaction parameter. Moreover, the persistent current retains exactly its value in the corresponding non-interacting system. As the interaction parameter exceeds the critical value, the current starts to drop. This drop is an exponential one, as can be seen from the logarithmic plot in figure 7.3. From the data plotted in figures 7.2 and 7.3, we can infer a critical value of \( r_S^c = 2.05 \).
7. Exact-exchange study of the Wigner crystal transition

Figure 7.3: A logarithmic version of the plot in figure 7.2. From the linear decay of the current in the logarithmic plot its exponential dependence on the interaction parameter (once the latter exceeds the critical value $r_S^c$) can be seen.

To understand this behaviour of the current, we calculate the electron localization function, which is shown in figure 7.4. If the interaction parameter is much less than the critical value $r_S^c$, we obtain the solid black line which corresponds to $r_S = 0.1$. The constant value $\eta = 0.5$ of the ELF signals a delocalized Fermi liquid state. Consequently, these uncorrelated electrons are unaffected by the “vanishing” impurity potential and their current equals that of the non-interacting system. The dashed red curve in figure 7.4 shows the ELF for an interaction parameter of $r_S = 2.06$, i.e. at the onset of the exponential decay of the current. The ELF is now no longer a constant but shows small oscillations with ten equidistant decay maxima that can be interpreted as the ten electrons which gradually localize at equidistant lattice sites. The rapidly increasing localization which is signaled by the dotted blue curve ($r_S = 2.5$) corresponds to the exponential decay of the current. Finally, at $r_S = 5.0$ the value of the current is merely about 1% of its non-interacting value and the ELF shows ten electrons completely localized ($\eta = 1$) at the equidistant lattice sites (the dash-dotted green curve in figure 7.4).

With the aid of the ELF, we can interpret the decay of the current as a transition from a delocalized system of uncorrelated electrons below the critical value of the interaction parameter to an increasingly localized collective state for values of $r_S$ above $r_S^c$. While the electrons in the Fermi liquid are unaffected by the “vanishing” impurity potential, the correlated system which we will call a Wigner molecule has to tunnel as a whole through the impurity. Due to the increased mass of the Wigner molecule compared to an individual electron, the tunneling is exponentially suppressed.

The evolution of the density as the system gets localized is plotted in figure 7.5. In the Fermi liquid state ($r_S = 0.1$), the density is homogeneous (the solid black line), apart from very weak Friedel oscillations which are due to the impurity potential and with an amplitude which is by far smaller than the scale of the plot. At the onset of the decay of the current, small oscillations start to build up in the electron density (dashed red line at $r_S = 2.06$). For increasingly localized electrons the density oscillations become more and more pronounced (dotted blue line at $r_S = 2.5$ and the dash-dotted green line at $r_S = 5.0$) and a charge-density waves is created.
7.2. Wigner crystallization of fully spin-polarized electrons

**Figure 7.4.:** The electron localization function in the presence of the “vanishing” impurity potential ($V_0 = 0.001$ meV) for different values of the interaction parameter. The solid black line corresponds to $r_S = 0.1$, the dashed red line to $r_S = 2.06$, the dotted blue line to $r_S = 2.5$ and the dash-dotted green line to $r_S = 5.0$.

**Figure 7.5.:** Electron density (multiplied by the ring circumference) in the presence of the “vanishing” impurity potential ($V_0 = 0.001$ meV) for different values of the interaction parameter. The solid black line corresponds to $r_S = 0.1$, the dashed red line to $r_S = 2.06$, the dotted blue line to $r_S = 2.5$ and the dash-dotted green line to $r_S = 5.0$. The scale of the vertical axis is chosen such that the oscillations are seen to build up on top of a uniform density.
7. Exact-exchange study of the Wigner crystal transition

Figure 7.6: Wave functions (multiplied by the ring circumference) of the lowest (solid red curve), the fifth (dashed green curve) and the tenth (highest) (dotted blue curve) occupied Kohn-Sham states. Top left: real part of the wave functions for the delocalized system \( r_S = 0.1 \). Top right: real part of the wave functions for the localized system \( r_S = 5.0 \). Bottom left and right: imaginary parts for the delocalized and localized system. In all cases the “vanishing” impurity \( V_0 = 0.001 \text{ meV} \) has been used.

Although there is no direct physical meaning in the Kohn-Sham orbitals, it is nevertheless interesting to see how they change from the delocalized to the localized state. We plot in figure 7.6 the real- and imaginary parts (top and bottom panels, respectively) of three Kohn-Sham orbitals, namely the lowest (solid red curve), the fifth (dashed green curve) and the tenth (i.e. the highest) (dotted blue curve) occupied one, both for the delocalized system with \( r_S = 0.1 \) (left) and the localized system with \( r_S = 5.0 \) (right).

The wave functions for all three considered levels get distorted in the localized system as compared to the delocalized one. The most drastic change is probably that the amplitude of the real part of the wave function corresponding to the highest occupied level (dotted blue curve) diminishes significantly, while some oscillations build up in the real part of the lowest occupied wave function (solid red curve). Still, the wave functions of all three levels cannot be considered as localized to some region, even in the case depicted in the right panel, where the system as a whole is clearly in a localized state. From this simple example we can already conclude that the Kohn-Sham orbitals cannot serve as a criterion to distinguish between the delocalized Fermi liquid and a collectively localized Wigner molecule.

The densities of the three Kohn-Sham orbitals under consideration are plotted in figure 7.7. The top panel shows the densities in the delocalized state (note the scale on the \( y \)-axis), where apart from small oscillations arising from the presence of the impurity potential, the density of each state is evenly spread over the whole system. The situation is different in the localized state (bottom panel), where the density of each of the depicted Kohn-Sham orbitals shows oscillations that remind us of the charge density wave which builds up in the system. The densities of the individual Kohn-Sham orbitals, however, do not correspond to individual electrons localized at the equidistant lattice sites.

From the numerical results discussed so far we can infer that exact-exchange density functional theory indeed describes the formation of a Wigner molecule in the quantum ring. The emergence of this correlated many-electron state can be detected by exclusively resorting to collective variables like the density and the paramagnetic current density. Being a mean-field theory, exact-exchange DFT tends to break the rotational symmetry—which we facilitate by the impurity potential—and map out the internal
7.2. Wigner crystallization of fully spin-polarized electrons

Figure 7.7.: Densities of the lowest (solid red curve), the fifth (dashed green curve) and the tenth (highest) (dotted blue curve) occupied Kohn-Sham states. Top panel: delocalized system \( r_S = 0.1 \). Bottom panel: localized system \( r_S = 5.0 \). In all cases the “vanishing” impurity \( V_0 = 0.001 \) meV has been used.

symmetry of the many-body state [Reimann et al., 1999]. In fact, in the Wigner crystal phase we observe pronounced density oscillations. This corresponds to the emergence of oscillations in the pair-correlation function—which gives insight into the internal structure of a many-body state—on decreasing the density in the quantum ring. Such a result was obtained by Pederiva et al. [2002] using the quantum Monte Carlo method. The decay of the persistent current density is of course a consequence of the pinning of the Wigner molecule and thus of the broken symmetry in the laboratory frame. In a perfectly clean ring with a rotational symmetry the current of the Wigner molecule is exactly the current of the respective non-interacting system [Hamer et al., 1987]. Note that this will not be observable in mean-field theories due to their tendency to break the symmetry. On the other hand, it is the formation of the symmetry-broken state that allows us to obtain information about the collective state directly from the persistent current density.

Flux-dependence of the transition point

So far we have studied the Wigner transition in the quantum ring which is penetrated by a flux of 0.3 flux quanta. But is the critical value \( r_S^c \) of the interaction parameter at which the transition is observed really independent of the flux? Clearly, this should be the case in a clean system (at least if it is not studied using a mean-field approach because we already know that the latter favours symmetry-broken states and thus mimics disorder). This is obvious, since the only influence a magnetic flux has on the clean, interacting system is to change the energy of a state with angular momentum \( M \) as \( M^2 \rightarrow (M - N \frac{\Phi}{\Phi_0})^2 \) \( (N \) is the particle number) leaving the internal structure of the many-body state unaffected [Viefers et al., 2003]. If, however, a weak impurity potential, which breaks the rotational symmetry, is present it may depend on the flux whether it actually pins the Wigner crystal or not. It has been found in exact-diagonalization studies that a pinned Wigner molecule is realized in a quantum ring containing up to three electrons [Chwiej and Szafran, 2009] or in a quantum dot containing up to four electrons [Szafran and Peeters, 2004] at those values of the magnetic field strength where the angular momentum of the ground state changes. The degeneracy (or near degeneracy) of states with different angular momenta allows to form a superposition of these states which results in a broken symmetry of the many-body state. This symmetry-broken state may then be pinned by an arbitrarily weak pinning potential.
To investigate a possible flux-dependence of the transition point in exact-exchange density functional theory, we perform calculations equivalent to those reported for $\Phi = 0.3\Phi_0$ for various values of the magnetic flux. For every value of the flux the persistent current is calculated numerically as a function of the interaction parameter. We do not show the individual resulting plots which are similar to figure 7.2. Instead, for each value of the magnetic flux a critical value of the interaction parameter is determined below which the persistent current is independent of $r_S$ whereas it drops exponentially for $r_S > r_S^c$. The resulting critical values $r_S^c$ are shown as a function of the magnetic flux in figure 7.8. The dots represent the calculated critical values $r_S^c$ which appear to depend quadratically on the flux. A parabola fitted to the data points is shown as the dotted curve.

It is clearly seen that the transition point depends strongly on the magnetic flux. For values of the flux close to zero or to one flux quantum (in general close to an integer number of flux quanta), $r_S^c$ is very small. From the data we can neither confirm nor exclude that it in fact vanishes. In contrast, close to $\Phi = 0.5\Phi_0$ the critical value of the interaction parameter is largest. Note that we cannot estimate $r_S^c$ resorting to the persistent current criterion exactly at $\Phi = 0.5\Phi_0$ since the current of the non-interacting system vanishes at this value of the magnetic flux in a system with an even particle number (see chapter 3). We can qualitatively explain the flux-dependence of $r_S^c$ by looking at the evolution of the non-interacting ground state as we increase the magnetic flux from zero to one flux quantum.

For an even particle number (as in the numerically studied system which contains ten electrons) the non-interacting ground state at zero flux is twofold degenerate. The state with angular momentum $M$ has the same energy as the state with angular momentum $-M$ and therefore any linear combination of the two states is also an eigenstate of the Hamiltonian with the same energy. On the other hand, a state which is a superposition of the states with angular momenta $M$ and $-M$ does not carry a paramagnetic current and since we consider the case of zero flux no diamagnetic current as well. According to our definition, this state is localized even in a non-interacting system. Note that a similar reasoning is true at the level crossing which occurs at $\Phi = \Phi_0$. The paramagnetic current carried by a state which is a superposition of
the states with angular momenta $M$ and $M + N$ is exactly canceled by the respective diamagnetic current and hence the total current vanishes as well at a flux of one flux quantum.

If, however, the ring is threaded by a non-integer number of flux quanta, the degeneracy between levels with different angular momenta is lifted. The difference in kinetic energy between two angular momentum states is largest at half-integer values of the magnetic flux (in units of the flux quantum). This is exactly where we find the largest value of the critical $r_S^c$.

In the delocalized Fermi liquid phase, the density is uniform apart from Friedel oscillations with a very small amplitude. We can thus infer that the delocalized system is (almost) in an angular-momentum eigenstate. In contrast, the localized phase shows pronounced density oscillations and thus has to be a superposition of states with different angular momenta. The increase in kinetic energy due to this superposition depends on the value of the magnetic flux and is largest for a half-integer number of flux quanta. Consequently, a stronger electron-electron interaction should be required to induce the transition from the delocalized to the localized state. This is in qualitative agreement with the numerically calculated dependence of $r_S^c$ on the number of flux quanta. Yet, this qualitative reasoning does not explain the apparently parabolic dependence of $r_S^c$ on the flux.

A brief overview of the Landau theory of second-order phase transitions

From the results presented above we can infer that at the transition point the symmetry of the many-electron density changes from the continuous rotational symmetry present in the Fermi liquid phase to a state with pronounced density oscillations in the Wigner crystal state. Note that we generate the density oscillations by the impurity potential which acts as a source field. Consequently, the Wigner crystal grows from the Friedel oscillations. In the case of the “vanishing” impurity potential this is not visible due to the very small amplitude of the Friedel oscillations (see figure 7.5) but it can nicely be seen if a strong impurity potential is placed in the ring (see figure 7.13). Quite generally, such a transition can be described by the Landau theory of second-order phase transitions. In the following we briefly recapitulate this theory as presented in Landau and Lifschitz [1969]. In the case under study in this thesis, the interaction parameter $r_S$ plays the role of the temperature in the usual thermodynamic theory.

We start by writing the “free energy” $F$ as a function of the interaction parameter and the order parameter $\delta$—a density variation in our case—and expand it around $\delta = 0$ in powers of the order parameter as

$$F(r_S; \delta) = F(r_S; 0) + A(r_S)\delta^2 + B(r_S)\delta^4 + \ldots$$

(7.17)

By symmetry, the expansion contains only even powers of the order parameter (see Landau and Lifschitz [1969]): to lowest order the change in the system’s energy does not depend on whether the system is expanded or compressed, corresponding to a change of the sign of the order parameter.

The second-order coefficient $A(r_S)$ has to vanish at the transition point because in the high-symmetry phase the minimum of $F$ has to correspond to $\delta = 0$ requiring $A > 0$. In contrast, in the low-symmetry phase the minimum corresponds to a nonzero value of the order parameter and thus $A < 0$ is required.

For the system to be in a stable state at the transition point, $F$ as a function of $\delta$ has to assume a minimum at the transition point where $\delta = 0$. This is indeed the case if the fourth order coefficient $B(r_S)$ is positive at the transition point and thus also in the vicinity of the latter.

If we restrict our considerations to those values of the interaction parameter which are close to its value at the transition point, we can expand the second order coefficient

$$A(r_S) \approx a (r_S - r_S^c)$$

(7.18)

to first order in $r_S$ around the critical value $r_S^c$. Note that $a$ has to be negative since the high-symmetry phase, in which $A > 0$, is assumed for $r_S < r_S^c$. To the fourth order coefficient we can assign its value at
the transition point, i.e. $B(r_S^c)$ and the expansion of $F$ reads
\[ F(r_S; \delta) = F(r_S; 0) + a (r_S - r_S^c) \delta^2 + B (r_S^c) \delta^4. \] (7.19)

The order parameter can now be found from the condition that $F$ has a minimum at the transition point, i.e.
\[ \frac{\partial F}{\partial \delta} = 2 \delta \left[ a (r_S - r_S^c) + 2B (r_S^c) \delta^2 \right] = 0. \] (7.20)

In the high-symmetry phase, i.e. $r_S < r_S^c$ the only real-valued solution is $\delta = 0$. In contrast, in the low-symmetry phase the order parameter differs from zero (the solution $\delta = 0$ corresponds to a maximum of $F$) and we find the respective solution of equation (7.20) to be
\[ \delta^2 = \frac{2|a|}{B} (r_S - r_S^c). \] (7.21)

In the low-symmetry phase the order parameter $\delta$ depends on the square root $\sqrt{r_S - r_S^c}$.

What happens if we place the system in some symmetry-breaking external field? In the expansion (7.17) of the “free energy”, the external potential $v$ is taken into account by adding the term $v \delta$ to $F$. After expansion of the second-order coefficient $A(r_S)$ around the transition point $r_S^c$ we obtain the expression
\[ F(r_S; \delta) = F(r_S; 0) + a (r_S - r_S^c) \delta^2 + B (r_S^c) \delta^4 + v \delta \] (7.22)

which is minimized for
\[ 2a \delta (r_S - r_S^c) + 4B (r_S^c) \delta^3 + v = 0. \] (7.23)

It is obvious that the symmetry-breaking field will lead to non-zero values of the order parameter $\delta$ over the whole range of values of the interaction parameter $r_S$. This means that the sharp transition from the high-symmetry phase (for $r_S < r_S^c$) to the low-symmetry phase (for $r_S > r_S^c$), which has been established in the clean system (i.e. without the external field $v$), vanishes. Instead of a distinct transition point characterized by the critical value $r_S^c$ of the interaction parameter, the transition will be smeared over a finite interval of the interaction strength.

### Wigner crystallization as a second-order phase transition

To verify that the Wigner crystal transition is indeed a second-order phase transition we need to identify an order parameter and show that it depends on the square root of the interaction parameter in the low-symmetry phase. Since the order parameter has to vanish identically throughout the high-symmetry phase (thus allowing a clear distinction between both phases), the amplitude of the density oscillations (see figure 7.5) is a natural candidate (one might also consider a particular Fourier component of the density oscillations).

In figure 7.9 we show the dependence of the amplitude of the density oscillations normalized to the average density as a function of the interaction parameter $r_S$. In fact, up to the critical value $r_S^c = 2.05$ the density oscillations are zero.\(^1\) As the interaction parameter exceeds the critical value, density oscillations start to build up and their amplitude follows very well the $\sqrt{r_S - r_S^c}$ behaviour (the dashed red curve in figure 7.9) which has been expected from the Landau theory of the second-order phase transition. Based on this theory we can expect that the clear signatures of the second-order phase transition (the behaviour of the density oscillations as we cross the transition point but also the transition of an $r_S$-independent persistent current to an exponentially decaying one) vanish as we increase the impurity potential strength and thereby break the symmetry of the high-symmetry phase. We will discuss this issue in the remainder of this section.

\(^1\)Note that we have to neglect the small Friedel oscillations due to the “vanishing” impurity potential. These are, nevertheless, much smaller than the scale of the density oscillations displayed in figure 7.9 and would be indistinguishable from zero in the plot.
7.2. Wigner crystallization of fully spin-polarized electrons

Figure 7.9: Amplitude of the density oscillations as a function of $r_S$ for the “vanishing” impurity potential ($V_0 = 0.001$ meV). The solid black curve shows the calculated data, the dashed red curve is a square root $\sqrt{r_S - r_S^c}$ behaviour.

Dependence of the transition on the impurity potential strength

So far we have seen that the electrons undergo a collective localization if we increase the interaction parameter and the resulting Wigner molecule is pinned by the “vanishing” impurity potential. But what happens if we place an impurity with a finite strength in the system? The resulting persistent currents—normalized to the non-interacting current in the presence of the “vanishing” impurity potential—for the Gaussian impurity potential with the strengths $V_0 = 0.001$ meV, $V_0 = 1.0$ meV, $V_0 = 5.0$ meV and $V_0 = 10.0$ meV are plotted in figure 7.10 as functions of $r_S$.

It is not surprising that the persistent current curve is shifted to lower values, compared to the case of a “vanishing” impurity. Even in the non-interacting case, an impurity potential that is not negligible compared to the individual single particle energy eigenvalues (which are of the order of $10^2$ meV) will clearly suppress the persistent current. There is, however, another difference between the curves in figure 7.10 that deserves more attention. For the “vanishing” impurity potential the current stays constant up to the critical value of the interaction parameter and subsequently decays exponentially as $r_S$ is further increased. In contrast, in the presence of a stronger impurity potential we do not find a sharp kink but rather a gradual reduction of the current. For the stronger potentials with $V_0 = 5.0$ meV and $V_0 = 10.0$ meV this gradual decay of the persistent current density sets in well before the transition point in the “clean” system. Only at large values of the interaction parameter, the exponential dependence of the current on $r_S$ is restored even for the two strongest impurity potentials considered (see the logarithmic plot in figure 7.11).

To understand this behaviour of the current, we plot in figure 7.12 the ELF for the system in the presence of an impurity potential with the strength $V_0 = 5.0$ meV. This value of the impurity potential strength is comparable to the average electrostatic energy $U$ between two electrons at a distance given by the average inter-electron distance $d = \frac{L}{N} = 20$ nm, i.e.

$$U = \frac{e^2}{4\pi \varepsilon \varepsilon_0} \frac{1}{d} = 5.75 \text{ meV}.$$  \hspace{1cm} (7.24)
7. Exact-exchange study of the Wigner crystal transition

Figure 7.10.: The persistent current \( j \) normalized to its value in the non-interacting system \( j_0 \) as a function of the interaction parameter \( r_S \) for different strengths of the impurity potential. The dashed line represents the current of the non-interacting system with \( V_0 = 0.001 \text{meV} \), which is independent of \( r_S \).

Figure 7.11.: A logarithmic version of the plot in figure 7.10.
7.2. Wigner crystallization of fully spin-polarized electrons

Figure 7.12.: The electron localization function in the presence of an impurity potential with a strength $V_0 = 5.0$ meV, that is comparable to the typical Coulomb energy per electron in the ring. The ELF is shown for different values of the interaction parameter. The solid black line corresponds to $r_S = 0.1$, the dashed red line to $r_S = 1.5$, the dotted blue line to $r_S = 2.0$, the dash-dotted green line to $r_S = 2.5$ and the long-dashed purple line to $r_S = 5.0$.

The solid black curve corresponds to $r_s = 0.1$ and shows that already in the almost non-interacting system the electron localization function is not a constant. In particular we find two regions in space next to the impurity potential located at $L = 100$ nm, where the electrons are slightly more localized. As we increase the interaction parameter to $r_S = 1.5$ (dashed red line), the electrons already start to localize which is seen from the increasing amplitude of the respective curve in figure 7.12. Note that next to the impurity potential there are two regions in space where the electrons are considerably more localized than in the rest of the system. A possible explanation is provided by the interplay between the short-range impurity potential and the long-range Coulomb potential, both being of the same order: the latter “pushes” the electrons against the impurity potential and thus localizes them. Further increasing the electron-electron interaction then localizes the electrons at the equidistant lattice sites, as in the case of the “vanishing” impurity potential. This is seen in particular from the long-dashed purple line, which corresponds to $r_S = 5.0$ and looks the same as the respective line in figure 7.4 that has been obtained for $V_0 = 0.001$ meV. Of course, for the larger values of the interaction parameter ($r_S = 2.5$ and $r_S = 5.0$), the Coulomb interaction between the electrons overweights the influence of the impurity potential and thus the difference between the system with a “vanishing” impurity potential and the system with a finite one starts to decrease.

The corresponding behaviour can also be seen in the density plot in figure 7.13. Initially for the almost non-interacting system (solid black curve corresponding to $r_S = 0.1$) we find Friedel oscillations that rapidly build up as we increase the interaction parameter. Thus, even if the interaction is very weak, the system is already in the low-symmetry phase. The symmetry-breaking field—which in our case is of course the impurity potential—already lowers the symmetry of the phase that would have been the high symmetry phase (the Fermi liquid) without an impurity (or with the “vanishing” impurity potential). It thus prevents the system from undergoing a second-order phase transition (see Landau and Lifschitz [1969]). Consequently, the sharp kink in the persistent current as a function of $r_S$ is replaced by a gradual localization.
7. Exact-exchange study of the Wigner crystal transition

Figure 7.13.: The electron density in the presence of an impurity potential with a strength $V_0 = 5.0 \text{ meV}$, that is comparable to the typical Coulomb energy per electron in the ring. The density is shown for different values of the interaction parameter. The solid black line corresponds to $r_S = 0.1$, the dashed red line to $r_S = 1.5$, the dotted blue line to $r_S = 2.0$, the dash-dotted green line to $r_S = 2.5$ and the long-dashed purple line to $r_S = 5.0$.

7.3. Spin-dependent Wigner crystallization

So far we have considered the exact-exchange Wigner transition for ten spinless (i.e. fully spin-polarized) electrons. In this section we include the electron spin degree of freedom in our calculations. In particular, we will focus on the differences between the Wigner transition of fully spin-polarized electrons and the Wigner transition of electrons explicitly including the spin degree of freedom. The results in this and the following section were previously presented by Arnold [2009] and are the subject of the publication [Arnold et al., 2010].

The first example we consider is a system of ten electrons with zero total spin, i.e. we consider five spin-up and five spin-down electrons. Analogous to the fully spin-polarized case we calculate the persistent currents of both spin-subsystems as functions of the interaction parameter. The latter refers to the total density and not to the individual spindensities. Interestingly, in the case of five spin-up and five spin-down electrons a spin-dependent impurity potential is required to ensure convergence. This breaking of the spin symmetry—which fixes the magnetic ordering, see below—corresponds to the requirement of some, albeit very small, impurity potential which breaks the spatial symmetry. In the calculations reported in this thesis the spin-up component of the impurity potential was chosen as $V_{0,\uparrow} = 0.001 \text{ meV}$ while the spin-down component was set to zero.

In figure 7.14 we show the persistent currents of the system with five spin-up and five spin-down electrons as functions of the interaction parameter $r_S$. The dotted blue curve shows the persistent current densities of the five spin-up and the five spin-down electrons. Since both spin subsystems contain the same number of electrons, the persistent current curves coincide. Hence the values of the total current density (which is the sum of the current densities of both spin subsystems) are simply twice the respective values of any of the two current densities. The total current density is represented by the dash-dotted black curve in figure 7.14.

As in the fully spin-polarized system we observe that the current density of both spin subsystems are
7.3. Spin-dependent Wigner crystallization

Figure 7.14.: Persistent current densities of five spin-up and five spin-down electrons as functions of the interaction parameter (dotted blue curve). The current densities are normalized to the total current of the non-interacting system. The total current density (i.e. the sum of both current densities)—normalized to its non-interacting value—is represented by the dash-dotted black curve.

In the delocalized phase both spin densities are homogeneously distributed throughout the system (not shown here). As the system starts to localize, spin density oscillations build up. In figure 7.15 the spin density is shown for a value of the interaction parameter of \( r_S = 0.10 \), i.e. in the Wigner crystal phase. The solid blue curve represents the density of the spin-up electrons and the dashed green curve the density of the spin-down electrons. One clearly observes a spin density wave where the local direction of the spin-magnetization is indicated by the black arrows.

The observation of antiferromagnetic ordering in the Wigner crystal phase is supported by the electron localization function shown in figure 7.16. In the Fermi liquid phase (\( r_S = 0.06 \)) the electrons are evenly distributed throughout the system. This is represented by the almost constant electron localization functions as shown by the black and red curve. The very small oscillations can be attributed to Friedel oscillations caused by the impurity potential with \( V_0 = 0.001 \) meV. Note that the ELF slightly deviates from one-half which is a consequence of the finite size of the system. In the Wigner crystal phase (at \( r_S = 0.10 \)), the electron localization functions for both spin subsystems show pronounced oscillations. The solid blue curve represents the ELF for the spin-up electrons and the dashed green curve shows the ELF for the spin-down electrons. The ELF shows that electrons with opposite spin are localized next to each other clearly displaying that in the Wigner crystal phase the electrons show an antiferromagnetic ordering (indicated by the black arrows which show the local direction of the spin-magnetization). Note that this antiferromagnetic ordering is in agreement with exact-diagonalization studies [Reimann et al., 1999] and current-spin density functional theory calculations using the local vorticity approximation [Viefers et al. 2000].
7. Exact-exchange study of the Wigner crystal transition

**Figure 7.15.** Spin density distribution of a system with five spin-up and five-spin down electrons in the Wigner crystal phase. The value of the interaction parameter is $r_S = 0.10$. The solid blue curve represents the density of the spin-up electrons and the dashed green curve the density of the spin-down electrons. The black arrows indicate the local direction of the spin-magnetization clearly showing an antiferromagnetic ordering.

**Figure 7.16.** Electron localization function for five spin-up and five spin-down electrons. The black and the red curve show the ELF of the spin-up and spin-down electrons, respectively, in the electron liquid ($r_S = 0.06$). The deviation from 0.5 is a finite size effect. The solid blue curve shows the ELF for the spin-up electrons and the dashed green curve shows the ELF for the spin-down electrons. Both the blue and the green curve correspond to the Wigner crystal phase with $r_S = 0.10$. The black arrows indicate the local value of the spin-magnetization clearly signaling antiferromagnetic ordering.
One more interesting situation is provided by a system with a nonzero spin magnetization. As an example we consider a system with eight spin-up and two spin-down electrons. Figure 7.17 shows the persistent current densities of the eight spin-up electrons (solid green curve) and the two spin-down electrons (dotted blue curve). The total current density is shown as the dash-dotted black curve and all current densities are normalized to the non-interacting value of the total current density. For small values of the interaction parameter, both current densities are constant (and hence also the total current density). On increasing the interaction parameter first the two spin-down electrons start to localize as signaled by the decay of the dotted blue curve. The localization of these two electrons gives rise to an increasingly strong electrostatic Hartree potential which in turn not only pins the other eight electrons but also washes out their localization transition. This behaviour is similar to the lack of a sharp transition in the presence of a strong pinning potential as discussed previously for ten fully spin-polarized electrons.

The evolution of the spin densities while the system undergoes subsequently the Wigner transition of the two spin-down electrons and the eight spin-up electrons is displayed in figure 7.18, where the solid green line corresponds to the eight spin-up electrons and the dotted blue line corresponds to the two spin-down electrons. The top panel shows both spin subsystems in the delocalized liquid phase. This corresponds to the top panel in figure 7.19 which shows the electron localization functions of the two spin-down electrons (dotted blue curve) and the eight spin-up electrons (solid green curve). In the liquid state the ELF is a constant for both spin subsystems. Note that the value of the ELF for the two spin-down electrons differs from one-half. This is due to the low particle number and can be considered a finite size effect.

The central panels in figures 7.18 and 7.19 show the system in a state where the two spin-down electrons have already undergone the Wigner transition. This is signaled by the two density maxima (dotted blue curve in central panel in figure 7.18) and the two localized electrons in the ELF plot (dotted blue curve in central panel in figure 7.19). In contrast, the eight spin-up electrons are still in the Fermi liquid phase as can be seen from the ELF plot. The two density minima seen in the solid green curve in the central panel
Figure 7.18.: Spin densities for two spin-down electrons (dotted blue curve) and eight spin-up electrons (solid green curve). The top panel shows the system in the delocalized state ($r_S = 0.08$). In the central panel ($r_S = 0.10$) the two spin-down electrons are localized while the eight spin-up electrons are still in the liquid phase. In the bottom panel ($r_S = 0.20$) both spin subsystems are localized.

in figure 7.18 appear due to the electrostatic Hartree repulsion of the eight spin-up electrons by the two localized spin-down electrons.

The completely localized system (at $r_S = 0.2$), where both the two spin-down and the eight spin-up electrons have undergone the Wigner transition, is shown in the bottom panels in figures 7.18 and 7.19. From the density plot we can infer a spin-ordering of the eight spin-up electrons between the two spin-down electrons. The ELF plot in figure 7.19 shows a similar picture. Note that the ELF signals a localization of the two spin-down electrons in a region which overlaps with the region where the adjacent spin-up electrons are localized. As can be seen from figure 7.18 this does not mean, however, that the densities of any of the two spin-down electrons overlaps significantly with the density of the spin-up electrons. This behaviour of the ELF is understandable from its very definition since the ELF measures the probability of finding a like-spin electron close to the reference electrons and does not carry any information (apart from that contained in the wave function which is in exact-exchange theory purely due to a classical electrostatic repulsion) about the subsystem with the opposite spin projection.

Dependence of the transition on the effective width of the ring

We have modeled the quasi one-dimensional quantum ring as a strictly one-dimensional system with a modified Coulomb interaction

$$V_{1D}^{1D}(x, x') = \frac{e^2}{4\pi\epsilon\epsilon_0 \min(|x - x'|^{-1}, a^{-1})}.$$  \hspace{1cm} (7.25)

While $V_{1D}^{1D}(x, x')$ resembles the usual $1/|x - x'|$-behaviour for large distances, it is cut off at distances smaller than $a$. The parameter $a$ is usually understood as the effective width of the ring (see the discussion and the related references in section 7.1).

Since the parameter $a$ enters the Hartree energy in the same way as the exchange energy, the Wigner transition of the system of fully spin-polarized electrons is unaffected by the choice of $a$. In contrast, in
7.3. Spin-dependent Wigner crystallization

![Graph showing electron localization function for two spin-down electrons (dotted blue curve) and eight spin-up electrons (solid green curve).](image)

Figure 7.19: Electron localization function for two spin-down electrons (dotted blue curve) and eight spin-up electrons (solid green curve). The top panel shows the system in the delocalized state ($r_S = 0.08$). The ELF for the two spin-down electrons differs significantly from one-half due to the low-particle number. The central panel ($r_S = 0.10$) shows the two localized spin-down electrons while the eight spin-up electrons are still in the liquid phase. In the bottom panel both spin subsystems are localized ($r_S = 0.20$).

In the spin-dependent system all electrons contribute to the Hartree potential while the exchange potential contains only contributions from the electrons with parallel spin. In the Wigner crystal phase electrons with opposite spin are situated next to each other.\(^2\) In exact-exchange theory the electrons with opposite spin interact only via the electrostatic Hartree repulsion. As a consequence the transition point acquires a dependence on the effective width of the ring. Numerical results are shown in table 7.1.

Table 7.1: Dependence of the critical value of the interaction parameter on the effective width $a$ (in units of the numerical lattice spacing which is 0.37 nm) of the quasi one-dimensional ring for different values of the total spin magnetic moment $M_S$

<table>
<thead>
<tr>
<th>$M_S$</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a = 0.05$</td>
<td>0.039</td>
<td>0.061</td>
<td>0.055</td>
<td>0.057</td>
<td>0.041</td>
<td>2.05</td>
</tr>
<tr>
<td>$a = 0.1$</td>
<td>0.062</td>
<td>0.099</td>
<td>0.088</td>
<td>0.090</td>
<td>0.064</td>
<td>2.05</td>
</tr>
<tr>
<td>$a = 1.0$</td>
<td>0.14</td>
<td>0.21</td>
<td>0.18</td>
<td>0.18</td>
<td>0.12</td>
<td>2.05</td>
</tr>
</tbody>
</table>

Except in the fully spin polarized system ($M_S = 5$)—where the transition point is independent of the effective width—the critical $r_S$ value decreases with a decreasing width of the ring. This result, which signifies that the Wigner molecule is formed the easier the more one-dimensional the system is, is in agreement with the results of a quantum Monte Carlo study of quasi one-dimensional quantum wires. Using a modified Coulomb interaction similar to the one employed in the present work, Shulenburger

\(^2\)Provided that the number of spin-up electrons equals the number of spin-down electron. Otherwise the electrons are distributed such that the electrons of the spin subsystem with the lower particle number are maximally separated: the electrons show ferrimagnetic ordering.
et al. [2008] found that a Wigner crystal forms in the quantum wire at higher densities as the width of the wire is decreased.

As expected, the dependence of the transition point on the effective width is most pronounced for $M_S = 0$ where the five spin-up and the five spin-down electrons show perfect antiferromagnetic ordering. Note again the small critical values of the interaction parameter in the spin-dependent case. The pronounced dependence of the transition point on the width of the ring—which is only seen in the spin-dependent case—also suggests a possible explanation for the very small critical values of the interaction parameter. In the fully spin-polarized case all electrons contribute to both the repulsive Hartree potential and the attractive exchange potential. In contrast, in the spin-dependent case only like-spin electrons contribute to the exchange potential whereas all electrons build up a common Hartree potential. Since the total Coulomb potential is the sum of the Hartree and the exchange potential, the Coulomb energy of spin-dependent electrons (in a system with the same total $r_S$) will be higher than the Coulomb energy of fully spin-polarized electrons. At the same time, the average kinetic energy per electron is lower in the spin-dependent case because two electrons with opposite spin are allowed to be in the same orbital state. We can thus expect that the Coulomb energy will become dominant at lower values of the interaction parameter as compared to the fully spin-polarized system. Consequently, the critical values $r_S^c$ should be smaller in the spin-dependent case. Yet, it remains questionable whether these arguments alone can explain the very small critical values of the interaction parameter and it seems plausible that there is also a relation to the flux-dependence of the transition point observed for the fully spin-polarized electrons. We explained this flux-dependence by the energy it costs to build a pinned Wigner molecule as a mixture of different angular momentum eigenstates. The energetic difference between different angular momentum eigenstates that may contribute to the formation of the Wigner molecule is, however, not only determined by the magnetic flux but depends also on the number of electrons and is thus affected by taking into account the electrons’ spin while keeping their number fixed.

### 7.4. Magnetization and structure of the ground state

We have so far discussed the spin-dependent Wigner crystallization fixing the total spin magnetic moment. To find the total spin and the structure of the ground state we perform self-consistent calculations for all admissible values of the total spin at various values of $r_S$. Obviously, the ground state at every $r_S$ value is the state with the lowest total energy. Whether the ground state is a Wigner molecule or a Fermi liquid is determined using the persistent current criterion.

In figure 7.20 we show the results of the calculations for six representative values of the interaction parameter. All calculations were done at a flux of $\Phi = 0.3 \Phi_0$ and in a ring with an effective width of $a = 0.1$ (in units of the numerical lattice spacing which is 0.37 nm). At high densities the ground state is an unpolarized Fermi liquid which is superseded by a Wigner molecule with antiferromagnetic spin-ordering at $r_S = 0.052$. Further increasing the interaction parameter we find that the Wigner molecule is stable up to $r_S = 0.198$. Its total spin magnetic moment is always zero and we always find the aforementioned antiferromagnetic ordering. At even larger $r_S$ values the ground state is a fully polarized ($M_S = 5$) Fermi liquid until it is superseded by a fully polarized Wigner molecule at $r_S = 2.05$. Converged spin-dependent calculations were possible up to $r_S = 1.01$ and the critical $r_S$ value for the transition from the fully polarized Fermi liquid to the fully polarized Wigner molecule has been obtained from the fully spin-polarized calculation reported earlier in this chapter. These results are summarized in table 7.2.

Due to the Pauli principle the kinetic energy is minimal if the total spin (of a system with an even number of electrons) is zero. Since in a weakly interacting system the kinetic energy is the most important contribution to the ground state energy it is understandable that we find an unpolarized Fermi liquid for small $r_S$ values. Our result is in agreement with results obtained using different methods such as the
7.4. Magnetization and structure of the ground state

Figure 7.20.: Ground state energy as a function of the total spin for different values of the interaction parameter (the lines are a guide to the eye). Top left panel: the ground state at $r_S = 0.060$ is an unpolarized Fermi liquid. Top right panel: the ground state at $r_S = 0.191$ is a Wigner crystal with antiferromagnetic order. Central left panel: the ground state at $r_S = 0.197$ is a Wigner crystal with antiferromagnetic order. Central right panel: the ground state at $r_S = 0.199$ is a fully polarized Fermi liquid. Bottom left panel: the ground state at $r_S = 0.201$ is a fully polarized Fermi liquid. Bottom right panel: the ground state at $r_S = 0.251$ is a fully polarized Fermi liquid. All calculations were done at a flux of $\Phi = 0.3\Phi_0$ and in a ring with an effective width of $a = 0.1$ (in units of the numerical lattice spacing which is $0.37 \text{ nm}$).

In view of the results presented in the previous section it comes as no surprise that the Fermi liquid state is superseded by a Wigner crystal state as the strength of the electron-electron interaction is increased. Both the emergence of the correlated state and its antiferromagnetic ordering are in agreement with “exact” calculations. The spatial correlation of the electrons has also been found in quantum Monte Carlo calculations [Pederiva et al., 2002; Emperador et al., 2003] and in exact-diagonalization studies [Liu et al., 2006, 2008]. Using the configuration-interaction method, Koskinen et al. [2001] found that the ground state of a quasi one-dimensional quantum ring can often be understood as a rotating Wigner molecule with antiferromagnetic spin ordering.

Surprisingly, as the interaction parameter is increased further, a fully polarized Fermi liquid state becomes the ground state. The formation of a fully polarized ground state is in agreement with the result from Hartree-Fock calculations [Bellucci and Onorato, 2009]. Both the Hartree-Fock method and exact-exchange SDFT emphasize the exchange contribution and thus are expected to favour a fully polarized ground state in the strongly interacting system. Interestingly, the inclusion of first-order correlations beyond the Hartree-Fock was found to have an effect only at those $r_S$ values where the transition from one ground state to the next one occurs and in particular leads to the same fully polarized ground state at large $r_S$ values [Bellucci and Onorato, 2009]. The possible existence of fully spin-polarized ground states in the strongly interacting system is also supported by “exact” calculations. Pederiva et al. [2002] reported results from a quantum Monte Carlo study of a six-electron quantum ring which indicate that at large $r_S$...
values states with different total spin (including the fully polarized state) become almost degenerate with the ground state. Similarly, Saiga et al. [2007] found in an exact-diagonalization study of quantum rings with up to five electrons that states with different total spin became degenerate with the ground state as the density was lowered by increasing the ring circumference. Although in these calculations the fully polarized state was never the unique ground state it is understandable that among the different degenerate (or nearly degenerate) states exact-exchange SDFT selects the fully polarized one due to its emphasized exchange contribution to the total energy.

Since the exchange energy is negative and contains only contributions from electrons with parallel spin the total Coulomb energy in the fully spin-polarized system is reduced as compared to the unpolarized case. Simultaneously, the total kinetic energy increases due to the Pauli principle because in the fully polarized system all electrons are in the same spin state. The combination of both effects—a reduced Coulomb energy and an increased kinetic energy—lead to the transition from a Wigner molecule to a fully spin-polarized Fermi liquid as the interaction parameter is increased beyond $r_S = 0.198$. Converged calculations were performed for $r_S$ values up to 1.01. Although we cannot strictly exclude the emergence of a ground state different from the fully polarized Fermi liquid our previously reported results for the fully spin-polarized quantum ring indicate that finally at $r_S = 2.05$ the fully spin-polarized Fermi liquid state will be superseded by a fully polarized Wigner molecule.

### 7.5. KLI versus OEP study of collective electron localization

In the first part of this chapter we have studied the Wigner localization of ten spinless (i.e. fully spin-polarized) electrons as well as the spin-dependent Wigner localization using the KLI approximation to the OEP equation. It is widely believed that the KLI approximation yields ground state results very close to the OEP results. Recently, however, it has been demonstrated by Kümmel et al. [2004], that the polarizabilities in a hydrogen chain computed from the KLI approximation are far worse than those obtained from a solution of the full OEP equation. This shortcoming of the KLI approximation has been attributed to a field-counteracting term only weakly present in the KLI potential. In view of this we will discuss the Wigner transition in the exact-exchange OEP formalism. Since the iterative calculation of the exact-exchange potential in each iteration step of the Kohn-Sham system is already computationally expensive we restrict our considerations to the fully spin-polarized case.

#### Iterative solution of the OEP equation: calculation of the orbital shifts

We begin our study of the Wigner transition in exact-exchange theory with a discussion of the iterative construction of the exact-exchange potential. We employ the method by Kümmel and Perdew [2003b] (see chapter 5), yet the calculation of the orbital shifts is done in a different way which proved to be
simple and efficient. In each iteration step of the self-consistent solution of the Kohn-Sham equation we first determine the KLI potential from the presently occupied Kohn-Sham orbitals \( \phi_k(x) \). Using the KLI potential as a first approximation for \( V_x \), we calculate the orbital shifts

\[
\psi_k(x) = \sum_{j \neq k} \frac{\phi_j(x)}{\varepsilon_j - \varepsilon_k} \int dx' \left( V_x(x') - u_k^*(x') \right) \phi_k(x') \phi_j^*(x').
\] (7.26)

In principle they can be calculated directly from the definition given above. This, however, involves the evaluation of the matrix elements

\[
\int dx' \left( V_x(x') - u_k^*(x') \right) \phi_k(x') \phi_j^*(x')
\] (7.27)

between occupied and unoccupied states and subsequent summation over all states (including unoccupied states) which makes the calculation computationally expensive.

Another possibility to calculate the orbital shifts is to use the differential equation (5.20), which results when operating with \( \hat{H}_{\text{KS}} - \varepsilon_k \) on the orbital shift \( \psi_k \),

\[
\left( \hat{H}_{\text{KS}} - \varepsilon_k \right) \psi_k(x) = - \left[ V_x(x) - u_k(x) - \left( V_{\text{xc}}^k - \bar{u}_k \right) \right] \phi_k(x).
\] (7.28)

The right-hand side is readily evaluated for a given \( V_x \) and for a given set of Kohn-Sham orbitals, i.e. the eigenfunctions of the Kohn-Sham Hamiltonian \( \hat{H}_{\text{KS}} \) with the eigenvalues \( \varepsilon_k \), which determine the orbital potentials \( u_k \). Yet, the operator \( \hat{H}_{\text{KS}} - \varepsilon_k \) cannot be inverted straight away, since there exists at least (in the case of non-degenerate Kohn-Sham eigenvalues) one non-trivial function \( \phi_k \) which is mapped onto zero by this operator. Of course, this function is precisely the Kohn-Sham orbital \( \phi_k \) with the energy eigenvalue \( \varepsilon_k \). Since the Kohn-Sham orbitals, being eigenfunctions of a Hermitian operator, form a complete basis, we can expand the orbital shift in the basis of the Kohn-Sham orbitals as

\[
\psi_k(x) = \sum_j c_j^k \phi_j(x)
\] (7.29)

with the expansion coefficients \( c_j^k \). However, being the first order perturbation of the Kohn-Sham orbital \( \phi_k \), the orbital shift \( \psi_k \) is orthogonal to \( \phi_k \) and—in the case of degeneracy—to all Kohn-Sham orbitals with the same energy eigenvalue. We therefore already know that this particular Kohn-Sham orbital—or these particular Kohn-Sham orbitals in the case of degeneracy—will not contribute to the orbital shift and we can thus exclude the respective subspace when inverting the operator \( \hat{H}_{\text{KS}} - \varepsilon_k \).

In a practical calculation using a basis set (see appendix A), the operator \( \hat{H}_{\text{KS}} - \varepsilon_k \) will be a matrix with one or more zero eigenvalues. A numerically feasible scheme to invert this matrix, together with the condition that the orbital shift \( \psi_k \) is orthogonal to all Kohn-Sham orbitals with the energy eigenvalue \( \varepsilon_k \), is the singular value decomposition [Press et al., 1996]. For our purpose it is sufficient to consider a square \( N_X \times N_X \) matrix \( \bar{A} \) (\( N_X \) will be the number of basis functions and thus determine the size of the Hamilton matrix). Now without actually proving it—which would be far beyond the scope of this thesis—we state the following theorem:

Any complex \( N_X \times N_X \) matrix \( \hat{A} \) can be written as a product of an \( N_X \times N_X \) unitary matrix \( \hat{U} \), a diagonal \( N_X \times N_X \) matrix \( \hat{W} \) and the Hermitian conjugate of an \( N_X \times N_X \) unitary matrix \( \hat{V} \):

\[
\hat{A} = \hat{U} \cdot \hat{W} \cdot \hat{V}^\dagger.
\]

The vanishing diagonal elements of the matrix \( \hat{W} \) are called the singular values.
If the matrix to be inverted would not have any singular values—i.e. if it were invertible—then we could easily find its inverse as

\[ \hat{A}^{-1} = \hat{V}^{-1} \cdot \hat{W}^{-1} \cdot \hat{U}^{-1}, \]  

(7.30)

where the inverse of a unitary matrix is simply its Hermitian conjugate (\( \hat{V}^{-1} = \hat{V}^\dagger \) and \( \hat{U}^{-1} = \hat{U}^\dagger \)) and the inverse of a diagonal matrix is again a diagonal matrix with the inverse elements. In our case, however, one or more of the elements of the diagonal matrix \( \hat{W} \) are zero, the number of singular values depending on the number of (degenerate) Kohn-Sham orbitals with the same energy eigenvalue \( \varepsilon_k \). The computation of the “best” inverse of the matrix \( \hat{H}_{\text{KS}} - \varepsilon_k \) now proceeds as follows: First, we calculate the singular value decomposition of the matrix \( \hat{H}_{\text{KS}} - \varepsilon_k \), for instance by using the ZGESVD-routine from the LAPACK library [Anderson et al., 1999]. Next, we can easily compute the inverse of the matrices \( \hat{V}^\dagger \) and \( \hat{U} \) by Hermitian conjugation. To find the inverse of the diagonal matrix \( \hat{W} \), we distinguish two possible cases for any of its diagonal values: either it is non-zero—or numerically sufficiently large—then we use its inverse value for the respective entry in the matrix \( \hat{W}^{-1} \), or it is zero—or numerically close to zero—then we replace the respective entry in the matrix \( \hat{W}^{-1} \) by zero. The latter choice might seem a very drastic one, but remember that all Kohn-Sham orbitals with the energy \( \varepsilon_k \) are orthogonal to the orbital shift \( \psi_k \) and hence do not contribute to the orbital shift. With this “appropriate” inverse matrix we can now act on the right-hand side of equation (7.28) to determine the orbital shift.

Inserting the latter ones calculated with the approximate exchange potential into the OEP equation yields the residual function

\[ S_V(x) = \sum_{k=1}^{N} \psi_k^*(x) \phi_k(x) + \text{c.c.} \]  

(7.31)

which measures the deviation of the presently used approximation for the exact-exchange potential from the correct solution of the OEP equation. A better approximation of \( V_x \) is then obtained by adding the residual function (multiplied by a constant \( \gamma \) for which we chose the numerical value of \( \gamma = 2 \)) to the approximate exchange potential

\[ V_x(x) \rightarrow V_x(x) + \gamma S_V(x). \]  

(7.32)

We have checked that this scheme can be iterated to find the exact-exchange potential which is the solution of the OEP equation (i.e. it corresponds to \( S_V(x) \equiv 0 \)). As it measures the error of the approximate exchange potential, the residual function \( S_V(x) \) can directly be used as the convergence criterion for the iterative construction of the exact-exchange potential. In our numerical calculation we consider this iteration to be converged if

\[ \max_x |S_V(x)| < 10^{-5}. \]  

(7.33)

In the Fermi liquid phase, where the density is uniform apart from very weak Friedel oscillations, the iterative solution of the OEP equation converges to the desired accuracy in typically five to six steps. In contrast, in the Wigner crystal phase the inhomogeneous density significantly complicates the iterative solution requiring between fifty and seventy iteration cycles.

**Exact-exchange study of the Wigner crystallization**

Using the iterative procedure described above we solve the problem of ten spinless—or fully spin-polarized—electrons on the quasi one-dimensional quantum ring in the framework of exact-exchange DFT. To pin the Wigner molecule we place a repulsive Gaussian impurity potential with a strength \( V_0 = 0.001 \) meV in the ring and induce a persistent current with a magnetic flux \( \Phi = 0.3 \Phi_0 \).

In figure 7.21 we compare the dependence of the persistent current density on the interaction parameter as obtained from the iterative solution of the OEP equation with the previously discussed result from the KLI calculation. We clearly see that both current densities coincide for small values of the interaction
7.5. KLI versus OEP study of collective electron localization

As we increase the latter the OEP current density drops significantly earlier than the KLI current density which signals that the exact-exchange OEP method predicts Wigner crystallization at considerably higher densities than the KLI approximation. For \( r_S > 2 \) converged data points could not be obtained from the exact-exchange OEP calculation. On the other hand there is no reason to believe that the current density should not go to zero in the exact-exchange OEP on further increasing the interaction parameter.

The question that arises at this point is why the OEP predicts a localization at higher densities than the KLI approximation does. An answer to this question is provided by figure 7.22 which shows the difference between the OEP and the KLI exchange potentials in the Wigner crystal phase at \( r_S = 2.0 \). Note that the difference is positive at density minima, i.e. the OEP yields potential barriers which are higher than the KLI potential barriers thus favouring stronger the separation between the electrons. In the Fermi liquid phase, the difference between the OEP exchange potential and the KLI exchange potential is much smaller (not shown here). Nevertheless, the OEP exchange potential drives the system slightly stronger to the Wigner crystal than the KLI exchange potential does.

It has been pointed out in the literature [Kümmel and Kronik, 2008] that this difference between the KLI exchange potential and the OEP exchange potential cannot be attributed to the self-interaction error which should try to delocalize the electrons. The self-interaction correction is related to a cancellation of the self-interaction in the Hartree term by the exchange-correlation functional used which is the exact-exchange functional in both the KLI and the OEP calculation. In particular, already the Slater potential provides the full self-interaction correction.

We conclude this section noting that our result agrees well with results found in the hydrogen chain mentioned above. Kümmel et al. [2004] found that the barriers between the hydrogen atoms are considerably higher in an exact-exchange OEP calculation than in the exact-exchange KLI approximation. In the hydrogen chain this difference between OEP and KLI does not manifest itself in the unperturbed ground state since the electron density is low between the atoms (or hydrogen dimers) where the KLI and
7. Exact-exchange study of the Wigner crystal transition

Figure 7.22.: Difference between the OEP and the KLI exchange potential as a function of the coordinate along the ring. The plot refers to a system in the Wigner crystal phase at $r_S = 2.0$.

The OEP exact exchange potentials differ. This can of course be explained by the fact that the external potential due to the hydrogen nuclei predominantly determines the electron density. In contrast, having in our case a purely electronic system without atomic nuclei, the same behaviour of the potential barriers leads eventually to different ground states: a Wigner molecule in OEP in contrast to a Fermi liquid in KLI.
Part II.

Exact-exchange current-density functional theory: gauge invariance and violation of the continuity equation in the Krieger-Li-lafrate type approximation
8 From density to current-density functional theory

As a consequence of the Hohenberg-Kohn theorem, we can determine all ground state properties of an interacting many-electron system from the knowledge of its density. The Kohn-Sham scheme provides a practical tool to determine the latter. This notion is still true in the presence of a magnetic field, albeit in this case all ground state properties depend parametrically on the external magnetic field. So why should we introduce another basic variable, which is, in the context of current-density functional theory, the paramagnetic current density? Following Vignale [1993], one can give essentially two answers to this question. First, explicitly including the paramagnetic current density as the variable conjugate to the magnetic field provides more flexibility in constructing approximations to the exchange-correlation functional. As an example, consider that we would try to construct a local approximation, where the density and the current density are at each point in space related as in the homogeneous electron gas. This would mean that the current vanishes everywhere, which is not true in the inhomogeneous system. The second reason, which is more important for the problem discussed in this thesis, is that the density determines the ground state properties only in principle. For instance, the paramagnetic current density is a functional of the density $j_p = j_p[n]$. However, in practice this functional is not known. Yet, if we minimize the energy functional not only with respect to the density but also with respect to the paramagnetic current density, then we can determine both the density and the paramagnetic current density (and hence the full physical current density) of the interacting system directly from the Kohn-Sham orbitals. The only approximation in this scheme is the one used for the exchange-correlation functional.

In this chapter, we will first introduce the energy functional and the Kohn-Sham equation in current-spin density functional theory. The derivation of the formalism will be succeeded by a discussion of the gauge invariance of the theory and its relation to the continuity equation. Our discussion will closely follow the seminal work by Vignale and Rasolt [1988].

8.1. The Kohn-Sham equation in current-density functional theory

We consider a many-electron system in the presence of an external electrostatic potential $V_{\text{ext}}(r)$ and an external magnetic field

$$\mathbf{B}_{\text{ext}}(r) = \nabla \times \mathbf{A}_{\text{ext}}(r).$$  \tag{8.1}

Following Vignale and Rasolt [1988], we restrict the discussion to the collinear approximation,\(^1\) where the coupling of the external magnetic field to the electron spin is incorporated into the spin-dependent external potential $V_{\text{ext},\sigma}$ defined in equation (4.47). Including the coupling of the orbital degrees of freedom to the

\(^1\)For an extension to the non-collinear case see e.g. Pittalis et al. [2006].
external vector potential, the Hamiltonian reads

\[
\hat{H} = \hat{H}_0 + \sum_{\sigma = 1, \downarrow} \int d^3r \ n_{\sigma}(r)V_{\text{ext,}\sigma}(r)
\]

+ \sum_{\sigma = 1, \downarrow} e \int d^3r \ \hat{j}_{p,\sigma}(r) \cdot \mathbf{A}_{\text{ext}}(r)

+ \sum_{\sigma = 1, \downarrow} \frac{e^2}{2m_0} \int d^3r \ n_{\sigma}(r)A_{\text{ext}}^2(r),
\]

with the operator of the paramagnetic current density given by

\[
\hat{j}_{p,\sigma}(r) = \frac{\hbar}{2m_0} \left[ \hat{\Psi}_\sigma^\dagger(r) \nabla \hat{\Psi}_\sigma(r) - \left( \nabla \hat{\Psi}_\sigma^\dagger(r) \right) \hat{\Psi}_\sigma(r) \right],
\]

\(\hat{n}_{\sigma}(r) = \hat{\Psi}_\sigma^\dagger(r)\hat{\Psi}_\sigma(r)\) denotes the spin density operator and \(\hat{H}_0\) is the Hamiltonian of the interacting system in the absence of the external fields. Extending the Hohenberg-Kohn theorem to include the paramagnetic current density as a second basic variable (in addition to the density or, as in the case under discussion here, the spin densities), Vignale and Rasolt [1988] showed that knowledge of the spin density \(n_{\sigma}(r)\) and the paramagnetic current density \(j_{p,\sigma}(r)\) uniquely determines the ground state wave function \(\Psi\). The proof proceeds by reductio ad absurdum, exactly as the original proof of the Hohenberg-Kohn theorem and thus shall not be repeated here (for the proof of the Hohenberg-Kohn theorem in density functional theory refer to section 4.1). There is, however, one striking difference that has already been noticed when going from density to spin density functional theory. While the densities determine the ground state wave function (uniquely if the ground state is non-degenerate, otherwise any member of the set of degenerate ground state wave functions can be obtained), they do not uniquely determine the potentials. This ambiguity, which is known as the non-uniqueness problem, has been analyzed for current-spin density functional theory by Capelle and Vignale [2002] and on a more general basis by Capelle et al. [2007]. Still, invoking the mapping between the densities and the wave function, one can define the energy functional

\[
E[n_{\sigma}, j_{p,\sigma}] = Q[n_{\sigma}, j_{p,\sigma}] + \sum_{\sigma = 1, \downarrow} \left[ \int d^3r \ n_{\sigma}(r)V_{\text{ext,}\sigma}(r) \right.
\]

\(\left. + e \int d^3r \ \hat{j}_{p,\sigma}(r) \cdot \mathbf{A}_{\text{ext}}(r) + \frac{e^2}{2m_0} \int d^3r \ n_{\sigma}(r)A_{\text{ext}}^2(r) \right] \).

The universal functional \(Q[n_{\sigma}, j_{p,\sigma}]\) is understood in the sense of the constrained search formalism, where the search runs over all \(N\)-particle wave functions \(\Psi\) that yield the densities \(n_{\sigma}\) and \(j_{p,\sigma}\). Employing the variational principle, it can now be shown [Vignale and Rasolt, 1988] that the energy functional assumes its minimum at the ground state spin density and paramagnetic current density. This minimum value equals the ground state energy.

Again, as in the case of density and spin density functional theory, the minimization of the energy functional with respect to the densities is formally equivalent to the solution of a single-particle Schrödinger equation

\[
\left[ \frac{1}{2m_0} (-i\hbar \nabla + eA_{k,\sigma}(r))^2 + V_{S,\sigma}(r) \right] \phi_{k,\sigma}(r) = \epsilon_{k,\sigma}\phi_{k,\sigma}(r)
\]

with the yet to be determined effective potentials \(A_{S,\sigma}(r)\) and \(V_{S,\sigma}(r)\). Following Vignale and Rasolt [1988], we first decompose the functional \(Q[n_{\sigma}, j_{p,\sigma}]\) into the non-interacting kinetic energy \(T_S\), the electrostatic Hartree energy \(E_{\text{HI}}\) and the exchange-correlation energy \(E_{\text{xc}}\) as

\[
Q[n_{\sigma}, j_{p,\sigma}] = T_S[n_{\sigma}, j_{p,\sigma}] + E_{\text{HI}}[n] + E_{\text{xc}}[n_{\sigma}, j_{p,\sigma}].
\]
The non-interacting kinetic energy

\[ T_S[n_\sigma, j_{p,\sigma}] = \Phi[n_\sigma, j_{p,\sigma}] - \frac{\hbar^2}{2m_0} \nabla^2 \Phi[n_\sigma, j_{p,\sigma}] \],

(8.7)
can be expressed in terms of the densities and the eigenvalues \( \varepsilon_{k,\sigma} \). \( \Phi[n_\sigma, j_{p,\sigma}] \) is a Slater determinant of non-interacting orbitals \( \phi_{k,\sigma} \) \( (k = 1, \ldots, N_\sigma) \) which yield the spin density \( n_\sigma \) and the paramagnetic current density \( j_{p,\sigma} \). We multiply equation (8.5) by \( \phi_{k,\sigma}^*(\mathbf{r}) \) from the left, integrate over \( \mathbf{r} \) and sum over \( k \) and \( \sigma \) to obtain:

\[
T_S[n_\sigma, j_{p,\sigma}] = \sum_{\sigma=\uparrow,\downarrow} \sum_{\sigma=\downarrow} \varepsilon_{k,\sigma} - \int d^3r n_\sigma(\mathbf{r}) V_{S,\sigma}(\mathbf{r}) \\
- e \sum_{\sigma=\uparrow,\downarrow} \int d^3r j_{p,\sigma}(\mathbf{r}) \cdot A_{S,\sigma}(\mathbf{r}) \\
- \frac{e^2}{2m_0} \sum_{\sigma=\uparrow,\downarrow} \int d^3r n_\sigma(\mathbf{r}) A_{S,\sigma}(\mathbf{r}).
\]

Inserting this expression, together with

\[ E_{\text{H}}[n] = \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \int \int d^3r d^3r' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \]

(8.9)

\( (n(\mathbf{r}) = n_\uparrow(\mathbf{r}) + n_\downarrow(\mathbf{r}) \), into the energy functional (8.4), we obtain the following functional which has to be minimized with respect to \( n_\sigma \) and \( j_{p,\sigma} \):

\[
E[n_\sigma, j_{p,\sigma}] = \sum_{\sigma=\uparrow,\downarrow} \sum_{\sigma=\downarrow} \varepsilon_{k,\sigma} + \int d^3r n_\sigma(\mathbf{r}) \left[ V_{\text{ext},\sigma}(\mathbf{r}) - V_{S,\sigma}(\mathbf{r}) \right] \\
+ e \sum_{\sigma=\uparrow,\downarrow} \int d^3r j_{p,\sigma}(\mathbf{r}) \cdot \left[ A_{\text{ext}}(\mathbf{r}) - A_{S,\sigma}(\mathbf{r}) \right] \\
+ \frac{e^2}{2m_0} \sum_{\sigma=\uparrow,\downarrow} \int d^3r n_\sigma(\mathbf{r}) \left[ A_{\text{ext}}^2(\mathbf{r}) - A_{S,\sigma}^2(\mathbf{r}) \right] \\
+ \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \int \int d^3r d^3r' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{\text{xc}}[n_\sigma, j_{p,\sigma}].
\]

(8.10)

The energy functional assumes its minimum if the effective potentials are

\[ A_{S,\sigma}(\mathbf{r}) = A_{\text{ext}}(\mathbf{r}) + A_{\text{xc},\sigma}(\mathbf{r}) \]

(8.11)

and

\[ V_{S,\sigma}(\mathbf{r}) = V_{\text{ext},\sigma}(\mathbf{r}) + V_{\text{H}}(\mathbf{r}) + V_{\text{xc},\sigma}(\mathbf{r}) + \frac{e^2}{2m_0} \left[ A_{\text{ext}}^2(\mathbf{r}) - A_{S,\sigma}^2(\mathbf{r}) \right], \]

(8.12)

where \( V_{\text{H}} \) is the Hartree potential defined by equation (4.20), \( V_{\text{xc},\sigma} \) is the scalar exchange-correlation potential (4.21) and

\[ eA_{\text{xc},\sigma}[n_\sigma, j_{p,\sigma}](\mathbf{r}) = \frac{\delta E_{\text{xc}}[n_\sigma, j_{p,\sigma}]}{\delta j_{p,\sigma}(\mathbf{r})} \]

(8.13)
defines the exchange-correlation vector potential.
8.2. Gauge invariance and the continuity equation

So far, we have formulated the Kohn-Sham equation of current-spin density functional theory using the spin density \( n_\sigma \) and the paramagnetic current density \( j_{p,\sigma} \) as the basic variables. The latter, however, is not gauge invariant.

Consider a gauge transformation that changes the external vector potential according to

\[
A_{\text{ext}}^E(r) \rightarrow A_{\text{ext}}^\Lambda(r) = A_{\text{ext}}^E(r) - \nabla \Lambda(r).
\]  

Clearly, such a gauge transformation leaves the external magnetic field \( B_{\text{ext}} \) unchanged and hence must not affect observables such as the ground state energy as well as the spin density and current density. Yet, it does change the paramagnetic current density from \( j_{p,\sigma}(r) \) to

\[
j_{p,\sigma}^\Lambda(r) = j_{p,\sigma}(r) + \frac{e}{m_0^*} n_\sigma(r) \nabla \Lambda(r).
\]

By explicitly requiring a gauge invariant energy functional, i.e.

\[
E[n_\sigma, j_{p,\sigma}^\Lambda] = Q \left[ n_\sigma j_{p,\sigma} + \frac{e}{m_0^*} n_\sigma \nabla \Lambda(r) \right] + \sum_{\sigma=\uparrow,\downarrow} \int d^3r n_\sigma(r) V_{\text{ext}}(r)
+ \sum_{\sigma=\uparrow,\downarrow} e \int d^3r j_{p,\sigma}(r) \cdot A_{\text{ext}}(r) + \sum_{\sigma=\uparrow,\downarrow} e \int d^3r j_{p,\sigma}(r) \cdot \nabla \Lambda(r)
+ \frac{e^2}{2m_0^*} \sum_{\sigma=\uparrow,\downarrow} \int d^3r n_\sigma(r) A_{\text{ext}}^2(r) + \frac{e^2}{2m_0^*} \sum_{\sigma=\uparrow,\downarrow} \int d^3r n_\sigma(r) (\nabla \Lambda(r))^2
\equiv E[n_\sigma, j_{p,\sigma}]
\]

we find that the functional \( Q[n_\sigma, j_{p,\sigma}] \) has to transform according to

\[
Q \left[ n_\sigma j_{p,\sigma} + \frac{e}{m_0^*} n_\sigma \nabla \Lambda(r) \right] = Q \left[ n_\sigma j_{p,\sigma} + \frac{e}{m_0^*} n_\sigma \nabla \Lambda(r) \right] + \sum_{\sigma=\uparrow,\downarrow} e \int d^3r j_{p,\sigma}(r) \cdot \nabla \Lambda(r)
+ \frac{e^2}{2m_0^*} \sum_{\sigma=\uparrow,\downarrow} \int d^3r n_\sigma(r) (\nabla \Lambda(r))^2.
\]

At this point we note that the transformation of this functional depends only on \( n_\sigma \) and \( j_{p,\sigma} \) and not on the ground state wave function. The same transformation thus applies to the non-interacting version of the functional, which is precisely \( T[n_\sigma, j_{p,\sigma}] \). The Hartree energy, as it depends only on the particle density, is clearly unaffected by the gauge transformation. Thus, we conclude that the exchange-correlation energy functional has to be gauge invariant, i.e.

\[
E_{xc} \left[ n_\sigma j_{p,\sigma} + \frac{e}{m_0^*} n_\sigma \nabla \Lambda(r) \right] = E_{xc}[n_\sigma, j_{p,\sigma}].
\]

Calculating the respective functional derivatives, we can infer the following transformation rules for the exchange-correlation scalar and vector potential from equation (8.18):

\[
V_{xc,\sigma}(r) \rightarrow V_{xc,\sigma}^\Lambda(r) = V_{xc,\sigma}(r) - \frac{e^2}{m_0^*} A_{xc,\sigma}(r) \cdot \nabla \Lambda(r)
\]

and

\[
A_{xc,\sigma}(r) \rightarrow A_{xc,\sigma}^\Lambda(r) = A_{xc,\sigma}(r).
\]
These transformations, when inserted into the Kohn-Sham equation of current-spin density functional theory, yield Kohn-Sham eigenvalues which in turn give a gauge-invariant ground state energy.

The gauge invariance of the exchange-correlation energy functional has yet another physically important consequence. It guarantees that the current of the interacting system satisfies the continuity equation because it ensures an appropriate form of the exchange-correlation vector potential. To see this, we note first that the gauge-invariance condition \( (8.18) \) has to hold for any gauge function \( \Lambda(\mathbf{r}) \). The exchange-correlation energy functional can thus be understood as a functional of gauge-invariant variables only, namely the spin density \( n_{\sigma}(\mathbf{r}) \) and a gauge-invariant combination of \( n_{\sigma}(\mathbf{r}) \) and the paramagnetic current density \( j_{p,\sigma}(\mathbf{r}) \). This combination is the vorticity

\[
\mathbf{v}_{\sigma}(\mathbf{r}) = \nabla \times \frac{j_{p,\sigma}(\mathbf{r})}{n_{\sigma}(\mathbf{r})},
\]

which is the curl of the velocity field. It is interesting to express the exchange-correlation vector potential as a functional derivative of the vorticity-dependent exchange-correlation energy

\[
\tilde{E}_{\text{xc}}[n_{\sigma}, \mathbf{v}_{\sigma}] = E_{\text{xc}}[n_{\sigma}, j_{p,\sigma}]
\]

with respect to the vorticity. One finds the expression

\[
e_{\mathbf{A}_{\text{xc},\sigma}}(\mathbf{r}) = \frac{1}{n(\mathbf{r})} \nabla \times \frac{\delta \tilde{E}_{\text{xc}}[n_{\sigma}, \mathbf{v}_{\sigma}]}{\delta \mathbf{v}_{\sigma}(\mathbf{r})},
\]

from which immediately follows:

\[
\nabla \cdot \left( n(\mathbf{r}) \mathbf{A}_{\text{xc},\sigma}(\mathbf{r}) \right) = 0.
\]

But why does this guarantee a current that satisfies the continuity equation? Well, first of all, the Kohn-Sham current

\[
j_{\text{KS},\sigma}(\mathbf{r}) = j_{p,\sigma}(\mathbf{r}) + e m_{0}^{-1} n_{\sigma}(\mathbf{r}) \mathbf{A}_{\text{k},\sigma}(\mathbf{r})
\]

which we define as the full current density of the Kohn-Sham system, naturally satisfies the (static) continuity equation

\[
\nabla \cdot j_{\text{KS},\sigma}(\mathbf{r}) = 0
\]

since it stems from the Hermitian Kohn-Sham Hamiltonian. By construction, the paramagnetic current density as well as the spin density of the Kohn-Sham system coincide (in principle) with the respective quantities of the interacting system. We can thus—in principle—rigorously calculate the correct full current density of the interacting system

\[
j_{\sigma}(\mathbf{r}) = j_{p,\sigma}(\mathbf{r}) + e m_{0}^{-1} n_{\sigma}(\mathbf{r}) \mathbf{A}_{\text{ext}}(\mathbf{r})
\]

which contains only the external vector potential but not the exchange-correlation vector potential. Obviously, this current is related to the Kohn-Sham current via

\[
j_{\text{KS},\sigma}(\mathbf{r}) = j_{\sigma}(\mathbf{r}) + e m_{0}^{-1} n_{\sigma}(\mathbf{r}) \mathbf{A}_{\text{xc},\sigma}(\mathbf{r})
\]

and thus the requirement that the full current density of the interacting system satisfies the continuity equation implies

\[
\nabla \cdot j_{\sigma}(\mathbf{r}) = \nabla \cdot \left[ j_{\text{KS},\sigma}(\mathbf{r}) - e m_{0}^{-1} n_{\sigma}(\mathbf{r}) \mathbf{A}_{\text{xc},\sigma}(\mathbf{r}) \right] = -e m_{0}^{-1} \nabla \cdot (n_{\sigma}(\mathbf{r}) \mathbf{A}_{\text{xc},\sigma}(\mathbf{r})) = 0.
\]

This, however, is exactly the same constraint on an admissible \( \mathbf{A}_{\text{xc},\sigma} \) as the one given above in equation (8.23), which was derived from the gauge invariance of the exchange-correlation energy functional.
9 The optimized effective potential method in current-density functional theory

We have already seen that there are several good reasons to study orbital-dependent functionals in density functional theory. In particular, the exact-exchange potential is self-interaction free and shows a derivative discontinuity. Yet, in many cases the LDA is applied successfully.

While Vignale and Rasolt [1988] have suggested a local approximation in terms of the density and the vorticity for current-density functional theory, the application of a local approximation in CDFT is problematic in general. In an increasing external magnetic field, the exchange-correlation energy per particle in a homogeneous electron gas shows derivative discontinuities whenever a new Landau level gets populated [Skudlarski and Vignale, 1993]. The resulting discontinuities in the corresponding exchange-correlation potential then appear incorrectly in the inhomogeneous system whenever its local density and vorticity coincide with the respective values of the homogeneous electron gas. While attempts have been made to circumvent this problem e.g. by designing functionals which interpolate between the high-field and the low-field limit [Wensauer and Rössler, 2004; Saarikoski et al., 2003], a more natural solution is to employ functionals which depend explicitly on the Kohn-Sham orbitals and only implicitly on the densities.

9.1. The optimized effective potential equations in current-density functional theory

As in DFT, the application of orbital-dependent functionals requires employing the OEP scheme to calculate the corresponding exchange-correlation scalar potential \( V_{\text{xc}} \) and vector potential \( A_{\text{xc}} \). Such an OEP procedure together with an approximation in the spirit of the KLI approximation has been derived by Pittalis et al. [2006] and Helbig et al. [2008]. In this section we outline the derivation of the current-density functional theory OEP (CDFT-OEP) equations. In contrast to the original work by Pittalis et al. [2006] and Helbig et al. [2008], who used the density \( n(\mathbf{r}) \) and the paramagnetic current density \( j_p(\mathbf{r}) \) as the basic variables, we resort to the density and the gauge-invariant vorticity \( \mathbf{v}(\mathbf{r}) \) in order to formulate the theory explicitly in a gauge-invariant way. The result, however, is the same if we finally express it by the variables \( n(\mathbf{r}) \) and \( j_p(\mathbf{r}) \).

First CDFT-OEP equation

Exactly as in ordinary density-functional OEP, we start by writing the derivative of the exchange-correlation energy—which is now understood as an implicit functional of the density and the vorticity—with respect to the Kohn-Sham potential \( V_S \) using the chain rule of functional differentiation as

\[
\frac{\delta E_{\text{xc}}}{\delta V_{S,\sigma}(\mathbf{r})} = \sum_{\sigma' = \uparrow, \downarrow} \int d^3 r' \left( \frac{\delta E_{\text{xc}}}{\delta n_{\sigma'}(\mathbf{r}')} \frac{\delta n_{\sigma'}(\mathbf{r}')}{\delta V_{S,\sigma}(\mathbf{r})} + \frac{\delta E_{\text{xc}}}{\delta \mathbf{v}_{\sigma'}(\mathbf{r}')} \frac{\delta \mathbf{v}_{\sigma'}(\mathbf{r}')}{\delta V_{S,\sigma}(\mathbf{r})} \right). \tag{9.1}
\]
Since $E_{xc}$ is—exactly as in DFT—an explicit functional of the Kohn-Sham orbitals, we can again express the above derivative as

$$
\frac{\delta E_{xc}}{\delta V_{\sigma}^{S}(\mathbf{r})} = \sum_{\sigma'=\uparrow,\downarrow} \sum_{k=1}^{N_{\sigma'}} \int d^{3}r' \frac{\delta E_{xc}}{\delta \phi_{k,\sigma'}^{\uparrow} (\mathbf{r}') \delta V_{\sigma}^{S}(\mathbf{r})} + \text{c.c.},
$$

(9.2)

where the sum runs over all occupied Kohn-Sham levels and c.c. denotes complex conjugation. Note that this is exactly the same expression as equation (5.5) in density-functional OEP and again, the functional derivatives $\frac{\delta E_{xc}}{\delta \phi_{k,\sigma'}^{\uparrow} (\mathbf{r}')}$ can be calculated explicitly. Combining both equations we obtain:

$$
\sum_{\sigma'=\uparrow,\downarrow} \int d^{3}r' \left[ \left( V_{xc,\sigma'}^{S}(\mathbf{r}') + eA_{xc,\sigma'}^{\uparrow} (\mathbf{r}') \right) \frac{\delta n_{\sigma'}(\mathbf{r}')}{\delta n_{\sigma}^{S}(\mathbf{r})} \right] + e\Gamma_{xc,\sigma'}^{\uparrow} \frac{\delta \mathbf{v}_{\sigma}(\mathbf{r}')}{\delta V_{\sigma}^{S}(\mathbf{r})} \right]

= \sum_{\sigma'=\uparrow,\downarrow} \sum_{k=1}^{N_{\sigma'}} \int d^{3}r' \frac{\delta E_{xc}}{\delta \phi_{k,\sigma'}^{\uparrow} (\mathbf{r}') \delta V_{\sigma}^{S}(\mathbf{r})} + \text{c.c.} \quad (9.3)
$$

Besides using the definition of the scalar exchange-correlation potential, which reads for an exchange-correlation energy functional depending on the density and vorticity

$$
V_{xc,\sigma}(\mathbf{r}) = \frac{\delta E_{xc}}{\delta n_{\sigma}(\mathbf{r})} - eA_{xc,\sigma}^{\uparrow} (\mathbf{r}) \cdot \frac{j_{p,\sigma}(\mathbf{r})}{n_{\sigma}(\mathbf{r})},
$$

(9.4)

we have defined the quantity

$$
e\Gamma_{xc,\sigma}(\mathbf{r}) = \frac{\delta E_{xc}}{\delta \mathbf{v}_{\sigma}(\mathbf{r})}
$$

(9.5)

which is related to the exchange-correlation vector potential $A_{xc,\sigma}$ via

$$
A_{xc,\sigma}(\mathbf{r}) = \frac{1}{n_{\sigma}(\mathbf{r})} \nabla \times \Gamma_{xc,\sigma}(\mathbf{r}).
$$

(9.6)

In order to calculate the functional derivatives of the Kohn-Sham orbitals—and hence of the density and the vorticity—with respect to the effective potentials from first order perturbation theory we require the variation of the Kohn-Sham Hamiltonian which is given by

$$
\delta \hat{H}_{S,\sigma}(\mathbf{r}) = \frac{1}{2m_{0}^{*}} (-i\hbar \nabla + e(A_{S,\sigma}(\mathbf{r}) + \delta A_{S,\sigma}(\mathbf{r}))^{2} + V_{S,\sigma}(\mathbf{r}) + \delta V_{S,\sigma}(\mathbf{r})

= - \frac{1}{2m_{0}^{*}} (-i\hbar \nabla + eA_{S,\sigma}(\mathbf{r}))^{2} - V_{S,\sigma}(\mathbf{r})

= - \frac{i\hbar e}{2m_{0}^{*}} \nabla \cdot \delta A_{S,\sigma}(\mathbf{r}) - \frac{i\hbar e}{2m_{0}^{*}} \delta A_{S,\sigma}(\mathbf{r}) \cdot \nabla + \frac{e^{2}}{m_{0}^{*}} A_{S,\sigma}(\mathbf{r}) \cdot \delta A_{S,\sigma}(\mathbf{r}) + \delta V_{S,\sigma}(\mathbf{r}).
$$

(9.7)

Quite generally, the variation of a Kohn-Sham orbital—i.e. its first order correction under the perturbation $\delta \hat{H}_{S,\sigma}$—reads

$$
\delta \phi_{k,\sigma}(\mathbf{r}) = \sum_{j \neq k} \frac{\phi_{j,\sigma}(\mathbf{r})}{\varepsilon_{k,\sigma} - \varepsilon_{j,\sigma}} \int d^{3}r' \phi_{j,\sigma}^{*}(\mathbf{r}') \delta \hat{H}_{S,\sigma}(\mathbf{r}') \phi_{k,\sigma}(\mathbf{r}').
$$

(9.8)

From this expression we can infer that the variation of a Kohn-Sham orbital with respect to the effective scalar potential is given by

$$
\frac{\delta \phi_{k,\sigma}(\mathbf{r})}{\delta V_{\sigma}^{S}(\mathbf{r}')} = \delta_{\sigma,\sigma'} \sum_{j \neq k} \frac{\phi_{j,\sigma}(\mathbf{r})}{\varepsilon_{k,\sigma} - \varepsilon_{j,\sigma}} \phi_{j,\sigma}^{*}(\mathbf{r}') \phi_{k,\sigma}(\mathbf{r}').
$$

(9.9)
This is precisely the same expression as the respective equation (5.8) in density-functional OEP, from which one readily obtains the variation of the density with respect to the effective scalar potential

\[
\frac{\delta n_\sigma (\mathbf{r})}{\delta V_{S,\sigma}(\mathbf{r}')} = \sum_{k=1}^{N_\sigma} \phi^*_{k,\sigma}(\mathbf{r}) \frac{\delta \phi_{k,\sigma}(\mathbf{r})}{\delta V_{S,\sigma}(\mathbf{r}')} + \text{c.c.} \\
= \delta_{\sigma,\sigma'} \sum_{k} \sum_{j \neq k} \left( \phi^*_{k,\sigma}(\mathbf{r}) \phi_{j,\sigma}(\mathbf{r}) \right) \left( \frac{\phi^*_{k,\sigma}(\mathbf{r})}{\varepsilon_{k,\sigma} - \varepsilon_{j,\sigma}} - \phi^*_{j,\sigma}(\mathbf{r}) \phi_{k,\sigma}(\mathbf{r}) + \text{c.c.} \right). 
\]

(9.10)

The calculation of the variation of the vorticity with respect to \( V_{S,\sigma} \) is not more involved, albeit slightly lengthy. Although the variation of the vorticity \( \delta \mathbf{v}_\sigma \) can be expressed directly through the variations of the Kohn-Sham orbitals, it is probably a bit more convenient to express \( \delta \mathbf{v}_\sigma \) using the variations of the density given by equation (9.10) and the variation of the paramagnetic current density

\[
\frac{\delta \mathbf{v}_\sigma (\mathbf{r})}{\delta V_{S,\sigma}(\mathbf{r}')} = \nabla \times \left( \frac{1}{n_\sigma (\mathbf{r})} \frac{\delta \mathbf{j}_{p,\sigma}(\mathbf{r})}{\delta V_{S,\sigma}(\mathbf{r}')} - \frac{\mathbf{j}_{p,\sigma}(\mathbf{r})}{n_\sigma^2 (\mathbf{r})} \frac{\delta n_\sigma (\mathbf{r})}{\delta V_{S,\sigma}(\mathbf{r}')} \right). 
\]

(9.11)

The latter can be easily calculated from the Kohn-Sham orbitals as

\[
\frac{\delta \mathbf{v}_\sigma (\mathbf{r})}{\delta V_{S,\sigma}(\mathbf{r}')} = -\delta_{\sigma,\sigma'} \sum_{k} \sum_{j \neq k} \phi^*_{j,\sigma}(\mathbf{r}) \phi_{k,\sigma}(\mathbf{r}) \nabla \times \left[ \frac{i \hbar}{2m_0} \frac{\phi^*_{k,\sigma}(\mathbf{r})}{\varepsilon_{k,\sigma} - \varepsilon_{j,\sigma}} \nabla \phi_{j,\sigma}(\mathbf{r}) - \phi_{j,\sigma}(\mathbf{r}) \nabla \phi^*_{k,\sigma}(\mathbf{r}) \right] + \text{c.c.} 
\]

(9.12)

With these explicitly orbital dependent expressions of the variations of the density and the paramagnetic current density, one finds

\[
\frac{\delta \mathbf{v}_\sigma (\mathbf{r})}{\delta V_{S,\sigma}(\mathbf{r}')} = -\delta_{\sigma,\sigma'} \sum_{k} \sum_{j \neq k} \phi^*_{j,\sigma}(\mathbf{r}) \phi_{k,\sigma}(\mathbf{r}) \nabla \times \left[ \frac{i \hbar}{2m_0} \frac{\phi^*_{k,\sigma}(\mathbf{r})}{\varepsilon_{k,\sigma} - \varepsilon_{j,\sigma}} \nabla \phi_{j,\sigma}(\mathbf{r}) - \phi_{j,\sigma}(\mathbf{r}) \nabla \phi^*_{k,\sigma}(\mathbf{r}) \right] + \frac{\mathbf{j}_{p,\sigma}(\mathbf{r})}{n_\sigma^2 (\mathbf{r})} \phi^*_{k,\sigma}(\mathbf{r}) \phi_{j,\sigma}(\mathbf{r}) + \text{c.c.} 
\]

(9.13)

Inserting the variations (9.10), (9.13) and (9.9) into equation (9.3) yields, after some algebra, the first CDFT-OEP equation

\[
\sum_{k} \phi_{k,\sigma}(\mathbf{r}) \sum_{j \neq k} \frac{\phi^*_{j,\sigma}(\mathbf{r})}{\varepsilon_{k,\sigma} - \varepsilon_{j,\sigma}} \int d^3 r' \left[ \left( V_{xc,\sigma}(\mathbf{r}') - u_{k,\sigma}(\mathbf{r}') \right) \phi^*_{k,\sigma}(\mathbf{r}') \phi_{j,\sigma}(\mathbf{r}') + \frac{i \hbar}{2m_0} A_{xc,\sigma} \left( \phi_{j,\sigma}(\mathbf{r}') \nabla \phi^*_{k,\sigma}(\mathbf{r}') - \phi^*_{k,\sigma}(\mathbf{r}') \nabla \phi_{j,\sigma}(\mathbf{r}') \right) \right] + \text{c.c.} = 0. 
\]

(9.14)

As in DFT-OEP, one can now define the orbital shift

\[
\psi_{k,\sigma}(\mathbf{r}) = \sum_{j \neq k} \frac{\phi_{j,\sigma}(\mathbf{r})}{\varepsilon_{k,\sigma} - \varepsilon_{j,\sigma}} \int d^3 r' \left[ \left( V_{xc,\sigma}(\mathbf{r}') - u^*_{k,\sigma}(\mathbf{r}') \right) \phi^*_{j,\sigma}(\mathbf{r}') \phi_{k,\sigma}(\mathbf{r}') - \frac{i \hbar}{2m_0} A_{xc,\sigma} \left( \phi^*_{j,\sigma}(\mathbf{r}') \nabla \phi_{k,\sigma}(\mathbf{r}') - \phi_{k,\sigma}(\mathbf{r}') \nabla \phi^*_{j,\sigma}(\mathbf{r}') \right) \right] 
\]

(9.15)

and rewrite the first CDFT-OEP equation in the compact form

\[
\sum_{k} \phi^*_{k,\sigma}(\mathbf{r}) \psi_{k,\sigma}(\mathbf{r}) + \text{c.c.} = 0. 
\]

(9.16)
Second CDFT-OEP equation

The second CDFT-OEP equation can be derived in an analogous manner, although the calculation is somewhat more cumbersome. As in the preceding case, we start with the variational derivative of the exchange-correlation energy functional but this time with respect to the self-consistent vector potential \(A_{S,\sigma}\), i.e.

\[
\frac{\delta E_{xc}}{\delta A_{S,\sigma}(\mathbf{r})} = \sum_{\sigma' = \uparrow, \downarrow} \int \frac{d^3r'}{2\pi^3} \left( \frac{\delta E_{xc}}{\delta n_{\sigma'}(\mathbf{r}')} - \frac{\delta E_{xc}}{\delta A_{S,\sigma}(\mathbf{r})} \frac{\delta A_{S,\sigma}(\mathbf{r})}{\delta n_{\sigma'}(\mathbf{r}')} \right)
\]

\[
= \sum_{\sigma' = \uparrow, \downarrow} \sum_{k=1}^{N_{\sigma}} \int \frac{d^3r'}{2\pi^3} \frac{\delta E_{xc}}{\delta \phi_{k,\sigma'}(\mathbf{r}')} \frac{\delta \phi_{k,\sigma'}(\mathbf{r}')}{\delta A_{S,\sigma}(\mathbf{r})} + \text{c.c.} \quad (9.17)
\]

Expressing the variational derivatives \(\frac{\delta E_{xc}}{\delta n_{\sigma'}(\mathbf{r}')}\) and \(\frac{\delta E_{xc}}{\delta A_{S,\sigma}(\mathbf{r})}\) in terms of the exchange-correlation potentials \(V_{xc,\sigma'}\) and \(A_{xc,\sigma'}\) (and the latter in terms of \(\Gamma_{xc,\sigma'}\) defined above) we can write this equation in the form

\[
\sum_{\sigma' = \uparrow, \downarrow} \int \frac{d^3r'}{2\pi^3} \left[ \left( V_{xc,\sigma'}(\mathbf{r}') + eA_{xc,\sigma'}(\mathbf{r}') \right) - \frac{\delta n_{\sigma'}(\mathbf{r}')}{\delta A_{S,\sigma}(\mathbf{r})} + e \Gamma_{xc,\sigma'}(\mathbf{r}') \frac{\delta n_{\sigma'}(\mathbf{r}')}{\delta A_{S,\sigma}(\mathbf{r})} \right]
\]

\[
= \sum_{\sigma' = \uparrow, \downarrow} \sum_{k=1}^{N_{\sigma}} \int \frac{d^3r'}{2\pi^3} \frac{\delta E_{xc}}{\delta \phi_{k,\sigma'}(\mathbf{r}')} \frac{\delta \phi_{k,\sigma'}(\mathbf{r}')}{\delta A_{S,\sigma}(\mathbf{r})} + \text{c.c.} \quad (9.18)
\]

The variation of the Kohn-Sham orbital \(\phi_{k,\sigma}\) with respect to \(A_{S,\sigma}\) can be extracted from the variation of the Kohn-Sham Hamiltonian given by equation (9.7). One finds

\[
\frac{\delta \phi_{k,\sigma}(\mathbf{r})}{\delta A_{S,\sigma}(\mathbf{r}')}(\mathbf{r}) = \delta_{\sigma,\sigma'} \sum_{j \neq k} \frac{\phi_{j,\sigma}(\mathbf{r})}{\varepsilon_{k,\sigma} - \varepsilon_{j,\sigma}} \left[ \frac{\hbar e}{2im_0} \left( \phi_{j,\sigma}(\mathbf{r}') \nabla' \phi_{k,\sigma}(\mathbf{r}) - \phi_{k,\sigma}(\mathbf{r}') \nabla' \phi_{j,\sigma}(\mathbf{r}) \right) \right.
\]

\[
+ \frac{e^2}{m_0} A_{S,\sigma}(\mathbf{r}') \phi_{j,\sigma}(\mathbf{r}') \phi_{k,\sigma}(\mathbf{r}') \right], \quad (9.19)
\]

where partial integration has been used to get rid of the term containing the derivative \(\nabla \delta A_{S,\sigma}\). Using this expression one can compute the variation of the density with respect \(A_{S,\sigma}\).

\[
\frac{\delta n_{\sigma}(\mathbf{r})}{\delta A_{S,\sigma}(\mathbf{r}')}(\mathbf{r}) = \delta_{\sigma,\sigma'} \sum_{k=1}^{N_{\sigma}} \left\{ \sum_{j \neq k} \frac{\phi_{j,\sigma}(\mathbf{r})}{\varepsilon_{k,\sigma} - \varepsilon_{j,\sigma}} \left[ \frac{\hbar e}{2im_0} \left( \phi_{j,\sigma}(\mathbf{r}') \nabla' \phi_{k,\sigma}(\mathbf{r}) - \phi_{k,\sigma}(\mathbf{r}') \nabla' \phi_{j,\sigma}(\mathbf{r}) \right) \right.
\]

\[
+ \frac{e^2}{m_0} A_{S,\sigma}(\mathbf{r}') \phi_{j,\sigma}(\mathbf{r}') \phi_{k,\sigma}(\mathbf{r}') \right] + \text{c.c.} \quad (9.20)
\]

To find the variation of the vorticity, it is again beneficial to express it via the variations of the density and the paramagnetic current density using equation (9.11). We exemplify the latter by the variation with respect to the \(\alpha\)-component of the effective vector potential

\[
\frac{\delta j_{\alpha,\sigma}(\mathbf{r})}{\delta A_{S,\sigma}(\mathbf{r}')}(\mathbf{r}) = \delta_{\alpha,\alpha'} \sum_{k=1}^{N_{\sigma}} \left[ \sum_{j \neq k} \frac{\phi_{j,\sigma}(\mathbf{r})}{\varepsilon_{k,\sigma} - \varepsilon_{j,\sigma}} \left[ - \frac{\hbar}{2m_0^*} \left( \phi_{j,\sigma}(\mathbf{r}') \nabla' \phi_{k,\sigma}(\mathbf{r}) - \phi_{k,\sigma}(\mathbf{r}') \nabla' \phi_{j,\sigma}(\mathbf{r}) \right) \right.
\]

\[
+ \frac{e}{m_0^*} A_{S,\sigma}(\mathbf{r}') \phi_{j,\sigma}(\mathbf{r}') \phi_{k,\sigma}(\mathbf{r}') \right] + \text{c.c.} \quad (9.21)
\]
Combining the variations of the density and the paramagnetic current density one eventually finds
\[
\frac{\delta \mathbf{v}_\sigma (\mathbf{r})}{\delta A_{\sigma,\sigma}^0 (r')} = -\delta_{\sigma,\sigma'} \nabla \times \frac{e}{\rho_{\sigma} (\mathbf{r})} \sum_{k=1}^{N_\sigma} \sum_{j \neq k} \frac{1}{\varepsilon_{k,\sigma} - \varepsilon_{j,\sigma}} \left[ \frac{i}{m_0} \left( \phi_{j,\sigma} (\mathbf{r}) \nabla \phi_{k,\sigma}^* (\mathbf{r}) - \phi_{k,\sigma}^* (\mathbf{r}) \nabla \phi_{j,\sigma} (\mathbf{r}) \right) - \frac{\hbar}{2im_0} \left( \phi_{j,\sigma} (\mathbf{r}) \phi_{k,\sigma} (\mathbf{r}) - \phi_{k,\sigma} (\mathbf{r}) \phi_{j,\sigma} (\mathbf{r}) \right) \right].
\]

Collecting all variations and putting them into equation (9.18) leads after a lengthy calculation, involving a partial integration to replace the term containing \( \Gamma_{xc,\sigma} \) by a term which contains the exchange-correlation vector potential \( A_{xc,\sigma} \) to the second CDFT-OEP equation
\[
\sum_{k=1}^{N_\sigma} \sum_{j \neq k} \left\{ \frac{1}{\varepsilon_{k,\sigma} - \varepsilon_{j,\sigma}} \left[ \frac{i}{2} \left( \phi_{j,\sigma} (\mathbf{r}) \nabla \phi_{k,\sigma}^* (\mathbf{r}) - \phi_{k,\sigma}^* (\mathbf{r}) \nabla \phi_{j,\sigma} (\mathbf{r}) \right) + A_{S,\sigma} (\mathbf{r}) \phi_{j,\sigma} (\mathbf{r}) \phi_{k,\sigma}^* (\mathbf{r}) \right] \cdot \int d^3 r' \left[ \left( V_{xc,\sigma} (r' - u_{k,\sigma}^* (r')) \right) \phi_{j,\sigma}^* (r') \phi_{k,\sigma} (r') \right. \\
- \frac{i\hbar}{2m_0} \left. A_{xc,\sigma} (r') \left( \phi_{j,\sigma}^* (r') \nabla' \phi_{k,\sigma} (r' - \phi_{k,\sigma} (r') \nabla' \phi_{j,\sigma}^* (r') \right) \right] + c.c. \right\} = 0.
\]

Note that the term containing \( A_{S} \) vanishes because this is precisely the first CDFT-OEP equation. With the definition (9.15) of the orbital shifts \( \psi_k \) we can finally write the second CDFT-OEP equation in the compact form
\[
\frac{1}{2i} \sum_{k=1}^{N_\sigma} \left[ \phi_{k,\sigma}^* (\mathbf{r}) \nabla \psi_k (\mathbf{r}) - \psi_k (\mathbf{r}) \nabla \phi_{k,\sigma}^* (\mathbf{r}) \right] + c.c. = 0.
\]

### 9.2. Krieger-Li-Lafraite type approximation to the current-density functional theory OEP equations

A simplifying approximation to the CDFT-OEP equations, which is in the spirit of the KLI approximation commonly used in DFT-OEP, has been proposed by Pittalis et al. [2006] and Helbig et al. [2008]. In this section we derive two approximate CDFT-OEP equations, which we will refer to as the CDFT-KLI equations.

As in density functional theory, the starting point for the derivation of the CDFT-KLI approximation is to replace the energy denominator \( \varepsilon_{k,\sigma} - \varepsilon_{j,\sigma} \) by some constant \( \Delta \varepsilon_{\sigma} \). Note that an alternative derivation—which exists in DFT and leads to the interpretation of the KLI approximation as a mean-field approximation of the OEP equation—is not known in CDFT. Applying this approximation to the orbital shift we find
\[
\psi_{k,\sigma} (\mathbf{r}) \approx \frac{1}{\Delta \varepsilon_{\sigma}} \left\{ \left( V_{xc,\sigma} (\mathbf{r}) - u_{k,\sigma}^* (\mathbf{r}) \right) \phi_{k,\sigma} (\mathbf{r}) + \frac{\hbar}{2im_0} A_{xc,\sigma} (\mathbf{r}) \left( 2 \nabla \phi_{k,\sigma} (\mathbf{r}) - \frac{\nabla n_{\sigma} (\mathbf{r})}{n_{\sigma} (\mathbf{r})} \phi_{k,\sigma} (\mathbf{r}) \right) \right. \\
- \left. \phi_{k,\sigma} (\mathbf{r}) \int d^3 r' \left[ \left( V_{xc,\sigma} (r' - u_{k,\sigma}^* (r')) \right) n_{k,\sigma} (r') + A_{xc,\sigma} (r') : j_{p,k,\sigma} (r') \right] \right\}. \tag{9.25}
\]

We may now insert the orbital shift in the KLI approximation into the first CDFT-OEP equation (9.16) and finally obtain
\[
n_{\sigma} (\mathbf{r}) V_{xc,\sigma} (\mathbf{r}) + j_{p,\sigma} (\mathbf{r}) \cdot A_{xc,\sigma} (\mathbf{r}) = \sum_{k=1}^{N_\sigma} n_{k,\sigma} (\mathbf{r}) \left[ \Re u_{k,\sigma} (\mathbf{r}) + V_{xc,\sigma}^k + \sum_{\sigma} A_{xc,\sigma}^k - \Re u_{\bar{\sigma}} (\mathbf{r}) \right], \tag{9.26}
\]
9. The optimized effective potential method in current-density functional theory

where we define the averages

\[ V_{xc,\sigma}^k = \int d^3r' n_{k,\sigma}(r')V_{xc,\sigma}(r') \quad (9.27a) \]

\[ A_{xc,\sigma}^k = \int d^3r' j_{p,k,\sigma}(r') \cdot A_{xc,\sigma}(r') \quad (9.27b) \]

\[ \bar{u}_{k,\sigma} = \int d^3r' n_{k,\sigma}(r')u_{k,\sigma}(r') \quad (9.27c) \]

Similarly, the second CDFT-KLI equation can be found by inserting the orbital shift (9.25) into the second CDFT-OEP equation (9.24). The actual calculation is again very lengthy but can be done without any fundamental difficulties. Eventually, one finds the second CDFT-KLI equation which reads

\[ j_{p,\sigma}(r)V_{xc,\sigma}(r) + \hat{N}_\sigma(r)A_{xc,\sigma}(r) \]

\[ = \sum_{k=1}^{N_s} \left\{ j_{p,k,\sigma}(r) \left[ \Re u_{k,\sigma}(r) + V_{xc,\sigma}^k + A_{xc,\sigma}^k - n_{k,\sigma}(r)\Re u_{k,\sigma} - \Re u_{k,\sigma} \right] - n_{k,\sigma}(r)\Im \nabla u_{k,\sigma}(r) \right\} . \quad (9.28) \]

Besides the averages defined in equations (9.27a)-(9.27c) we introduced the 3 × 3-matrix (for a system with three spatial dimensions) \( \hat{N}_\sigma \) with the matrix elements

\[ \hat{N}_{\alpha,\beta,\sigma}(r) = \frac{\hbar}{m_0} \sum_{k=1}^{N_s} \left( \frac{\partial \phi_{k,\sigma}^*(r)}{\partial r_\alpha} \frac{\partial \phi_{k,\sigma}(r)}{\partial r_\beta} + \text{c.c.} \right) - \frac{\hbar}{m_0} \frac{1}{4n^2_\sigma(r)} \frac{\partial n_\sigma(r)}{\partial r_\alpha} \frac{\partial n_\sigma(r)}{\partial r_\beta} . \quad (9.29) \]

9.3. Gauge invariance of the CDFT-OEP and CDFT-KLI equations

We have already discussed that the gauge invariance of current-density functional theory requires a specific transformation of the exchange-correlation potentials under a gauge transformation of the external vector potential \( A_{ext}(r) \rightarrow A_{ext}(r) - \nabla \Lambda(r) \). In this section we will show that the CDFT-OEP and the CDFT-KLI potentials indeed transform according to

\[ V_{xc,\sigma}(r) \rightarrow V_{xc,\sigma}^\Lambda(r) = V_{xc,\sigma}(r) - \frac{\epsilon^2}{m_0^2} A_{xc,\sigma}(r) \cdot \nabla \Lambda(r) \quad (9.30a) \]

\[ A_{xc,\sigma}(r) \rightarrow A_{xc,\sigma}^\Lambda(r) , \quad (9.30b) \]

which is the transformation that guarantees that the Kohn-Sham eigenvalues and the ground state energy are gauge invariant.

To this end we first note that the Kohn-Sham orbitals transform under this gauge transformation according to

\[ \phi_{k,\sigma}(r) \rightarrow \phi_{k,\sigma}^\Lambda(r) = \phi_{k,\sigma}(r)e^{i\Lambda(r)} . \quad (9.31) \]

Replacing the Kohn-Sham orbitals \( \phi_{k,\sigma} \) and the scalar exchange-correlation potential \( V_{xc,\sigma} \) in the orbital shift (9.15) by the respective gauge transformed quantities \( \phi_{k,\sigma}^\Lambda \) and \( V_{xc,\sigma}^\Lambda \), it is easy to show that the relation between the gauge transformed orbital shift \( \psi_{k,\sigma}^\Lambda \) and the original one is exactly the same as the relation between \( \phi_{k,\sigma} \) and \( \phi_{k,\sigma}^\Lambda \), i.e.

\[ \psi_{k,\sigma}^\Lambda(r) = e^{i\Lambda(r)} \psi_{k,\sigma}(r) . \quad (9.32) \]
Additionally, we have used that $A_{xc,\sigma}$ is left unchanged under the gauge transformation and the gauge invariance of the orbital potentials $u_{k,\sigma}$ follows directly from the gauge invariance of the exchange-correlation energy functional. Inserting the transformed orbital shift into the CDFT-OEP equations preserves their form. Consequently, if $V_{xc,\sigma}$ and $A_{xc,\sigma}$ are solutions of the CDFT-OEP equations for the set of Kohn-Sham orbitals $\{\phi_{k,\sigma}\}$, then $V_{xc,\sigma} - \frac{e^2}{m_0} A_{xc,\sigma} \cdot \nabla \Lambda$ and $A_{xc,\sigma}$ are the solutions of the CDFT-OEP equations for the gauge-transformed set of Kohn-Sham orbitals $\{\phi_{k,\sigma} e^{i\Lambda}\}$, exactly as required by the gauge invariance of the exchange-correlation energy functional.

The gauge invariance of the CDFT-KLI equations can be shown similarly. Obviously, the gauge-transformed first CDFT-KLI equation (9.26) must be given by

$$n_{\sigma}(r) V_{xc,\sigma}^\Lambda(r) + j_{p,\sigma}^\Lambda(r) \cdot A_{xc,\sigma}(r) = \sum_{k=1}^{N_\sigma} n_{k,\sigma}(r) \left[ \text{Re} u_{k,\sigma}(r) + \nabla^\Lambda_{xc,\sigma} + \bar{A}^k_{xc,\sigma} - \text{Re} \bar{\pi}_{k,\sigma} \right]$$

(9.33)

(the density, the exchange-correlation vector potential and the orbital potentials are not altered under the gauge transformation). If we now insert the gauge-transformed paramagnetic current (8.15) and scalar exchange-correlation potential (9.30a), we recover exactly the original first CDFT-KLI equation (9.26).

Analogously, we can write the gauge transformed second CDFT-KLI equation as

$$j_{p,\sigma}^\Lambda(r) V_{xc,\sigma}^\Lambda(r) + \tilde{N}_\sigma^\Lambda(r) A_{xc,\sigma}(r) = \sum_{k=1}^{N_\sigma} j_{p,k,\sigma}^\Lambda(r) \left[ \text{Re} u_{k,\sigma}(r) + \nabla^\Lambda_{xc,\sigma} + \bar{A}^k_{xc,\sigma} - \text{Re} \bar{\pi}_{k,\sigma} \right]$$

(9.34)

From the gauge transformation of the Kohn-Sham orbitals, we can infer that the elements of the $3 \times 3$ matrix $\tilde{N}_\sigma$ transform according to

$$N_{\alpha,\beta,\sigma}(r) \to \tilde{N}_{\alpha,\beta,\sigma}^\Lambda(r) = N_{\alpha,\beta,\sigma}(r) + \frac{\hbar}{m_0} \frac{\partial \Lambda(r)}{\partial r_\alpha} \frac{\partial \Lambda(r)}{\partial r_\beta} n_\sigma(r)$$

$$+ \frac{\partial \Lambda(r)}{\partial r_\alpha} j_{p,\sigma}^\alpha(r) + \frac{\partial \Lambda(r)}{\partial r_\beta} j_{p,\sigma}^\beta(r),$$

(9.35)

where $j_{p,\sigma}^\alpha$ is the $\alpha$-component of the paramagnetic current vector. If we now express, in equation (9.34), $V_{xc,\sigma}^\Lambda$, $j_{p,\sigma}^\Lambda$ and $\tilde{N}_\sigma^\Lambda$ by the respective untransformed quantities, we recover exactly the original second CDFT-KLI equation (9.28). Again, this means that if $V_{xc,\sigma}$ and $A_{xc,\sigma}$ are solutions of the CDFT-KLI equations for the set of Kohn-Sham orbitals $\{\phi_{k,\sigma}\}$, then $V_{xc,\sigma} - \frac{e^2}{m_0} A_{xc,\sigma} \cdot \nabla \Lambda$ and $A_{xc,\sigma}$ are the solutions of the CDFT-KLI equations for the gauge-transformed set of Kohn-Sham orbitals $\{\phi_{k,\sigma} e^{i\Lambda}\}$.
Exact-exchange current-density functional theory: symmetry-broken system and violation of the continuity equation by the Krieger-Li-Iafrate approximation

Current-density functional theory provides a highly efficient way to calculate—in principle exactly—both the density and the paramagnetic current density in the ground state of an interacting inhomogeneous many-electron system. In a practical calculation one usually employs the Kohn-Sham scheme which defines a fictitious system of non-interacting particles moving in an effective scalar potential $V_S(r)$ and vector potential $A_S(r)$. The effective potentials are constructed such that the ground state density and paramagnetic current density of the Kohn-Sham system coincide with the respective quantities in the interacting system. From the paramagnetic current density $j_p(r)$ and the density $n(r)$ we can directly calculate the full current density of the interacting system which is given by

$$j(r) = j_p(r) + \frac{e}{m_0} n(r) A_{\text{ext}}(r) \quad (10.1)$$

where $A_{\text{ext}}(r)$ is an external vector potential.

As usual, the effective potentials contain an exchange-correlation contribution that has to be approximated. An adequate approximation of the exchange-correlation potentials has to satisfy certain exact properties and in our case a very important requirement is that the current density of the interacting system satisfies the static continuity equation

$$\nabla \cdot j(r) = 0 \quad (10.2)$$

which expresses the particle conservation. Since the Kohn-Sham equation is equivalent to a single-particle Schrödinger equation—in particular the Kohn-Sham Hamiltonian is a Hermitian operator—is clear that the full current density of the Kohn-Sham system

$$j_{KS}(r) = j_p(r) + \frac{e}{m_0} n(r) A_S(r) \quad (10.3)$$

obeys the continuity equation. The full current density of the Kohn-Sham system and that of the interacting system differ by the diamagnetic term $\frac{e}{m_0} n(r) A_{xc}(r)$ containing the exchange-correlation vector potential $A_{xc}(r)$. Therefore, the requirement $\nabla \cdot j(r) = 0$ is equal to

$$\nabla \cdot [n(r) A_{xc}(r)] = 0. \quad (10.4)$$

In fact, solely based on the gauge invariance of the exchange-correlation functional—which is required to ensure the gauge invariance of the ground state energy—Vignale and Rasolt [1988] proved that the true exchange-correlation vector potential satisfies this condition. We can, however, not infer a priori that for
any approximate exchange-correlation vector potential the condition (10.4) will also hold. In particular, since the aforementioned proof by Vignale and Rasolt relies on the fact that the exchange-correlation vector potential is calculated as the functional derivative of the gauge-invariant exchange-correlation energy functional $E_{xc}$ with respect to the paramagnetic current density, it is not obvious that the CDFT-KLI exchange-correlation vector potential obeys the condition (10.4). While the exchange-correlation vector potential which is obtained as the solution of the CDFT-OEP equations is by construction a functional derivative of $E_{xc}$ with respect to $j_p$, this is not true for the exchange-correlation vector potential which solves the CDFT-KLI equations since the latter are only an approximation to the CDFT-OEP equations. It is thus at least questionable whether or not the CDFT-KLI exchange-correlation vector potential will eventually lead to a full current of the interacting system that satisfies the static continuity equation.

Previous applications of the CDFT-KLI method employing the gauge-invariant exact-exchange functional (5.2) have been restricted to spherically symmetric systems [Pittalis et al., 2006; Helbig et al., 2008]. Symmetry already guarantees then that the CDFT-KLI exact-exchange vector potential satisfies the condition (10.4).

In this chapter we address the question if the CDFT-KLI equations also provide such an admissible exchange-correlation vector potential if the rotational symmetry of the system is broken explicitly. We use the numerical example of a one-dimensional quantum ring in which a persistent current is induced by a magnetic flux $\Phi = 0.30\Phi_0$ that penetrates the ring. We break the rotational symmetry by placing a repulsive Gaussian impurity potential with a strength $V_0 = 10\text{ meV}$ in the ring. This is sufficiently strong to induce Friedel oscillations in the non-interacting system with a maximal amplitude comparable to the average density (to avoid numerical problems we checked that the density significantly differs from zero everywhere in the ring). The results presented in this chapter are the subject of the publication [Siegmund and Pankratov, 2010].

A note on the gauge invariance of quasi one-dimensional current-density functional theory

The numerical model we study in this thesis is one-dimensional. It is therefore not immediately obvious how to transfer the three-dimensional considerations of gauge-invariance and its relation to the continuity equation in the framework of current-density functional theory to our model since they explicitly involve the curl of a vector field. We thus reexamine the respective relations in the one-dimensional quantum ring.

The first question we have to answer in this context is, what a gauge transformation in the one-dimensional model looks like. In our model of a quantum ring pierced by a magnetic flux, such that the electrons move in a field-free region, the observables depend only on the flux

$$\Phi = \int dS \cdot B$$

(10.5)

but not directly on the magnetic field $B$. Thus, the requirement of gauge invariance means that the flux must not change under a gauge transformation of the external vector potential. Employing the Stokes theorem and noting that the external vector potential has only a non-vanishing tangential component we find

$$\Phi = \int dS \cdot B = \int dS \cdot \nabla \times A_{ext} = \oint_{\partial S} d1 \cdot A_{ext} = R \int_0^{2\pi} d\varphi A_{ext}(\varphi),$$

(10.6)

where $\partial S$ denotes the boundary of the surface $S$ and $A_{ext}$ is the modulus of the vector potential $A_{ext}$. Obviously, the flux will not change, if we add to $A_{ext}$ the derivative of any $2\pi$-periodic function, since

$$\int_0^{2\pi} d\varphi \frac{d}{d\varphi}\Lambda(\varphi) = \Lambda(2\pi) - \Lambda(0).$$

(10.7)
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But we already know that any gauge transformation $A_{\text{ext}} \rightarrow A_{\text{ext}} - \frac{d}{d\varphi} \Lambda$ will change the paramagnetic current density according to

$$j_{p,\sigma}(\varphi) \rightarrow j_{p,\sigma}(\varphi) + \frac{e}{m_0} n_{\sigma}(\varphi) \frac{d}{d\varphi} \Lambda(\varphi),$$

which suggests to define the gauge invariant quantity

$$\nu_{\sigma} = \int_0^{2\pi} d\varphi \frac{j_{p,\sigma}(\varphi)}{n_{\sigma}(\varphi)}$$

as the one-dimensional analogue of the vorticity. Note that $\nu_{\sigma}$ is simply a number and thus the derivative $\frac{\partial E_{\text{xc}}}{\partial \nu_{\sigma}}$ (where the exchange-correlation energy functional is considered as a functional of the density and $\nu_{\sigma}$) will also be position-independent. This derivative is closely related to the one-dimensional version of the exchange-correlation vector potential via

$$eA_{\text{xc},\sigma}(\varphi) = \frac{\delta E_{\text{xc}}}{\delta j_{p,\sigma}(\varphi)} = \frac{\partial E_{\text{xc}}}{\partial \nu_{\sigma}} \frac{\delta \nu_{\sigma}}{\delta j_{p,\sigma}(\varphi)} = \frac{1}{n_{\sigma}(\varphi)} \frac{\partial E_{\text{xc}}}{\partial \nu_{\sigma}}.$$

The latter expression ensures that $n_{\sigma}(\varphi) A_{\text{xc},\sigma}(\varphi) = \text{const.}$ which in turn guarantees that the physical current of the interacting system obeys the continuity equation (see the general three-dimensional discussion above). In one dimension this means that this current is simply a constant.

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Solution of the CDFT-KLI equations

The CDFT-KLI equations are a set of coupled Fredholm integral equations of the second kind with a separable kernel. Thus, in principle any of these equations can be solved separately with the method used for the solution of the DFT-KLI equation (cf. section 5.2), provided that some approximation for the other exchange-correlation potential is already available. This technique therefore suggests an iterative solution of the CDFT-KLI equations, which can be implemented in different ways. For instance, one could use the exchange-correlation potentials from the previous iteration cycle of the Kohn-Sham system as an input and solve the CDFT-KLI equations for the new exchange-correlation potentials [Pittalis et al., 2006; Helbig et al., 2008]. A different iterative method is to compute both the exchange-correlation vector potential $A_{\text{xc},\sigma}$ and the exchange-correlation scalar potential $V_{\text{xc},\sigma}$ for a given and fixed set of Kohn-Sham orbitals. While this solution might be a bit slower than the simultaneous iteration of the Kohn-Sham system and the CDFT-KLI equations, it allows somewhat better control over the solution of the CDFT-KLI equations. For this reason we implemented the latter technique, which will be outlined in the following. Since the restriction to the one-dimensional system is straightforward we prefer to present the general three-dimensional case.

First, the CDFT-KLI equations are transformed into algebraic equations for the averaged potentials $\overline{V}_{\text{xc},\sigma}^k$ and $\overline{A}_{\text{xc},\sigma}^k$. To this end we multiply equation (9.26) by $n_j(r)$ and integrate over $r$ to find

$$\overline{V}_{\text{xc},\sigma}^j + \overline{A}_{\text{n,\sigma}}^j = \overline{V}_{\text{Slater},\sigma}^j + \sum_k M_{V,\sigma}^{j,k} \left[ \overline{V}_{\text{xc},\sigma}^k + \overline{A}_{\text{xc},\sigma}^k - \Re \eta_{k,\sigma} \right],$$
where the abbreviations

\[ \overline{A}_{\sigma}^j = \int d^3r \frac{n_j,\sigma(r)}{n_\sigma(r)} j_{p,\sigma}(r) \cdot A_{xc,\sigma}(r) \]  
(10.12a)

\[ V_{\text{Slater}}^j = \int d^3r n_j,\sigma(r) \sum_{k=1}^{N_\sigma} \frac{n_k,\sigma(r)}{n_\sigma(r)} \Re u_{k,\sigma}(r) \]  
(10.12b)

\[ M_{\sigma}^{k,j} = \int d^3r \frac{n_k,\sigma(r)n_j,\sigma(r)}{n_\sigma(r)} \]  
(10.12c)

have been defined. The freedom to add a constant to the scalar exchange-correlation potential is reflected by the fact that the rank of the \( N_\sigma \times N_\sigma \)-matrix (for a system of \( N_\sigma \) particle with spin \( \sigma \)) \( \hat{1} - \hat{M}_{xc,\sigma} \) is \( N_\sigma - 1 \) (see the discussion about fixing the asymptotic behaviour of the exchange-correlation potential in section 5.2). Consequently, one has to solve \( N_\sigma - 1 \) independent linear equations and the remaining average \( \overline{V}_{xc,\sigma} \) is set equal to \( \Re \eta_{N_\sigma,\sigma} \) which imposes the correct asymptotics [Krieger et al., 1992a,b]. Given that some approximation for the exchange-correlation vector potential \( A_{xc,\sigma} \) is already known, one can solve equation (10.11) by exactly the same technique used in the solution of the DFT-KLI equation.

Similarly, after multiplying equation (9.28) with the inverse matrix \( \hat{N}^{-1}_{xc,\sigma} \) and doing a scalar multiplication with \( j_{p,j,\sigma}(r) \) we integrate over \( r \) to obtain:

\[ \overline{A}_{xc,\sigma}^j + \overline{V}_{c,\sigma}^j = \overline{A}_{\text{Slater},\sigma}^j + \sum_{j=1}^{N_\sigma} M_{A,\sigma}^{j,k} \left[ \overline{V}_{xc,\sigma}^k + \overline{A}_{xc,\sigma}^k - \Re \eta_{k,\sigma} \right] , \]  
(10.13)

where we have introduced the abbreviations

\[ \overline{V}_{c,\sigma}^j = \int d^3r j_{p,j,\sigma}(r) \cdot \left( \hat{N}^{-1}_{xc,\sigma}(r) j_{p,\sigma}(r) \right) V_{xc,\sigma}(r) \]  
(10.14a)

\[ \overline{A}_{\text{Slater},\sigma}^j = \int d^3r j_{p,j,\sigma}(r) \cdot \sum_{k=1}^{N_\sigma} \hat{N}^{-1}_{xc,\sigma}(r) \left[ j_{p,k,\sigma}(r) \Re u_{k,\sigma}(r) - n_{k,\sigma}(r) \Im \nabla u_{k,\sigma}(r) \right] \]  
(10.14b)

\[ M_{A,\sigma}^{k,j} = \int d^3r j_{p,k,\sigma}(r) \cdot \left( \hat{N}^{-1}_{xc,\sigma}(r) j_{p,j,\sigma}(r) \right) . \]  
(10.14c)

The name "\( \overline{A}_{\text{Slater},\sigma}^j \)" has been chosen since this term corresponds to the average of the Slater potential in the DFT-KLI and the first CDFT-KLI equations. It might, however, be somewhat misleading and in particular it should not be considered as a close analogue of the Slater potential being a local approximation to the Hartree-Fock potential.

The iterative solution of the CDFT-KLI equations can now be done as follows. First, set \( A_{xc,\sigma} = 0 \) and solve equation (10.11) for the scalar exchange-correlation potential \( \overline{V}_{xc,\sigma} \) averaged with the partial densities (see section 5.2). With the averages \( \overline{V}_{xc,\sigma} \) one can compute the scalar exchange-correlation potential \( V_{xc,\sigma} \) from the first CDFT-KLI equation (9.26), which in turn is plugged into equation (10.13) to determine the exchange-correlation vector potential \( \overline{A}_{xc,\sigma}^j \) averaged with the partial current densities. Finally, from the averages \( \overline{A}_{xc,\sigma}^j \) the exchange-correlation vector potential \( A_{xc,\sigma} \) is calculated using the second CDFT-KLI equation (9.28). This scheme can be iterated to obtain converged exchange-correlation scalar and vector potentials.

In order to check whether we have found a converged solution, we used two different tests. The first, and more obvious one, is to insert the exchange-correlation scalar and vector potential into the right-hand side of the CDFT-KLI equations and compare the resulting exchange-correlation potentials to the original
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As a second test we computed the CDFT-KLI exchange-correlation potentials using an independent method. This method basically expands all functions in the spline-basis (see section A.1) and hence expresses the CDFT-KLI equations themselves as matrix equations. These two matrix equations may now be combined into one matrix equation which is solved in a single step without the need for any iterative procedure. We always found that the potentials agree to within the numerical accuracy.

Iterative solution of the CDFT-OEP equations: the general three-dimensional case

An iterative solution of the full CDFT-OEP equations can be implemented in the spirit of the method proposed by Kümmel and Perdew [2003b,a], which has already been introduced in section 5.3 as our method of choice for the solution of the DFT-OEP equation. This iterative scheme has been extended to non-collinear spin-density functional theory and later to current-spin density functional theory by Sharma et al. [2007a,b].

As in density functional theory OEP, we compute the orbital shifts for some approximate solution of the exchange-correlation scalar and vector potential using a fixed set of Kohn-Sham orbitals. Since these approximate exchange-correlation potentials were probably not the solutions of the OEP equations, instead of giving zero, they yield the residuals

\[ S_{V,\sigma}(r) = \sum_{k=1}^{N_\sigma} \phi_k^* \psi_k \psi_k^* \phi_k^* + \text{c.c.} \quad \text{and} \]
\[ S_{A,\sigma}(r) = \frac{1}{2i} \sum_{k=1}^{N_\sigma} \left[ \phi_k^* \nabla \psi_k - \psi_k \nabla \phi_k^* + \text{c.c.} \right] \]

We can use the residuals \( S_{V,\sigma} \) and \( S_{A,\sigma} \) to improve the approximate exchange-correlation potentials by performing an update according to

\[ V_{xc,\sigma}^{\text{new}}(r) = V_{xc,\sigma}(r) + \gamma_{V,\sigma} S_{V,\sigma}(r) \quad \text{and} \]
\[ A_{xc,\sigma}^{\text{new}}(r) = A_{xc,\sigma}(r) + \gamma_{A,\sigma} S_{A,\sigma}(r) \]

The positive constants \( \gamma_{V,\sigma} \) and \( \gamma_{A,\sigma} \) can in practice be obtained by trial without problems.

For the calculation of the orbital shift, Sharma et al. [2007a,b] employed directly its definition (9.15) which involves a summation over all orbitals, including unoccupied orbitals. In our implementation we pursue a different scheme similar to the one used to calculate the DFT-OEP orbital shift in section 5.3. To find a differential equation which determines the orbital shift we start by acting on equation (5.13) with the operator \( \hat{H}_{S,\sigma} - \varepsilon_{k,\sigma} \), which allows us to get rid of the energy denominator \( \varepsilon_{k,\sigma} - \varepsilon_{j,\sigma} \) and we obtain
the expression

$$\left( \hat{H}_{S,\sigma} - \varepsilon_{k,\sigma} \right) \psi_{k,\sigma}(r) = - \sum_{j \neq k} \phi_{j,\sigma}(r) \int d^3r' \left\{ V_{xc,\sigma}(r') - u_{k,\sigma}^*(r') \right\} \phi_{j,\sigma}(r') \phi_{k,\sigma}(r')$$

$$- \frac{i\hbar}{2m_0^*} A_{xc,\sigma}(r') \cdot \left( \phi_{j,\sigma}(r') \nabla' \phi_{k,\sigma}(r') - \phi_{k,\sigma}(r') \nabla' \phi_{j,\sigma}(r') \right) \right\}$$

$$= - \int d^3r' \left\{ \phi_{k,\sigma}(r') \left( V_{xc,\sigma}(r') - u_{k,\sigma}^*(r') \right) \sum_{j} \phi_{j,\sigma}^*(r') \phi_{j,\sigma}(r) \right\} \right\}$$

$$- \frac{i\hbar}{2m_0^*} A_{xc,\sigma}(r') \cdot \left[ \left( \nabla' \phi_{k,\sigma}(r') \right) \sum_{j} \phi_{j,\sigma}^*(r') \phi_{j,\sigma}(r) \right\}$$

$$- \phi_{k,\sigma}(r') \nabla' \sum_{j} \phi_{j,\sigma}^*(r') \phi_{j,\sigma}(r) \right\}$$

$$+ \phi_{k,\sigma}(r) \left( \frac{V^k_{xc,\sigma}}{\hbar_0} + \frac{A^k_{xc,\sigma}}{\hbar_0} - \overline{u}_{k,\sigma}^* \right).$$

Performing a partial integration, the term $$\frac{i\hbar}{2m_0^*} \int d^3r' A_{xc,\sigma}(r') \phi_{k,\sigma}(r') \nabla' \sum_{j} \phi_{j,\sigma}^*(r') \phi_{j,\sigma}(r)$$ can be written

$$\frac{i\hbar}{2m_0^*} \int d^3r' A_{xc,\sigma}(r') \phi_{k,\sigma}(r') \nabla' \sum_{j} \phi_{j,\sigma}^*(r') \phi_{j,\sigma}(r)$$

$$= - \frac{i\hbar}{2m_0^*} \int d^3r' \sum_{j} \phi_{j,\sigma}^*(r') \phi_{j,\sigma}(r) \nabla' A_{xc,\sigma}(r') \phi_{k,\sigma}(r')$$

and we find the differential equation

$$\left( \hat{H}_{S,\sigma} - \varepsilon_{k,\sigma} \right) \psi_{k,\sigma}(r) = - \left( V_{xc,\sigma}(r) - u_{k,\sigma}^*(r) \right) \phi_{k,\sigma}(r) + \frac{i\hbar}{m_0^*} A_{xc,\sigma}(r) \cdot \left( \nabla \phi_{k,\sigma}(r) \right)$$

$$+ \frac{i\hbar}{2m_0^*} \left( \nabla \cdot A_{xc,\sigma}(r) \right) \phi_{k,\sigma}(r) + \left( \overline{V}^k_{xc,\sigma} + \overline{A}^k_{xc,\sigma} - \overline{u}_{k,\sigma}^* \right) \phi_{k,\sigma}(r).$$

As already discussed when presenting the construction of the DFT orbital shift in section 5.3, the operator $$\hat{H}_{S,\sigma} - \varepsilon_{k,\sigma}$$ is not invertible since there exists at least one function which satisfies $$\left( \hat{H}_{S,\sigma} - \varepsilon_{k,\sigma} \right) \phi_{k,\sigma}(r) = 0$$. Yet, in the subspace orthogonal to the subspace spanned by all functions which are mapped onto zero, it can be inverted using the technique based on a singular value decomposition described in section 5.3. Acting with this inverse on the right-hand side of equation (10.19)—which can easily be computed for a given approximation of the exchange-correlation potentials and a given set of Kohn-Sham orbitals—one obtains the orbital shifts. The orbital shifts can then be used to calculate the residuals (10.15a) and (10.15b) which in turn yield new approximations for the exchange-correlation potentials via the updates given by equations (10.16a) and (10.16b). At this point, one enforces the correct asymptotics for the scalar
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Exchange-correlation potential by requiring

\[ V_{xc,\sigma}^{N_\sigma} = \Re \pi_{N_\sigma,\sigma}, \]  

(10.20)

which can be done by subtracting the term

\[ \int d^3r \left[ V_{xc,\sigma}(r) - \Re u_{N_\sigma,\sigma}(r) \right] n_{N_\sigma,\sigma}(r) \]  

(10.21)

from \( V_{xc,\sigma} \).

Finally, we should mention that the residuals—since they measure the deviation between an approximate solution of the CDFT-OEP equations and the correct one—can be directly used to determine whether the iterations has already converged or not. In practice, it turns out that the exchange-correlation vector potential converges much slower than the scalar exchange-correlation potential. It is therefore the residual \( S_{A,\sigma} \) which should be monitored.

Iterative solution of the quasi one-dimensional CDFT-OEP equations: a numerical example

For comparison to the CDFT-KLI exchange potentials we also compute the CDFT-OEP potentials using the iterative solution method outlined above. In the following we use the quasi one-dimensional quantum ring model to illustrate the iterative method. For simplicity we neglect the electron spin throughout the remainder of this chapter which does not qualitatively alter our conclusions.

For the one-dimensional model system under consideration containing \( N = 10 \) electrons the CDFT-OEP equations read

\[ \sum_{k=1}^{N} \psi_k^*(x) \phi_k(x) + \text{c.c.} = 0 \]  

(10.22a)

\[ \frac{1}{2i} \sum_{k=1}^{N} \left[ \phi_k^*(x) \frac{d}{dx} \psi_k(x) - \psi_k(x) \frac{d}{dx} \phi_k^*(x) \right] + \text{c.c.} = 0 \]  

(10.22b)

where \( x \) denotes the coordinate along the ring. Given an orbital-dependent exchange-correlation energy functional—for which we take the quasi one-dimensional exact-exchange functional containing the modified quasi one-dimensional Coulomb interaction (7.6)—the CDFT-OEP equations have to be solved for the potentials \( V_x(x) \) and \( A_x(x) \) for a given set of Kohn-Sham orbitals \( \{ \phi_k \} \). We will solve the CDFT-OEP equations iteratively, starting with \( V_x = 0 \) and \( A_x = 0 \).

Using the fixed set of Kohn-Sham orbitals and the present exchange potentials \( V_x \) and \( A_x \), the orbital shifts \( \psi_k(r) \) are obtained in every iteration step from the differential equation (10.19) which reads in the one-dimensional case

\[ \left( \hat{H}_S - \varepsilon_k \right) \psi_k(x) = - \left( V_x(x) - u_k^*(x) \right) \phi_k(x) + \frac{i\hbar}{m_0} A_x(x) \frac{d}{dx} \phi_k(x) \]

\[ + \frac{i\hbar}{2m_0} \left( \frac{d}{dx} A_x(x) \right) \phi_k(x) + \left( V_x^k + A_x^k - \overline{u_k}^k \right) \phi_k(x). \]  

(10.23)

The orbital shifts computed with some approximate \( V_x \) and \( A_x \) will not satisfy the CDFT-OEP equations, i.e. the right hand sides of the equations (10.22a) and (10.22b) will not vanish but rather yield the residual functions \( S_V(x) \) and \( S_A(x) \). Following Kümmel and Perdew [2003b], Sharma et al. [2007b] and the
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Discussion presented above, we use the residual functions to find better approximations $V_x(x)$ and $A_x(x)$ by updating the potentials according to

$$V_x(x) \rightarrow V_x(x) + \gamma_V S_V(x) \quad \text{(10.24a)}$$

$$A_x(x) \rightarrow A_x(x) + \gamma_A S_A(x) \quad \text{(10.24b)}$$

For the positive constants $\gamma_V$ and $\gamma_A$ a value of two was chosen, which results in a stable convergence in the present study.

If the iterative scheme converges, then the deviation between the approximate potentials and the true solution of the CDFT-OEP equations should decrease in the course of the iteration. The residual functions $S_V(x)$ and $S_A(x)$ provide a measure for this deviation. Indeed, we can infer from the top panel in figure 10.1 which shows the initial values of the residual function $S_A(x)$, i.e. those obtained from $A_x = 0$ and $V_x = 0$ (solid black curve) as well as the respective values after two (dashed red curve), five (dotted blue curve) and twenty (dash-dotted green curve) iterations that $S_A(x)$ approaches zero.

Unfortunately, it is by far not enough to use twenty iteration steps as can be seen from figure 10.2 where we plot the exact-exchange vector potential $A_x(x)$ as obtained after twenty iterations (solid black curve), fifty iterations (dashed red curve), one hundred iterations (dotted blue curve) and two hundred iterations (dash-dotted green curve). The respective residual functions are shown in the bottom panel of figure 10.1. Doing up to 250 iteration steps we checked that the exact-exchange vector potential is indeed converged after around 200 iterations.

At the beginning of the iterative solution of the CDFT-OEP equations, $A_x$ largely overshoots to negative values as can be seen from the initial value of the residual $S_A$ shown as the solid black curve in the top panel of figure 10.1 (after the first iterations step, $A_x$ is simply given by $S_A(x)$ multiplied by the constant $\gamma_A$). From this large negative values, the exchange vector potential subsequently evolves slowly towards

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**Figure 10.1.**: Residual $S_A$ as a function of the coordinate along the ring.
Top panel: The solid black curve is the initial value of the residual, i.e. calculated with $A_x = 0$ and $V_x = 0$. The dashed red curve is the residual after two iterations, the dotted blue curve after five iterations and the dash-dotted green curve after 20 iterations.
Bottom panel: The solid black curve shows the residual $S_A$ after twenty iterations (same as the dash-dotted green curve in the top panel), the dashed red curve after fifty iterations, the dotted blue curve after one hundred iterations and the dash-dotted green curve after two hundred iterations.
the converged small positive values. The large number of iteration cycles needed can thus be partially traced back to the overshooting at the beginning of the iteration. A straightforward remedy is to start the iterative solution of the CDFT-OEP equations in the next iteration cycle of the Kohn-Sham system using the previously obtained $V_x$ and $A_x$ as initial values instead of zero.

Simultaneous with the calculation of the exchange vector potential, the scalar exchange potential $V_x(x)$ has to be found. In fact, the calculation of $V_x$ poses no special difficulty and converges much faster than the calculation of $A_x$. To illustrate this, we plot in figure 10.3 the residual function $S_V(x)$ as obtained after ten iterations (solid black curve), forty iterations (dashed red curve), seventy iterations (dotted blue curve) and two hundred iterations (dash-dotted green curve).

The error of the scalar exchange potential measured by the residual $S_V(x)$ clearly converges much faster to zero than the error of the exchange vector potential. After seventy iteration steps we can consider $V_x$ to be converged. This is seen from figure 10.4, where we plot the scalar exchange potential as obtained after ten iterations (solid black curve), forty iterations (dashed red curve) and after seventy iterations (dotted blue curve). Nevertheless, we further iterate $V_x$ together with $A_x$ and checked that $V_x$ is left unchanged during the remaining iteration steps. To speed up computation one might consider to stop the iteration of $V_x$ considerably earlier than the iteration of $A_x$.

### 10.2. OEP vs. KLI exchange potentials: implications for the persistent current

In this section we present the results of converged ground state CDFT calculations for the model system described above. We compare the density, current density and the exchange potentials $V_x(x)$ and $A_x(x)$ as obtained from a CDFT-KLI calculation with those found from a CDFT-OEP calculations. In every iteration step of the Kohn-Sham system, the CDFT-OEP equations have been solved using the method outlined in the previous section.
10. Exact-exchange CDFT: symmetry-broken system and violation of the continuity equation in the KLI approximation

**Figure 10.3.** The residual $S_V(x)$ as a function of the coordinate along the ring after ten iterations (solid black curve), forty iterations (dashed red curve), seventy iterations (dotted blue curve) and two hundred iterations (dash-dotted green curve).

**Figure 10.4.** The scalar exact-exchange potential $V_x$ as a function of the coordinate along the ring after ten iterations (solid black curve), forty iterations (dashed red curve) and seventy iterations (dotted blue curve). The inset shows a zoom into the region around the global maximum where the deviations between the potentials obtained in different iterations steps are most prominent.
10.2. OEP vs. KLI exchange potentials: implications for the persistent current

First, we show in figure 10.5 a comparison between the scalar CDFT-KLI exchange potential and the scalar CDFT-OEP exchange potential. We observe only a minor difference between both potentials. The oscillations of the exact CDFT-OEP potential (the dashed blue curve) are slightly more pronounced, yet for the system presently under consideration the difference is small enough so that it does not influence the density. The latter is shown in figure 10.6 where we find that the ground state density found from the CDFT-KLI calculation coincides very well with the ground state density obtained from the CDFT-OEP calculation.

Next, we compare the exchange vector potential obtained from a solution of the CDFT-OEP equations to the respective potential computed using the CDFT-KLI approximation. Figure 10.7 displays a striking difference between both potentials. While the CDFT-OEP vector potential is inversely proportional to the density (see inset in figure 10.7), the CDFT-KLI vector potential—which differs significantly from the CDFT-OEP vector potential—clearly does not satisfy the condition \( n(x)A_x(x) = \text{const.} \). The latter is the one-dimensional (exchange-only) analogue of the general three-dimensional condition \( \nabla \cdot [n(r)A_{xc}(r)] = 0 \) which ensures that the current of the interacting system obeys the continuity equation. Consequently, the CDFT-KLI current shown as the solid green curve in figure 10.8 is not constant and thus clearly violates the continuity equation. In contrast, the latter is satisfied by the constant CDFT-OEP current (the dashed blue line in figure 10.8). As is seen from the spatially constant Kohn-Sham currents displayed in the inset in figure 10.8, the violation of the continuity equation can indeed be traced back to the CDFT-KLI exchange vector potential \( A_x \) which does not meet the requirement \( n(x)A_x(x) = \text{const.} \).

Finally we mention that we also checked numerically, that both the CDFT-KLI scalar and vector exchange potentials and the CDFT-OEP scalar and vector exchange potentials transform under a gauge...
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**Figure 10.6.** The ground state density of the ten-electron quantum ring. The solid green curve shows the CDFT-KLI result, the dashed blue curve the CDFT-OEP result.

**Figure 10.7.** The exchange vector potential $A_x(x)$ as a function of the coordinate along the ring for the ten-electron system. The solid green curve shows the CDFT-KLI potential, the dashed blue curve the CDFT-OEP potential. The inset shows the exchange vector potentials multiplied by the density.
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Figure 10.8.: The ground state current density of the ten-electron quantum ring. The solid green curve shows the CDFT-KLI result which clearly violates the continuity equation, the dashed blue curve shows the CDFT-OEP result. The inset shows the full Kohn-Sham currents, which both obey the continuity equation.

The transformation \( A_{\text{ext}} \rightarrow A_{\text{ext}} + \frac{d}{dx} \Lambda(x) \) according to equations (8.19a) and (8.19b), i.e. according to

\[
V_x(x) \rightarrow V^\Lambda_x(x) = V_x(x) - \frac{e^2}{m^*_0} A_x(x) \frac{d}{dx} \Lambda(x) \quad (10.25a)
\]

\[
A_x(x) \rightarrow A^\Lambda_x(x) = A_x(x) \quad (10.25b)
\]

Both the CDFT-KLI and the CDFT-OEP equations thus yield exchange potentials which lead to Kohn-Sham eigenvalues and a ground state energy that are gauge invariant. But isn’t this an obvious contradiction to a very general statement based on linear response theory that gauge invariance and compliance with the continuity equation are just two different aspects of the same thing [Pines and Nozieres, 1966]? In fact, it is not. On one hand, the Kohn-Sham current, which is the full current of the non-interacting Kohn-Sham particles subjected to the effective vector potential \( A_S \) obeys the continuity equation and is gauge invariant. On the other hand, Vignale and Rasolt [1988] showed that the same is true for the full current of the interacting system calculated from the CDFT Kohn-Sham orbitals provided that the exchange-correlation vector potential is the functional derivative of \( E_{xc} \) with respect to the paramagnetic current density. The apparent violation of the continuity equation in the present example is caused by an approximate exchange-correlation vector potential which only satisfies one of two—in principle equivalent—conditions: it transforms correctly under a gauge transformation but it does not obey the condition \( \nabla \cdot [n(r)A_{xc}(r)] = 0 \) thus leading to the wrong interacting current density.
10. Exact-exchange CDFT: symmetry-broken system and violation of the continuity equation in the KLI approximation

Figure 10.9.: Densities (top panel), scalar exchange potentials (central panel) and exchange vector potential (bottom panel) obtained from a DFT-OEP calculation and a CDFT-OEP calculation. The solid green lines represent the CDFT-OEP results, the dashed blue lines the DFT-OEP results. No difference between the DFT-OEP and CDFT-OEP densities and scalar exchange potentials is seen. The oscillations in the exchange vector potential can be considered as a numerical artifact. The impurity potential is chosen to be $V_0 = 0.1 \, \text{meV}$ and the interaction parameter is $r_S = 1.0$. The system is in the Fermi liquid phase.

10.3. Density functional theory vs. current-density functional theory

We have previously studied the Wigner crystallization in the framework of exact-exchange DFT employing the persistent current of the DFT Kohn-Sham system as the localization criterion (see chapter 7). This current usually provides a reasonable approximation to the true current density of the interacting system. Strictly speaking, however, one should resort to current-density functional theory where besides the density the paramagnetic current density is—in principle—guaranteed to coincide exactly with the respective quantity of the interacting system. As shown above, we can unfortunately not resort to the CDFT-KLI approximation since in the Wigner crystal phase (where the rotational symmetry is broken) the latter leads to a current of the interacting system that violates the continuity equation. On the other hand, the CDFT-OEP calculation is computationally even more demanding than the DFT-OEP calculation. For this reason, the calculation of the persistent current density for various values of the interaction parameter is not feasible. Still, while the persistent currents may differ in CDFT-OEP and DFT-OEP, so far we do not have reason to believe that the transition itself should be affected. Therefore, we will consider only two particular cases. First, the system with a weak impurity potential in the Fermi liquid phase and second, the system in the presence of a strong impurity potential which creates a strongly non-uniform density.

Let us first consider a system of ten spinless—or fully spin-polarized—electrons in the presence of an impurity potential with a strength $V_0 = 0.1 \, \text{meV}$ which is still weak enough not to influence the individual electrons considerably but leads to a faster convergence than the impurity potential with $V_0 = 0.001 \, \text{meV}$. Comparing a converged DFT-OEP and a converged CDFT-OEP calculation we do not find a notable difference. The CDFT-OEP calculation yields a persistent current density of $109381 \, \text{s}^{-1}$, whereas the DFT-OEP calculation predicts a persistent current density of $109380 \, \text{s}^{-1}$. We cannot consider this
10.3. Density functional theory vs. current-density functional theory

Figure 10.10: Densities (top panel), scalar exchange potentials (central panel) and exchange vector potential (bottom panel) obtained from a DFT-OEP calculation and a CDFT-OEP calculation. The solid green lines represent the CDFT-OEP results, the dashed blue lines the DFT-OEP results. The impurity potential is chosen to be $V_0 = 10$ meV and the interaction parameter is $r_S = 1.0$.

Differences to be significant. In figure 10.9 we show that also the densities (top panel) and the scalar exchange potentials (central panel) obtained from the CDFT-OEP (solid green lines) and the DFT-OEP (dashed blue lines) calculations almost coincide. The exchange vector potential shows oscillations with an amplitude of $10^{-6}$ (in units of the magnetic flux) which we can consider a numerical artifact: As can be seen from the bottom panel in figure 10.9 these oscillations do not show the $\frac{1}{n}$-behaviour required to ensure that the current of the interacting system obeys the continuity equation. In contrast, the $\frac{1}{n}$-behaviour of the exchange vector potential was always found in a system with more pronounced density oscillations. We are thus lead to the conclusion that in the one-dimensional rotationally invariant system DFT-OEP and CDFT-OEP coincide since the exchange vector potential in the latter vanishes. In fact, it can be shown that also the CDFT-KLI vector potential vanishes in a one-dimensional rotationally invariant system thus giving a correct approximation to the CDFT-OEP vector potential in this special case.

Of course, the more interesting case is a system which shows pronounced density oscillations. As it has not been possible due to the computational cost to perform a calculation of the Wigner transition using the CDFT-OEP method we will instead create a non-uniform density by placing a strong impurity potential with $V_0 = 10$ meV in the system. Again, we perform converged ground state calculations for the ten-electron ring threaded by a magnetic flux $\Phi = 0.3\Phi_0$ in DFT-OEP and CDFT-OEP. In both cases the interaction parameter is chosen to be $r_S = 1.0$.

The top panel of figure 10.10 shows the densities as obtained in the CDFT-OEP calculation (solid green curve) and in the DFT-OEP calculation (dashed blue curve). Clearly, the oscillation in the DFT-OEP density are much more pronounced than the oscillations in the CDFT-OEP density. The corresponding behaviour in the scalar exchange potential is shown in the central panel of figure 10.10. Consistently with the densities, the DFT-OEP potential (dashed blue curve) shows stronger oscillations than the scalar CDFT-OEP potential (solid green curve). The exchange vector potential (bottom panel) shows exactly the required $\frac{1}{n}$-behaviour (see also figure 10.7 which shows the CDFT-OEP exchange vector potential obtained with the same set of parameters). Having in mind the more homogeneous density distribution and scalar exchange potential in the CDFT-OEP result, it is not surprising that the persistent current
densities differ as well. From the CDFT-OEP calculation we obtain a value of $104551\,\text{s}^{-1}$, where the DFT-OEP calculation yields a persistent current density of $76271\,\text{s}^{-1}$, i.e. only about 73% of the value in the CDFT-OEP calculation. It was previously reported that an application of the CDFT-OEP method leads to a stronger paramagnetic current in bulk Germanium than the calculation employing the DFT-OEP method [Sharma et al., 2007b]. While this system is clearly very different from our model system at least the tendency of the CDFT-OEP method to predict stronger currents than the DFT-OEP method agrees with our result.

Comparing the Kohn-Sham currents, which are $76271\,\text{s}^{-1}$ in the DFT-OEP calculation and $95693\,\text{s}^{-1}$ in the CDFT-OEP calculation (which differ only by about 20%), it is clear that we can only partly attribute this increase in the persistent current density in the CDFT-OEP calculation to the presence of an additional exchange vector potential. The strength of the latter is only about 2% of the strength of the external vector potential. Another important reason for the enhanced current density in the CDFT-OEP calculation is the reduced amplitude in the scalar exchange potential as compared to the DFT-OEP calculation. In other words, CDFT-OEP tends to delocalize the electrons. It remains to be seen how this can affect the Wigner transition.
11 Summary and conclusion

A Wigner molecule is a correlated many-electron state with electrons forming a certain crystal-like configuration. At low electron densities such a crystalline state supersedes the Fermi liquid state as the Coulomb interaction becomes dominant over the kinetic energy. In a perfectly clean system, i.e. without any pinning potential, the Wigner molecule can slide such that the crystalline order can be visible only in a co-moving reference frame. Indeed, quantum Monte Carlo calculations revealed that the pair correlation function shows no structure in the weakly interacting quantum ring whereas pronounced oscillations are observed in the strongly interacting case [Pederiva et al., 2002; Emperador et al., 2003]. In contrast to the Fermi liquid state, the Wigner molecule can be pinned by an arbitrarily weak pinning potential which has no discernible effect on individual electrons. This pinning results in a collective localization of electrons in the laboratory frame.

The main purpose of this work is to investigate the formation of a pinned Wigner molecule in the framework of exact-exchange density (DFT) and spin-density functional theory (SDFT). To distinguish the Fermi liquid from the correlated state we resort exclusively to simple collective variables like the density and the persistent current density. Such collective variables are perfectly accessible within the density functional theory which casts the many-electron problem exclusively in terms of density (in DFT), spin-density (in SDFT) or paramagnetic current density (in current density functional theory, CDFT). Most applications of DFT—including the ones presented in this work—employ the Kohn-Sham scheme. The latter defines an auxiliary system of non-interacting particles moving in an effective local potential such that its ground-state density (spin-density or paramagnetic current density) coincides with the respective quantity of the interacting system. While DFT is formally exact, a practical calculation requires a suitable approximation for the exchange-correlation energy functional which accounts for all quantum many-body effects. Already a simple approximation based on the homogeneous electron gas (like the local density approximation, LDA) might be suitable for describing the Wigner state provided that the homogeneous reference system contains Wigner crystal-type correlations in the low-density limit. Yet, the LDA suffers from the self-interaction error which leads to delocalization of electrons and thus opposes the formation of a Wigner molecule. One needs here a more sophisticated self-interaction free functional capable to describe strongly correlated systems. In this work we employ the probably most prominent such functional which is the exact-exchange functional. The latter is the Fock exchange energy evaluated with the Kohn-Sham orbitals.

An orbital-dependent exchange-functional requires the application of the optimized effective potential (OEP) method which allows to determine the local effective Kohn-Sham potential from a functional that depends only implicitly on the density. Unfortunately, the OEP equation for the effective potential is a very complicated integral equation. The problem is dramatically simplified by using the Krieger-Li-Iafrate (KLI) approximation which typically yields the ground state quantities (e.g. the ground state energy) very close to the OEP values. We carried out most of the calculations using the KLI approximation. We found, however, that the KLI approximation has its limitations which become most crucial when the current-DFT is employed (see below).

The model system we study consists of ten electrons on a quasi one-dimensional quantum ring. The ring is penetrated by a magnetic flux which induces a persistent current and a very weak Gaussian impurity potential is placed in the ring that pins the Wigner molecule but leaves the individual electrons essentially unaffected.
First, we study the model of fully spin-polarized electrons confined to the quasi one-dimensional quantum ring. Starting from an almost non-interacting system, we increase the electron-electron interaction (expressed via the dimensionless parameter \( r_S \)) and calculate the persistent current density in the quantum ring as a function of the interaction parameter. For electrons in the Fermi liquid state the persistent current density equals that of the non-interacting system. In particular, it is independent of \( r_S \). As the interaction between the electrons is increased, the Coulomb repulsion becomes more and more dominant over the kinetic energy. The latter favours the delocalized state while the Coulomb repulsion tends to localize electrons at discrete lattice sites to minimize the Coulomb energy. At some critical \( r_S \) value the persistent current density drops sharply below its non-interacting value. On further increasing the interaction parameter, the persistent current density decays exponentially. Simultaneously, oscillations in the electron density and the electron localization function (ELF) start to build up. The ELF is closely related to the pair correlation function and provides a real-space picture of electron localization. Thus the decay of the persistent current density signifies the formation of a Wigner molecule which is pinned by the impurity potential.

Choosing the amplitude of the charge-density oscillations as the order parameter, we show that at the critical value of the interaction parameter the system undergoes a second-order quantum phase transition from the uniform electron liquid to the pinned Wigner molecule. In agreement with the Landau theory of the second order phase transition, the amplitude of the density oscillations vanishes in the high-symmetry phase (i.e. the Fermi liquid state encountered at low \( r_S \) values) and shows a square-root dependence \( \sim \sqrt{r_S - r_{cS}} \) in the Wigner crystal phase (i.e. for values of the interaction parameter which exceed the critical value \( r_{cS} \)). Replacing the very weak impurity potential by a potential with the strength comparable to the electron Coulomb interaction results in a gradual (instead of an abrupt) localization transition. This is reflected by a persistent current density which now depends on the interaction parameter for all values of \( r_S \). This behaviour fits very well into the mean-field Landau theory which predicts the smearing out of the phase transition by a symmetry-breaking external field.

A very interesting behaviour involving two subsequent Wigner transitions is found if we include the electrons’ spin degree of freedom in our model. Considering a system with fixed numbers \( N_{↑} \) and \( N_{↓} \) of spin-up and spin-down electrons (without loss of generality we can assume \( N_{↑} \geq N_{↓} \)) we find that the spin subsystem with the smaller number of electrons (e.g. the spin-down subsystem) undergoes a Wigner transition at higher density compared to the fully spin-polarized case. This transition is signaled by a sharp decrease of the persistent current of the respective spin subsystem. The localized charge density of the spin-down subsystem provides a strong pinning potential to the spin-up subsystem which consequently shows a rather smooth Wigner transition. After both subsystems have undergone a Wigner transition we find an antiferromagnetic ordering of the electrons. Both the existence of the Wigner molecule and the antiferromagnetic spin ordering are in a very good agreement with the results obtained using the configuration interaction method [Koskinen et al., 2001; Liu et al., 2006, 2008] and with quantum Monte Carlo calculations [Pederiva et al., 2002; Emperador et al., 2003]. Interestingly, in contrast to the fully spin-polarized case, the critical \( r_{cS} \) in the spin-dependent calculations depends on the effective width of the ring. We find that in the spin-dependent systems \( r_{cS} \) is smaller for the rings with a smaller effective width. This observation is in good qualitative agreement with exact results. Using the quantum Monte Carlo method, Shulenburger et al. [2008] found that a Wigner crystal is formed in quasi one-dimensional wire. If the effective width of the wire was made smaller (similar to the present work the finite width was incorporated into a modified Coulomb interaction), the Wigner crystallization was observed at a higher critical density.

The spin magnetization and the structure of the ground state are obtained for various values of the interaction parameter by calculating the ground state energy and the persistent current for all admissible values of the magnetization \( |N_{↑} - N_{↓}| \), i.e. under the constraint \( N_{↑} + N_{↓} = N = \text{const} \). We find that at small values of the interaction parameter, the ground state is an unpolarized Fermi liquid state. At
intermediate $r_S$ a Wigner molecule with an antiferromagnetic spin ordering supersedes the Fermi liquid state and finally at large $r_S$ values a fully polarized Fermi liquid state is the ground state. From the fully spin-polarized calculation reported above we can infer that eventually also this polarized Fermi liquid ground state will be replaced by a fully spin-polarized Wigner molecule at an $r_S$ value that is an order of magnitude larger than the $r_S$ value at which the polarization transition is observed. The existence of a fully spin polarized ground state at the strongly interacting quantum ring is in agreement with Hartree-Fock calculations [Bellucci and Onorato, 2009]. While this does not come as a surprise (because the exact-exchange DFT and the Hartree-Fock method both emphasize the exchange contribution), Bellucci and Onorato [2009] found that including first-order correlations beyond the Hartree-Fock has a significant influence on these $r_S$ values where the transition from one ground state to the next one occurs. In the strongly interacting system, the inclusion of first-order correlations leads to the same fully spin-polarized ground state as in the Hartree Fock calculation. The possible emergence of a fully spin-polarized ground state is also supported by “exact” calculations. Using the quantum Monte Carlo method, Pederiva et al. [2002] reported that in a quasi one-dimensional quantum ring containing six electrons, there are states with different total spin which are almost degenerate with the ground state at large $r_S$ values. A similar result was found by Saiga et al. [2007] who studied a one-dimensional quantum ring containing up to five electrons by exact diagonalization. While in this calculation the state with maximal total spin was never the unique ground state, states with different total spin became degenerate when the ring circumference was increased, i.e. the density was decreased. Since exact-exchange density functional theory emphasizes the exchange contribution to the total energy, it is understandable that it selects among the degenerate ground states (or the states nearly degenerate with the ground state) the fully spin-polarized one.

In most of the calculations we computed the exact-exchange potential within the KLI approximation to the OEP equations. To validate the KLI approximation we study the Wigner transition of the fully spin-polarized system iteratively solving the full OEP equation. We find that a full solution of the OEP equation tends to localize the system at higher densities than the KLI approximation does. This result can be explained by the higher potential barriers separating the electrons which are found from the full solution of the OEP equation. The higher potential barriers resulting in the exact OEP solution are in agreement with previously published results for a chain of hydrogen atoms [Kümmel et al., 2004]. Since the precise value of the transition point depends on the system parameters (e.g. on the magnetic flux penetrating the ring) one might think that a mere shift of the transition point is unimportant. Yet, this result should also be seen as a warning: the KLI approximation may predict a delocalized state for a system which in reality is already in a localized state (at least within exact-exchange density functional theory).

Finally, shouldn’t we have used the current-spin density functional theory instead of spin-density functional theory? In principle yes, since only the former can yield the exact current density. Yet, the exact-exchange current-spin density functional theory calculation is computationally much more expensive. The bad news is that we cannot employ the CDFT-KLI approximation, not even as an approximation to the full solution of the CDFT-OEP equations. We have shown that the solution of the CDFT-KLI equations leads to the current of the interacting system that violates the continuity equation. In contrast, the full solution of the CDFT-OEP equations does not suffer from this shortcoming. Due to the computational cost of a full CDFT-OEP calculation we report only two examples. First, in the Fermi liquid phase the persistent currents calculated using the DFT-OEP and the CDFT-OEP methods coincide. Second, placing a strong impurity potential in the system we explicitly break the rotational invariance which results in a non-uniform density. Surprisingly, the currents calculated from a solution of the CDFT-OEP equations and the DFT-OEP equation differ by almost thirty percent and the electron density shows considerably stronger oscillations in the DFT-OEP solution. Thus CDFT-OEP favours the electron delocalization. It remains to be seen how this affects the Wigner transition.
A Numerics

The numerical solution of the Kohn-Sham and optimized effective potential equations requires a repre-
sentation which can be implemented on the computer. Generally speaking, the following two different
approaches are feasible: The first one is a discrete real space representation of the position-dependent
functions on a grid, which means that only the values at the grid points are stored. The second method is
the expansion of all functions in a basis.\footnote{Obviously, the choice of a \( \delta \)-basis leads to a representation of the first kind.}

A basis which is frequently used in solid-state DFT codes is the plane-wave basis since it is particularly
well suited for extended or periodic systems. However, the description of localized electrons requires a
large number of plane waves which makes it inefficient for the problems treated in this thesis. While a
discrete real space representation would reduce the computational effort related to the large basis, it has
the drawback, that all derivatives and matrix elements have to be computed numerically. An appealing
way to profit both from the localized functions as well as from the easy computation of derivatives and
matrix elements is the choice of localized \( C^2 \)-functions. One such basis is the b-spline basis \cite{Hofmann et al., 2001}. In this work we will exclusively discuss a quasi one-dimensional model and thus restrict
ourselves to the representation of one-dimensional functions and the corresponding matrix elements in
the spline-basis. The numerical code we use is based on the code used by Hofmann \cite{2005b}.

A.1. The spline basis

Consider any function \( f_i(x) \) which shall be defined on an interval \( 0 \leq x \leq L \). This function can be
represented by an expansion in the b-spline basis as

\[
 f_i(x) = \sum_{\mu=1}^{N_X} f_i^\mu b_\mu(x)
\]

with the either real or complex valued expansion coefficients \( f_i^\mu \) and the size of the basis \( N_X \) limits the
real space resolution which is given by \( \Delta x = \frac{L}{N_X} \). The b-spline basis functions are real third order
polynomials which are defined by

\[
b_\mu(x) = \begin{cases} 
  \frac{1}{4} \left( 2 + \frac{x-x_\mu}{h} \right)^3 & : -2 < \frac{x-x_\mu}{h} \leq -1 \\
  1 - \frac{3}{2} \left( \frac{x-x_\mu}{h} \right)^2 - \frac{3}{4} \left( \frac{x-x_\mu}{h} \right)^3 & : -1 < \frac{x-x_\mu}{h} \leq 0 \\
  1 - \frac{3}{2} \left( \frac{x-x_\mu}{h} \right)^2 + \frac{3}{4} \left( \frac{x-x_\mu}{h} \right)^3 & : 0 < \frac{x-x_\mu}{h} \leq 1 \\
  \frac{1}{4} \left( 2 - \frac{x-x_\mu}{h} \right)^3 & : 1 < \frac{x-x_\mu}{h} \leq 1 \frac{1}{2} \\
  0 & : \text{else.}
\end{cases}
\]

The b-spline \( b_\mu(x) \) is centered around \( x_\mu \) and the distance between two adjacent splines is \( h \) which equals
the real space resolution \( \Delta x \). A single b-spline is shown in figure A.1.

Since any b-spline is different from zero in the interval \( x_\mu - 2h \leq x \leq x_\mu + 2h \), it overlaps with the
splines centered at \( x_{\mu-3} = x_\mu - 3h, x_{\mu-2} = x_\mu - 2h, x_{\mu-1} = x_\mu - h, x_{\mu+1} = x_\mu + h, x_{\mu+2} = x_\mu + 2h \)
Figure A.1.: A single b-spline \( b_\mu(x) \) centered at \( x_\mu \).

Figure A.2.: Overlap of a b-spline centered at \( x_\mu \) with the splines centered at \( x_{\mu-2}, x_{\mu-1}, x_{\mu+1} \) and \( x_{\mu+2} \).
and \( x_{\mu+3} = x_\mu + 3h \) as shown in figure A.2. The spline basis is therefore a non-orthogonal basis with the non-diagonal overlap matrix

\[
S_{\mu,\nu} = \int dx \, b_\mu(x) b_\nu(x) .
\]  
(A.3)

The matrix elements of \( S_{\mu,\nu} \) depend only on the absolute value of the difference between the indices \( |\mu - \nu| \) and can easily be calculated analytically. They are given in table A.1.

**Table A.1.:** Non-zero elements of the overlap matrix

| \( |\mu - \nu| \) | 0 | 1 | 2 | 3 |
|------------------|---|---|---|---|
| \( S_{\mu,\nu} \) | 15h | 119h | 3h | 56h |

A very useful feature of the b-splines is that they are twice continuously differentiable. This makes the calculation of the first and second derivatives of a function \( f_i(x) \) particularly simple, i.e.

\[
f'_i(x) = \sum_{\mu=1}^{N_X} f_i^\mu b'_\mu(x) \]  
(A.4)

and

\[
f''_i(x) = \sum_{\mu=1}^{N_X} f_i^\mu b''_\mu(x) \]  
(A.5)

The first derivative of a b-spline centered at \( x_\mu \) is explicitly given by

\[
b'_\mu(x) = \begin{cases} 
\frac{3}{4\pi} \left( 2 + \frac{x-x_\mu}{h} \right)^2 : & -2 < \frac{x-x_\mu}{h} \leq -1 \\
-\frac{3}{h} \frac{x-x_\mu}{h} - \frac{9}{4\pi} \left( \frac{x-x_\mu}{h} \right)^2 : & -1 < \frac{x-x_\mu}{h} \leq 0 \\
-\frac{3}{h} \frac{x-x_\mu}{h} + \frac{9}{4\pi} \left( \frac{x-x_\mu}{h} \right)^2 : & 0 < \frac{x-x_\mu}{h} \leq 1 \\
-\frac{3}{4\pi} \left( 2 - \frac{x-x_\mu}{h} \right)^2 : & 1 < \frac{x-x_\mu}{h} \leq 2 \\
0 : & \text{else}
\end{cases} 
\]  
(A.6)

and the second derivative by

\[
b''_\mu(x) = \begin{cases} 
\frac{3}{2\pi^2} \left( 2 + \frac{x-x_\mu}{h} \right) : & -2 < \frac{x-x_\mu}{h} \leq -1 \\
-\frac{3}{h^2} - \frac{9}{2\pi^2} \frac{x-x_\mu}{h} : & -1 < \frac{x-x_\mu}{h} \leq 0 \\
-\frac{3}{h^2} + \frac{9}{2\pi^2} \frac{x-x_\mu}{h} : & 0 < \frac{x-x_\mu}{h} \leq 1 \\
\frac{3}{2\pi^2} \left( 2 - \frac{x-x_\mu}{h} \right) : & 1 < \frac{x-x_\mu}{h} \leq 2 \\
0 : & \text{else}
\end{cases} 
\]  
(A.7)

In the numerical implementation, the b-splines and their derivatives are evaluated merely at the grid points which are given by the centers \( x_\mu \) of the splines. However, the matrix elements which will be discussed in the next section are calculated (mostly) analytically employing the full analytic form of the basis functions.
Figure A.3.: The first derivative of a b-spline centered at $x_\mu$.

Figure A.4.: The second derivative of a b-spline centered at $x_\mu$. 
A.2. The Kohn-Sham equation in the b-spline basis

After having introduced the b-spline basis which will be used in the numerical implementation, we can proceed to the representation of the Kohn-Sham equation in the spline basis. The Kohn-Sham equation of current-density functional theory has been discussed in section 8. For the one-dimensional model system it is given by

\[ \frac{1}{2m_0^*} \left( -i\hbar \partial_x + eA_{S,\sigma}(x) \right)^2 + V_{S,\sigma}(x) \phi_{k,\sigma}(x) = \varepsilon_{k,\sigma}\phi_{k,\sigma}(x) \]  

(A.8)

with the effective potentials \( A_{S,\sigma} \) and \( V_{S,\sigma} \). The Kohn-Sham orbitals \( \phi_i \) can be expanded in the spline basis

\[ \phi_{i,\sigma}(x) = \sum_{\mu} a_{i,\sigma}^\mu b_\mu(x). \]  

(A.9)

After multiplication of the Kohn-Sham equation with \( b_\nu \) from the left and integration over \( x \) we find the generalized eigenvalue equation

\[ \sum_{\mu} H_{\sigma,\nu,\mu}^\sigma a_{i,\sigma}^\mu = \varepsilon_{i,\sigma} \sum_{\mu} S_{\nu,\mu,\sigma} a_{i,\sigma}^\mu \]  

(A.10)

where the overlap matrix \( S_{\nu,\mu,\sigma} \) has already been introduced in the preceding section and the Hamilton matrix is given by

\[ H_{\nu,\mu}^\sigma = \int dx\ b_\nu(x) \left[ \frac{1}{2m_0^*} \left( -i\hbar \partial_x + eA_{S,\sigma}(x) \right)^2 + V_{S,\sigma}(x) \right] b_\mu(x). \]  

(A.11)

Obviously, the matrix \( H_{\nu,\mu}^\sigma \) consists of four different types of matrix elements, namely

1. matrix elements of the kinetic energy operator \(-\frac{1}{2} \partial_x^2\),
2. matrix elements containing the derivative of \( A_{S,\sigma} \),
3. matrix elements containing the derivative of the b-spline and
4. matrix elements containing the function \( V_{S,\sigma} \).  

\(^2\)The exchange-correlation vector potential appears only linearly in the Kohn-Sham Hamiltonian. The square of the external vector potential can be included in the effective scalar potential. For details, please refer to section 8.

Matrix elements of the kinetic energy operator

Due to translational invariance, the matrix elements of the kinetic energy operator

\[ T_{\mu,\nu} = -\frac{1}{2} \int dx\ b_\mu(x) \partial_x^2 b_\nu(x) \]  

depend only on the absolute value of the difference \(|x_\mu - x_\nu|\). The integrals can be calculated analytically and are tabulated in the code. The numerical values are listed in table A.2.
A. Numerics

Table A.2.: Non-zero matrix elements of the kinetic energy operator. Values taken from reference [Hofmann, 2005b].

| \(|\mu - \nu|\) | 0   | 1   | 2   | 3   |
|-----------------|-----|-----|-----|-----|
| \(T_{\mu,\nu}\) | \(-\frac{3}{3h}\) | \(-\frac{9}{6h}\) | \(-\frac{9}{30h}\) | \(-\frac{3}{320h}\) |

Matrix elements of the local potential operator

A little bit more work is required to calculate the matrix elements of the local potential operator \(V_S(x)\). Of course, since \(V_S(x)\) is not known \textit{a priori}, these matrix elements cannot simply be tabulated. The numerical effort, however, can be significantly reduced if we first expand \(V_S(x)\) in the spline-basis as

\[
V_{S,\sigma}(x) = \sum_{\mu} V_{\mu,\sigma}^{\mu} b_{\mu}(x). \tag{A.13}
\]

Inserting this expansion into the matrix element we find

\[
V_{\mu,\nu} = \int dx b_{\mu}(x) V_{S,\sigma}(x) b_{\nu}(x) = \sum_{\lambda} V_{\mu,\sigma}^{\lambda} \int dx b_{\mu}(x) b_{\lambda}(x) b_{\nu}(x). \tag{A.14}
\]

Before we rush into the actual computation of the integrals \(B_{\mu,\nu,\lambda}\) we note that the number of different values of \(B_{\mu,\nu,\lambda}\) can be significantly reduced by the following exact properties of the integral:

- Obviously, the integral \(B_{\mu,\nu,\lambda}\) is invariant under a permutation of the indices as well as under a rigid shift of the whole integral. We can therefore always choose one index to be zero and give the remaining indices relative to this one.

- Furthermore, since any two b-splines overlap only if their centers are not further apart than \(3h\), the integral vanishes if the difference between any two indices exceeds \(3\).

As a consequence of these properties we are left with only seven different values of \(B_{\mu,\nu,\lambda}\) which are listed in table A.3.

Table A.3.: The seven different values of the integral \(B_{\mu,\nu,\lambda}\). Without loss of generality, the index \(\mu\) has been set to zero. Values taken from reference [Hofmann, 2005b].

<table>
<thead>
<tr>
<th>((\mu, \nu, \lambda))</th>
<th>(0, 0, 0)</th>
<th>(0, 0, 1)</th>
<th>(0, 0, 2)</th>
<th>(0, 0, 3)</th>
<th>(0, 1, 2)</th>
<th>(0, 1, 3)</th>
<th>else</th>
</tr>
</thead>
<tbody>
<tr>
<td>(B_{\mu,\nu,\lambda})</td>
<td>\frac{1979}{2240}</td>
<td>\frac{18871}{53760}</td>
<td>\frac{31}{1020}</td>
<td>\frac{1}{53760}</td>
<td>\frac{85}{1792}</td>
<td>\frac{17}{53760}</td>
<td>0</td>
</tr>
</tbody>
</table>

Matrix elements containing derivatives

The remaining two matrix elements \(\int dx b_{\mu}(x) [\partial_x A_{S,\sigma}(x)] b_{\nu}(x)\) and \(\int dx b_{\mu}(x) A_{S,\sigma}(x) \partial_x b_{\nu}(x)\) can be treated simultaneously. To this end we insert the expansion of the effective vector potential \(A_{S,\sigma}\) in the
A.2. The Kohn-Sham equation in the b-spline basis

The Kohn-Sham equation in the b-spline basis

\[ A_{S,\sigma}(x) = \sum_{\lambda} N_X A_{S,\sigma,\lambda} b\lambda(x). \]  
(A.15)

into the matrix elements to obtain

\[ \int dx \, b_\mu(x) \left[ \partial_x A_{S,\sigma}(x) \right] b_\nu(x) = \sum_{\lambda} N_X A_{S,\sigma,\lambda} \int dx \, b_\mu(x) b_\lambda'(x) b_\nu(x) \]  
(A.16)

and

\[ \int dx \, b_\mu(x) A_{S,\sigma}(x) \partial_x b_\nu(x) = \sum_{\lambda} N_X A_{S,\sigma,\lambda} \int dx \, b_\mu(x) b_\lambda(x) b_\nu'(x), \]  
(A.17)

respectively. We note that we can calculate both matrix elements by permuting the indices of

\[ D_{\mu,\nu,\lambda} = \int dx \, b_\mu(x) b_\nu(x) b_\lambda'(x). \]  
(A.18)

While the calculation of the integral \( D_{\mu,\nu,\lambda} \) is not more cumbersome than the calculation of \( B_{\mu,\nu,\lambda} \) we cannot exploit that many exact properties to reduce the number of integrals to be calculated. Still, the whole integral is translationally invariant which allows us to set the index corresponding to the derivative of the b-spline to zero (the index \( \lambda \) in the definition of \( D_{\mu,\nu,\lambda} \) above). Furthermore, it follows directly from the odd symmetry of the derivative of the b-spline with respect to its center (taken to be zero here), that the integral obeys the symmetry relation

\[ D_{\mu,\nu,\lambda} = -D_{-\mu,-\nu,\lambda}, \]  
(A.19)

where the indices \( \mu \) and \( \nu \) may still be interchanged without altering the value of the integral. We are thus left with the calculation of the ten integrals with \( \lambda = 0 \) and \( \mu \) and \( \nu \) taking the values \((-3, -3), (-3, -2), (-3, -1), (-3, 0), (-2, -2), (-2, -1), (-2, 0), (-1, -1) \) and \((-1, 0)\) (the integrals \( D_{-1,1,0} = D_{1,-1,0} \) and \( D_{0,0,0} \) vanish due to the odd symmetry of the derivative of the b-spline). The numerical values are listed in table A.4.

Table A.4.: The non-zero values of the integral \( D_{\mu,\nu,\lambda} \). The value \( D_{-\mu,-\nu,\lambda} \) is the negative of the respective value \( D_{\mu,\nu,\lambda} \). Without loss of generality, the index \( \lambda \) corresponding to the derivative of the b-spline has been set to zero.

<table>
<thead>
<tr>
<th>( \mu )</th>
<th>( \nu )</th>
<th>( \frac{1}{576} )</th>
<th>( \frac{43}{17920} )</th>
<th>( \frac{9}{4480} )</th>
<th>( \frac{1}{10752} )</th>
<th>( \frac{1}{2560} )</th>
<th>( \frac{1}{2240} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>(-3)</td>
<td>(-3)</td>
<td>(\frac{1}{576})</td>
<td>(\frac{43}{17920})</td>
<td>(\frac{9}{4480})</td>
<td>(\frac{1}{10752})</td>
<td>(\frac{1}{2560})</td>
<td>(\frac{1}{2240})</td>
</tr>
<tr>
<td>(-3)</td>
<td>(-2)</td>
<td>(\frac{43}{17920})</td>
<td>(\frac{81}{1120})</td>
<td>(\frac{271}{1792})</td>
<td>(\frac{81}{2240})</td>
<td>(\frac{1}{2560})</td>
<td>(\frac{1}{2240})</td>
</tr>
<tr>
<td>(-3)</td>
<td>(-1)</td>
<td>(\frac{9}{4480})</td>
<td>(\frac{271}{1792})</td>
<td>(\frac{5947}{8960})</td>
<td>(\frac{2635537}{7947520})</td>
<td>(\frac{2635537}{7947520})</td>
<td>(\frac{7947520}{7947520})</td>
</tr>
<tr>
<td>(-3)</td>
<td>(0)</td>
<td>(\frac{1}{10752})</td>
<td>(\frac{81}{2240})</td>
<td>(\frac{2635537}{7947520})</td>
<td>(0)</td>
<td>(-\frac{2635537}{7947520})</td>
<td>(-\frac{7947520}{7947520})</td>
</tr>
<tr>
<td>(-3)</td>
<td>(1)</td>
<td>(0)</td>
<td>(\frac{1}{2560})</td>
<td>(0)</td>
<td>(-\frac{2635537}{7947520})</td>
<td>(-\frac{5947}{8960})</td>
<td>(\frac{5947}{8960})</td>
</tr>
</tbody>
</table>
B-spline expansion

To evaluate the matrix elements containing the effective scalar potential and the effective vector potential we represented \( V_{S,\sigma}(x) \) and \( A_{S,\sigma}(x) \) in the spline-basis. Before we actually carry out this expansion [Hofmann, 2005b] we note first that the set of the \( N_X \) b-splines \( \{b_\mu(x)\} \) which are evaluated at the \( N_X \) grid points can be understood as a symmetric, positive definite \( N_X \times N_X \)-matrix \( B \). It is a general feature of any symmetric, positive definite matrix, and hence of the matrix \( B \), that it can be represented as a product of an upper (or lower) triangular matrix \( D \) and its transpose:

\[
B = DD^T. \tag{A.20}
\]

The matrix \( D \) can be obtained by means of a Cholesky decomposition [Press et al., 1996]. We can exploit this decomposition, which needs to be carried out only once in the self-consistent cycle, to solve equation A.1 for the expansion coefficients \( f^\mu_i \). To this end, we first write the b-spline expansion of a function \( f_i(x) \) in matrix form as

\[
f_i = B b_i, \tag{A.21}
\]

where \( f_i \) is the \( N_X \)-dimensional vector containing the values of the function \( f_i(x) \) at the grid points and \( b_i \) is the \( N_X \)-dimensional vector of the expansion coefficients \( f^\mu_i \). Equation (A.21) can formally be written as two matrix equations with the auxiliary vector \( y \):

\[
\begin{align*}
    f_i &= Dy, & \text{(A.22)} \\
    y &= D^T f_i. & \text{(A.23)}
\end{align*}
\]

Since \( D \) (and hence \( D^T \)) is a triangular matrix, it is particularly easy to first solve equation (A.22) for the auxiliary vector \( y \) and subsequently equation (A.23) for the expansion coefficients.

A.3. Self-consistent solution of the Kohn-Sham equation

The effective potentials \( V_S \) and \( A_S \) which enter the Kohn-Sham Hamiltonian are functionals of the density and the paramagnetic current density. In turn, the Kohn-Sham Hamiltonian determines the Kohn-Sham orbitals from which the density and paramagnetic current density are calculated. The Kohn-Sham equation thus has to be solved self-consistently.

Before we begin the self-consistent iteration, we calculate once the matrix of the b-splines, the overlap matrix \( S \) and their Cholesky decompositions. We then set up the Hamilton matrix of the non-interacting system, i.e. we choose \( V_{S,\sigma} \) and \( A_{S,\sigma} \) to be equal to the external potentials \( V_{\text{ext}} \) and \( A_{\text{ext}} \) which are expanded in the spline-basis to calculate the corresponding matrix elements. The resulting generalized eigenvalue equation (A.10) is first transformed into a standard eigenvalue equation using the Cholesky decomposition of the overlap matrix: \( S = LL^T \). This standard eigenvalue equation reads

\[
\left( L^{-1} H^\sigma L^{T^{-1}} \right) \left( L^T a_{k,\sigma} \right) = \varepsilon_{k,\sigma} \left( L^T a_{k,\sigma} \right), \tag{A.24}
\]

where \( a_{k,\sigma} \) is the vector of the expansion coefficients of the \( k \)-th eigenstate. The matrix \( L^{-1} H^\sigma L^{T^{-1}} \) is diagonalized using the \texttt{ZHGEV} routine from the LAPACK library [Anderson et al., 1999] and from the resulting eigenvector \( L^T a_{k,\sigma} \) the original eigenvector \( a_{k,\sigma} \) can be obtained. The non-interacting eigenstates constitute the starting point for the self-consistent iteration.

At the beginning of each of the subsequent iteration cycles, the Hartree potential, the scalar exchange potential and the exchange vector potential need to be calculated from the eigenfunctions of the previous

\[^3\text{Note that the overlap matrix is a symmetric positive definite matrix and thus can be Cholesky-decomposed.}\]
A.3. Self-consistent solution of the Kohn-Sham equation

Iteration. To this end, the density matrix \( \rho_{\sigma,\sigma'}^{i,j}(x) = \phi_{i,\sigma}^*(x)\phi_{j,\sigma'}(x) \) is expressed in terms of the expansion coefficients given by the vectors \( a_{k,\sigma}(k = 1, \ldots, N) \) according to

\[
\rho_{\sigma,\sigma'}^{i,j}(x) = \sum_{\mu,\nu} a_{i,\sigma}^\mu a_{j,\sigma'}^\nu b_{\mu}(x)b_{\nu}(x).
\]  

(A.25)

At this point, a subtle difficulty arises. Remember that we have used the exact, analytical form of the b-splines to calculate the matrix elements which enter the generalized eigenvalue equation (A.10). Therefore, the eigenvectors \( a_{i,\sigma} \) are ortho-normalized with respect to the exact overlap matrix \( S \). In contrast, when we numerically evaluate the integrals containing \( \rho_{\sigma,\sigma'}^{i,j}(x) \)—which we encounter in the calculation of the orbital potentials, see chapter 5—we only use the values of the b-splines at the grid points. Consequently, the value of the numerically evaluated integral differs from the exact value and in particular, if we numerically integrate the density \( n_{i,\sigma}(x) = \rho_{\sigma,\sigma}^{i,i}(x) \) of the \( i \)-th eigenstate, we may find a value different from one. This can lead to instabilities in the self-consistent iteration. We can solve this problem if we divide \( n_{i,\sigma}(x) \) by the value of the numerically calculated integral or, in the case of \( \rho_{\sigma,\sigma'}^{i,j}(x) \), by the product of the square roots of the numerically evaluated integrals of \( n_{i,\sigma}(x) \) and \( n_{j,\sigma'}(x) \) [Hofmann, 2005a]. The Hartree potential can now be calculated directly by numerical integration and the exchange potentials are found from the solution of the CDFT-KLI equations or the CDFT-OEP equations, respectively, without encountering further numerical difficulties.

Potential mixing

Once we have found the new potentials we can proceed to set up the Hamiltonian for the next iteration step. We should, however, not rush into the next iteration with the new potentials straight away since an exclusive use of the new potentials will most likely not lead to stable convergence. There exist several schemes to stabilize and speed up convergence the most simple one probably being linear mixing. Instead of taking the full new potential from the \( n \)-th iteration step to construct the Hamiltonian for the \( n + 1 \)-th step we only take a fraction \( \alpha < 1 \) of the new potential and add a fraction \( 1 - \alpha \) of the potential from the \( n - 1 \)-th step (i.e. of the input potential used for the \( n \)-th iteration)

\[
\tilde{V}_{n+1} = (1 - \alpha)\tilde{V}_n + \alpha V_n,
\]

(A.26)

where \( \tilde{V}_{n+1} \) is the input potential for the \( n + 1 \)-th iteration step, \( \tilde{V}_n \) is the input potential used in the \( n \)-th step and \( V_n \) is the new potential obtained from the eigenfunctions of the \( n \)-th iteration step (i.e. the eigenfunctions corresponding to the input potential \( \tilde{V}_n \)). Choosing a very small value of the mixing parameter \( \alpha \) means that the system will evolve only slowly into a new direction given by the new potential. On the other hand, a large value of \( \alpha \) can speed up the self-consistent cycle but a too large value can easily lead to overshooting and hence introduce instabilities. The best value of \( \alpha \) for a particular calculation needs to be chosen empirically. For the calculations discussed in this work a value of \( \alpha = 0.2 \) always lead to a stable convergence without slowing down convergence too drastically.

Convergence criteria

With the new potentials, the new Hamiltonian is set up and diagonalized as described before which closes the self-consistency cycle. At this point we have to make a decision whether the iteration is converged or not. There exist various convergence criteria, each based on a different quantity. We could for instance compare the densities, wave functions or potentials in subsequent iterations. This, however, means that we would have to deal with position dependent quantities which would complicate the comparison. A way to overcome this problem is the definition of a suitable norm, for instance we could look only at
A. Numerics

the maxima of the absolute values of these functions. Yet it is still easier to compare just plain numbers. Therefore we use in this work the difference of the eigenvalues from two subsequent iterations as the convergence criterion. We found that all three convergence criteria—the one based on the comparison of the eigenvalues as well as those based on the potential and on the wave functions—lead to the same results [Arnold, 2010].

Let \( \varepsilon_{i,\sigma}^{(n)} \) be the \( i \)-th eigenvalue in the \( n \)-th iteration. We then compute

\[
\Delta_n = \max_{i} \left| \varepsilon_{i,\sigma}^{(n)} - \varepsilon_{i,\sigma}^{(n-1)} \right|
\]

and compare it to some threshold value \( \Delta \). If

\[
\Delta_n < \Delta
\]

we consider the iteration to be converged. The crucial point here is the choice of the threshold \( \Delta \). A value of \( \Delta \) which is chosen too large will lead to non converged results. In the case of a Wigner transition (with the non-interacting system as the starting point) this means that we find a delocalized system for a value of the interaction parameter \( r_S \) where the fully converged system is found to be localized. On the other hand, if \( \Delta \) is chosen very small, this unnecessarily prolongs the computation time. Unfortunately, the system is very unstable in the vicinity of the transition requiring a very small value \( \Delta \). We find that the threshold has to be as small as

\[
\Delta = 10^{-10} \text{ meV}
\]

(A.29)

To illustrate the convergence and the choice of the threshold \( \Delta \) we plot the total energy and the convergence parameter \( \Delta_n \) as functions of the iteration number \( n \). In figure A.5 we show these values for a system of ten interacting electrons in the presence of a very weak Gaussian impurity potential with a maximum strength \( V_0 = 10^{-3} \text{ meV} \) which have undergone a Wigner transition but the system is still close to the transition point. The convergence parameter first decreases until it reaches a minimum value which is about \( 2.77 \cdot 10^{-9} \text{ meV} \). As the iteration proceeds, it rises again and the total energy begins to drop. The (local) maximum value that \( \Delta_n \) acquires, corresponds to the steepest decay of the total energy. As the total energy saturates to its converged value, the convergence parameter decreases again and finally falls below the previously defined threshold value. The crucial point is that \( \Delta_n \) already falls to values close to \( 10^{-9} \text{ meV} \) while the system is still in the delocalized phase \(^4\) and the total energy has not yet begun to decrease. If we would have chosen the threshold \( \Delta \) larger than the first minimum value of \( \Delta_n \), we would not have found this system to be in a localized state.

A.4. Convergence test: the size of the basis

We have now introduced all necessary ingredients to perform a self-consistent calculation of a one-dimensional system using the b-spline basis. Before we use this method to study Wigner crystallization in exact-exchange theory on a quasi one-dimensional ring, we will perform some convergence tests to estimate the number of the basis functions required to give reliable values for the current and the ground state energy. As a test system we consider ten electrons on the quasi one-dimensional ring with a circumference \( L = 200 \text{ nm} \) and add a repulsive Gaussian impurity potential with a strength of \( V_0 = 10 \text{ meV} \) which creates a non-uniform density. A persistent current will be induced by a tangential vector

\(^4\)The localized phase can be distinguished from the delocalized phase by the persistent current. At this point in the iteration cycle, the value of the persistent current is still equal to the value found in the delocalized phase and it only starts to decrease in the course of the self-consistent iteration when the total energy decreases. See chapter 6 for details on the persistent current as a localization criterion.
potential corresponding to a flux $\Phi = 0.3 \Phi_0$ ($\Phi_0 = \frac{\hbar}{e}$ is the flux quantum). We perform self-consistent calculations using the KLI approximation to the exact-exchange OEP equations for various numbers of basis functions.

In a static one-dimensional system, the continuity equation requires the current to be a constant. However, doing a numerical calculation with a finite basis set, we will not obtain a strictly constant value of the current. Nevertheless, we can expect that the deviations decrease as we increase the size of the basis.

We calculate the persistent current of the system using between 50 and 650 basis functions. We find that the current shows an oscillatory behaviour around its average value. However, due to the presence of the impurity—which creates Friedel oscillations and a pronounced density minimum at the impurity site—there is no spatially constant amplitude of the oscillations. We thus prefer to speak of the maximal and minimal value of the current. For each size of the basis we determine the difference between the maximum and the minimum value of the current and divide it by the average value of the current. We plot this quantity (here termed oscillation amplitude) together with the average value of the current as a function of the number of basis functions in figure A.6. One sees that the current becomes more and more constant as we increase the size of the basis. Using 550 basis functions the relative deviation from the constant value has dropped to $\sim 2 \cdot 10^{-6}$. At the same time, the average value—which of course converges to the actual value of the constant current—decreases and we find that it has well converged if the size of the basis exceeds 500.

Next we check if the ground state energy converges as well with increasing basis size. Figure A.7 shows that this is indeed the case and we see that the energy has converged if the basis consists of 500 b-splines or more.

To conclude, we expect that we can obtain reliable results for the ten electron ring with a circumference of $L = 200$ nm if we choose a basis consisting of more than 500 b-splines. Therefore all calculations are carried out using 540 basis functions.
Figure A.6.: The average value of the persistent current and the amplitude of the persistent current oscillations relative to the average value of the current with respect to the size of the basis. The numbers are calculated for a ten electron ring with a magnetic flux $\Phi = 0.3\Phi_0$ and a repulsive Gaussian impurity potential with a strength of $V_0 = 10$ meV using the exact-exchange KLI potential. The squares and dots represent the calculated values, the lines are guides to the eye.

Figure A.7.: The ground state energy of a ten-electron ring with a magnetic flux $\Phi = 0.3\Phi_0$ and a Gaussian impurity potential with a strength of $V_0 = 10$ meV as a function of the number of basis functions. The calculations have been performed employing the exact-exchange functional and using the KLI approximation. The squares represent the calculated values and the line serves as a guide to the eye.
Bibliography


HOFMANN, M., 2005a, private communication.


Kohn, W., 1964, Phys. Rev. 133(1A), A171.


WIGNER, E., 1934, Phys. Rev. 46(11), 1002.


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