

Part II

**Current Density Functional
Theory**

Chapter 5

Theoretical Foundations

Historically, the extension of density-functional theory to systems in an external magnetic field was a two-step process. General DFT was first extended to spin-density-functional theory (SDFT) which allows the treatment of spin-polarized systems [56]. The coupling to an external magnetic field within this formalism is solely described by a Zeeman term, i.e. the magnetic field only couples to the spin degrees of freedom but not to the orbital angular momentum. This limitation has been overcome by Vignale and Rasolt in 1987 [17, 18] introducing current-spin-density-functional theory (CSDFT). Within this theory the Hamiltonian contains, in addition to the external scalar potential v_0 , an external magnetic field \mathbf{B}_0 and the corresponding vector potential \mathbf{A}_0 . The two are connected via the usual relation

$$\mathbf{B}_0(\mathbf{r}) = \nabla \times \mathbf{A}_0(\mathbf{r}). \quad (5.1)$$

Due to the two additional potentials, there are two additional densities introduced in the theory, namely the spin magnetization \mathbf{m} and the paramagnetic current density \mathbf{j}_p .

Extending the approximations from DFT to CSDFT proved to be significantly more difficult than extending the theory itself. LDA and all GGAs rely on the homogeneous electron gas (HEG) for their construction. If we apply an external magnetic field to the HEG and change its strength, the energy density changes discontinuously whenever a new Landau level is filled [19], see Fig. 5.1. The filling of Landau levels is a physical effect, however, the consequences of the kinks in the energy density are quite severe. The exchange-correlation potential, given as a functional derivative, suffers from divergencies at these magnetic fields. Therefore, it is impossible to directly implement an LDA or GGA potential in a numerical calculation. The only solution to this problem so far is an interpolation between two different approximations at high and low magnetic fields. The kinks in the energy density are smoothed out and the corresponding divergencies in the exchange-correlation potential, therefore, avoided. In addition, the discontinuities and respective divergencies occur whenever the *local* densities coincide with the positions of the discontinuities in the HEG. In general, these positions do not correspond to the Landau levels of

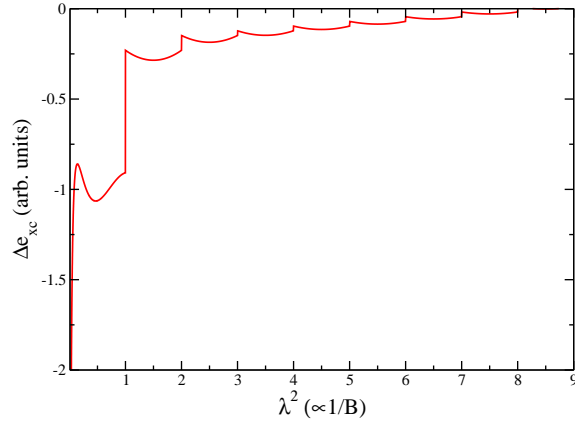


Figure 5.1: Energy density of the homogeneous electron gas as a function of the inverse of an external magnetic field [19].

the inhomogeneous system and lead to unphysical effects. The interpolation solves this problem only partially, the potential does not diverge but still shows strong features at the respective, and hence wrong, positions. Due to these problems with LDA and GGAs the use of orbital functionals is a necessity within CSDFT rather than an option. Therefore, we need to extend the OEP formalism to CSDFT.

In this Chapter, we first extend the Hohenberg-Kohn theorem to CSDFT and introduce the corresponding Kohn-Sham system in Section 5.1. In Section 5.2 we briefly comment on collinear magnetism which is frequently employed in the literature and which we use for the applications in Chapter 6. The OEP formalism within CSDFT is presented in Section 5.3, and the effect of the KLI approximation [66] on the resulting equations in Section 5.4. Section 5.5 discusses the OEP equations in collinear magnetism with and without the KLI approximation. We conclude this chapter with Section 5.6 by introducing the exact-exchange functional employed in Chapter 6.

5.1 Hohenberg-Kohn Theorem and Kohn-Sham System

The non-relativistic Hamiltonian for N electrons in an external magnetic field reads

$$H = \sum_{j=1}^N \left[\frac{1}{2} \left(-i\nabla_j + \frac{1}{c} \mathbf{A}_0(\mathbf{r}_j) \right)^2 + v_0(\mathbf{r}_j) + g\mu_B \boldsymbol{\sigma}_j \mathbf{B}_0(\mathbf{r}_j) \right] + \frac{1}{2} \sum_{\substack{j,k=1 \\ j \neq k}}^N \frac{1}{|\mathbf{r}_j - \mathbf{r}_k|}, \quad (5.2)$$

where the magnetic field couples both to the spin degrees of freedom via the Zeeman term and to the spatial variables via the minimal coupling to the vector potential.

Here, ∇_j denotes a gradient with respect to \mathbf{r}_j and $\boldsymbol{\sigma}_j = (\sigma_{xj}, \sigma_{yj}, \sigma_{zj})$ is the vector of Pauli matrices acting on the j^{th} particle. g and μ_B are the gyromagnetic ratio and the Bohr magneton, respectively.

In their original paper Vignale and Rasolt claimed that one can extend the Hohenberg-Kohn proof and establish a one-to-one correspondence between the three external potentials v_0 , \mathbf{B}_0 and \mathbf{A}_0 and the three ground-state densities

$$n_{\text{GS}}(\mathbf{r}) = \sum_{\sigma} \sum_{j=1}^N \int d\mathbf{x}_1 \dots d\mathbf{x}_N \Psi_{\text{GS}}^*(\mathbf{x}_1, \mathbf{x}_2 \dots \mathbf{x}_N) \delta(\mathbf{x} - \mathbf{x}_j) \Psi_{\text{GS}}(\mathbf{x}_1, \mathbf{x}_2 \dots \mathbf{x}_N), \quad (5.3)$$

$$\mathbf{m}_{\text{GS}}(\mathbf{r}) = -g\mu_B \sum_{\sigma} \sum_{j=1}^N \int d\mathbf{x}_1 \dots d\mathbf{x}_N \Psi_{\text{GS}}^*(\mathbf{x}_1, \mathbf{x}_2 \dots \mathbf{x}_N) \times \boldsymbol{\sigma}_j \delta(\mathbf{x} - \mathbf{x}_j) \Psi_{\text{GS}}(\mathbf{x}_1, \mathbf{x}_2 \dots \mathbf{x}_N), \quad (5.4)$$

$$\mathbf{j}_{p\text{GS}}(\mathbf{r}) = \frac{1}{2i} \sum_{\sigma} \sum_{j=1}^N \int d\mathbf{x}_1 \dots d\mathbf{x}_N \Psi_{\text{GS}}^*(\mathbf{x}_1, \mathbf{x}_2 \dots \mathbf{x}_N) \times [-\nabla_j \delta(\mathbf{x} - \mathbf{x}_j) - \delta(\mathbf{x} - \mathbf{x}_j) \nabla_j] \Psi_{\text{GS}}(\mathbf{x}_1, \mathbf{x}_2 \dots \mathbf{x}_N) \quad (5.5)$$

which are the density, the spin magnetization and the paramagnetic current density, respectively. The variable \mathbf{x} is a combined space-spin variable, i.e. $\mathbf{x} = (\mathbf{r}, \sigma)$ and the integral over \mathbf{x} stands for an integral over space and a sum over spin, $\int d\mathbf{x} = \sum_{\sigma} \int d\mathbf{r}$. In their original work on spin-DFT [56] von Barth and Hedin already mention that under certain circumstances the potentials are non-unique. Recently, it was shown by Capelle and Vignale that, also in CSDFT, there are certain physical systems where the potentials leading to a specific set of densities are not unique [67, 68]. We immediately see that an explicit construction of the potentials from an inversion of the Schrödinger equation, as used in conventional DFT, is impossible, since we have three different potentials. Hence, a direct generalization of the HK theorem fails.

The one-to-one correspondence between the ground-state wave function and the three densities, however, is still valid. Assuming that two different ground-state wave functions Ψ_{GS} and Ψ'_{GS} , which necessarily correspond to two different sets of potentials $\{v_0, \mathbf{B}_0, \mathbf{A}_0\}$ and $\{v'_0, \mathbf{B}'_0, \mathbf{A}'_0\}$ yield the same set of densities $n'_{\text{GS}} = n_{\text{GS}}$, $\mathbf{m}'_{\text{GS}} = \mathbf{m}_{\text{GS}}$ and $\mathbf{j}'_{p\text{GS}} = \mathbf{j}_{p\text{GS}}$ one finds (again both ground-states are assumed to be non-degenerate)

$$\begin{aligned} E_{\text{GS}} &= \langle \Psi_{\text{GS}} | \hat{H} | \Psi_{\text{GS}} \rangle < \langle \Psi'_{\text{GS}} | \hat{H} | \Psi'_{\text{GS}} \rangle \\ &< \langle \Psi'_{\text{GS}} | \hat{H}' + \hat{V} - \hat{V}' + \hat{B} - \hat{B}' + \hat{A} - \hat{A}' | \Psi'_{\text{GS}} \rangle \\ &< E'_{\text{GS}} + \int d^3r n_{\text{GS}}(\mathbf{r}) \left[v_0(\mathbf{r}) - v'_0(\mathbf{r}) + \frac{1}{2c^2} (\mathbf{A}_0^2(\mathbf{r}) - \mathbf{A}'_0{}^2(\mathbf{r})) \right] \\ &\quad - \int d^3r \mathbf{m}_{\text{GS}}(\mathbf{r}) [\mathbf{B}_0(\mathbf{r}) - \mathbf{B}'_0(\mathbf{r})] + \int d^3r \mathbf{j}_{p\text{GS}}(\mathbf{r}) [\mathbf{A}_0(\mathbf{r}) - \mathbf{A}'_0(\mathbf{r})]. \end{aligned} \quad (5.6)$$

Starting with the primed system we derive

$$\begin{aligned}
E'_{\text{GS}} &= \langle \Psi'_{\text{GS}} | \hat{H}' | \Psi'_{\text{GS}} \rangle < \langle \Psi_{\text{GS}} | \hat{H}' | \Psi_{\text{GS}} \rangle \\
&< E_{\text{GS}} + \int d^3r n_{\text{GS}}(\mathbf{r}) \left[v'_0(\mathbf{r}) - v_0(\mathbf{r}) + \frac{1}{2c}(\mathbf{A}'_0{}^2(\mathbf{r}) - \mathbf{A}_0{}^2(\mathbf{r})) \right] \\
&\quad - \int d^3r \mathbf{m}_{\text{GS}}(\mathbf{r}) [\mathbf{B}'_0(\mathbf{r}) - \mathbf{B}_0(\mathbf{r})] + \int d^3r \mathbf{j}_{p\text{GS}}(\mathbf{r}) [\mathbf{A}'_0(\mathbf{r}) - \mathbf{A}_0(\mathbf{r})].
\end{aligned} \tag{5.7}$$

Adding the two equations, leads to the contradiction

$$E_{\text{GS}} + E'_{\text{GS}} < E_{\text{GS}} + E'_{\text{GS}}. \tag{5.8}$$

Therefore, the three ground-state densities n_{GS} , \mathbf{m}_{GS} , and $\mathbf{j}_{p\text{GS}}$ uniquely determine the ground-state wave function of the system. As a consequence, any observable of a system in its ground-state is a functional of the three densities.

The non-uniqueness of the potentials is indeed a problem for the calculation of excited-state properties. However, it seems to be restricted to a small number of very specific systems, for example semi-metals [67], while for most systems the one-to-one correspondence holds. Also, the non-uniqueness might be an artefact of the restriction to collinear magnetism, where the magnetization density \mathbf{m} is restricted to be parallel to the magnetic field. To the best of the authors knowledge no numerical problems due to non-uniqueness have been reported in the literature.

The ground-state energy of the system can be obtained by minimizing the expectation value of the Hamiltonian with respect to an antisymmetric wave function. Splitting this minimization process into one minimization with respect to the three densities, and a second over all wave functions which lead to a specific set of densities, one defines the energy as a functional of the densities, i.e.

$$\begin{aligned}
E_{\text{GS}} &= \min_{\Psi} \langle \Psi | \hat{H} | \Psi \rangle \\
&= \min_{n, \mathbf{m}, \mathbf{j}_p} \left[\min_{\Psi \rightarrow n, \mathbf{m}, \mathbf{j}_p} \langle \Psi | \hat{H} | \Psi \rangle \right] \\
&= \min_{n, \mathbf{m}, \mathbf{j}_p} E[n, \mathbf{m}, \mathbf{j}_p].
\end{aligned} \tag{5.9}$$

As a direct consequence the ground-state energy satisfies

$$E_{\text{GS}} \leq E[n, \mathbf{m}, \mathbf{j}_p], \tag{5.10}$$

where the equality holds if and only if $n \equiv n_{\text{GS}}$, $\mathbf{m} \equiv \mathbf{m}_{\text{GS}}$, and $\mathbf{j}_p \equiv \mathbf{j}_{p\text{GS}}$. This part of the HK theorem allows us to find the ground-state density from a minimization of the total energy.

Part three of the Hohenberg-Kohn theorem introduces a universal functional F which is independent of the external potential. The Hamiltonian (5.2) can be split

into a kinetic part \hat{T} , the interaction part \hat{W} , and the external potential part. The energy functional $E[n, \mathbf{m}, \mathbf{j}_p]$ can hence be expressed as

$$\begin{aligned} E[n, \mathbf{m}, \mathbf{j}_p] &= \min_{\Psi \rightarrow n, \mathbf{m}, \mathbf{j}_p} \left[\langle \Psi | \hat{T} + \hat{W} | \Psi \rangle + \langle \Psi | \hat{V}_0 + \hat{B}_0 + \hat{A}_0 | \Psi \rangle \right] \\ &= F[n, \mathbf{m}, \mathbf{j}_p] + \int d^3r n(\mathbf{r}) \left[v_0(\mathbf{r}) + \frac{1}{2c^2} \mathbf{A}_0^2(\mathbf{r}) \right] \\ &\quad - \int d^3r \mathbf{m}(\mathbf{r}) \mathbf{B}_0(\mathbf{r}) + \int d^3r \mathbf{j}_p(\mathbf{r}) \mathbf{A}_0(\mathbf{r}) \end{aligned} \quad (5.11)$$

with the functional F given by

$$F[n, \mathbf{m}, \mathbf{j}_p] = \min_{\Psi \rightarrow n, \mathbf{m}, \mathbf{j}_p} \langle \Psi | \hat{T} + \hat{W} | \Psi \rangle. \quad (5.12)$$

The functional dependence of F on the density is universal, i.e. it is the same for all systems where the particles interact via the Coulomb interaction \hat{W} , it does not depend on the external potentials.

Due to the one-to-one correspondence between the set of densities and the wave function we can introduce a Kohn-Sham (KS) system, i.e. a non-interacting system that reproduces the densities of the interacting system. The KS Hamiltonian is given by

$$\left[\frac{1}{2} \left(-i\nabla + \frac{1}{c} \mathbf{A}_s(\mathbf{r}) \right)^2 + v_s(\mathbf{r}) + g\mu_B \boldsymbol{\sigma} \mathbf{B}_s(\mathbf{r}) \right] \Phi_k(\mathbf{r}) = \epsilon_k \Phi_k(\mathbf{r}), \quad (5.13)$$

where the KS orbitals Φ_k are Pauli spinors. The effective potentials resulting from a minimization of the total energy read

$$\begin{aligned} v_s(\mathbf{r}) &= v_0(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc}(\mathbf{r}) + \frac{1}{2c^2} (\mathbf{A}_0^2(\mathbf{r}) - \mathbf{A}_s^2(\mathbf{r})), \\ \mathbf{B}_s(\mathbf{r}) &= \mathbf{B}_0(\mathbf{r}) + \mathbf{B}_{xc}(\mathbf{r}), \\ \mathbf{A}_s(\mathbf{r}) &= \mathbf{A}_0(\mathbf{r}) + \mathbf{A}_{xc}(\mathbf{r}). \end{aligned} \quad (5.14)$$

Note that the definition of the scalar potential is changed with respect to standard DFT. The additional term is due to the coupling of the term quadratic in \mathbf{A} to the density. The exchange correlation potentials are, as in standard DFT, defined as functional derivatives of the exchange-correlation energy E_{xc} with respect to the corresponding densities

$$v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}}{\delta n(\mathbf{r})}, \quad (5.15)$$

$$\mathbf{B}_{xc}(\mathbf{r}) = -\frac{\delta E_{xc}}{\delta \mathbf{m}(\mathbf{r})}, \quad (5.16)$$

$$\frac{1}{c} \mathbf{A}_{xc}(\mathbf{r}) = \frac{\delta E_{xc}}{\delta \mathbf{j}_p(\mathbf{r})}. \quad (5.17)$$

Finally, we can calculate the density

$$n(\mathbf{r}) = \sum_{k=1}^{\text{occ}} \Phi_k^\dagger(\mathbf{r}) \Phi_k(\mathbf{r}), \quad (5.18)$$

the magnetization density

$$\mathbf{m}(\mathbf{r}) = -g\mu_B \sum_{k=1}^{\text{occ}} \Phi_k^\dagger(\mathbf{r}) \boldsymbol{\sigma} \Phi_k(\mathbf{r}), \quad (5.19)$$

and the paramagnetic current density

$$\mathbf{j}_p(\mathbf{r}) = \frac{1}{2i} \sum_{k=1}^{\text{occ}} \left(\Phi_k^\dagger(\mathbf{r}) \nabla \Phi_k(\mathbf{r}) - (\nabla \Phi_k^\dagger(\mathbf{r})) \Phi_k(\mathbf{r}) \right) \quad (5.20)$$

of the KS system. The iteration starts from a guess for the densities, for example one can use densities of a non-interacting system. Then one evaluates the functional derivatives (5.15)-(5.17) at these given densities. The resulting KS potentials are used in Eq. (5.13) to obtain a new set of KS spinors from which a new set of densities via Eqs. (5.18-5.20) is calculated. This procedure is repeated till self-consistency is reached, i.e. until the potentials or the densities remain unchanged in consecutive iterations.

Once the calculation has converged the total energy of the interacting system is calculated from

$$\begin{aligned} E[n, \mathbf{m}, \mathbf{j}_p] &= T_s[n, \mathbf{m}, \mathbf{j}_p] + E_H[n] + E_{xc}[n, \mathbf{m}, \mathbf{j}_p] + \int d^3r v_0(\mathbf{r})n(\mathbf{r}) \\ &- \int d^3r \mathbf{m}(\mathbf{r})\mathbf{B}_0(\mathbf{r}) + \frac{1}{c} \int d^3r \mathbf{j}_p(\mathbf{r})\mathbf{A}_0(\mathbf{r}) + \frac{1}{2c^2} \int d^3r n(\mathbf{r})\mathbf{A}_0^2(\mathbf{r}), \end{aligned} \quad (5.21)$$

where

$$T_s = \sum_{k=1}^{\text{occ}} \Phi_k^\dagger(\mathbf{r}) \left(-\frac{\nabla^2}{2} \right) \Phi_k(\mathbf{r}) \quad (5.22)$$

is the kinetic energy of the KS system while

$$E_H = \frac{1}{2} \iint d^3r d^3r' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \quad (5.23)$$

denotes its Hartree energy. Using the KS equation (5.13) one can rewrite this equation as

$$\begin{aligned} E[n, \mathbf{m}, \mathbf{j}_p] &= \sum_{k=1}^{\text{occ}} \epsilon_k + E_{xc}[n, \mathbf{m}, \mathbf{j}_p] - \frac{1}{2} \int d^3r v_H(\mathbf{r})n(\mathbf{r}) \\ &- \int d^3r v_{xc}(\mathbf{r})n(\mathbf{r}) + \int d^3r \mathbf{m}(\mathbf{r})\mathbf{B}_{xc}(\mathbf{r}) - \frac{1}{c} \int d^3r \mathbf{j}_p(\mathbf{r})\mathbf{A}_{xc}(\mathbf{r}). \end{aligned} \quad (5.24)$$

Note that the term quadratic in \mathbf{A}_{xc} is absent. The second formula does not contain the second derivative of the KS spinors which is part of the kinetic energy in (5.21). Therefore, one prefers Eq. (5.24) in the numerical implementation.

Whenever one is working with electromagnetic potentials one has to ensure that all observable quantities are invariant under gauge transformations. The total energy is certainly an observable and since the combined kinetic plus external energy, and also the Hartree energy, are gauge invariant the exchange-correlation energy has to satisfy gauge invariance as well. This requirement leads to the restriction that E_{xc} depends on \mathbf{j}_p only through the vorticity [18]

$$\nu(\mathbf{r}) = \nabla \times \frac{\mathbf{j}_p(\mathbf{r})}{n(\mathbf{r})}, \quad (5.25)$$

i.e.

$$E_{xc}[n, \mathbf{j}_p, \mathbf{m}] = \bar{E}_{xc}[n, \nu, \mathbf{m}]. \quad (5.26)$$

As a consequence the exchange-correlation vector potential \mathbf{A}_{xc} has to satisfy

$$\nabla (n(\mathbf{r})\mathbf{A}_{xc}(\mathbf{r})) = 0. \quad (5.27)$$

In addition, Capelle and Gross showed [69] that the dependence on the magnetization density is only through $\nabla \times \mathbf{m}$, i.e.

$$E_{xc}[n, \mathbf{j}_p, \mathbf{m}] = \tilde{E}_{xc}[n, \mathbf{j}_p, -c\nabla \times \mathbf{m}]. \quad (5.28)$$

This condition implies that

$$\mathbf{B}_s = \nabla \times \mathbf{A}_s \quad (5.29)$$

which ensures that the KS magnetic field and vector potential resemble true physical fields. CSDFT itself treats the magnetic field and the vector potential as independent variables which do not necessarily satisfy Eq. (5.29). Therefore, the approximation for E_{xc} has to be carefully chosen not to violate (5.29). LDA and GGAs do not depend on the magnetization density only through its curl, and hence, lead to a violation of Eq. (5.29).

5.2 Collinear Magnetism

One commonly applied additional approximation restricts the spin magnetization \mathbf{m} to be parallel or anti-parallel to the effective magnetic field which is taken to point in the same direction throughout space. Without loss of generality one can then choose the magnetic field to be along the z -direction, and hence

$$\mathbf{B}(\mathbf{r}) = B(\mathbf{r})\mathbf{e}_z, \quad \mathbf{m}(\mathbf{r}) = m(\mathbf{r})\mathbf{e}_z. \quad (5.30)$$

The Zeeman term in the KS equation (5.13) reduces to

$$\mu_B \begin{pmatrix} B_s & 0 \\ 0 & -B_s \end{pmatrix}, \quad (5.31)$$

and the whole equation for the two spin components decouples. As a consequence, the KS spinors can be chosen as purely spin-up or spin-down, i.e.

$$\Phi_k(\mathbf{r}) = \begin{pmatrix} \varphi_{k\uparrow}(\mathbf{r}) \\ 0 \end{pmatrix} \quad \text{or} \quad \Phi_k(\mathbf{r}) = \begin{pmatrix} 0 \\ \varphi_{k\downarrow}(\mathbf{r}) \end{pmatrix}, \quad (5.32)$$

and the resulting KS equation reads

$$\left[\frac{1}{2} \left(-i\nabla + \frac{1}{c} \mathbf{A}_s(\mathbf{r}) \right)^2 + v_s(\mathbf{r}) \pm g\mu_B B_s(\mathbf{r}) \right] \varphi_{k\sigma}(\mathbf{r}) = \epsilon_{k\sigma} \varphi_{k\sigma}(\mathbf{r}), \quad (5.33)$$

where the + sign corresponds to spin-up ($\sigma = \uparrow$) and the – sign to spin-down ($\sigma = \downarrow$). One defines a spin-dependent scalar potential

$$v_{s\sigma}(\mathbf{r}) = v_s(\mathbf{r}) \pm g\mu_B B_s(\mathbf{r}) \quad (5.34)$$

and the corresponding spin densities

$$n_\sigma(\mathbf{r}) = \sum_k^{\text{occ}} |\varphi_{k\sigma}(\mathbf{r})|^2. \quad (5.35)$$

The total density and the z -component of the spin magnetization are then given by

$$n(\mathbf{r}) = n_\uparrow(\mathbf{r}) + n_\downarrow(\mathbf{r}), \quad (5.36)$$

$$m(\mathbf{r}) = -g\mu_B (n_\uparrow(\mathbf{r}) - n_\downarrow(\mathbf{r})). \quad (5.37)$$

From these two equations we can conclude that instead of writing $E_{xc}[n, m, \mathbf{j}_p]$, we might use $E_{xc}[n_\uparrow, n_\downarrow, \mathbf{j}_p]$ since there is a one-to-one correspondence between $\{n, m\}$ and $\{n_\uparrow, n_\downarrow\}$. Defining spin-dependent scalar exchange-correlation potentials

$$v_{xc\sigma}(\mathbf{r}) = \frac{\delta E_{xc}}{\delta n_\sigma(\mathbf{r})} \quad (5.38)$$

one obtains from the chain rule

$$\frac{\delta E_{xc}}{\delta n_\sigma(\mathbf{r})} = \int d^3r' \frac{\delta E_{xc}}{\delta n(\mathbf{r}')} \frac{\delta n(\mathbf{r}')}{\delta n_\sigma(\mathbf{r})} + \frac{\delta E_{xc}}{\delta m(\mathbf{r}')} \frac{\delta m(\mathbf{r}')}{\delta n_\sigma(\mathbf{r})} \quad (5.39)$$

$$= \int d^3r' v_{xc}(\mathbf{r}') \delta(\mathbf{r} - \mathbf{r}') \pm g\mu_B B_{xc}(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}'). \quad (5.40)$$

In other words, the spin-dependent scalar exchange-correlation potentials are given by

$$v_{xc\sigma}(\mathbf{r}) = v_{xc}(\mathbf{r}) \pm g\mu_B B_{xc}(\mathbf{r}). \quad (5.41)$$

The KS equation can then be written in a very compact form as

$$\left[\frac{1}{2} \left(-i\nabla + \frac{1}{c} \mathbf{A}_s(\mathbf{r}) \right)^2 + v_{s\sigma}(\mathbf{r}) \right] \varphi_{k\sigma}(\mathbf{r}) = \epsilon_{k\sigma} \varphi_{k\sigma}(\mathbf{r}). \quad (5.42)$$

In their original papers [17, 18] Vignale and Rasolt introduced a spin-dependent vector potential $\mathbf{A}_{s\sigma}$ with the associated paramagnetic current densities $\mathbf{j}_{p\sigma}$. Although external vector potentials are spin-independent the inclusion of spin-dependent KS vector potentials allows for direct access to the spin components of the paramagnetic current density. If the vector potential is spin-independent, only the total KS paramagnetic current is required to coincide with the one of the interacting system. As a disadvantage of a spin-dependent vector potential the relation (5.29) between \mathbf{B}_s and \mathbf{A}_s becomes unusable since the functional dependence of the total \mathbf{A}_s on its two spin-components $\mathbf{A}_{s\sigma}$ is unknown. Here, we choose to work with a spin-independent KS vector potential.

5.3 Optimized Effective Potential Method in CSDFT

In conventional DFT there are not only functionals which depend explicitly on the density but also orbital functionals which show an implicit dependence. We have also seen that the extension of explicit density functionals to CSDFT is problematic. Since these problems are caused by the filling of Landau levels, an orbital effect, orbital functionals are the natural solution. The concept of orbital functionals can be transferred to any extension of DFT. In CSDFT, the dependence on the densities (5.18)-(5.20) is replaced by a dependence on the KS orbitals which, via the extended HK theorem, are functionals of the complete set of densities. Of course, the functional derivatives with respect to the densities, in CSDFT Eqs. (5.15)-(5.17), become non-trivial to evaluate. Hence, we have to extend the whole optimized effective potential (OEP) method [70, 71]. The OEP equations can be derived keeping in mind that the exchange-correlation energy in CSDFT is an implicit functional of the densities (5.18), (5.19), and (5.20). In analogy to conventional DFT, we vary the exchange-correlation energy with respect to all three potentials using the chain rule with respect to all three densities. This leads to more complicated equations but does not introduce any fundamental difficulty. Applying the chain rule also with respect to the KS spinors we find

$$\begin{aligned} \frac{\delta E_{xc}}{\delta v_s(\mathbf{r})} &= \int d^3r' \left(v_{xc}(\mathbf{r}') \frac{\delta n(\mathbf{r}')}{\delta v_s(\mathbf{r})} + \frac{1}{c} \mathbf{A}_{xc}(\mathbf{r}') \frac{\delta \mathbf{j}_p(\mathbf{r}')}{\delta v_s(\mathbf{r})} - \mathbf{B}_{xc}(\mathbf{r}') \frac{\delta \mathbf{m}(\mathbf{r}')}{\delta v_s(\mathbf{r})} \right) \\ &= \sum_{j=1}^N \int d^3r' \left(\frac{\delta E_{xc}}{\delta \Phi_j(\mathbf{r}')} \frac{\delta \Phi_j(\mathbf{r}')}{\delta v_s(\mathbf{r})} + \frac{\delta E_{xc}}{\delta \Phi_j^\dagger(\mathbf{r}')} \frac{\delta \Phi_j^\dagger(\mathbf{r}')}{\delta v_s(\mathbf{r})} \right), \end{aligned} \quad (5.43)$$

$$\begin{aligned} \frac{\delta E_{xc}}{\delta \mathbf{B}_s(\mathbf{r})} &= \int d^3r' \left(v_{xc}(\mathbf{r}') \frac{\delta n(\mathbf{r}')}{\delta \mathbf{B}_s(\mathbf{r})} + \frac{1}{c} \mathbf{A}_{xc}(\mathbf{r}') \frac{\delta \mathbf{j}_p(\mathbf{r}')}{\delta \mathbf{B}_s(\mathbf{r})} - \mathbf{B}_{xc}(\mathbf{r}') \frac{\delta \mathbf{m}(\mathbf{r}')}{\delta \mathbf{B}_s(\mathbf{r})} \right) \\ &= \sum_{j=1}^N \int d^3r' \left(\frac{\delta E_{xc}}{\delta \Phi_j(\mathbf{r}')} \frac{\delta \Phi_j(\mathbf{r}')}{\delta \mathbf{B}_s(\mathbf{r})} + \frac{\delta E_{xc}}{\delta \Phi_j^\dagger(\mathbf{r}')} \frac{\delta \Phi_j^\dagger(\mathbf{r}')}{\delta \mathbf{B}_s(\mathbf{r})} \right), \end{aligned} \quad (5.44)$$

$$\begin{aligned}
\frac{\delta E_{xc}}{\delta \mathbf{A}_s(\mathbf{r})} &= \int d^3r' \left(v_{xc}(\mathbf{r}') \frac{\delta n(\mathbf{r}')}{\delta \mathbf{A}_s(\mathbf{r})} + \frac{1}{c} \mathbf{A}_{xc}(\mathbf{r}') \frac{\delta \mathbf{j}_p(\mathbf{r}')}{\delta \mathbf{A}_s(\mathbf{r})} - \mathbf{B}_{xc}(\mathbf{r}') \frac{\delta \mathbf{m}(\mathbf{r}')}{\delta \mathbf{A}_s(\mathbf{r})} \right) \\
&= \sum_{j=1}^N \int d^3r' \left(\frac{\delta E_{xc}}{\delta \Phi_j(\mathbf{r}') \delta \mathbf{A}_s(\mathbf{r})} + \frac{\delta E_{xc}}{\delta \Phi_j^\dagger(\mathbf{r}') \delta \mathbf{A}_s(\mathbf{r})} \right). \tag{5.45}
\end{aligned}$$

The exact functional derivatives of the orbitals with respect to the KS potentials are calculated from first order perturbation theory of the Hamiltonian (5.13) perturbed by small fields δv_s , $\delta \mathbf{B}_s$, and $\delta \mathbf{A}_s$. This leads to

$$\frac{\delta \Phi_j(\mathbf{r}')}{\delta v_s(\mathbf{r})} = \sum_{\substack{k=1 \\ k \neq j}}^{\infty} \frac{\Phi_k^\dagger(\mathbf{r}) \Phi_j(\mathbf{r})}{\epsilon_j - \epsilon_k} \Phi_k(\mathbf{r}), \tag{5.46}$$

$$\frac{\delta \Phi_j(\mathbf{r}')}{\delta \mathbf{B}_s(\mathbf{r})} = \mu_B \sum_{\substack{k=1 \\ k \neq j}}^{\infty} \frac{\Phi_k^\dagger(\mathbf{r}) \boldsymbol{\sigma} \Phi_j(\mathbf{r})}{\epsilon_j - \epsilon_k} \Phi_k(\mathbf{r}), \tag{5.47}$$

and

$$\frac{\delta \Phi_j(\mathbf{r}')}{\delta \mathbf{A}_s(\mathbf{r})} = \frac{1}{c} \sum_{\substack{k=1 \\ k \neq j}}^{\infty} \frac{\frac{1}{2i} \left[\Phi_k^\dagger(\mathbf{r}) \nabla \Phi_j(\mathbf{r}) - (\nabla \Phi_k^\dagger(\mathbf{r})) \Phi_j(\mathbf{r}) \right] + \frac{1}{c} \mathbf{A}_s(\mathbf{r}') \Phi_k^\dagger(\mathbf{r}) \Phi_j(\mathbf{r})}{\epsilon_j - \epsilon_k} \Phi_k(\mathbf{r}). \tag{5.48}$$

The functional derivatives of the densities are calculated from their definitions in terms of the KS spinors, Eqs. (5.18)-(5.20), e.g.

$$\frac{\delta n(\mathbf{r}')}{\delta v_s(\mathbf{r})} = \sum_j^{\text{occ}} \int d^3r'' \left(\Phi_j^\dagger(\mathbf{r}'') \frac{\delta \Phi_j(\mathbf{r}'')}{\delta v_s(\mathbf{r})} + \frac{\delta \Phi_j^\dagger(\mathbf{r}'')}{\delta v_s(\mathbf{r})} \Phi_j(\mathbf{r}'') \right). \tag{5.49}$$

The derivatives of the exchange-correlation energy can be evaluated once an approximate orbital functional is specified. The final OEP equations read

$$\sum_{j=1}^N \left(\Phi_j^\dagger(\mathbf{r}) \Psi_j(\mathbf{r}) + h.c. \right) = 0, \tag{5.50}$$

$$-\mu_B \sum_{j=1}^N \left(\Phi_j^\dagger(\mathbf{r}) \boldsymbol{\sigma} \Psi_j(\mathbf{r}) + h.c. \right) = 0, \tag{5.51}$$

$$\left[\frac{1}{2i} \sum_{j=1}^N \left(\Phi_j^\dagger(\mathbf{r}) \nabla \Psi_j(\mathbf{r}) - (\nabla \Phi_j^\dagger(\mathbf{r})) \Psi_j(\mathbf{r}) \right) \right] + h.c. = 0. \tag{5.52}$$

These equations (5.50)-(5.52) form a set of coupled integral equations for the three unknown exchange-correlation potentials. We introduced the ‘‘orbital shifts’’ [71,

72, 73]

$$\Psi_j(\mathbf{r}) = \sum_{\substack{k=1 \\ k \neq j}}^{\infty} \frac{D_{jk}^\dagger \Phi_k(\mathbf{r})}{\epsilon_j - \epsilon_k} \quad (5.53)$$

with

$$\begin{aligned} D_{jk}^\dagger = & \int d^3 r' \left(v_{xc}(\mathbf{r}') \Phi_k^\dagger(\mathbf{r}') \Phi_j(\mathbf{r}') \right. \\ & \left. + g\mu_B \mathbf{B}_{xc}(\mathbf{r}') \Phi_k^\dagger(\mathbf{r}') \boldsymbol{\sigma} \Phi_j(\mathbf{r}') - \Phi_k^\dagger(\mathbf{r}') \frac{\delta E_{xc}}{\delta \Phi_j^\dagger(\mathbf{r}')} \right) \\ & + \frac{1}{2ic^2} \mathbf{A}_{xc}(\mathbf{r}') \left[\Phi_k^\dagger(\mathbf{r}') \nabla' \Phi_j(\mathbf{r}') - \left(\nabla' \Phi_k^\dagger(\mathbf{r}') \right) \Phi_j(\mathbf{r}') \right]. \quad (5.54) \end{aligned}$$

In first-order perturbation theory, the orbital shifts Ψ_j would correspond to a perturbation whose matrix elements are given by D_{jk}^\dagger . Hence, the OEP equations (5.50)-(5.52) have the simple physical interpretation that the densities do not change under this perturbation. The perturbation in CSDFT contains two additional terms, one for \mathbf{A}_{xc} and one for \mathbf{B}_{xc} , compared to conventional DFT.

For $\mathbf{A}_{xc} = 0$ in Eqs. (5.50) and (5.51) reduce to the OEP equations in spin-DFT [74], as expected. In collinear (spin-) DFT, a technique for solving the OEP equations has recently been developed which is based on a direct computation of the orbital shifts [72, 73]. A similar technique has been used to solve the OEP equations in non-collinear spin-DFT [74] and could also be employed here. However, we do not follow this approach but use the simplifying approximation by Krieger, Li, and Iafrate (KLI) [75, 66] which is also frequently employed in spin-DFT calculations.

5.4 Approximation of Krieger, Li, and Iafrate

The derivation of the OEP equations in the last section resulted in three coupled integral equations (5.50)-(5.52) for the three exchange-correlation potentials. The approximation by Krieger, Li, and Iafrate (KLI) [75, 66] transforms these equations into a set of coupled algebraic equations simplifying the numerical treatment considerably. As in DFT, one replaces the energy denominator $\epsilon_j - \epsilon_k$ in the definition (5.53) of Ψ_j by a constant $\Delta\epsilon$ leading to

$$\Psi_j(\mathbf{r}) = \frac{1}{\Delta\epsilon} \left\{ \sum_{k=1}^{\infty} D_{jk}^\dagger \Phi_k(\mathbf{r}) - D_{jj}^\dagger \Phi_j(\mathbf{r}) \right\}. \quad (5.55)$$

The sum over k can then be performed analytically due to the closure relation

$$\sum_{k=1}^{\infty} \Phi_k^\dagger(\mathbf{r}') \Phi_k(\mathbf{r}) = \delta(\mathbf{r} - \mathbf{r}'). \quad (5.56)$$

The three OEP equations in the KLI approximation are then most conveniently written in the matrix notation

$$\mathcal{D}(\mathbf{r})\mathcal{V}_{xc}(\mathbf{r}) = \mathcal{R}(\mathbf{r}), \quad (5.57)$$

where we defined the vector of exchange-correlation potentials as

$$\mathcal{V}_{xc}^T(\mathbf{r}) = \left(v_{xc}(\mathbf{r}), \mathbf{B}_{xc}^T(\mathbf{r}), \frac{1}{c} \mathbf{A}_{xc}^T(\mathbf{r}) \right). \quad (5.58)$$

The 7×7 matrix \mathcal{D} is given by

$$\mathcal{D}(\mathbf{r}) = \begin{pmatrix} n(\mathbf{r}) & -\mathbf{m}^T(\mathbf{r}) & \mathbf{j}_p^T(\mathbf{r}) \\ -\mathbf{m}(\mathbf{r}) & g^2 \mu_B^2 n(\mathbf{r}) \mathbb{1} & \mathcal{J}(\mathbf{r}) \\ \mathbf{j}_p(\mathbf{r}) & \mathcal{J}^T(\mathbf{r}) & \mathcal{N}(\mathbf{r}) \end{pmatrix}, \quad (5.59)$$

where $\mathbb{1}$ is the 3×3 unit matrix. The matrix elements of the 3×3 matrices \mathcal{J} and \mathcal{N} are defined by

$$\mathcal{J}_{\alpha\beta}(\mathbf{r}) = -\frac{g\mu_B}{2i} \sum_{j=1}^N \left(\Phi_j^\dagger(\mathbf{r}) \sigma_\alpha \frac{\partial \Phi_j(\mathbf{r})}{\partial r_\beta} - \frac{\partial \Phi_j^\dagger(\mathbf{r})}{\partial r_\beta} \sigma_\alpha \Phi_j(\mathbf{r}) \right), \quad (5.60)$$

and

$$\mathcal{N}_{\alpha\beta}(\mathbf{r}) = \frac{1}{2} \sum_{j=1}^N \left(\frac{\partial \Phi_j^\dagger(\mathbf{r})}{\partial r_\alpha} \frac{\partial \Phi_j(\mathbf{r})}{\partial r_\beta} + \frac{\partial \Phi_j^\dagger(\mathbf{r})}{\partial r_\beta} \frac{\partial \Phi_j(\mathbf{r})}{\partial r_\alpha} \right) - \frac{1}{4n(\mathbf{r})} \frac{\partial n(\mathbf{r})}{\partial r_\alpha} \frac{\partial n(\mathbf{r})}{\partial r_\beta}, \quad (5.61)$$

where $\alpha = 1, 2, 3$ correspond to the Cartesian coordinates $x, y,$ and $z,$ respectively. The seven components of the vector $\mathcal{R}(\mathbf{r})$ on the right hand side of Eq. (5.57) are given by

$$\mathcal{R}_1(\mathbf{r}) = \frac{1}{2} \sum_{j=1}^N \left(\Phi_j^\dagger(\mathbf{r}) \frac{\delta E_{xc}}{\delta \Phi_j^\dagger(\mathbf{r})} + n_j(\mathbf{r}) D_{jj}^\dagger + h.c. \right), \quad (5.62)$$

$$\mathcal{R}_{1+\alpha}(\mathbf{r}) = \frac{1}{2} \sum_{j=1}^N \left(-\mu_B \Phi_j^\dagger(\mathbf{r}) \sigma_\alpha \frac{\delta E_{xc}}{\delta \Phi_j^\dagger(\mathbf{r})} + m_{j\alpha}(\mathbf{r}) D_{jj}^\dagger + h.c. \right), \quad (5.63)$$

$$\mathcal{R}_{4+\alpha}(\mathbf{r}) = \frac{1}{2} \sum_{j=1}^N \left(\frac{1}{2i} \Phi_j^\dagger(\mathbf{r}) \frac{\partial}{\partial r_\alpha} \frac{\delta E_{xc}}{\delta \Phi_j^\dagger(\mathbf{r})} - \frac{1}{2i} \frac{\partial \Phi_j^\dagger(\mathbf{r})}{\partial r_\alpha} \frac{\delta E_{xc}}{\delta \Phi_j^\dagger(\mathbf{r})} + j_{pj\alpha}(\mathbf{r}) D_{jj}^\dagger + h.c. \right), \quad (5.64)$$

where the density $n_j,$ the magnetization density $\mathbf{m}_j,$ and the paramagnetic current density \mathbf{j}_{pj} correspond to a single orbital $\Phi_j(\mathbf{r}),$ i.e.

$$n_j(\mathbf{r}) = \Phi_j^\dagger(\mathbf{r}) \Phi_j(\mathbf{r}), \quad (5.65)$$

$$\mathbf{m}_j(\mathbf{r}) = -\mu_B \Phi_j^\dagger(\mathbf{r}) \boldsymbol{\sigma} \Phi_j(\mathbf{r}), \quad (5.66)$$

$$\mathbf{j}_{pj}(\mathbf{r}) = \frac{1}{2i} \left(\Phi_j^\dagger(\mathbf{r}) \nabla \Phi_j(\mathbf{r}) - (\nabla \Phi_j^\dagger(\mathbf{r})) \Phi_j(\mathbf{r}) \right). \quad (5.67)$$

In order to derive the KLI equations in this form we made use of Eq. (5.27), i.e. we employed the gauge invariance of $E_{xc}.$

5.5 OEP Equations for Collinear Magnetism

As introduced in Section 5.2, a common approximation restricts the magnetization of the system to be collinear with the magnetic field and the KS equation decomposes into two independent spinor components. Therefore, the orbital shifts (5.53), being spinor quantities in general, also reduce to spin-orbital shifts, i.e.

$$\psi_{j\sigma}(\mathbf{r}) = \sum_{\substack{k=1 \\ k \neq j}}^{\infty} \frac{D_{jk\sigma}^* \varphi_{k\sigma}(\mathbf{r})}{\epsilon_j - \epsilon_k}. \quad (5.68)$$

The matrix elements $D_{jk\sigma}$ also inherit the spin-dependence and are given by

$$D_{jk\sigma}^* = \int d^3r' \left(v_{xc\sigma}(\mathbf{r}') \varphi_{j\sigma}(\mathbf{r}') \varphi_{k\sigma}^*(\mathbf{r}') - \varphi_{k\sigma}^*(\mathbf{r}') \frac{\delta E_{xc}}{\delta \varphi_{j\sigma}^*(\mathbf{r}')} \right. \\ \left. + \frac{1}{2ic} \mathbf{A}_{xc}(\mathbf{r}') [\varphi_{k\sigma}^*(\mathbf{r}') \nabla' \varphi_{j\sigma}(\mathbf{r}') - \varphi_{j\sigma}(\mathbf{r}') \nabla' \varphi_{k\sigma}^*(\mathbf{r}')] \right) \quad (5.69)$$

with the spin-dependent scalar potential defined in Eq. (5.34).

The OEP equations (5.50)-(5.52) reduce to a sum over their two spin components

$$\sum_{\sigma=\uparrow,\downarrow} \sum_{j=1}^{N_\sigma} \varphi_{j\sigma}^*(\mathbf{r}) \psi_{j\sigma}(\mathbf{r}) + c.c. = 0, \quad (5.70)$$

$$-\mu_B \sum_{\sigma=\uparrow,\downarrow} \sum_{j=1}^{N_\sigma} \pm \varphi_{j\sigma}^*(\mathbf{r}) \psi_{j\sigma}(\mathbf{r}) + c.c. = 0, \quad (5.71)$$

$$\left[\frac{1}{2ic} \sum_{\sigma=\uparrow,\downarrow} \sum_{j=1}^{N_\sigma} [\varphi_{j\sigma}^*(\mathbf{r}) \nabla \psi_{j\sigma}(\mathbf{r}) - \psi_{j\sigma}(\mathbf{r}) \nabla \varphi_{j\sigma}^*(\mathbf{r})] \right] + c.c. = 0, \quad (5.72)$$

where the upper sign in Eq. (5.71) is for the spin up and the lower signs for the spin down direction. Note that Eq. (5.71) simplifies from a 3-component vector equation to a pure scalar equation for collinear magnetism. By adding and subtracting the first two equations, the two spin directions can be decoupled, i.e.

$$\sum_{j=1}^{N_\sigma} \varphi_{j\sigma}^*(\mathbf{r}) \psi_{j\sigma}(\mathbf{r}) + c.c. = 0 \quad (5.73)$$

has to be satisfied separately for each spin component. The third equation, however, does not decouple into its spin components because the vector potential does not depend on spin.

The KLI approximation can be used in complete analogy to Section 5.4. Since the number of densities is reduced, the KLI approximation results in a 5×5 matrix equation

$$\mathcal{D}(\mathbf{r}) \mathcal{V}_{xc}(\mathbf{r}) = \mathcal{R}(\mathbf{r}), \quad (5.74)$$

where the vector of exchange-correlation potentials is now given by

$$\mathcal{V}_{xc}^T(\mathbf{r}) = \left(v_{xc\uparrow}(\mathbf{r}), v_{xc\downarrow}(\mathbf{r}), \frac{1}{c} \mathbf{A}_{xc}^T(\mathbf{r}) \right), \quad (5.75)$$

and the matrix \mathcal{D} reads

$$\mathcal{D}(\mathbf{r}) = \begin{pmatrix} n_{\uparrow}(\mathbf{r}) & 0 & \mathbf{j}_{p\uparrow}^T(\mathbf{r}) \\ 0 & n_{\downarrow}(\mathbf{r}) & \mathbf{j}_{p\downarrow}^T(\mathbf{r}) \\ \mathbf{j}_{p\uparrow}(\mathbf{r}) & \mathbf{j}_{p\downarrow}(\mathbf{r}) & \mathcal{N}(\mathbf{r}) \end{pmatrix}. \quad (5.76)$$

The matrix elements of the 3×3 matrix \mathcal{N} are also given as a sum over both spin directions

$$\mathcal{N}_{\alpha\beta}(\mathbf{r}) = \frac{1}{2} \sum_{\sigma=\uparrow,\downarrow} \sum_{j=1}^{N_{\sigma}} \left(\frac{\partial \varphi_{j\sigma}^*(\mathbf{r})}{\partial r_{\alpha}} \frac{\partial \varphi_{j\sigma}(\mathbf{r})}{\partial r_{\beta}} + \frac{\partial \varphi_{j\sigma}^*(\mathbf{r})}{\partial r_{\beta}} \frac{\partial \varphi_{j\sigma}(\mathbf{r})}{\partial r_{\alpha}} \right) - \frac{1}{4n(\mathbf{r})} \frac{\partial n(\mathbf{r})}{\partial r_{\alpha}} \frac{\partial n(\mathbf{r})}{\partial r_{\beta}}, \quad (5.77)$$

where $\alpha = 1, 2, 3$ again correspond to the Cartesian coordinates $x, y,$ and $z,$ respectively. The five components of the vector $\mathcal{R}(\mathbf{r})$ on the right hand side of Eq. (5.74) can be written as

$$\mathcal{R}_1(\mathbf{r}) = \frac{1}{2} \sum_{j=1}^{N_{\uparrow}} \left(\varphi_{j\uparrow}^*(\mathbf{r}) \frac{\delta E_{xc}}{\delta \varphi_{j\uparrow}^*(\mathbf{r})} + n_{j\uparrow}(\mathbf{r}) D_{jj\uparrow}^* + c.c. \right), \quad (5.78)$$

$$\mathcal{R}_2(\mathbf{r}) = \frac{1}{2} \sum_{j=1}^{N_{\downarrow}} \left(\varphi_{j\downarrow}^*(\mathbf{r}) \frac{\delta E_{xc}}{\delta \varphi_{j\downarrow}^*(\mathbf{r})} + n_{j\downarrow}(\mathbf{r}) D_{jj\downarrow}^* + c.c. \right), \quad (5.79)$$

$$\begin{aligned} \mathcal{R}_{2+\alpha}(\mathbf{r}) = & \frac{1}{2} \sum_{\sigma=\uparrow,\downarrow} \sum_{j=1}^{N_{\sigma}} \left(\frac{1}{2i} \varphi_{j\sigma}^*(\mathbf{r}) \frac{\partial}{\partial r_{\alpha}} \frac{\delta E_{xc}}{\delta \varphi_{j\sigma}^*(\mathbf{r})} - \frac{1}{2i} \frac{\partial \varphi_{j\sigma}^*(\mathbf{r})}{\partial r_{\alpha}} \frac{\delta E_{xc}}{\delta \varphi_{j\sigma}^*(\mathbf{r})} \right. \\ & \left. + \mathbf{j}_{pj\sigma\alpha}(\mathbf{r}) D_{jj\sigma}^* + c.c. \right). \end{aligned} \quad (5.80)$$

5.6 Exact Exchange

The derivations in Sections 5.3 to 5.5 are completely general and valid for any orbital dependent functional E_{xc} . For the application in Chapter 6 we restrict ourselves to the most commonly used functional, namely the exact-exchange functional E_{xc}^{EXX} . In terms of the KS spinors E_{xc}^{EXX} is given by

$$E_{xc}^{\text{EXX}} = -\frac{1}{2} \sum_{j,k=1}^N \iint d^3r d^3r' \frac{\Phi_j^{\dagger}(\mathbf{r}) \Phi_j(\mathbf{r}') \Phi_k^{\dagger}(\mathbf{r}') \Phi_k(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|}. \quad (5.81)$$

Applying the collinear approximation, (5.81) simplifies to

$$E_{xc}^{\text{EXX}} = -\frac{1}{2} \sum_{\sigma=\uparrow,\downarrow} \sum_{j,k}^{N_\sigma} \iint d^3r d^3r' \frac{\varphi_{j\sigma}^*(\mathbf{r})\varphi_{j\sigma}(\mathbf{r}')\varphi_{k\sigma}^*(\mathbf{r}')\varphi_{k\sigma}(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|}. \quad (5.82)$$

A comparison with conventional DFT reveals an advantage of orbital functionals. They remain unchanged when the theory is extended to include additional potentials and densities. All the dependence on any new density is automatically accounted for because the KS orbitals depend on the new density.

