

Part I

Reduced Density Matrix Functional Theory

Chapter 2

Theoretical Foundations

Quantum mechanics teaches us that all information about a system is contained in its wave function. Equivalently, one can describe a system of N particles by the N -body density matrix

$$\Gamma^{(N)}(\mathbf{x}_1 \dots \mathbf{x}_N, ; \mathbf{x}'_1 \dots \mathbf{x}'_N) = \Psi^*(\mathbf{x}'_1 \dots \mathbf{x}'_N) \Psi(\mathbf{x}_1 \dots \mathbf{x}_N), \quad (2.1)$$

where \mathbf{x} is understood as a combined space-spin coordinate $\mathbf{x} = (\mathbf{r}, \sigma)$ and $\int d\mathbf{x} = \sum_{\sigma} \int d\mathbf{r}$. The wave function is normalized such that

$$\int d\mathbf{x}_1 \dots d\mathbf{x}_N \Psi^*(\mathbf{x}_1 \dots \mathbf{x}_N) \Psi(\mathbf{x}_1 \dots \mathbf{x}_N) = 1. \quad (2.2)$$

For the wave function one has to store a function depending on $3N$ spatial variables. However, nature was kind enough to provide us with electrons that can be described with two-particle interactions only. Consequently, the Hamiltonian can be written as

$$\hat{H} = \int d\mathbf{x} \hat{\psi}^\dagger(\mathbf{x}) \left(-\frac{\nabla^2}{2} \right) \hat{\psi}(\mathbf{x}) + \frac{1}{2} \iint d\mathbf{x} d\mathbf{x}' \frac{\hat{\psi}^\dagger(\mathbf{x}) \hat{\psi}^\dagger(\mathbf{x}') \hat{\psi}(\mathbf{x}') \hat{\psi}(\mathbf{x})}{|\mathbf{r} - \mathbf{r}'|}. \quad (2.3)$$

The field operators are given by

$$\hat{\psi}^\dagger(\mathbf{x}) = \sum_k \psi_k^*(\mathbf{x}) c_k^\dagger, \quad (2.4)$$

$$\hat{\psi}(\mathbf{x}) = \sum_k \psi_k(\mathbf{x}) c_k, \quad (2.5)$$

where the set $\{\psi_k\}$ forms a basis of the single-particle Hilbert space. The creation (annihilation) operators c_k^\dagger (c_k) fulfill the usual anti-commutation relations

$$\{c_j, c_k\} = \{c_j^\dagger, c_k^\dagger\} = 0, \quad \{c_j, c_k^\dagger\} = \delta_{jk}. \quad (2.6)$$

We introduce the p^{th} order reduced density matrix

$$\Gamma^{(p)}(\mathbf{x}_1 \dots \mathbf{x}_p; \mathbf{x}'_1 \dots \mathbf{x}'_p) = \binom{N}{p} \int d\mathbf{x}_{p+1} \dots d\mathbf{x}_N \Psi^*(\mathbf{x}'_1 \dots \mathbf{x}'_p, \mathbf{x}_{p+1} \dots \mathbf{x}_N) \Psi(\mathbf{x}_1 \dots \mathbf{x}_N) \quad (2.7)$$

which is the expectation value of the operator

$$\hat{\Gamma}^{(p)}(\mathbf{x}_1 \dots \mathbf{x}_p; \mathbf{x}'_1 \dots \mathbf{x}'_p) = \frac{1}{p!} \hat{\psi}^\dagger(\mathbf{x}'_p) \dots \hat{\psi}^\dagger(\mathbf{x}'_1) \hat{\psi}(\mathbf{x}_1) \dots \hat{\psi}(\mathbf{x}_p). \quad (2.8)$$

For the special case $p = 1$, (2.7) reduces to

$$\Gamma^{(1)}(\mathbf{x}; \mathbf{x}') = \int d\mathbf{x}_2 \dots d\mathbf{x}_N \Psi^*(\mathbf{x}'_1, \mathbf{x}_2, \dots, \mathbf{x}_N) \Psi(\mathbf{x}_1, \dots, \mathbf{x}_N). \quad (2.9)$$

We can then rewrite the Hamiltonian (2.3) as

$$\begin{aligned} \hat{H} &= \int d\mathbf{x} \hat{\psi}^\dagger(\mathbf{x}) \left(-\frac{\nabla^2}{2} \right) \hat{\psi}(\mathbf{x}) + \iint d\mathbf{x} d\mathbf{x}' \frac{\hat{\Gamma}^{(2)}(\mathbf{x}, \mathbf{x}'; \mathbf{x}, \mathbf{x}')}{|\mathbf{r} - \mathbf{r}'|} \\ &= \int d\mathbf{x} \lim_{\mathbf{x}' \rightarrow \mathbf{x}} \left(-\frac{\nabla^2}{2} \right) \hat{\Gamma}^{(1)}(\mathbf{x}; \mathbf{x}') + \iint d\mathbf{x} d\mathbf{x}' \frac{\hat{\Gamma}^{(2)}(\mathbf{x}, \mathbf{x}'; \mathbf{x}, \mathbf{x}')}{|\mathbf{r} - \mathbf{r}'|}. \end{aligned} \quad (2.10)$$

Specifying appropriate boundary conditions one can, in principle, solve the static Schrödinger equation $\hat{H}\Psi_\alpha = E_\alpha\Psi_\alpha$. The total energy of the system, i.e. the expectation value of the above Hamiltonian, however, is completely determined by the one-body reduced density matrix (1-RDM) and the diagonal of the two-body reduced density matrix. Any other information present in the wave function is irrelevant for the total energy. At the same level of complication we can add an external potential to the Hamiltonian which also couples only to the 1-RDM, i.e.

$$\begin{aligned} \hat{H} &= \int d\mathbf{x} \lim_{\mathbf{x}' \rightarrow \mathbf{x}} \left(-\frac{\nabla^2}{2} \right) \hat{\Gamma}^{(1)}(\mathbf{x}; \mathbf{x}') + \iint d\mathbf{x} d\mathbf{x}' \frac{\hat{\Gamma}^{(2)}(\mathbf{x}, \mathbf{x}'; \mathbf{x}, \mathbf{x}')}{|\mathbf{r} - \mathbf{r}'|} \\ &\quad + \iint d\mathbf{x} d\mathbf{x}' v_0(\mathbf{x}, \mathbf{x}') \hat{\Gamma}^{(1)}(\mathbf{x}'; \mathbf{x}). \end{aligned} \quad (2.11)$$

The physical, i.e. local, potentials are given by $v_0(\mathbf{x}, \mathbf{x}') = v_0(\mathbf{x})\delta(\mathbf{x} - \mathbf{x}')$. We nevertheless keep the more general form of the Hamiltonian because the necessary HK-type theorem can be proven for the more general form.

The total energy of the system of N interacting electrons is the expectation value of the Hamiltonian and, therefore, reads

$$\begin{aligned} E_{\text{total}} &= \int d\mathbf{x} \lim_{\mathbf{x}' \rightarrow \mathbf{x}} \left(-\frac{\nabla^2}{2} \right) \Gamma^{(1)}(\mathbf{x}; \mathbf{x}') + \iint d\mathbf{x} d\mathbf{x}' \frac{\Gamma^{(2)}(\mathbf{x}, \mathbf{x}'; \mathbf{x}, \mathbf{x}')}{|\mathbf{r} - \mathbf{r}'|} \\ &\quad + \iint d\mathbf{x} d\mathbf{x}' v_0(\mathbf{x}, \mathbf{x}') \Gamma^{(1)}(\mathbf{x}'; \mathbf{x}). \end{aligned} \quad (2.12)$$

In other words, the density matrix operators, present in the Hamiltonian, are replaced by their respective expectation values. From the definition of the reduced density matrices (2.9) one can see that the p^{th} and $(p-1)^{\text{st}}$ order density matrices are connected via

$$\Gamma^{(p-1)}(\mathbf{x}_1 \dots \mathbf{x}_{p-1}; \mathbf{x}'_1 \dots \mathbf{x}'_{p-1}) = \frac{p}{N-p+1} \int d\mathbf{x}_p \Gamma^{(p)}(\mathbf{x}_1 \dots \mathbf{x}_{p-1}, \mathbf{x}_p; \mathbf{x}'_1 \dots \mathbf{x}'_{p-1}, \mathbf{x}_p), \quad (2.13)$$

and, in particular for $p = 2$,

$$\Gamma^{(1)}(\mathbf{x}_1; \mathbf{x}'_1) = \frac{2}{N-1} \int d\mathbf{x}_2 \Gamma^{(2)}(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}'_1, \mathbf{x}_2). \quad (2.14)$$

Consequently, we can rewrite the total energy (2.12) as a functional of $\Gamma^{(2)}$ alone. Minimizing this functional should then result in the ground-state energy of the system. However, there is one additional complication. One has to ensure that the set of two-body density matrices over which we minimize only contains physical $\Gamma^{(2)}$ which are N -representable, i.e. correspond to a properly anti-symmetrized wave function via Eq. (2.9). The set of necessary *and* sufficient conditions for $\Gamma^{(2)}$ to be N -representable is not known completely. Recently, a set of necessary conditions has been introduced which is however not sufficient [21, 22]. The conditions for ensemble N -representability are known, however, for the one-body density matrix $\Gamma^{(1)}$, where they even turn out to be very simple. Therefore, the idea of using $\Gamma^{(1)}$ as the basic variable is appealing. From Eq. (2.12) the kinetic and external energies are known explicitly as functionals of $\Gamma^{(1)}$. Also, as we discuss later in this Chapter, the Hartree and exchange energies can be written exactly in terms of $\Gamma^{(1)}$. Only the so-called correlation energy remains to be approximated which, in general, is a small percentage of the total energy. Reduced-density matrix functional theory can be regarded as an intermediate step going from DFT to solving the full problem. In DFT, the kinetic energy is unknown in terms of the density and the difference of the kinetic energies of the true system and the KS system is part of the exchange-correlation energy. In other words, the part of the total energy that needs to be approximated in DFT is larger than in RDMFT.

In order to use $\Gamma^{(1)}$ as the basic variable one has to prove a Hohenberg-Kohn type theorem which was done by Gilbert [23]. Before we review his proof in Section 2.2 we introduce some important properties of $\hat{\Gamma}^{(1)}$, especially its eigenfunctions and eigenvalues in Section 2.1. There, we also state the conditions which ensure the N -representability of $\Gamma^{(1)}$. The proof that these conditions are indeed necessary *and* sufficient can be found in Appendix A. The ground-state energy as a functional of $\Gamma^{(1)}$ is discussed in Section 2.3 with special emphasis on the needed approximations. The concept of orbital functionals can be transferred with only minor modifications to RDMFT and is presented in Section 2.4. For reasons that we discuss in Section 2.5 there exists *no* KS system in RDMFT such that the energy has to be minimized directly. The corresponding equations are also presented in Section 2.5. We conclude this introductory chapter with a discussion of spin degrees of freedom in Section 2.6.

2.1 Natural Orbitals and Occupation Numbers

Diagonalizing the one-body reduced density matrix operator (see Eq. (2.8)) yields

$$\hat{\Gamma}^{(1)}(\mathbf{x}; \mathbf{x}') = \sum_{j=1}^{\infty} \varphi_j^*(\mathbf{x}') \varphi_j(\mathbf{x}) c_j^\dagger c_j, \quad (2.15)$$

with the basis for the single-particle Hilbert space chosen to be the eigenfunctions φ_j of $\hat{\Gamma}^{(1)}$. These eigenfunctions are referred to as natural orbitals. Due to the appearance of the number operator of orbital j in the above expression the eigenvalues are called occupation numbers and denoted by n_j . Therefore, the one-body reduced density matrix (1-RDM) can be written as

$$\Gamma^{(1)}(\mathbf{x}; \mathbf{x}') = \sum_{j=1}^{\infty} n_j \varphi_j(\mathbf{x}) \varphi_j^*(\mathbf{x}'). \quad (2.16)$$

In position-space representation the operator $\hat{\Gamma}^{(1)}$ is an integral operator and its eigenvalue equation reads

$$\int d\mathbf{x}' \Gamma^{(1)}(\mathbf{x}; \mathbf{x}') \varphi_j(\mathbf{x}') = n_j \varphi_j(\mathbf{x}). \quad (2.17)$$

The natural orbitals form a complete orthonormal set, i.e.

$$\int d\mathbf{x} \varphi_j^*(\mathbf{x}) \varphi_k(\mathbf{x}) = \delta_{jk}, \quad (2.18)$$

$$\sum_{j=1}^{\infty} \varphi_j(\mathbf{x}) \varphi_j^*(\mathbf{x}') = \delta(\mathbf{x} - \mathbf{x}'). \quad (2.19)$$

In order for the one-particle density matrix to be N -representable, i.e. to correspond to an anti-symmetric wave function Ψ via (2.9), the conditions

$$0 \leq n_j \leq 1, \quad (2.20)$$

$$\sum_{j=1}^{\infty} n_j = N \quad (2.21)$$

have to be satisfied. The proof that these conditions indeed ensure N -representability is very technical and given in Appendix A.¹ The special case where exactly N occupation numbers have the value one and the rest are zero describes a system of non-interacting particles. This is a consequence of the fact that the ground-state wave function of a non-interacting system is a single Slater determinant. The single particle orbitals in the determinant are identical to the natural orbitals of the resulting density matrix, and these orbitals have occupation number equal to 1. For interacting particles the wave function can be expressed as an expansion in the complete (infinite) set of Slater determinants constructed from the natural orbitals. Any single particle orbital that is not part of each determinant of the expansion results in an occupation number smaller than 1 in the density matrix.

The 1-RDM is, via (2.16), a functional of the occupation numbers and natural orbitals $\Gamma^{(1)}(\mathbf{x}; \mathbf{x}') = \Gamma^{(1)}[\{n_j\}, \{\varphi_j\}](\mathbf{x}; \mathbf{x}')$. The spectral representation (2.16) of

¹Actually, the proof ensures ensemble N -representability which, however, is sufficient as discussed in Section 2.2.

the density matrix is unique unless $\Gamma^{(1)}(\mathbf{x}; \mathbf{x}')$ has degenerate eigenvalues. Hence, we can write the occupation numbers and natural orbitals as functionals of the one-particle density matrix, i.e.

$$n_j = n_j[\Gamma^{(1)}], \quad (2.22)$$

$$\varphi_j(\mathbf{x}) = \varphi_j[\Gamma^{(1)}](\mathbf{x}). \quad (2.23)$$

These equations imply that we can also write the energy as a functional of the occupation numbers and natural orbitals instead of the 1-RDM. Therefore, the concept of orbital functionals, commonly used in DFT, can also be employed in RDMFT, where the KS orbitals are replaced by the natural orbitals and one has an additional dependence on the occupation numbers.

If there are two or more degenerate natural orbitals one can change the basis in the degenerate subspace by performing a unitary transformation. These unitary transformations leave $\Gamma^{(1)}$ unchanged. The total energy, being a functional of $\Gamma^{(1)}$, is then also independent of the basis in the degenerate subspace. In other words, $\Gamma^{(1)}$ and E_{total} are invariant under the same set of unitary transformations. As long as we only employ approximations which are *explicit* functionals of $\Gamma^{(1)}$ this property is automatically satisfied. However, when orbital functionals are used special attention has to be paid not to violate this property. Strictly speaking, any approximation for E_{total} which is not invariant under the same unitary transformations as $\Gamma^{(1)}$ is *not* a functional of $\Gamma^{(1)}$. We come back to this point when we discuss the approximations in Chapter 3.

2.2 Gilbert Theorem

As already mentioned before, the many-body wave function Ψ describes a quantum mechanical system completely. The Hohenberg-Kohn theorem of DFT, however, shows that all information about the system is already contained in its ground-state density $n_{\text{GS}}(\mathbf{r})$. Using the one-body reduced density matrix $\Gamma^{(1)}$ instead of the density n the kinetic energy is known exactly. To take advantage of this fact, a HK like theorem needs to be proven which was done by Gilbert in 1975 [23].

The proof starts from the Schrödinger equation

$$\left[\sum_{j=1}^N \left(-\frac{\nabla_j^2}{2} \right) + \frac{1}{2} \sum_{\substack{j,k=1 \\ j \neq k}}^N \frac{1}{|\mathbf{r}'_j - \mathbf{r}'_k|} \right] \Psi_\alpha(\mathbf{x}_1 \dots \mathbf{x}_N) \quad (2.24)$$

$$+ \sum_{j=1}^N \int d\mathbf{x}'_1 \dots d\mathbf{x}'_N \prod_{\substack{k=1 \\ k \neq j}}^N \delta(\mathbf{x}_k - \mathbf{x}'_k) v_0(\mathbf{x}_j, \mathbf{x}'_j) \Psi_\alpha(\mathbf{x}'_1 \dots \mathbf{x}'_N) = E_\alpha \Psi_\alpha(\mathbf{x}_1 \dots \mathbf{x}_N),$$

where now the external potential v_0 can be non-local. This includes all physical, and hence local, potentials. However, we state the proof in a form as general as

possible. As an additional advantage, the use of pseudo-potentials, which are often non-local in space, is well founded within RDMFT.

In analogy to the HK proof, the ground-state wave function is determined by the external potential if it is non-degenerate. The corresponding one-body density matrix is then given by Eq. (2.9) and hence, the external potential determines it uniquely, i.e.

$$v_0 \rightarrow \Psi_{\text{GS}} \rightarrow \Gamma_{\text{GS}}^{(1)}. \quad (2.25)$$

In contrast to the HK theorem, however, part of the inverse direction breaks down. The ground-state wave function does not uniquely determine the non-local potential v_0 . As a simple example, consider the case of N non-interacting electrons. The ground-state many-body wave function is then given by a single Slater determinant of N single-particle orbitals φ_j . Hence, the one-body reduced density matrix reads

$$\Gamma^{(1)}(\mathbf{x}; \mathbf{x}') = \sum_{j=1}^N \varphi_j^*(\mathbf{x}') \varphi_j(\mathbf{x}), \quad (2.26)$$

where the natural orbitals are exactly the single particle orbitals of the Slater determinant. If we add an arbitrary function f of the operator $\hat{\Gamma}^{(1)}$ to the non-interacting Hamiltonian, i.e. we change the potential according to

$$v_0(\mathbf{x}, \mathbf{x}') \rightarrow v_0(\mathbf{x}, \mathbf{x}') + \langle \mathbf{x} | f(\hat{\Gamma}^{(1)}) | \mathbf{x}' \rangle, \quad (2.27)$$

the same Slater determinant remains an eigenfunction of the new Hamiltonian. For some functions f this Slater determinant also remains the ground-state. The relation between v_0 and Ψ_{GS} is, therefore, many-to-one

$$v_0(\mathbf{x}, \mathbf{x}') \xleftrightarrow{\text{many-one}} \Psi_{\text{GS}}(\mathbf{x}_1 \dots \mathbf{x}_N), \quad (2.28)$$

provided we restrict ourselves to non-degenerate ground states.

One can still prove that the ground-state one-body reduced density matrix $\Gamma_{\text{GS}}^{(1)}$ uniquely determines the ground-state wave function Ψ_{GS} by reductio ad absurdum. We assume that two different ground-state wave functions Ψ_{GS} and Ψ'_{GS} lead to the same density matrix $\Gamma_{\text{GS}}^{(1)} = \Gamma'_{\text{GS}}{}^{(1)}$. The two different ground-state wave functions then, due to (2.28), have to originate from two different potentials v_0 and v'_0 . The ground-state energies of the two systems are then given by

$$\begin{aligned} E_{\text{GS}} &= \langle \Psi_{\text{GS}} | \hat{H} | \Psi_{\text{GS}} \rangle, \\ E'_{\text{GS}} &= \langle \Psi'_{\text{GS}} | \hat{H}' | \Psi'_{\text{GS}} \rangle. \end{aligned} \quad (2.29)$$

Applying Ritz' theorem we can conclude

$$\begin{aligned} E_{\text{GS}} &= \langle \Psi_{\text{GS}} | \hat{H} | \Psi_{\text{GS}} \rangle < \langle \Psi'_{\text{GS}} | \hat{H} | \Psi'_{\text{GS}} \rangle \\ &< E'_{\text{GS}} + \int d\mathbf{x} d\mathbf{x}' \Gamma_{\text{GS}}^{(1)}(\mathbf{x}'; \mathbf{x}) [v_0(\mathbf{x}, \mathbf{x}') - v'_0(\mathbf{x}, \mathbf{x}')] \end{aligned} \quad (2.30)$$

and on the other hand

$$\begin{aligned} E'_{\text{GS}} &= \langle \Psi'_{\text{GS}} | \hat{H}' | \Psi'_{\text{GS}} \rangle < \langle \Psi_{\text{GS}} | \hat{H}' | \Psi_{\text{GS}} \rangle \\ &< E_{\text{GS}} + \int d\mathbf{x}d\mathbf{x}' \Gamma_{\text{GS}}^{(1)}(\mathbf{x}'; \mathbf{x}) [v'_0(\mathbf{x}, \mathbf{x}') - v_0(\mathbf{x}, \mathbf{x}')]. \end{aligned} \quad (2.31)$$

Adding the two equations, under the assumption that $\Gamma_{\text{GS}}^{(1)} = \Gamma'^{(1)}_{\text{GS}}$, we arrive at the contradiction

$$E_{\text{GS}} + E'_{\text{GS}} < E_{\text{GS}} + E'_{\text{GS}}. \quad (2.32)$$

Therefore, the relation between the ground-state 1-RDM and the ground-state wave function is indeed one-to-one,

$$\Psi_{\text{GS}}(\mathbf{x}_1 \dots \mathbf{x}_N) \xleftrightarrow{1-1} \Gamma_{\text{GS}}^{(1)}(\mathbf{x}; \mathbf{x}'). \quad (2.33)$$

As we have just shown, Gilbert's proof establishes a one-to-one correspondence between the ground-state 1-RDM and the ground-state wave function. Therefore, any observable of the system in its ground-state can be written as a functional of the 1-RDM. We emphasize this subtle but important difference: while in DFT the ground-state density uniquely determines any wave function (also for excited states), here, only the ground-state wave function is uniquely determined. Hence, only all *ground-state* observables are functionals of the ground-state density matrix $\Gamma_{\text{GS}}^{(1)}$. Of course, this difference is a direct consequence of the non-uniqueness of the non-local potential.

The second and third part of the Hohenberg-Kohn theorem can be transferred to the 1-RDM formalism with only minor modifications. For all N -representable 1-RDMs, the energy has a minimum at the ground-state 1-RDM, i.e.

$$E_{\text{GS}} \leq E[\Gamma^{(1)}], \quad (2.34)$$

where the equality only holds if $\Gamma^{(1)} = \Gamma_{\text{GS}}^{(1)}$. We can also introduce a universal functional F

$$F[\Gamma^{(1)}] = \min_{\Psi \rightarrow \Gamma^{(1)}} \langle \Psi | \hat{T} + \hat{W} | \Psi \rangle, \quad (2.35)$$

where \hat{T} is the kinetic energy operator and \hat{W} is the Coulomb interaction. The functional is universal in the sense that it does not depend on the potential $v_0(\mathbf{x}, \mathbf{x}')$, it is the same for all systems that interact via Coulomb interaction. The total energy then reads

$$E[\Gamma^{(1)}] = F[\Gamma^{(1)}] + \iint d\mathbf{x}d\mathbf{x}' \Gamma^{(1)}(\mathbf{x}'; \mathbf{x}) v_0(\mathbf{x}, \mathbf{x}'). \quad (2.36)$$

At this point, we have to address the N -representability problem again. Actually, the proof in Appendix A shows that the conditions (2.20) and (2.21) ensure *ensemble* N -representability. The density matrix of an ensemble is given by

$$\Gamma^{(1)}(\mathbf{x}; \mathbf{x}') = \sum_k c_k \Gamma_k^{(1)}(\mathbf{x}; \mathbf{x}'), \quad (2.37)$$

where each $\Gamma_k^{(1)}(\mathbf{x}; \mathbf{x}')$ is connected to an N -particle wave function via (2.9). The coefficients c_k satisfy

$$\sum_k c_k = 1, \quad (2.38)$$

such that the normalization of the density matrix is preserved. If we denote the pure-state N -representable $\Gamma_k^{(1)}(\mathbf{x}; \mathbf{x}')$ which yields the lowest energy in Eq. (2.36) by $\Gamma_l^{(1)}(\mathbf{x}; \mathbf{x}')$ then we can rewrite (2.37) as

$$\Gamma^{(1)}(\mathbf{x}; \mathbf{x}') = c_l \Gamma_l^{(1)}(\mathbf{x}; \mathbf{x}') + \sum_{k \neq l} c_k \Gamma_k^{(1)}(\mathbf{x}; \mathbf{x}'). \quad (2.39)$$

In the non-degenerate case, one can lower the energy in the system by increasing c_l and decreasing the other coefficients. The lowest possible energy is obtained for $c_l = 1$ and all other coefficients $c_k = 0$. In other words, the set of ensemble N -representable density matrices obtains its lowest energy at a pure-state N -representable density matrix anyway. Therefore, it is sufficient to restrict the 1-RDMs to ensemble N -representable matrices in the minimization process. Of course, this argument only applies to the exact total energy and only holds for approximations which are convex (see Section 3.1). In case the ground-state of the system is degenerate, i.e. two or more different density matrices $\Gamma_k^{(1)}$ yield the same energy, the minimization leads to any linear combination of these matrices with the correct ground-state energy of the real system.

2.3 Total Energy as a functional of $\Gamma^{(1)}$

The total energy of an electronic system is given by

$$E_{\text{total}}[\Gamma^{(1)}] = E_{\text{kin}}[\Gamma^{(1)}] + E_{\text{ext}}[\Gamma^{(1)}] + E_{\text{int}}[\Gamma^{(1)}], \quad (2.40)$$

where E_{kin} , E_{ext} and E_{int} are the kinetic, external and interaction energy respectively. As a big advantage of RDMFT, the kinetic energy is known exactly as a functional of the one-body reduced density matrix

$$E_{\text{kin}}[\Gamma^{(1)}] = \iint d\mathbf{x}d\mathbf{x}' \delta(\mathbf{x} - \mathbf{x}') \left(-\frac{\nabla^2}{2} \right) \Gamma^{(1)}(\mathbf{x}; \mathbf{x}'). \quad (2.41)$$

The external energy can also be written as a functional of the one-particle density matrix

$$E_{\text{ext}}[\Gamma^{(1)}] = \iint d\mathbf{x}d\mathbf{x}' v_0(\mathbf{x}, \mathbf{x}') \Gamma^{(1)}(\mathbf{x}'; \mathbf{x}). \quad (2.42)$$

Only the interaction part, in our case the Coulomb interaction, cannot be easily expressed as a functional of the one-body reduced density matrix. However, parts

of the interaction are known. We therefore split the interaction energy

$$E_{\text{int}}[\Gamma^{(1)}] = \min_{\Gamma^{(N)} \rightarrow \Gamma^{(1)}} \frac{1}{2} \sum_{\substack{j,k=1 \\ j \neq k}}^N \int d\mathbf{x}_1 \dots d\mathbf{x}_N \frac{\Gamma^{(N)}(\mathbf{x}_1, \dots, \mathbf{x}_N; \mathbf{x}_1 \dots \mathbf{x}_N)}{|\mathbf{r}_j - \mathbf{r}_k|}, \quad (2.43)$$

further into

$$E_{\text{int}}[\Gamma^{(1)}] = E_{\text{H}}[\Gamma^{(1)}] + E_x[\Gamma^{(1)}] + E_c[\Gamma^{(1)}]. \quad (2.44)$$

The Hartree energy E_{H} is known in terms of 1-RDMs and reads

$$E_{\text{H}}[\Gamma^{(1)}] = \frac{1}{2} \iint d\mathbf{x} d\mathbf{x}' \frac{\Gamma^{(1)}(\mathbf{x}; \mathbf{x}) \Gamma^{(1)}(\mathbf{x}'; \mathbf{x}')}{|\mathbf{r} - \mathbf{r}'|}, \quad (2.45)$$

It represents the interaction energy between two charge clouds at \mathbf{r} and \mathbf{r}' . It is, therefore, often referred to as the classical part of the interaction. The exchange energy E_x in Eq. (2.44) is given by

$$E_x[\Gamma^{(1)}] = -\frac{1}{2} \iint d\mathbf{x} d\mathbf{x}' \frac{\Gamma^{(1)}(\mathbf{x}; \mathbf{x}') \Gamma^{(1)}(\mathbf{x}'; \mathbf{x})}{|\mathbf{r} - \mathbf{r}'|}. \quad (2.46)$$

Only the remaining correlation energy E_c needs to be approximated. We emphasize at this point that the exchange energy here differs from the exchange energy in DFT and also from the exchange energy in Hartree-Fock. The density matrices in (2.46) have, in general, fractional occupation numbers while in DFT and Hartree-Fock they are restricted to the sum of fully occupied orbitals. If $\hat{\Gamma}^{(1)}$ has fractional occupation numbers, the exchange energy as defined by (2.46) contains energy contributions which usually (in DFT and HF) are considered part of the correlation energy. In addition, we conclude from (2.41) that the exchange-correlation energy within RDMFT does not contain any kinetic energy contributions. The consequence of this property, as well as other properties of the exchange and correlation energy functionals, E_x and E_c , are discussed in Chapter 3, where we also present possible approximations to E_c .

2.4 Orbital Functionals

In Section 2.2 we have presented the proof of Gilbert which ensures that we can write the ground-state energy as a functional of the one-body reduced density matrix $\Gamma^{(1)}(\mathbf{x}; \mathbf{x}')$. From the diagonalization of $\Gamma^{(1)}$ one can directly conclude that the ground-state energy can then also be written as a functional of the occupation numbers n_j and the natural orbitals φ_j . In addition, as long as $\Gamma^{(1)}$ does not possess degenerate eigenvalues, its diagonalization is unique and the occupation numbers and natural orbitals are functionals of $\Gamma^{(1)}$ as well. In this case, any functional of n_j and φ_j is automatically a functional of $\Gamma^{(1)}$. The dependence on $\Gamma^{(1)}$, however,

might be implicit so that it might not be possible to make all the dependencies of n_j and φ_j on $\Gamma^{(1)}$ explicit. As an example we compare the following two terms

$$\sum_{j=1}^{\infty} n_j \varphi_j^*(\mathbf{x}') \varphi_j(\mathbf{x}), \quad (2.47)$$

$$\sum_{j=1}^{\infty} \sqrt{n_j} \varphi_j^*(\mathbf{x}') \varphi_j(\mathbf{x}). \quad (2.48)$$

While the first term can easily be replaced by $\Gamma^{(1)}(\mathbf{x}; \mathbf{x}')$ such a substitution is impossible for the second term. Nevertheless, also this term is a functional of $\Gamma^{(1)}$ but the dependence is implicit. From this little example we can see the big advantage of orbital functionals: The flexibility in possible approximations has grown enormously. As we discuss in Chapter 3 most of the currently used approximations are indeed orbital functionals. As usual, there is a price to pay for this advantage. Here, functional derivatives with respect to the density matrix $\Gamma^{(1)}$ cannot be evaluated directly. Instead we have to employ the chain rule with respect to n_j and φ_j . While this is not a principle problem, it increases the number of terms in the equations. For a functional $G[\{n_j\}, \{\varphi_j\}]$ the derivative with respect to $\Gamma^{(1)}$ is hence calculated according to

$$\frac{\delta G}{\delta \Gamma^{(1)}(\mathbf{x}; \mathbf{x}')} = \sum_{j=1}^{\infty} \left[\frac{\delta G}{\delta n_j} \frac{\delta n_j}{\delta \Gamma^{(1)}(\mathbf{x}; \mathbf{x}')} + \int d\mathbf{y} \left(\frac{\delta G}{\delta \varphi_j(\mathbf{y})} \frac{\delta \varphi_j(\mathbf{y})}{\delta \Gamma^{(1)}(\mathbf{x}; \mathbf{x}')} + c.c. \right) \right]. \quad (2.49)$$

The derivatives of G with respect to n_j and φ_j can be calculated directly if G is an orbital functional. The functional derivatives of the occupation numbers and natural orbitals with respect to the 1-RDM can be obtained from first order perturbation theory applied to the eigenvalue equation of the 1-RDM (2.17)

$$\int d\mathbf{x} \Gamma^{(1)}(\mathbf{x}; \mathbf{x}') \varphi_j(\mathbf{x}') = n_j \varphi_j(\mathbf{x}). \quad (2.50)$$

The resulting derivatives are given by

$$\frac{\delta n_j}{\delta \Gamma^{(1)}(\mathbf{x}; \mathbf{x}')} = \varphi_j^*(\mathbf{x}) \varphi_j(\mathbf{x}'), \quad (2.51)$$

$$\frac{\delta \varphi_j(\mathbf{y})}{\delta \Gamma^{(1)}(\mathbf{x}; \mathbf{x}')} = \sum_{\substack{k=1 \\ k \neq j}}^{\infty} \frac{\varphi_k^*(\mathbf{x}) \varphi_j(\mathbf{x}')}{n_j - n_k} \varphi_k(\mathbf{y}). \quad (2.52)$$

Here, the second equation is only valid for non-degenerate occupation numbers. In case of degeneracies, one has to obtain the expression from degenerate perturbation theory. The infinite sums, of course, have to be truncated in a numerical implementation. We come back to this point when we discuss numerical results in Chapter 4.

2.5 Direct Minimization

In the previous sections we have introduced the foundations of RDMFT. We now tackle the question how to determine the ground-state energy in practice. Due to the second part of Gilbert's theorem we can find the ground-state energy by minimizing the energy functional with respect to $\Gamma^{(1)}$. In DFT the total energy is minimized with respect to the density and the direct minimization is replaced by solving the non-interacting Kohn-Sham system. In RDMFT there is *no* Kohn-Sham system. There is simply no non-interacting system that reproduces the one-body reduced-density matrix of the interacting one because the density matrix of a non-interacting system is idempotent, i.e. $\Gamma^{(1)}$ fulfills

$$\int d\mathbf{x}'' \Gamma^{(1)}(\mathbf{x}; \mathbf{x}'') \Gamma^{(1)}(\mathbf{x}''; \mathbf{x}') - \Gamma^{(1)}(\mathbf{x}; \mathbf{x}') = 0. \quad (2.53)$$

Expanding the density matrix in any set of complete orthonormal orbitals ψ_j Eq. (2.53) reads

$$\sum_k \Gamma_{jk}^{(1)} \Gamma_{kj}^{(1)} - \Gamma_{jj}^{(1)} = 0 \quad (2.54)$$

with

$$\Gamma_{jk}^{(1)} = \iint d\mathbf{x} d\mathbf{x}' \psi_j^*(\mathbf{x}) \Gamma^{(1)}(\mathbf{x}; \mathbf{x}') \psi_k(\mathbf{x}') \quad (2.55)$$

$$\Gamma^{(1)}(\mathbf{x}; \mathbf{x}') = \sum_{j,k} \Gamma_{jk}^{(1)} \psi_k^*(\mathbf{x}') \psi_j(\mathbf{x}). \quad (2.56)$$

Using the natural orbitals of $\Gamma^{(1)}$ as the set of basis functions for the expansion the off-diagonal elements vanish and Eq. (2.54) reduces further to

$$n_j^2 - n_j = 0, \quad (2.57)$$

where n_j are the occupation numbers of $\Gamma^{(1)}$. Equation (2.57) has only the two solutions $n_j = 0$ and $n_j = 1$. Therefore, any one-body density matrix fulfilling (2.53) represents a system of non-interacting particles: The many-body ground-state wave function is a single Slater determinant built out of natural orbitals with occupation number 1. From Eqs. (2.53)-(2.57) we can also conclude that the ground-state one-body density matrix of any interacting system, where the ground-state wave function cannot be written as a single Slater determinant, does not fulfill (2.53). Therefore, one *cannot* find a non-interacting system that reproduces the one-body density matrix of an interacting system. If we want to determine the ground-state energy within RDMFT we need to perform the minimization directly.

The total energy E_{total} has to be minimized under the subsidiary condition that the 1-RDM is N -representable, i.e. conditions (2.20) and (2.21) have to be satisfied. The constraint that the 1-RDM has to integrate to the particle number N can be

implemented with a Lagrange multiplier μ . The functional to be minimized then reads

$$F[\Gamma^{(1)}] = E_{\text{total}}[\Gamma^{(1)}] - \mu \left(\int d\mathbf{x} \Gamma^{(1)}(\mathbf{x}; \mathbf{x}) - N \right). \quad (2.58)$$

Numerically, the minimization is realized by taking the functional derivative of F with respect to $\Gamma^{(1)}$ which equals zero at a true minimum. However, the second constraint, $n_j \in [0; 1]$, cannot be made explicit in terms of the 1-RDM in a form useful for the numerical implementation. One can either use $n_j = \sin^2 \theta_j$ and minimize with respect to θ_j instead of n_j , or one can keep n_j between zero and one explicitly in the numerical treatment. In both cases, to minimize with respect to $\Gamma^{(1)}$, we make use of the chain rule with respect to the natural orbitals and the occupation numbers n_j (θ_j)

$$\frac{\delta F}{\delta \Gamma^{(1)}(\mathbf{x}; \mathbf{x}')} = \sum_{j=1}^{\infty} \left[\frac{\delta F}{\delta n_j(\theta_j)} \frac{\delta n_j(\theta_j)}{\delta \Gamma^{(1)}(\mathbf{x}; \mathbf{x}')} + \int d\mathbf{y} \left(\frac{\delta F}{\delta \varphi_j(\mathbf{y})} \frac{\delta \varphi_j(\mathbf{y})}{\delta \Gamma^{(1)}(\mathbf{x}; \mathbf{x}')} + c.c \right) \right]. \quad (2.59)$$

Since the N -representability condition can only be implemented in a way similar to orbital functionals, compare Eq. (2.49), using orbital functionals does not introduce any further complications.

We like to add a few more words about the problem of keeping the occupation numbers between zero and one. If one includes this constraint explicitly in the numerical treatment one simply puts n_j back to zero or one, whenever the minimization procedure would move it out of the interval. However, this leads to a violation of the minimum condition $\delta F / \delta n_j = 0$. The derivative is bigger than zero (at zero) or smaller than zero (at one) as it is typical for a border minimum. Therefore, the constraint leads to $\delta F / \delta n_j \neq 0$ at the minimum of F in all directions where n_j takes values at the border of the interval $[0; 1]$. We refer to these states as pinned states because the corresponding occupation numbers are pinned to the values zero or one. From (2.59), we can see that then $\delta F / \delta \Gamma^{(1)}$ is not zero either at its minimum due to these pinned states. If we instead replace n_j with $\sin^2 \theta_j$ and minimize with respect to θ_j F always has a minimum. However, we have to pay special attention whenever θ_j is a multiple of $\pi/2$. Then the derivative $\delta F / \delta \theta_j$ is zero and the conjugate gradient scheme leaves θ_j unchanged in the following iteration. One avoids this by moving θ_j a bit (e.g. 10^{-5}) away from $\pi/2$. For a pinned state the next iteration recovers the $\theta_j = \pi/2$ solution.

2.6 Spin Dependent Formalism

In all previous sections we considered a combined space-spin variable $\mathbf{x} = (\mathbf{r}, \sigma)$. The natural orbitals can be written as two-component spinors

$$\varphi_j(\mathbf{x}) = \begin{pmatrix} a_{j\uparrow} \varphi_{j\uparrow}(\mathbf{r}) \\ a_{j\downarrow} \varphi_{j\downarrow}(\mathbf{r}) \end{pmatrix}, \quad |a_{j\uparrow}|^2 + |a_{j\downarrow}|^2 = 1. \quad (2.60)$$

The 1-RDM is then given as a 2×2 matrix in spin-space

$$\Gamma^{(1)}(\mathbf{x}; \mathbf{x}') = \begin{pmatrix} \Gamma_{\uparrow\uparrow}^{(1)}(\mathbf{r}; \mathbf{r}') & \Gamma_{\uparrow\downarrow}^{(1)}(\mathbf{r}; \mathbf{r}') \\ \Gamma_{\downarrow\uparrow}^{(1)}(\mathbf{r}; \mathbf{r}') & \Gamma_{\downarrow\downarrow}^{(1)}(\mathbf{r}; \mathbf{r}') \end{pmatrix} \quad (2.61)$$

with

$$\Gamma_{\sigma\sigma'}^{(1)}(\mathbf{r}; \mathbf{r}') = \sum_{j=1}^{\infty} n_j a_{j\sigma'}^* a_{j\sigma} \varphi_{j\sigma'}^*(\mathbf{r}') \varphi_{j\sigma}(\mathbf{r}) . \quad (2.62)$$

However, there are several physical applications where the treatment can be significantly simplified. As long as the Hamiltonian does not mix the two different spin directions, like for **LS** coupling or inhomogeneous external magnetic fields, and the symmetry is also not broken spontaneously, the two spin directions decouple. For example for homogeneous magnetic fields (no **LS** coupling), the quantization axis of the spinors can be chosen such that one can directly work with spin dependent occupation numbers and natural orbitals, i.e. there is a different set of occupation numbers and orbitals for each spin channel. For closed-shell systems both spin directions are completely identical even if the **LS** coupling is taken into account (no magnetic field). Therefore, one can work with natural orbitals that only depend on \mathbf{r} and use occupation numbers between zero and two. As an intermediate and only approximate method, one can allow for spin dependent occupation numbers but keep the spin-independent natural orbitals. This method is in the spirit of restricted open-shell Hartree-Fock, and we therefore call it Restricted Open-Shell RDMFT. Hence, there are the following four possibilities:

I **Restricted RDMFT** (Spin independent treatment)

The occupation numbers and the natural orbitals are independent of the spin of the electron. The occupation numbers are restricted to the interval $[0; 2]$. The method is suitable for closed-shell systems.

II **Restricted open-shell RDMFT** (Spin dependent $n_{j\sigma}$)

The occupation numbers are spin dependent while the natural orbitals are still identical for both spin channels. The states calculated with this method are eigenstates of the total spin operators \mathbf{S}_z and \mathbf{S}^2 .

III **Unrestricted RDMFT** (Spin dependent $n_{j\sigma}$ and $\varphi_{j\sigma}$)

Both the occupation numbers as well as the natural orbitals depend on spin. The numerical treatment is more expensive and the resulting states are in general not eigenstates of the total spin operator \mathbf{S}^2 .

IV **Full Spinor treatment**

Each electron is described with a spinor and a Pauli equation is solved. This method is necessary, for example, to include **LS** coupling.

Since we do not describe **LS** coupling or other effects that require a full spinor treatment, we do not consider the last method in the following chapters. We do not employ spin-dependent natural orbitals either (method III) because we require the system to be an eigenstate of the total spin operator.