



## DIPLOMARBEIT

# Dynamics of correlated many body systems: propagating reduced two-particle density matrices without wave functions

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# 1. Introduction

The fundamental problem of describing a system of more than three interacting particles has troubled physicists since the early days of Newton. A general analytic solution of the many-body problem in classical mechanics turned out to be intractable but sophisticated  $N$ -body simulations allow to calculate trajectories corresponding to thousands of interacting particles with high numerical accuracy. In the quantum regime the dynamics requires the propagation of the many-body wave function which renders the numerical treatment far more intricate. In fact, a direct numerical solution of the Schrödinger equation in three dimensions is feasible only for two interacting particles. Many-body quantum systems are pivotal in many different areas of research ranging from atomic and molecular physics to solid state and nuclear physics. The significance of quantum many-body problems has led to a dedicated search for the basic laws underlying these systems. However, due to the complexity and the large number of degrees of freedom an exact treatment of quantum many-body systems is limited to a few very specific model systems [1]. The generic case requires well suited approximations that capture essential features of the complete problem. Starting with the 1920s, the need for accurate approximations for atoms, the prime example for a quantum many-body system, has led to the development of a wide range of different theories. One of the first approaches was the Hartree-Fock method for fermions developed by D. R. Hartree, J. C. Slater and V. A. Fock as a mean-field theory [2]. Within this approximation the many-body wave function is assumed to be a single Slater determinant reducing the many-body problem to an effective one-body problem. Originally this method has been developed for stationary states but it was soon adapted to time-dependent problems by allowing the orbitals to vary in time [3]. This approach explains crucial atomic properties like the Aufbau principle and gives a good estimate for the energy spectrum and the dynamics induced by time-dependent external potentials. However, it is not accurate enough to trace the behaviour of atomic and molecular systems if the interaction between the electrons forces the wave function into superposition of several determinants. The description of such correlated systems is significantly more complicated because the electrons are no longer individual particles but rather a collective that has to be described as a whole. In particular, time-dependent problems such as atoms in high-intense laser fields triggering non-linear response such as high-harmonic generation or tunnel ionization require sophisticated time-dependent methods beyond the Hartree-Fock approximation. A quite recent numerically demanding approach is based on a linear combination of Slater determinants whose time-dependent coefficients and orbitals are determined by a time-dependent action principle. The theory is referred to as the multiconfiguration time-dependent Hartree Fock (MCTDHF) method and enables a quantitatively correct description of complex many-particle systems thus providing a state of the art reference [4, 5]. A similar theory for bosons called multiconfiguration time-dependent Hartree method for bosons (MCTDHB) enables to treat systems where mean field approximations such as the Gross-Pitaevskii equation fail [6]. For systems including more

than a few particles the number of required orbital configurations increases rapidly rendering calculations unfeasible. A computationally less demanding approach to many-body dynamics which is based on the particle density is given by the time-dependent density functional theory (TDDFT) [7]. This theory is an efficient alternative to MCTDHF calculations because it reduces to an effective one-particle problem. However, to account for correlation effects the use of an exchange-correlation potential is required whose exact form is unknown. This fundamental drawback makes DFT hard to develop further from first principles. The unknown energy functional can be circumvented by using the two-particle reduced density matrix (2-RDM) as the basic object since in this case the energy functional is known exactly [8–10]. Such a theory based on the 2-RDM has the key advantage of reducing the overwhelming information stored in the wave function to the essential information necessary to calculate expectation values of two-particle operators such as the Hamiltonian [11–13]. This suggests the intriguing possibility of turning many-body problems into effective two-body problems. Variational calculations for ground states based on the 2-RDM energy functional showed that it is crucial to take into account additional constraints which assure that the 2-RDM can be obtained from an actual many-body wave function [13]. Although great effort was dedicated to finding these constraints, called the  $N$ -representability conditions, the problem still remains unsolved. However, recent progress transformed the variational 2-RDM method into a convenient alternative to expensive multiconfigurational calculations [14].

By now theories employing the 2-RDM directly without the use of the wave function have primarily been used for ground state energies of molecular systems. The aim of this work is to develop a new approach based on the 2-RDM to treat time-dependent problems. Central point of our method is the reconstruction of the three-particle reduced density matrix (3-RDM) via the 2-RDM. To deal with the  $N$ -representability problem we incorporate purification methods known from the literature and in addition develop new approaches which take into account further  $N$ -representability conditions. To test the accuracy of the new theory we calculate the electron dynamics of a lithium hydrate molecule subject to high-intense laser fields. As a suitable reference for the exact propagation we utilize the MCTDHF method in a twofold way. First, we use the MCTDHF results to compare with the approximate 2-RDM results for quantities such as the energy and the dipole moment. Second, the MCTDHF method allows at each time step to estimate the error arising from the reconstruction of the 3-RDM and from purification. This feedback is essential in further developing and optimizing the 2-RDM method.

This thesis is organized as follows: In [chapter 2](#) we review the theoretical basis for the time-dependent 2-RDM method including the definition and general properties of reduced density matrices as well as the 2-RDM energy functional and its theoretical consequences. Further, we derive self-consistent equations of motion for RDMs using a reconstruction scheme to express higher-order RDMs by lower-order ones. We exploit a time-dependent orbital basis to solve the equations of motion in a numerically efficient way. Finally, we discuss the  $N$ -representability problem and we develop a new purification scheme that extends the number of implemented conditions. In [chapter 3](#) we apply the theory to the one-dimensional lithium hydrate molecule in intense laser fields and compare the results to those obtained from the MCTDHF method. In addition, we identify the influence of the purification on the time evolution of the 2-RDM. We summarize our results and give an outlook to further studies in [chapter 4](#). In the Appendix

detailed derivations of several properties discussed in [chapter 2](#) are presented.





## 2. Theory

In this chapter we present an introduction to the mechanics of reduced density matrices (RDMs) including their general definition and their application to the many-body problem. We show that the total energy can be written as a two-particle RDM functional and discuss the associated variational principle, before we turn to the contracted Schrödinger equation and the approximation of higher-order density matrices by lower-order ones. Finally, we treat the N-representability problem which lies at the heart of the reduced density matrix mechanics and poses a challenge to every application.

### 2.1. Reduced density matrices

In 1927 [15] John von Neumann investigated the probabilistic character of the new born quantum mechanics finding that every state of a quantum system can be described via an operator, the density matrix  $\hat{\rho}$ . Since then, density matrices have become an essential tool in describing systems that are in a statistical ensemble of different states such as subsystems in contact with an environment.

The defining property of the density matrix is that the probability to find a system in a specific state  $|\Phi\rangle$  is given by the element  $P_\Phi = \langle\Phi|\hat{\rho}|\Phi\rangle$ . This fundamental relation leads to three basic characteristics of the density matrix:

1. Hermiticity: Since for all  $|\Phi\rangle$  the probability  $P_\Phi$  must be real,  $P_\Phi^* = \langle\Phi|\hat{\rho}^\dagger|\Phi\rangle = P_\Phi$ , the density matrix is hermitian  $\hat{\rho}^\dagger = \hat{\rho}$ .
2. Positivity: For all  $|\Phi\rangle$  the probability  $P_\Phi$  must be positive  $P_\Phi = \langle\Phi|\hat{\rho}|\Phi\rangle > 0$
3. Normalization:  $\text{Tr}(\hat{\rho}) = \sum_i \langle\Phi_i|\hat{\rho}|\Phi_i\rangle = 1$ .

For a system described by  $|\Psi\rangle$  the probability to measure the state  $|\Phi\rangle$  is given by

$$P_\Phi = |\langle\Phi|\Psi\rangle|^2 = \langle\Phi|\Psi\rangle\langle\Psi|\Phi\rangle, \quad (2.1)$$

such that the corresponding density matrix is

$$\hat{\rho} = |\Psi\rangle\langle\Psi|, \quad (2.2)$$

and the system is in a pure state in which case the density matrix is idempotent, i.e.,  $\hat{\rho} = \hat{\rho}^2$ . Von Neumann's description of quantum systems via density matrices is very general and the set of physical states that can be described by density matrices includes not only pure states but also statistical ensembles of different states called mixed states with

$$\hat{\rho} = \sum_i p_i |\Psi_i\rangle\langle\Psi_i| \quad \text{and} \quad \sum_i p_i = 1. \quad (2.3)$$

Such mixed states are essential for the description of subsystems embedded in a larger closed system. In a natural way the Hilbert space of the closed supersystem can be divided into a subsystem and an environment spanned by the associated basis functions  $|s_i\rangle$  and  $|e_j\rangle$ , respectively. Assuming the closed system to be in the pure state

$$|\Psi\rangle = \sum_{i,j} c_{i,j} |s_i\rangle |e_j\rangle, \quad (2.4)$$

the probability to find the subsystem in a specific state  $|\Phi_s\rangle$  is given by

$$P_{\Phi_s} = \langle \Psi | \left( \sum_j |\Phi_s\rangle |e_j\rangle \langle \Phi_s| \langle e_j| \right) | \Psi \rangle \quad (2.5)$$

$$= \langle \Phi_s | \left( \sum_{j,i,i'} |s_i\rangle c_{i,j} c_{i',j}^* \langle s_{i'}| \right) | \Phi_s \rangle. \quad (2.6)$$

Therefore, the appropriate description of the subsystem is given by the RDM

$$\hat{\rho}_s = \sum_{j,i,i'} |s_i\rangle c_{i,j} c_{i',j}^* \langle s_{i'}|. \quad (2.7)$$

Using the basis representation  $\rho_{i,j,i',j'} = \langle s_i | \langle e_j | \hat{\rho} | e_{j'} \rangle | s_{i'} \rangle$  the reduction of the density matrix of the supersystem to the RDM of the subsystem has a very simple form:

$$\rho_{i,i'} = \langle s_i | \hat{\rho}_s | s_{i'} \rangle = \sum_j \rho_{i,j,i',j}. \quad (2.8)$$

The degrees of freedom corresponding to the environment have been traced out and the operation that leads to the RDM of the subsystem is known as partial trace. The resulting RDM of the subsystem corresponds to a pure state only if the environment and the subsystem are not entangled. In this case the expansion coefficients can be written as a dyadic product  $c_{i,j} = a_i b_j$ . In general, however, since the number of entangled states is much larger than the number of product states the interaction between the subsystem and the environment creates a mixed state for the subsystem. The reduction process (Equation 2.8) is one of the key ingredients in modern decoherence theory [16].

Since many years the idea of decomposing a large system into a subsystem and an environment has been applied to the quantum  $N$ -body problem by considering the subsystem of  $p$ -particles to interact with the remaining  $(N - p)$ -particles which form the environment. In this spirit the  $p$ -particle reduced density matrix ( $p$ -RDM)  $D(x_1 \dots x_p; x'_1 \dots x'_p)$  of the  $p$ -particle subspace is determined by tracing out the coordinates of the remaining particles:

$$D(x_1 \dots x_p; x'_1 \dots x'_p) = \binom{N}{p} \int \Psi(x_1 \dots x_p, x_{p+1} \dots x_N) \Psi^*(x'_1 \dots x'_p, x_{p+1} \dots x_N) dx_{p+1} \dots dx_N. \quad (2.9)$$

Note that contrary to a classical system of  $N$  particles with  $\binom{N}{p}$  different  $p$ -particle subsystems the indistinguishability of particles in quantum mechanics renders all  $p$ -particle subsystems

indistinguishable as well. Thereby, the  $p$ -RDM does not describe one specific  $p$ -particle subsystem but rather all of them simultaneously as an ensemble of  $p$ -particle states. In the case of a single determinant wave function, for example, the occupied orbitals representing different one-particle subsystems are eigenfunctions of the 1-RDM (see [Appendix A](#)). Eigenvalues and eigenfunctions of the 1-RDM are commonly used in quantum chemistry and are called natural occupation numbers and natural orbitals, respectively. In the general case of arbitrary many-body wave functions of interacting particles the natural orbitals are the closest analogy to individual one-particle states. In the same spirit, the eigenvectors and the eigenvalues of the 2-RDM are called geminals and geminal occupation numbers, respectively.

Most of the results presented in this work apply equally to fermions and bosons in one dimension. Therefore, we define the coordinates  $x_i$  to comprise the space coordinates  $z_i$  and the spin coordinates  $s_i$  to handle both spin- $\frac{2n+1}{2}$  fermions and spin- $2n$  bosons ( $n$  being a natural number) in the same manner. The fundamental difference between fermions and bosons is reflected in the symmetry or antisymmetry of the density matrices with respect to a permutation of left coordinates  $x_1 \dots x_p$  and right coordinates  $x'_1 \dots x'_p$ . Both for fermions and bosons the RDM is hermitian under the exchange of the left and the right coordinates as a whole. Throughout this work we will use the convention that the number of indices implicitly specifies the particle number of the reduced density matrix. For coordinate-independent formulations we denote the  $p$ -RDM by  $D_p$ .

While the definition of the  $p$ -RDM in first quantization might be more familiar, some concepts are easier to describe in second quantization. The wave function can be expressed in second quantization using the field operator  $\hat{\Phi}(x)$  and the vacuum state  $|0\rangle$ :

$$\Psi(x_1, \dots, x_N) = \frac{1}{\sqrt{N!}} \langle 0 | \hat{\Phi}(x_N) \dots \hat{\Phi}(x_1) | \Psi \rangle. \quad (2.10)$$

Note that  $|\Psi\rangle$  is a  $N$ -particle state. To obtain the  $p$ -RDMs in second quantization we insert this expression into [Equation 2.9](#)

$$D(x_1 \dots x_p; x'_1 \dots x'_p) = \frac{1}{N!} \binom{N}{p} \int \langle \Psi | \hat{\Phi}^\dagger(x'_1) \dots \hat{\Phi}^\dagger(x'_p) | 0 \rangle \langle 0 | \hat{\Phi}(x_N) \dots \hat{\Phi}(x_1) | \Psi \rangle dx_{p+1} \dots dx_N. \quad (2.11)$$

This equation can be simplified using the fact that the wave function  $|\Psi\rangle$  is a  $N$ -particle state. The annihilation operator acting  $N$ -times on  $|\Psi\rangle$  gives a result that is proportional to  $|0\rangle$  and the inner projection operator  $|0\rangle\langle 0|$  acts as an identity:

$$D(x_1 \dots x_p; x'_1 \dots x'_p) = \frac{1}{N!} \binom{N}{p} \int \langle \Psi | \hat{\Phi}^\dagger(x'_1) \dots \hat{\Phi}^\dagger(x'_p) \hat{\Phi}(x_N) \dots \hat{\Phi}(x_1) | \Psi \rangle dx_{p+1} \dots dx_N. \quad (2.12)$$

Further simplification can be achieved by using the particle number operator

$$\hat{N} = \int \hat{\Phi}^\dagger(x) \hat{\Phi}(x) dx \quad (2.13)$$

to get

$$\begin{aligned}
D(x_1 \dots x_p; x'_1 \dots x'_p) &= \frac{1}{N!} \binom{N}{p} \int \langle \Psi | \hat{\Phi}^\dagger(x'_1) \dots \hat{\Phi}^\dagger(x_N) \hat{\Phi}(x_N) \dots \hat{\Phi}(x_1) | \Psi \rangle dx_{p+1} \dots dx_N \\
&= \frac{1}{N!} \binom{N}{p} \int \langle \Psi | \hat{\Phi}^\dagger(x'_1) \dots \hat{\Phi}^\dagger(x_{N-1}) \hat{N} \hat{\Phi}(x_{N-1}) \dots \hat{\Phi}(x_1) | \Psi \rangle dx_{p+1} \dots dx_{N-1} \\
&= \frac{1}{N!} \binom{N}{p} 1 \cdot \int \langle \Psi | \hat{\Phi}^\dagger(x'_1) \dots \hat{\Phi}^\dagger(x_{N-2}) \hat{N} \hat{\Phi}(x_{N-2}) \dots \hat{\Phi}(x_1) | \Psi \rangle dx_{p+1} \dots dx_{N-2} \\
&= \frac{1}{N!} \binom{N}{p} 1 \cdot 2 \cdot \int \langle \Psi | \hat{\Phi}^\dagger(x'_1) \dots \hat{\Phi}^\dagger(x_{N-3}) \hat{N} \hat{\Phi}(x_{N-3}) \dots \hat{\Phi}(x_1) | \Psi \rangle dx_{p+1} \dots dx_{N-3} \\
&\quad \vdots \\
&= \frac{1}{p!} \langle \Psi | \hat{\Phi}^\dagger(x'_1) \dots \hat{\Phi}^\dagger(x'_p) \hat{\Phi}(x_p) \dots \hat{\Phi}(x_1) | \Psi \rangle. \tag{2.14}
\end{aligned}$$

The expression for  $D_p$  in second quantization has the advantage that the coordinates of the additional  $(N - p)$  particles do not enter explicitly which simplifies many calculations.

For applications, the representation of RDMs in a given orbital basis  $\phi_i(x)$  is often beneficial. For electrons each spatial orbital comes in two different spin configurations  $\phi_i(z, \uparrow)$  and  $\phi_i(z, \downarrow)$  effectively doubling the number of actual orbitals. In our notation we merge the spin configuration into the orbital index. In analogy to [Equation 2.14](#) the representation of  $D_p$  in any (spin) orbital basis reads

$$D_{j_1, \dots, j_p}^{i_1, \dots, i_p} = \frac{1}{p!} \langle \Psi | \hat{a}_{i_1}^\dagger \dots \hat{a}_{i_p}^\dagger \hat{a}_{j_p} \dots \hat{a}_{j_1} | \Psi \rangle, \tag{2.15}$$

with the creation and annihilation operators

$$\hat{a}_i = \int \phi_i(x) \hat{\Phi}(x) dx \quad \hat{a}_i^\dagger = \int \phi_i^*(x) \hat{\Phi}^\dagger(x) dx. \tag{2.16}$$

The relation between the space and the orbital representation is given by

$$\begin{aligned}
D_{j_1, \dots, j_p}^{i_1, \dots, i_p} &= \int D(x_1 \dots x_p; x'_1 \dots x'_p) \phi_{i_1}^*(x_1) \dots \phi_{i_p}^*(x_p) \phi_{j_1}(x'_1) \dots \phi_{j_p}(x'_p) dx_1 \dots dx_p dx'_1 \dots dx'_p \\
D(x_1 \dots x_p; x'_1 \dots x'_p) &= D_{j_1, \dots, j_p}^{i_1, \dots, i_p} \phi_{i_1}(x_1) \dots \phi_{i_p}(x_p) \phi_{j_1}^*(x'_1) \dots \phi_{j_p}^*(x'_p), \tag{2.17}
\end{aligned}$$

where we apply Einstein notation whenever a sum over orbital indices appears. The expansion of the RDM in an orbital basis is essential for technical reasons: The numerical discretization of space requires, in general, a large number of grid points such that even the RDMs of lowest order become very large matrices.

Following [9] the factor  $\binom{N}{p}$  in the definition of the RDMs (see [Equation 2.9](#)) is chosen in such a way that the  $p$ -RDM is normalized to

$$\int D(x_1 \dots x_p; x_1 \dots x_p) dx_1 \dots dx_p = \binom{N}{p}. \tag{2.18}$$

There is no general convention for the normalization of  $p$ -RDMs and many different conventions can be found in literature. Our convention is convenient since the particle number  $N$  does not enter the equations of motion (see [Equation 2.79](#) below) and the diagonal elements  $D(x_1 \dots x_p; x_1 \dots x_p)$  have a nice interpretation in terms of expectation values for  $p$ -particle tuples (see [Appendix B](#)). Tuples are the generalization of pairs and triples to arbitrary integers. Another feature of this normalization is that  $p$ -RDMs obtained from single determinant wave functions have exactly  $\binom{N}{p}$  eigenvalues equal to one while the remaining eigenvalues vanish making the  $p$ -RDMs idempotent  $D_p = D_p^2$  (see [Appendix A](#)). In particular for the 1-RDM the idempotence  $D_1 = D_1^2$  gives a necessary and sufficient condition for the wave function to be a single determinant.<sup>1</sup>

## 2.2. Energy as a 2-RDM functional

As mentioned in [section 2.1](#), the defining property of the density matrix is that the probability to find the system in a specific state  $|\Phi\rangle$  is given by  $P_\Phi = \langle \Phi | \hat{\rho} | \Phi \rangle$ . A similar result holds in the case of  $p$ -RDMs, i.e., the element

$$T_\Phi = \int \Phi^*(x_1 \dots x_p) D(x_1 \dots x_p; x'_1 \dots x'_p) \Phi(x'_1 \dots x'_p) dx_1 dx'_1 \dots dx_p dx'_p. \quad (2.19)$$

is the mean number of  $p$ -particle tuples in the  $p$ -particle state  $\Phi(x_1 \dots x_p)$ . This gives a convenient method for the calculation of expectation values and probabilities of  $p$ -particle operators with the help of  $D_p$  without using the wave function. For example, the average number of pairs in the 2-particle state  $\Phi(x_1, x_2)$  is given by

$$T_\Phi = \int \Phi^*(x_1, x_2) D(x_1 x_2; x'_1 x'_2) \Phi(x'_1, x'_2) dx_1 dx_2 dx'_1 dx'_2. \quad (2.20)$$

Similarly, the average number of pairs with coordinates  $(x_1, x_2)$  is given by the two-particle density

$$\rho(x_1, x_2) = D(x_1 x_2; x_1 x_2), \quad (2.21)$$

and the average number of pairs with momenta  $(k_1, k_2)$  is

$$P(k_1, k_2) = \frac{1}{(2\pi)^2} \int e^{ik_1(x'_1 - x_1)} e^{ik_2(x'_2 - x_2)} D(x_1 x_2; x'_1 x'_2) dx_1 dx_2 dx'_1 dx'_2. \quad (2.22)$$

This property of the 2-RDM has an important consequence for systems whose dynamics is fully determined by pairwise interactions between the particles. In this case the Hamiltonian has the general form

$$H(x_1, \dots, x_N) = \sum_i h(x_i) + \sum_{i < j} V_{\text{int}}(x_i, x_j), \quad (2.23)$$

---

<sup>1</sup> Note that for RDMs normalized to one the idempotence is a necessary and sufficient condition for the  $p$ -particle subsystem to be in a pure state.  $p$ -particle subsystems of Slater determinants cannot be described by pure states and the  $p$ -RDM is idempotent if and only if it is normalized to  $\binom{N}{p}$ .

where  $h(x_i) = -(\hbar^2/2m)\Delta_i + V_{\text{ext}}(x_i)$  is the one-particle operator containing the kinetic energy and the external potential, and  $V_{\text{int}}$  is the interaction potential between two particles. Such systems include, e.g., atoms and molecules, ultra cold atoms in trapping potentials or electrons in a solid. Since the Hamilton operator for such systems is given by a 2-particle operator the 2-RDM contains all information needed to calculate the total energy of the many-body system. This result can be obtained by

$$\begin{aligned}
E = \langle \hat{H} \rangle &= \int \Psi^*(x_1, \dots, x_N) \left( \sum_i h(x_i) + \sum_{i < j} V_{\text{int}}(x_i, x_j) \right) \Psi(x_1, \dots, x_N) dx_1 \dots dx_N \\
&= N \int \Psi^*(x_1, \dots, x_N) h(x_1) \Psi(x_1, \dots, x_N) dx_1 \dots dx_N \\
&+ \binom{N}{2} \int \Psi^*(x_1, \dots, x_N) V_{\text{int}}(x_1, x_2) \Psi(x_1, \dots, x_N) dx_1 \dots dx_N \\
&= \int h(x'_1) D(x'_1; x_1) |_{x'_1 \rightarrow x_1} dx_1 + \int V_{\text{int}}(x_1, x_2) D(x_1 x_2; x_1 x_2) dx_1 dx_2, \quad (2.24)
\end{aligned}$$

where we have used the fact that the expression  $\Psi^*(x_1, \dots, x_N) \Psi(x_1, \dots, x_N)$  remains invariant under particle exchange. An alternative to obtain the expression for the energy is based on the Hamiltonian in second quantization

$$\hat{H} = \int \hat{\Phi}^\dagger(x_1) h(x_1) \hat{\Phi}(x_1) dx_1 + \frac{1}{2} \int \hat{\Phi}^\dagger(x_2) \hat{\Phi}^\dagger(x_1) V_{\text{int}}(x_1, x_2) \hat{\Phi}(x_1) \hat{\Phi}(x_2) dx_1 dx_2. \quad (2.25)$$

On this level, the additional coordinates that make the expressions in first quantization somewhat clumsy are avoided from the start and the energy functional is obtained in a convenient way by taking the expectation value  $E = \langle \Psi | \hat{H} | \Psi \rangle$ . Further simplification can be achieved by rewriting the Hamiltonian as a pure 2-particle operator

$$\hat{H} = \frac{1}{2} \int \hat{\Phi}^\dagger(x_2) \hat{\Phi}^\dagger(x_1) H_2(x_1, x_2) \hat{\Phi}(x_1) \hat{\Phi}(x_2) dx_1 dx_2 \quad (2.26)$$

with

$$H_2(x_1, x_2) = \frac{h(x_1) + h(x_2)}{N - 1} + V_{\text{int}}(x_1, x_2). \quad (2.27)$$

Taking the expectation value leads to the formula for the total energy:

$$E = \langle \hat{H} \rangle = \int H_2(x_1, x_2) D(x_1 x_2; x_1 x_2) dx_1 dx_2 = \text{Tr}(H_2 D_2). \quad (2.28)$$

From a conceptual point of view this result has a nice interpretation. Each eigenstate  $\Psi_{E_i}(x_1, x_2)$  of the Hamiltonian  $H_2(x_1, x_2)$  contains the average number of pairs  $P_{E_i}$

$$P_{E_i} = \int \Psi_{E_i}^*(x_1, x_2) D(x_1 x_2; x'_1 x'_2) \Psi_{E_i}(x'_1, x'_2) dx_1 dx_2 dx'_1 dx'_2, \quad (2.29)$$

and the total energy is nothing else but the sum over all contributions<sup>2</sup>

$$E = \sum_i E_i P_{E_i}. \quad (2.30)$$

The energy functional in terms of  $D_2$  has an important consequence known as Rosina's theorem [17] which states that the 2-RDM of a non-degenerate ground state contains the complete information on the ground state many-body wave function, i.e., there exists only one wave function whose partial trace is the ground state 2-RDM. The proof for this theorem uses reductio ad absurdum and relies essentially on the 2-RDM energy functional: Consider two wave functions that reduce to the same ground state 2-RDM. Then by Equation 2.28 their expectation value for the energy is equal to the ground state energy which is only possible if the ground state is degenerate which we have excluded from the beginning. We show that this result can be generalized to arbitrary eigenstates of the Hamiltonian. We employ the fact that the energy functional is stationary

$$\delta E[\Psi] = 0 \quad (2.31)$$

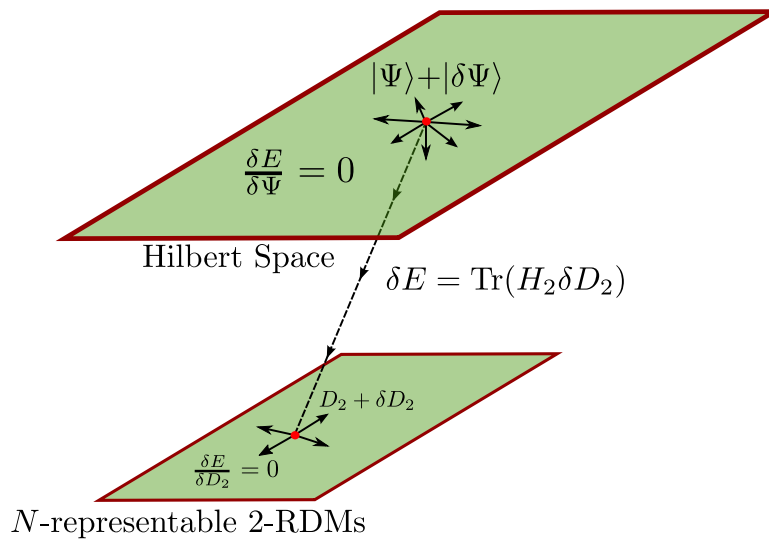
under variations  $|\Psi\rangle + |\delta\Psi\rangle$  constrained by  $\langle\Psi|\Psi\rangle = 1$  if and only if  $|\Psi\rangle$  is an eigenstate. Since every variation of the 2-RDM subject to the  $N$ -representability<sup>3</sup> condition is represented by at least one variation of the wave function, the variational principle for the wave function can be mapped to a variational principle for the 2-RDM. In particular, the 2-RDM corresponding to a wave function is stationary if and only if the wave function itself is stationary and therefore an eigenstate (see Figure 2.1). If the 2-RDM corresponds to two wave functions with the same energy expectation value where one of them is an eigenstate the other has to be an eigenstate as well. The 2-RDM of non-degenerate eigenstates thus contains enough information to reconstruct the whole eigenstate. This theorem justifies the reconstruction procedure we will encounter in subsection 2.3.2 since by this theorem all higher-order RDMs can be reconstructed from the 2-RDM, at least when the state can be associated with an eigenstate.

In the early 1950s, the 2-RDM energy functional triggered interest in the 2-RDM as a convenient object for the description of many-body systems and the fascinating idea arose that the problem of calculating the energy of many-body systems could be reduced to an effective two-body problem [9, 10, 18, 19]. In a first try, the Rayleigh-Ritz variational principle based on the 2-RDM as a trial object for the ground state energy of a gas of electrons immersed in a uniform positive charge produced ground state energies well below the exact result [18]. The reason for this unsuccessful attempt is that within the variational process the energy is minimized such that the trial 2-RDM takes on a form that cannot be derived from any actual many-body wave function. Therefore, additional constraints have to be applied in such a way that the partial trace of at least one wave function leads to the 2-RDM at hand. These sufficient and necessary conditions have been called  $N$ -representability conditions [20, 21].

Simultaneously with first attempts based on the 2-RDM, Walter Kohn has launched one of the great success stories in many-body quantum mechanics, i.e., density functional theory

<sup>2</sup> Note that by summing over all pairs the one-particle contribution to the total energy is over-counted ( $N-1$ ) times giving rise to the denominator in Equation 2.27

<sup>3</sup>  $N$ -representability means that the RDM can be obtained from at least one wave function, for more details see section 2.5



**Figure 2.1.:** Every variation  $|\delta\Psi\rangle$  of the wave function in Hilbert space can be mapped onto a variation  $\delta D_2$  of the corresponding 2-RDM and in return every variation of the 2-RDM under  $N$ -representability condition can be assigned at least one variation of the associated wave function. The variation of the energy is a functional of the variation of the 2-RDM and, therefore, the wave function is stationary if and only if the corresponding 2-RDM is stationary.

(DFT) [22] building on previous work by Llewellyn Thomas and Enrico Fermi [23]. The key fact of DFT is the existence of an energy functional depending solely on the electron density

$$\rho(z) = D(z \uparrow; z \uparrow) + D(z \downarrow; z \downarrow) \quad (2.32)$$

whose minimum yields the exact ground state energy. In contrast to the 2-RDM energy functional, however, the exact form of this functional remains undetermined. The  $N$ -representability conditions on the other hand are satisfied for any reasonable density. In particular, every electron density that is non-negative, normalizable, and fulfills

$$\int |\nabla \sqrt{\rho(z)}|^2 dz < \infty, \quad (2.33)$$

corresponds to at least one wave function [23]. The present unsatisfying situation is that within DFT the  $N$ -representability problem is solved but the energy functional remains unknown, whereas within the 2-RDM approach the energy functional is known but a complete set of  $N$ -representability conditions is inaccessible in general and one is restricted to an approximate set of conditions [14, 24] (see section 2.5). For many years the variational approach to the ground state based on the 2-RDM was put aside due to the complexity of the  $N$ -representability problem. Only in the late 1990's with the help of semidefinite programming and new theoretical insights this method became a feasible alternative for ground state calculations of highly correlated molecules and atoms [14].

Beside the variational approach to the ground state another method based on the contracted Schrödinger equation has emerged in the early 1990's. Since our method of propagating the 2-RDM is based on a similar contraction of the time-dependent Schrödinger equation we review this approach in the next section.



### 2.3. Contracted Schrödinger equation

The fundamental equation that governs the dynamics of the N-body quantum wave function  $\Psi(x_1, \dots, x_N, t)$  is the Schrödinger equation

$$i\partial_t \Psi(x_1, \dots, x_N; t) = \left( \sum_i^N h(x_i) + \sum_{i<j}^N V_{\text{int}}(x_i, x_j) \right) \Psi(x_1, \dots, x_N; t). \quad (2.34)$$

Solving the Schrödinger equation yields a complete description of the N-body quantum system. However, for more than two particles in three dimensions the direct (numerical) solution of this partial differential equation is inaccessible, except for a few special cases. The source of this complexity is the tremendous amount of information stored in the wave function. For many applications the complete wave function contains much more information than necessary and it is therefore of considerable interest to reduce the Schrödinger equation in such a way that the obtained equation describes the propagation of the significant information only. Such a reduced Schrödinger equation is known by the name contracted Schrödinger equation (CSE) which is the central equation of this diploma thesis. Depending on whether the contraction is applied to the time-dependent or the time-independent Schrödinger equation two related but substantially different equations arise. For many years the time-independent CSE has been used as the fundamental equation for the direct calculation of the ground state 2-RDM. The CSE for  $D_p$  is obtained by multiplying the Schrödinger equation with  $\Psi^*(x_1, \dots, x_N)$  and tracing out the coordinates of all but  $p$  particles. This results in the following expression for the  $p^{\text{th}}$ -order CSE:

$$\begin{aligned} ED(x_1 \dots x_p; x'_1 \dots x'_p) &= \\ &= \binom{N}{p} \int \Psi^*(x'_1 \dots x'_p, x_{p+1} \dots x_N) \left( \sum_i^N h(x_i) + \sum_{i<j}^N V_{\text{int}}(x_i, x_j) \right) \Psi(x_1 \dots x_p, x_{p+1} \dots x_N) dx_{p+1} \dots dx_N \\ &= \left( \sum_{i=1}^p h(x_i) + \sum_{i<j}^p V_{\text{int}}(x_i, x_j) \right) D(x_1 \dots x_p; x'_1 \dots x'_p) \\ &+ (p+1) \int \left( h(x_{p+1}) + \sum_{i=1}^p V_{\text{int}}(x_i, x_{p+1}) \right) D(x_1 \dots x_p x_{p+1}; x'_1 \dots x'_p x_{p+1}) dx_{p+1} \\ &+ \frac{(p+1)(p+2)}{2} \int V_{\text{int}}(x_{p+1}, x_{p+2}) D(x_1 \dots x_p x_{p+1} x_{p+2}; x'_1 \dots x'_p x_{p+1} x_{p+2}) dx_{p+1} dx_{p+2}. \end{aligned} \quad (2.35)$$

By a result of Nakatsuji's the  $p^{\text{th}}$ -order CSE for  $p > 1$  is necessary and sufficient for the underlying wave function to be an eigenstate of the Schrödinger equation [25]. This means that there is a direct mapping between the eigenfunction with energy  $E$  and the chain of  $N$ -representable RDMs  $D_p, D_{p+1}, D_{p+2}$  that solve the CSE for the same  $E$ . The second-order CSE is the first equation in this hierarchy and by Nakatsuji theorem the 4-particle RDM is sufficient to determine all non-degenerate eigenstates. While in principle, the second-order CSE is a closed equation for the 4-RDM subject to  $N$ -representability conditions, the 4-RDM is not a feasible object in any practical application due to its complexity and a more promising approach

was made by Valdemoro who derived reconstruction functionals for  $D_3$  and  $D_4$  in terms of  $D_2$  and  $D_1$  in order to make the second order CSE a closed equation [26]. Before we turn to the reconstruction we discuss in the next section the contraction of the time-dependent Schrödinger equation.

### 2.3.1. Equations of motion for RDMs

A convenient starting point for the derivation of the time-dependent contracted Schrödinger equation is the von Neumann equation for the density matrix

$$\begin{aligned} i\partial_t D(x_1 \dots x_N; x'_1 \dots x'_N; t) &= [\hat{H}, D_N] = \\ &= \left[ \sum_i^N h(x_i) + \sum_{i<j}^N V_{\text{int}}(x_i, x_j) - \sum_i^N h(x'_i) - \sum_{i<j}^N V_{\text{int}}(x'_i, x'_j) \right] D(x_1 \dots x_N; x'_1 \dots x'_N; t) = \\ &= K(x_1 \dots x_N; x'_1 \dots x'_N; t) - K^*(x'_1 \dots x'_N; x_1 \dots x_N; t) \end{aligned} \quad (2.36)$$

with

$$K(x_1 \dots x_N; x'_1 \dots x'_N; t) = \left[ \sum_i^N h(x_i) + \sum_{i<j}^N V_{\text{int}}(x_i, x_j) \right] D(x_1 \dots x_N; x'_1 \dots x'_N; t). \quad (2.37)$$

By tracing out all but  $p$  particles we arrive at the equation of motion for the  $p$ -RDM

$$i\partial_t D(x_1 \dots x_p; x'_1 \dots x'_p; t) = \int K(x_1 \dots x_N; x'_1 \dots x'_N; t) - K^*(x'_1 \dots x'_N; x_1 \dots x_N; t) dx_{p+1} \dots dx_N, \quad (2.38)$$

where the right hand side is given by the subtraction of two terms, one being equivalent to the right hand side of Equation 2.35 and the other being the conjugated term with the replacement of  $x_i$  by  $x'_i$ . This subtraction causes the integration over  $D_{p+2}$  and  $D_{p+1}$  with  $h(x_{p+1})$  to cancel:

$$\begin{aligned} \int [h(x_{p+1}) - h(x'_{p+1})] D(x_1 \dots x_p x_{p+1}; x'_1 \dots x'_p x'_{p+1}; t) dx_{p+1} &= 0 \\ \int [V_{\text{int}}(x_{p+1}, x_{p+2}) - V_{\text{int}}(x'_{p+1}, x'_{p+2})] D(x_1 \dots x_p x_{p+1} x_{p+2}; x'_1 \dots x'_p x'_{p+1} x'_{p+2}; t) dx_{p+1} dx_{p+2} &= 0. \end{aligned} \quad (2.39)$$

The remaining terms form the equations of motion for the  $p$ -RDM [27]

$$i\hbar\partial_t D^p(x_1, \dots, x_p; x'_1, \dots, x'_p; t) - [H, D^p(t)] = (p+1)F(x_1, \dots, x_p; x'_1, \dots, x'_p; t), \quad (2.40)$$

where

$$\begin{aligned} [H, D^p(t)] &= \left( \sum_{i=1}^p h(x_i) + \sum_{i<j}^p V_{\text{int}}(x_i, x_j) - \sum_{i=1}^p h(x'_i) + \sum_{i<j}^p V_{\text{int}}(x'_i, x'_j) \right) D(x_1 \dots x_p; x'_1 \dots x'_p; t) \\ F(x_1, \dots, x_p; x'_1, \dots, x'_p; t) &= I(x_1, \dots, x_p; x'_1, \dots, x'_p; t) - I^*(x'_1, \dots, x'_p; x_1, \dots, x_p; t) \end{aligned} \quad (2.41)$$

and

$$I(x_1, \dots, x_p; x'_1, \dots, x'_p; t) = \int \sum_{i=1}^p V_{\text{int}}(x_i, x_{p+1}) D(x_1 \dots x_p x_{p+1}; x'_1 \dots x'_p x'_{p+1}; t) dx_{p+1}. \quad (2.42)$$

This equation is similar to the time-independent case but there are some major differences. The most important point is that the time derivation of  $D_p$  depends solely on  $D_p$  and  $D_{p+1}$ . When combined, the set of all equations forms as coupled chain that is at least as complicated as solving the original Schrödinger equation. In statistical physics a very similar result is known as the Bogoliubov-Born-Green-Kirkwood-Yvon hierarchy [27]. In contrast to the  $p^{\text{th}}$ -order CSE which is, in principle, a closed equation for  $D_{p+2}$ , the time-dependent equation is not a closed equation for the evolution of  $D_{p+1}$ . In general, practical applications require a truncation of this chain at some finite order  $p$  by approximating  $D_{p+1}$  in terms of lower-order RDMs. Before we turn to the approximation scheme we give an intuitive interpretation of Equation 2.40. Since for systems with pairwise interaction the 2-RDM allows to calculate the total energy and related 2-particle properties we focus on the equations of motions for the 2-RDM:

$$i\partial_t D(x_1 x_2; x'_1 x'_2; t) - [H, D_2(t)] = 3F(x_1 x_2; x'_1 x'_2; t). \quad (2.43)$$

For two-particle systems the 3-RDM is equal to zero and the equation reduces to the well known von Neumann equation for the density matrix. In the case of more than two particles the F-operator describes the pairwise interaction between pairs and the surrounding particles. The similarity between Equation 2.40 and the Boltzmann equation for classical systems suggests to interpret the F-operator as a two-body collision integral. Therefore, the physical meaning of this term becomes more obvious in momentum representation where the diagonal element

$$F_2(k_1 k_2; k_1 k_2; t) = I(k_1 k_2; k_1 k_2; t) - I^*(k_1 k_2; k_1 k_2; t) \quad (2.44)$$

describes how the occupation number of pairs with momenta  $(k_1, k_2)$  changes in time due to the presence of the surrounding particles.

The term with the positive sign corresponds to processes which increases the number of pairs with  $(k_1, k_2)$  whereas the term with the negative sign stands for processes in which the pair is scattered out of the momentum configuration  $(k_1, k_2)$ . To investigate the mechanism behind these processes we interpret the interaction potential in momentum space,

$$V_{\text{int}}(k_1, k_\tau; k_\mu, k_\sigma) = \int e^{i(k_1 - k_\mu)x_1 + i(k_\tau - k_\sigma)x_2} V_{\text{int}}(x_1, x_2) dx_1 dx_2, \quad (2.45)$$

as the coupling strength for a particle pair to undergo a transition from  $(k_\mu, k_\sigma)$  to  $(k_1, k_\tau)$ . Based on this interpretation the explicit formulas for the momentum representation of  $I(k_1 k_2; k_1 k_2; t)$  and  $I^*(k_1 k_2; k_1 k_2; t)$ :

$$I(k_1 k_2; k_1 k_2; t) = \int V_{\text{int}}(k_\mu, k_\sigma; k_1, k_\tau) D(k_1 k_\tau k_2; k_\mu k_\sigma k_2; t) dk_\mu dk_\sigma dk_\tau \quad (2.46)$$

$$+ \int V_{\text{int}}(k_\mu, k_\sigma; k_2, k_\tau) D(k_2 k_\tau k_1; k_\mu k_\sigma k_1; t) dk_\mu dk_\sigma dk_\tau$$

$$I^*(k_1 k_2; k_1 k_2) = \int V_{\text{int}}(k_1, k_\tau; k_\mu, k_\sigma) D(k_\mu k_\sigma k_2; k_1 k_\tau k_2; t) dk_\mu dk_\sigma dk_\tau$$

$$+ \int V_{\text{int}}(k_2, k_\tau; k_\mu, k_\sigma) D(k_\mu k_\sigma k_1; k_2 k_\tau k_1; t) dk_\mu dk_\sigma dk_\tau \quad (2.47)$$



**Figure 2.2.:** Scattering events leading to (a) the formation of a particle pair with momentum configuration  $(k_1, k_2)$  and (b) to the annihilation of such a pair.

show that  $I(k_1 k_2; k_1 k_2; t)$  contains the sum over all scattering events that lead to the momentum configuration  $(k_1, k_2)$  whereas the negative contribution  $I^*(k_1 k_2; k_1 k_2; t)$  is the sum over all possibilities to destroy such a momentum configuration (see [Figure 2.2](#)).

The interpretation of  $F$  as a collision integral clarifies why the diagonal of  $F$  in space representation  $F(x_1 x_2; x_1 x_2; t)$  is zero since the pair density  $D(x_1 x_2; x_1 x_2; t)$  is not immediately altered by scattering events. At first sight the equations of motion for the diagonal part of the 2-RDM,

$$i\partial_t D(x_1 x_2; x_1 x_2; t) = [H, D_2(x_1 x_2; x_1 x_2; t)], \quad (2.48)$$

seems to be closed but since  $H$  contains derivations with respect to  $x_1$  and  $x_2$  the diagonal of the 2-RDM is not sufficient to calculate the right-hand side. Consequently the interaction with the surrounding particles does effect the pair distribution via off-diagonal components.

### 2.3.2. Approximating higher-order density matrices

The indeterminate nature of the CSE requires a reconstruction procedure that allows to express higher-order RDMs in terms of lower-order ones. The theoretical basis for this reconstruction is that for eigenstates, in particular for ground states, all RDMs can be written as functionals of the 2-RDM (see [section 2.2](#)). This theorem assures that the 2-RDM is a sufficient resource for the reconstruction of the wave function if the 2-RDM can be associated with some eigenstate. However, applications are restricted to approximations since the explicit form of this functional is not known by now. The one-to-one correspondence between the 2-RDM and the wave function breaks down for superpositions of eigenstates. In particular, if the ground state is perturbed by time-dependent external fields (see [subsection 3.1.2](#)) the time-dependent method requires the reconstruction of 3-RDMs for a wave packet. The reconstruction in this general time-dependent case is based on neglecting the ambiguity in the 3-RDM originating from the lack of a direct mapping between the time-dependent 2-RDM and a time-dependent wave function. Although the theoretical basis for this assumption is not yet developed, the results in [subsection 3.1.2](#) suggest that the assumption is well suited to describe the systems under consideration. The first reconstruction procedure was developed in 1992 by Valdemoro [26, 28] via the particle-hole duality in the search for an approximate solution of the second-order time-independent CSE, see [Appendix C](#). A more systematic approach to the reconstruction process is based on the

cumulant theory for RDMs developed by Mazziotti [29]. Starting point of this method is the generating functional of the RDMs

$$\Gamma(J, J^\dagger) = \langle \Psi | \hat{O} \exp \left( \int \hat{\Phi}^\dagger(x) J(x) + \hat{\Phi}(x) J^\dagger(x) dx \right) | \Psi \rangle, \quad (2.49)$$

where  $J(x), J^\dagger(x)$  are anti-commutating variables  $[J(x), J(x')]_+ = [J(x), J^\dagger(x')]_+ = 0$  for fermions and commutating variables for bosons. The normal ordering operator  $\hat{O}$  assures that in the Taylor expansion of the exponential all creation operators are on the left side of the annihilation operators which makes the exponential a well defined function. Similar to the moment generating function in probability theory  $J(x), J^\dagger(x)$  have no physical meaning and vanish in final expressions. The special property of the generating functional is that the RDMs appear as the coefficients of its Taylor expansion:

$$D(x_1 \dots x_p; x'_1 \dots x'_p) = \lim_{J, J^\dagger \rightarrow 0} \frac{\partial^p \Gamma}{\partial J^\dagger(x_1) \dots \partial J^\dagger(x_p) \partial J(x'_1) \dots \partial J(x'_p)}. \quad (2.50)$$

For more details see [Appendix F](#). In analogy with the definition of cumulants in probability theory the cumulant generating functional in reduced density mechanics is given by  $W = \ln(\Gamma)$  leading to the following expression for the  $p$ -particle cumulant  $\Delta_p$ :

$$\Delta_p(x_1 \dots x_p; x'_1 \dots x'_p) = \lim_{J, J^\dagger \rightarrow 0} \frac{\partial^p W}{\partial J^\dagger(x_1) \dots \partial J^\dagger(x_p) \partial J(x'_1) \dots \partial J(x'_p)}. \quad (2.51)$$

Using the chain rule several times the cumulants can be expanded in terms of the RDMs. In a short hand calculation the coefficients can be derived from expanding  $\frac{d^p}{dx^p} \log(y(x))|_{x \rightarrow 0}$  in terms of the derivatives of  $y(x)$  and using  $y(0) = 1$ :

$$\begin{aligned} \frac{d}{dx} \log(y(x))|_{x \rightarrow 0} &= \frac{y'(0)}{y(0)} = y'(0) \\ \frac{d^2}{dx^2} \log(y(x))|_{x \rightarrow 0} &= y''(0) - y'(0)y'(0) \\ \frac{d^3}{dx^3} \log(y(x))|_{x \rightarrow 0} &= y^{(3)}(0) - 3y''(0)y'(0) + 2y'(0)y'(0)y'(0) \\ \frac{d^4}{dx^4} \log(y(x))|_{x \rightarrow 0} &= y^{(4)}(0) - 4y^{(3)}(0)y'(0) - 3y''(0)y''(0) + 12y''(0)y'(0)y'(0) \\ &\quad - 6y'(0)y'(0)y'(0)y'(0). \end{aligned}$$

A more involved calculation for the  $p$ -particle cumulants  $\Delta_p$  for fermions gives (see [Appendix F](#)):

$$\Delta_1 = D_1 \quad (2.52)$$

$$\Delta_2 = D_2 - D_1 \wedge D_1 \quad (2.53)$$

$$\Delta_3 = D_3 - 3D_2 \wedge D_1 + 2D_1^3 \quad (2.54)$$

$$\Delta_4 = D_4 - 4D_3 \wedge D_1 - 3D_2^2 \wedge D_2^2 + 12D_2 \wedge D_1^2 - 6D_1^4, \quad (2.55)$$

with  $D_1^2 = D_1 \wedge D_1$  and the wedge product defined as the antisymmetrization of the tensor product  $D_p \otimes D_q$

$$\begin{aligned} D_p \wedge D_q &= \\ &= \frac{1}{(p+q)!} \sum_{\sigma, \tau} \text{sgn}(\sigma) \text{sgn}(\tau) D(x_{\sigma(1)} \dots x_{\sigma(p)}; x'_{\tau(1)} \dots x'_{\tau(p)}) D(x_{\sigma(p+1)} \dots x_{\sigma(p+q)}; x'_{\tau(p+1)} \dots x'_{\tau(p+q)}) \\ &= \frac{1}{(p+q)!} \hat{\mathcal{A}}[D_p \otimes D_q], \end{aligned} \quad (2.56)$$

where  $\text{sgn}(\sigma)$  denotes the sign of the permutation  $\sigma$  and  $\hat{\mathcal{A}}$  is the antisymmetrization operator.

To illustrate the significance of cumulants we consider a  $N$ -particle system that can be decomposed into a subsystem of  $N_s$ -particles and an environment consisting of  $(N - N_s)$  particles. In general, if there is any interaction between the particles of the subsystem and the environment both systems will be non-separable. However, if the total system decouples into a non-interacting composition of subsystem and environment the wave function of the composite systems is separable and may be expressed using the antisymmetrization operator as:

$$\Psi(x_1, \dots, x_N) = \frac{1}{\sqrt{N!}} \hat{\mathcal{A}}[\Psi^S(x_1, \dots, x_p) \Psi^E(x_{p+1}, \dots, x_N)]. \quad (2.57)$$

The wave functions  $\Psi^S(x_1, \dots, x_p)$  and  $\Psi^E(x_{p+1}, \dots, x_N)$  can be decomposed into determinants build up exclusively by basis orbitals  $\phi_i^S$  and  $\phi_i^E$  associated with the corresponding system. Together the combined set of orbitals  $\{\phi_i^S, \phi_i^E\}$  builds up a complete set of orbitals for the total system. To see the structure of the 2-RDM for such a non-interacting composition we consider its basis representation in the combined set of orbitals

$$D_{j_1, \dots, j_p}^{i_1, \dots, i_p} = \frac{1}{p!} \langle \Psi | \hat{a}_{i_1}^\dagger \dots \hat{a}_{i_p}^\dagger \hat{a}_{j_p} \dots \hat{a}_{j_1} | \Psi \rangle, \quad (2.58)$$

where each index now belongs either to the subsystem or to the environment. In general,  $D_{j_1, \dots, j_p}^{i_1, \dots, i_p}$  is non-zero only if the number of indices associated with the subsystem is equal in the upper and the lower row because in this case the number of creation operators equals the number annihilation operators leaving the total number of particles in the subsystem unchanged. For the 1-RDM this means that either both indices correspond to the subsystem or the environment but mixed terms vanish making the 1-RDM a separable quantity

$$D_{j_1}^{i_1} = {}^S D_{j_1}^{i_1} + {}^E D_{j_1}^{i_1}. \quad (2.59)$$

${}^S D_{j_1}^{i_1}$  and  ${}^E D_{j_1}^{i_1}$  are the 1-RDMs of the subsystem and the environment, respectively. The 2-RDM, however, cannot be separated. This becomes obvious by assuming that such a separation exists

$$D_{j_1, j_2}^{i_1, i_2} = {}^S D_{j_1, j_2}^{i_1, i_2} + {}^E D_{j_1, j_2}^{i_1, i_2}. \quad (2.60)$$

Taking the trace on both sides would lead to the statement that the number of pairs is additive which is not the case. For example, a system with two particles consists of one pair but the

combined system of two such systems contains six pairs. In contrast, the cumulant  $\Delta_{j_1, \dots, j_p}^{i_1, \dots, i_p}$  is an additive quantity in the case of non-interacting subsystems

$$\Delta_{j_1, \dots, j_p}^{i_1, \dots, i_p} = {}^S \Delta_{j_1, \dots, j_p}^{i_1, \dots, i_p} + {}^E \Delta_{j_1, \dots, j_p}^{i_1, \dots, i_p}, \quad (2.61)$$

because it is only non-zero if all indices correspond to the same subsystem [30]. The 1-RDM is the only RDM that is equal to its cumulant and thereby the only RDM that is additive, see Equation 2.52. Loosely speaking, this is a consequence of the logarithm appearing in the definition of the cumulants. This property of cumulants has a very significant consequence. If the number of particles in the subsystem  $N_s$  is smaller than the order  $N_s < p$  the cumulant of the subsystem has to vanish  ${}^S \Delta_p = 0$ . Since for a quantum system all  $p$ -particle subsystems are indistinguishable, assuming  $\Delta_{p+1} = 0$  yields the approximation that the system contains at most  $p$  simultaneously interacting particles where all other particles are sufficiently far away to be considered statistically independent.

Therefore, setting  $\Delta_p$  to zero in the reconstruction functionals (see Equation 2.62) is a convenient way to approximate  $p$ -RDM by lower-order RDMs which becomes increasingly more accurate with increasing  $p$  resembling the perturbation theory for many body systems. In analogy with the convention for Green's functions in quantum field theory which follow a similar construction the part of the  $p$ -RDM that cannot be written as a wedge product of lower-order RDMs is called the connected  $p$ -RDM and corresponds to  $\Delta_p$  while the approximation by lower-order RDMs represents the unconnected  $p$ -RDM [17].

The first order approximation,  $\Delta_2 = 0$ , is equivalent to independent and non-interacting particles. This corresponds to the Hartree-Fock approximation where the wave function is a single Slater determinant constructed from  $N$  orbitals. In this case the reconstruction is exact and follows a simple scheme (see Appendix H). Since in the present work we want to propagate the 2-RDM we assume  $\Delta_3 = 0$  and get the following approximation for the 3-RDM:

$$D_3 \approx 3D_2 \wedge D_1 - 2D_1^3. \quad (2.62)$$

This approximation would be correct if at any time there are no three particles simultaneously influencing each other. Higher order methods for the reconstruction of the 3-RDM that account for three particle correlations are based on the reconstruction of the connected 3-RDM  $\Delta_3$  from lower-order RDMs. Such methods haven been proposed by Nakatsuji and Yasuda [31] or Mazziotti [17]. As we show in subsection 3.3.1 the reconstruction via Equation 2.62 is accurate enough to approximate the time-dependent 3-RDM for the systems investigated in the present thesis.

## 2.4. Equations of motion in second quantization

In practical applications, propagating  $D_2(x_1 x_2; x'_1 x'_2; t)$  in coordinate space is possible only for sparse spatial grids. A more convenient approach is to expand  $D_2$  in some given orthonormal orbital basis:

$$D(x_1 x_2; x'_1 x'_2, t) = D_{j_1, j_2}^{i_1, i_2}(t) \phi_{i_1}(x_1, t) \phi_{i_2}(x_2, t), \phi_{j_1}^*(x'_1, t) \phi_{j_2}^*(x'_2, t), \quad (2.63)$$

where both the expansion coefficients  $D_{j_1, j_2}^{i_1, i_2}(t)$  and the orbitals  $\phi_{i_1}(x_1, t)$  are time-dependent. For the sake of simplicity we drop the time-dependence of operators in orbital representation. With this expansion the propagation separates into two parts. First, the evolution of the orbitals is given by

$$i\hbar\partial_t\phi_i(x, t) = f_i[\phi_k(x, t)], \quad (2.64)$$

where  $f_i$  is a functional that ensures unitary propagation of the orbitals. Second, the equations of motion for the 2-RDM expansion coefficients are obtained by inserting Equation 2.63 into Equation 2.43:

$$\begin{aligned} i\hbar\partial_t D_{j_1, j_2}^{i_1, i_2} &= \\ &= D_{j_1, j_2}^{k_1, k_2} \int \phi_{i_1}^*(x_1, t)\phi_{i_2}^*(x_2, t) [H(x_1, x_2)\phi_{k_1}(x_1, t)\phi_{k_2}(x_2, t) - i\partial_t(\phi_{k_1}(x_1, t)\phi_{k_2}(x_2, t))] dx_1 dx_2 \\ &+ D_{k_1, k_2}^{i_1, i_2} \int \phi_{j_1}(x_1, t)\phi_{j_2}(x_2, t) [H(x_1, x_2)\phi_{k_1}^*(x_1, t)\phi_{k_2}^*(x_2, t) - i\partial_t(\phi_{k_1}^*(x_1, t)\phi_{k_2}^*(x_2, t))] dx_1 dx_2 \\ &+ \int F(x_1 x_2; x'_1 x'_2)\phi_{i_1}^*(x_1, t)\phi_{i_2}^*(x_2, t)\phi_{j_1}(x'_1, t)\phi_{j_2}(x'_2, t) dx_1 dx_2 dx'_1 dx'_2. \end{aligned} \quad (2.65)$$

At this point Equation 2.64 is in its most general form, where no specific form for the functional  $f_i$  is determined. Given any unitary propagation of the orbitals, Equation 2.65 describes the time evolution of the expansion coefficients. As a particular choice one might, e.g., keep the orbitals time independent and propagate only the expansion coefficients. However time independent orbitals will, in general, require a large number of basis orbitals to account for the full dynamics of the system. If for technical reasons the number of basis orbitals is too low the dynamics will be unphysically truncated. Thus, one has to deal with the antagonism that for technical reasons the number of orbitals should be as low as possible while for physical reasons it should be large enough to capture the full dynamics. This calls for an optimization algorithm for the equations of motion for the orbitals and ultimately to a time-dependent basis. This optimization is incorporated within the multiconfigurational time-dependent Hartree-Fock (MCTDHF) approach via the variational principle. As a consequence the orbital equations of motion are coupled to the time evolution of the 2-RDM:

$$i\hbar\partial_t\phi_i = f^{\text{MC}}[\phi_i, D_2]. \quad (2.66)$$

To obtain the equations of motion for the orbitals we take a closer look at the MCTDHF in the next section.

### 2.4.1. Multiconfigurational time-dependent Hartree-Fock method

Starting point of the MCTDHF method is the expansion of the many-body wave function into determinants build up from  $r$  orbitals  $\phi_i$

$$|\Psi\rangle = \sum_{\vec{n}} C_{\vec{n}} |\vec{n}\rangle. \quad (2.67)$$



Each of the determinant is denoted by  $|\vec{n}\rangle = |n_1, n_2, \dots, n_r\rangle$ , where  $n_i$  is the occupation of the orbital  $\phi_i$ . For fermions,  $r$  is the number of spin orbitals and must be larger than  $N$ . The equations of motion for the orbitals and the expansion coefficients  $C_{\vec{n}}$  can be determined via the time-dependent variational principle for the action

$$S[\Psi] = \int_{t_0}^t \langle \Psi | \left( \hat{H} - i\partial_t \right) | \Psi \rangle, \quad (2.68)$$

which gives

$$\delta S = \int_{t_0}^t \langle \delta \Psi | \left( \hat{H} | \Psi \rangle - i\partial_t | \Psi \rangle \right) + \langle \Psi | \left( \hat{H} | \delta \Psi \rangle - i\partial_t | \delta \Psi \rangle \right) = 0. \quad (2.69)$$

For the time evolution of the wave function the action has to be stationary with respect to independent variations of the expansion coefficients  $\delta C_{\vec{n}}$  and variations of the orbitals  $\delta \phi_i$ . Altogether, the total variation of the wave function can be expressed as

$$|\delta \Psi\rangle = \sum_{\vec{n}} |\vec{n}\rangle \delta C_{\vec{n}} + \delta |\vec{n}\rangle C_{\vec{n}}. \quad (2.70)$$

This variation of the action leads, after some algebraic manipulations (see e.g. [32]), to the equations of motion for the orbitals

$$i\partial_t \phi_i(x, t) = f^{\text{MC}}[\phi_i, D_2] = \hat{Q} \left( h(x) \phi_i(x, t) + \hat{\Gamma}_u(x, t) (D^{-1})_i^u \right), \quad (2.71)$$

where

$$\hat{Q} = 1 - \sum_{i=1}^r |\phi_i\rangle \langle \phi_i| \quad (2.72)$$

is the orbital projection operator assuring unitary time evolution of the basis orbitals,  $(D^{-1})_i^u$  is the inverse of the 1-RDM in the orbital representation, and

$$\hat{\Gamma}_u(x, t) = D_{u,t}^{v,w} \phi_v(x, t) \int \phi_w(x', t) \phi_t^*(x', t) V_{\text{int}}(x, x') dx' \quad (2.73)$$

is the coupling term between the orbitals originating from the interaction between the particles. Without this term the equations of motion for the orbitals reduce to

$$i\partial_t \phi_i(x, t) = \hat{h}(x) \phi_i(x, t), \quad (2.74)$$

which is the Schrödinger equation for a single particle in the external potential. [Equation 2.74](#) could, in principle, be used for the propagation of the 2-RDM as well but since the evolution of the orbitals is not adapted to the evolution of the interacting system, this potentially would lead to very large basis sets to describe the physical system accurately. The last term in [Equation 2.71](#) accounts for the optimization of the basis and couples the time evolution of the orbitals to the equations of motion for the 2-RDM.

In the MCTDHF approach the variation of the action with respect to the expansion coefficients leads to equations of motion for  $C_{\vec{n}}$

$$i\partial_t C_{\vec{n}} = \sum_{\vec{m}} \langle \vec{m} | H | \vec{n} \rangle - \delta_{\vec{n}, \vec{m}} \langle \Psi | H | \Psi \rangle \quad (2.75)$$

which in combination with the orbitals contain the complete information on the total many-body wave function. Especially for systems with a large number of particles the equations of motion for  $C_{\vec{n}}$  become very time consuming since the number of determinants  $N_C$  scales factorially with the number of particles  $N$  for bosons

$$N_C^b = \binom{N - r + 1}{N}, \quad (2.76)$$

as well as for fermions

$$N_C^f = \binom{r}{N}, \quad (2.77)$$

where the number of orbitals needed for convergence is roughly given by  $r \approx 2N$  [33].

Our approach is based on the assumption that the complete propagation of the expansion coefficients is dispensable since the time propagation of the orbitals depends solely on the 2-RDM and the 1-RDM. We thus replace the equations of motion for  $C_{\vec{n}}$  by the equation of motion for the 2-RDM coefficients [Equation 2.65](#). Due to the projection operator the orbital propagation is not only unitary but fulfills the more stringent condition

$$\int \phi_i^*(x, t) \partial_t \phi_j(x, t) dx = 0, \quad (2.78)$$

which can be used to simplify [Equation 2.65](#) according to

$$i\hbar \partial_t D_{j_1, j_2}^{i_1, i_2} = H_{k_1, k_2}^{i_1, i_2} D_{j_1, j_2}^{k_1, k_2} - D_{k_1, k_2}^{i_1, i_2} H_{j_1, j_2}^{k_1, k_2} + 3F_{j_1, j_2}^{i_1, i_2} \quad (2.79)$$

with

$$H_{j_1, j_2}^{i_1, i_2} = \int H(x_1, x_2) \phi_{i_1}^*(x_1, t) \phi_{i_2}^*(x_2, t), \phi_{j_1}(x_1, t) \phi_{j_2}(x_2, t) dx_1 dx_2 dx'_1 dx'_2 \quad (2.80)$$

$$F_{j_1, j_2}^{i_1, i_2} = I_{j_1, j_2}^{i_1, i_2} - I_{i_1, i_2}^{*j_1, j_2} \quad I_{j_1, j_2}^{i_1, i_2} = V_{j_1, j_\tau}^{i_\sigma, i_\mu} D_{j_\sigma, j_2, j_\mu}^{i_1, i_2, i_\tau} + V_{j_2, j_\tau}^{i_\sigma, i_\mu} D_{j_\sigma, j_1, j_\mu}^{i_2, i_1, i_\tau} \quad (2.81)$$

and

$$V_{j_1, j_2}^{i_1, i_2} = \int V(x_1, x_2) \phi_{i_1}^*(x_1, t) \phi_{i_2}^*(x_2, t), \phi_{j_1}(x_1, t) \phi_{j_2}(x_2, t) dx_1 dx_2 dx'_1 dx'_2. \quad (2.82)$$

[Equation 2.79](#) in combination with [Equation 2.71](#) constitutes the basic equation for the time-dependent 2-RDM method.

The equations of motion for the 2-RDM coefficients have a different scaling than the equations of motion for the  $C_{\vec{n}}$  because they are independent of the actual number of particles  $N$ . The computationally most demanding procedure is the evaluation of the  $F$ -operator in the orbital

representation via [Equation 2.82](#) which, in general, scales as  $r^7$ . However, if the system under consideration is in the electronic singlet spin state the required number of numerical operations can be reduced because the 2-RDM vanishes if the total spin of the upper indices is not equal to the total spin of the lower indices. Further, using the fact that the singlet state is invariant under the spin flip ( $\uparrow$ )  $\leftrightarrow$  ( $\downarrow$ ) the complete information on the 2-RDM is contained in the two spin blocks

$$D_{j_1\uparrow, j_2\uparrow}^{i_1\uparrow, i_2\uparrow} \neq 0 \qquad D_{j_1\uparrow, j_2\downarrow}^{i_1\uparrow, i_2\downarrow} \neq 0. \quad (2.83)$$

Exploiting this property allows to reduce the number of required operations for the calculation of the F-operator to  $4 \left(\frac{r}{2}\right)^7$ .

### 2.4.2. Equations of motion within a two-particle basis

The rather complicated form of the equations of motion for the orbitals ([Equation 2.71](#)) is a consequence of describing the dynamics of a many-body system with pairwise interactions in terms of one-particle orbitals. A more natural choice would be to use a two-particle basis to account for the interaction already on the level of the two-particle basis functions  $\Phi_i(x_1, x_2, t)$ . The expansion of  $D_2$  in such a basis is given by

$$D_2(x_1x_2; x'_1x'_2; t) = \lambda_j^i \Phi_i(x_1, x_2, t) \Phi_j^*(x'_1, x'_2, t), \quad (2.84)$$

where the symmetry of the 2-RDM with respect to particle exchange is reflected in the symmetry of  $\Phi_i(x_1, x_2, t)$ . The equations of motion for  $\lambda_j^i$  can be derived by inserting [Equation 2.84](#) into [Equation 2.43](#) which yields

$$\begin{aligned} i\partial_t \lambda_j^i &= \lambda_j^k \int \Phi_i^*(x_1, x_2) [H(x_1, x_2) \Phi_k(x_1, x_2) - i\partial_t \Phi_k(x_1, x_2)] dx_1 dx_2 \\ &+ \lambda_k^i \int \Phi_j(x_1, x_2) [H(x_1, x_2) \Phi_k^*(x_1, x_2) + i\partial_t^* \Phi_k(x_1, x_2)] dx_1 dx_2 \\ &+ \int F(x_1x_2; x'_1x'_2) \Phi_i^*(x_1, x_2) \Phi_j(x'_1, x'_2) dx_1 dx_2 dx'_1 dx'_2. \end{aligned} \quad (2.85)$$

This equation is analogous to [Equation 2.65](#) within the one-particle basis. Although the similarity is striking there are some major differences. The main difference is that odd number RDMs like the 1-RDM or the 3-RDM do not have a similarly simple representation within the two-particle basis. While for one-particle orbitals the  $F$ -operator can be obtained solely from the orbital representation of the potential and the orbital representation of the 3-RDM via [Equation 2.82](#) this is not possible within the two-particle basis and requires the evaluation of the integral

$$F_j^i = \int F(x_1x_2; x'_1x'_2) \Phi_i^*(x_1, x_2) \Phi_j(x'_1, x'_2) dx_1 dx_2 dx'_1 dx'_2 \quad (2.86)$$

at each time step. By using the reconstruction functional for  $D_3$  ([Equation 2.62](#)) the  $F$ -operator can be written in terms of  $\lambda_j^i$  as

$$F_j^i = I_j^i - I_i^{*j} \quad (2.87)$$

$$I_j^i = \gamma_{j, i_1, i_2}^{i, j_1, j_2} \lambda_{j_1}^{i_1} \lambda_{j_2}^{i_2} - \kappa_{j, i_1, i_2, i_3}^{i, j_1, j_2, j_3} \lambda_{j_1}^{i_1} \lambda_{j_2}^{i_2} \lambda_{j_3}^{i_3}. \quad (2.88)$$

The quadratic term in  $\lambda_j^i$  originates from  $D_2 \wedge D_1$ , the cubic term originates from  $D_1 \wedge D_1 \wedge D_1$ . From a technical point of view [Equation 2.88](#) is computationally more demanding than [Equation 2.82](#) because the evaluation of the coefficient  $\kappa_{j,i_1,i_2,i_3}^{i,j_1,j_2,j_3}$  requires, for general systems, four integrals from [Equation 2.86](#) and three additional integrals because of the projection of the two particle basis into the one-particle subspace to evaluate the 1-RDM:

$$D(x_1; x'_1) = \int D(x_1 x_2; x'_1 x_2) dx_2 = \lambda_j^i \int \Phi_i(x_1, x_2) \Phi_j^*(x'_1, x_2) dx_2. \quad (2.89)$$

This makes the evaluation of  $\kappa_{j,i_1,i_2,i_3}^{i,j_1,j_2,j_3}$  via integration at each time step practically impossible. However, for a system of bosons with short-range interaction the evaluation of the coefficients  $\gamma, \kappa$  can be reduced to a sequence of one-dimensional integrals (see [Appendix G](#)). A possible choice to decompose [Equation 2.85](#) which circumvents many of the above difficulties is given by the choice

$$i\partial_t \Phi_i(x_1, x_2) = H(x_1, x_2) \Phi_i(x_1, x_2) \quad (2.90)$$

and

$$i\partial_t \lambda_j^i = F_j^i. \quad (2.91)$$

In particular, if the two-particle basis functions are the eigenstates of  $H(x_1, x_2)$ ,

$$H(x_1, x_2) \Phi_i(x_1, x_2) = E_i \Phi_i(x_1, x_2), \quad (2.92)$$

the time propagation reduces to  $\Phi_i(x_1, x_2, t) = \exp(-iE_i t) \Phi_i(x_1, x_2, 0)$ . The coefficients  $\gamma, \kappa$  can be calculated at the beginning for the initial state and then evolve by accumulating the phase

$$\gamma_{j,i_1,i_2}^{i,j_1,j_2}(t) = e^{i(E_i - E_j)t} e^{i(E_{j_1} - E_{i_1})t} e^{i(E_{j_2} - E_{i_2})t} \gamma_{i,i_1,i_2}^{j,j_1,j_2}(0) \quad (2.93)$$

$$\kappa_{j,i_1,i_2,i_3}^{i,j_1,j_2,j_3}(t) = e^{i(E_i - E_j)t} e^{i(E_{j_1} - E_{i_1})t} e^{i(E_{j_2} - E_{i_2})t} e^{i(E_{j_3} - E_{i_3})t} \kappa_{i,i_1,i_2,i_3}^{j,j_1,j_2,j_3}(0). \quad (2.94)$$

A good estimate for the number of basis functions that have to be taken into account is the mean energy of the many-body system  $\langle \Psi | E | \Psi \rangle$  which has to be much smaller than the largest  $E_i$ .

## 2.5. The $N$ -representability problem

Every density matrix that is (i) hermitian, (ii) normalized, (iii) antisymmetric/symmetric under particle permutation for fermions/bosons, and (iv) positive semidefinite accounting for positive probabilities can be related to an actual physical state of a system. While these four conditions are necessary and sufficient for density matrices the situation is much more complicated in the case of reduced density matrices. A reduced density matrix is called  $N$ -representable if it can be derived from a many-body wave function. It turns out that the four conditions for density matrices (i)-(iv) are necessary but not sufficient for RDMs to be  $N$ -representable. A variational procedure based on the energy functional ([Equation 2.28](#)) imposing only these four conditions

leads to ground state energies well below the exact result [18]. Further conditions are necessary to ensure the  $N$ -representability of RDMs called  $N$ -representability conditions. The search for a complete set of conditions for the 2-RDM has lasted for over half a century [24, 34, 35]. Still the actual form of such a complete set of conditions remains undetermined.

In this section we review the 2-positivity conditions which represent the most important set of conditions. In [Appendix D](#) we discuss more complex conditions like the  $T_1/T_2$  conditions and the general construction of higher-order conditions.

### 2.5.1. 2-positivity conditions

Condition (iv) states that any  $p$ -RDM has to be positive semidefinite which means that

$$X_{i_1, \dots, i_p}^* D_{j_1, \dots, j_p}^{i_1, \dots, i_p} X_{j_1, \dots, j_p} \geq 0 \quad \forall X_{j_1, \dots, j_p} \in \mathbb{C}^{r \cdot p}. \quad (2.95)$$

This result is based on positivity of probabilities:

$$\begin{aligned} X_{i_1, \dots, i_p}^* D_{j_1, \dots, j_p}^{i_1, \dots, i_p} X_{j_1, \dots, j_p} &= \frac{1}{p!} \langle \Psi | X_{i_1, \dots, i_p}^* \hat{a}_{i_1}^\dagger \dots \hat{a}_{i_p}^\dagger \hat{a}_{j_p} \dots \hat{a}_{j_1} X_{j_1, \dots, j_p} | \Psi \rangle \\ &= \frac{1}{p!} \langle \tilde{\Psi} | \tilde{\Psi} \rangle \quad \text{with} \quad |\tilde{\Psi}\rangle = \hat{a}_{j_p} \dots \hat{a}_{j_1} X_{j_1, \dots, j_p} | \Psi \rangle, \end{aligned} \quad (2.96)$$

Note that we employ the Einstein sum convention to simplify notation. A direct generalization can be made to arbitrary hermitian operators of the form

$$M_p = M_{j_1, \dots, j_p}^{i_1, \dots, i_p} = \langle \Psi | \hat{C}_{i_1, \dots, i_p}^\dagger \hat{C}_{j_1, \dots, j_p} | \Psi \rangle, \quad (2.97)$$

where  $\hat{C}_p = \hat{C}_{j_1, \dots, j_p}$  is a polynomial of degree  $p$  in the creation/annihilation operators making  $M_p$  a  $p$ -particle operator. In this general formulation the positivity of the  $p$ -RDM occurs as a special case with  $\hat{C}_p = \hat{a}_{j_p} \dots \hat{a}_{j_1}$ . The conditions that all matrices  $M_p$  are positive semidefinite denoted by  $M_p \geq 0$  are called  $p$ -positivity conditions:

$$M_p = \langle \Psi | \hat{C}_{i_1, \dots, i_p}^\dagger \hat{C}_{i_1, \dots, i_p} | \Psi \rangle \geq 0. \quad (2.98)$$

These conditions are always fulfilled for any physical state of the system. The crucial point is that since  $M_p$  is a  $p$ -particle operator the  $p$ -positivity conditions can be formulated in term of the  $p$ -RDM only. In this way the  $p$ -positivity conditions represent a set of  $N$ -representability conditions on the level of the  $p$ -RDM without involving the wave function.

Instead of testing the positivity for all matrices  $M_p$ , which leads to an infinite number of conditions, it is sufficient to show the positivity for only a finite number of special matrices  $M_p$ . These conditions are called extreme  $p$ -positivity conditions [36]. For the 1-positivity the set of extreme conditions is given by

$$\hat{C}_i = \hat{a}_i \quad (2.99)$$

$$\hat{C}_i = \hat{a}_i^\dagger, \quad (2.100)$$

corresponding to the positivity of the two matrices

$$D_j^i = \langle \Psi | \hat{a}_i^\dagger \hat{a}_j | \Psi \rangle \quad (2.101)$$

$$Q_j^i = \langle \Psi | \hat{a}_j \hat{a}_i^\dagger | \Psi \rangle. \quad (2.102)$$

While the first matrix corresponds to the 1-RDM the second matrix describes the distribution of holes rather than particles. This can be understood by interpreting the annihilation operator  $\hat{a}_i$  as the creation operator  $\hat{b}_i^\dagger$  of holes. In the case of fermions these holes fulfill the same commutation relations. The particle-hole duality enables an equivalent description of the many-particle system in terms of holes. A system of  $N$  fermions described by  $r$  orbitals can be converted into a system of  $(r - N)$  holes. Therefore, the matrix  $Q_j^i$  describes the distribution of holes and it is normalized to  $(r - N)$ . In the case of bosons the particle-hole duality is broken in the fact that bosonic holes obey a different canonical commutation relation which is reflected by the normalization of the 1-hole-RDM to  $(r + N)$  in the bosonic case:

$$\begin{aligned} \sum_i^r Q_i^i &= \sum_i^r \langle \Psi | \hat{a}_i \hat{a}_i^\dagger | \Psi \rangle \\ &= \sum_i^r \langle \Psi | \hat{a}_i^\dagger \hat{a}_i | \Psi \rangle + \sum_i^r 1 \\ &= N + r. \end{aligned} \quad (2.103)$$

Nonetheless, the construction of hole RDMs for bosons is still beneficial in the derivation of bosonic  $N$ -representability conditions although their interpretation lacks intuition. We focus on the fermionic case for the rest of this chapter, the corresponding expressions for bosons can be derived in a similar way. Both descriptions in holes and particles can be converted into each other by

$$Q_j^i + D_j^i = \delta_j^i. \quad (2.104)$$

Therefore, they carry the same information on the state of the system. Nevertheless, the conditions  $Q_1 \geq 0$  and  $D_1 \geq 0$  are independent. While  $D_1 \geq 0$  demands positive natural occupation numbers,  $Q_1 \geq 0$  requires the natural occupation numbers to be smaller than one. Altogether, both conditions restrict the eigenvalues of the 1-RDM to the interval  $[0 : 1]$ . For the 1-RDM these two conditions are already sufficient for the 1-RDM to be  $N$ -representable [20]. In this exceptional case, the 1-positivity conditions for the 1-RDM form a complete set of  $N$ -representability conditions. In general the  $p$ -positivity of the  $p$ -RDM is necessary but not sufficient for  $N$ -representability.

The next conditions in this hierarchy are the 2-positivity conditions represented by the positivity of the three extreme matrices [14, 21, 37]

$$D_{j_1, j_2}^{i_1, i_2} = \langle \Psi | \hat{a}_{i_1}^\dagger \hat{a}_{i_2}^\dagger \hat{a}_{j_2} \hat{a}_{j_1} | \Psi \rangle \geq 0 \quad (2.105)$$

$$Q_{j_1, j_2}^{i_1, i_2} = \langle \Psi | \hat{a}_{j_1} \hat{a}_{j_2} \hat{a}_{i_2}^\dagger \hat{a}_{i_1}^\dagger | \Psi \rangle \geq 0 \quad (2.106)$$

$$G_{j_1, j_2}^{i_1, i_2} = \langle \Psi | \hat{a}_{i_1}^\dagger \hat{a}_{j_2} \hat{a}_{i_2}^\dagger \hat{a}_{j_1} | \Psi \rangle \geq 0. \quad (2.107)$$

These conditions are called the D, Q and G-condition, respectively. The positivity of these matrices represents independent conditions although the matrices are interconvertible by a rearrangement of the creation/annihilation operators (for more details see [Appendix C](#))

$$Q_{j_1, j_2}^{i_1, i_2} = \delta_{j_1}^{i_1} \wedge \delta_{j_2}^{i_2} - 2\delta_{j_1}^{i_1} \wedge D_{j_2}^{i_2} + D_{j_1, j_2}^{i_1, i_2} \quad (2.108)$$

$$G_{j_1, j_2}^{i_1, i_2} = \frac{1}{2}\delta_{j_1}^{i_1} D_{j_2}^{i_2} - D_{j_1, i_2}^{i_1, j_2}, \quad (2.109)$$

or in a basis independent notation

$$Q_2 = \delta^2 - 2\delta \wedge D_1 + D_2 \quad (2.110)$$

$$G_2 = \frac{1}{2}\delta D_1 - \bar{D}_2, \quad (2.111)$$

where  $\bar{D}_{2j_1, j_2}^{i_1, i_2} = D_{2j_1, i_2}^{i_1, j_2}$  and  $\delta^2 = \delta_{j_1}^{i_1} \wedge \delta_{j_2}^{i_2}$ .

Similar to the 1-positivity conditions the 2-positivity conditions require that the occupation number of particle pairs, hole pairs, or particle-hole pairs in any two-particle state is always positive which is essential for the  $N$ -representability of the 2-RDM. In contrast to the 1-positivity of the 1-RDM, however, the 2-positivity conditions are necessary but not sufficient for  $N$ -representability of the 2-RDM. Further positivity conditions and a constructive method to generate a complete set of  $N$ -representability conditions for the 2-RDM is reviewed in [Appendix D](#).

## 2.5.2. Purifications

In the previous chapter we reviewed the conditions arising from  $N$ -representability on the 2-RDM. These conditions are necessary to guarantee that the 2-RDM describes a physical state of the many-body system. Since the equations of motion in [Equation 2.43](#) determine the propagation of the exact 2-RDM the  $N$ -representability is fulfilled at all times. This means that by starting from an  $N$ -representable 2-RDM the time evolution incorporating the exact 3-RDM leaves the  $N$ -representability of the 2-RDM unchanged. However, as it turns out, the reconstruction of the 3-RDM via the functional [Equation 2.62](#) introduces an error that causes the 2-RDM to violate  $N$ -representability after few iterations (see the results in [subsection 3.3.2](#) below). Using an intuitive picture, the set of  $N$ -representable 2-RDMs forms a subspace of all matrices in which the exact 2-RDM propagates. The error due to the approximation of the 3-RDM, however, causes the 2-RDM to depart from this subspace. To prevent the 2-RDM from leaving the subspace a procedure that projects the 2-RDM back onto the subspace at each time step is essential. Such a procedure is called purification. Several types of purifications have been discussed in literature and are used primarily for the iterative solution of the second order CSE to find a self-consistent  $N$ -representable solution for the ground state of molecules [[38](#), [39](#)].

The purification procedure that we follow was introduced by Mazziotti [[38](#)]. Starting point is the following decomposition of antisymmetric hermitian matrices into three components which contain different information on the contractions

$$D_2 = D_{2;0} + D_{2;1} + D_{2;2}, \quad (2.112)$$

with

$$D_{2;0} = \frac{2\text{Tr}(D_2)}{r(r-1)}\delta^2 \quad (2.113)$$

$$D_{2;1} = \frac{4}{r-2}D_1 \wedge \delta - \frac{4\text{Tr}(D_2)}{r(r-2)}\delta^2 \quad (2.114)$$

$$D_{2;2} = D_2 - \frac{4}{r-2}D_1 \wedge \delta - \frac{4\text{Tr}(D_2)}{(r-1)(r-2)}\delta^2. \quad (2.115)$$

Central property of this decomposition is that the contraction into the one-particle subspace vanishes for  $D_{2;2}$

$$\sum_k D_{2;2}^{i_1,k} = 0, \quad (2.116)$$

such that the complete information on the trace as well as the 1-RDM is contained in  $D_{2;0}$  and  $D_{2;1}$ . Since the definition is basis independent this decomposition is invariant under unitary basis transformations and is called unitary decomposition for this reason.

The purification scheme is now divided into two steps. In the first step the 1-RDM is purified by enforcing the eigenvalues to lie in the interval  $[0, 1]$  which is sufficient for the 1-RDM to be  $N$ -representable. Following Mazziotti this is achieved by setting all negative eigenvalues to zero and adding their sum to the largest eigenvalue before setting all eigenvalues larger one to one and subtracting their sum from the smallest eigenvalue. This assures that the norm of the new 1-RDM,  $\tilde{D}_1$ , remains invariant. To obtain the new 2-RDM,  $\tilde{D}_2$ , which contracts to the new 1-RDM we employ the unitary decomposition and replace  $D_1$  by  $\tilde{D}_1$ :

$$\tilde{D}_2 = D_2 + \frac{4}{r-2}(\tilde{D}_1 - D_1) \wedge \delta + \text{Tr}(\tilde{D}_1 - D_1)\delta^2 \quad (2.117)$$

As a technical side remark we note that if the traces of  $D_1$  and  $\tilde{D}_1$  are not exactly equal but differ by a small complex number due to numerical inaccuracy, the error doubles each time the purification is applied because of the term  $\text{Tr}(\tilde{D}_1 - D_1)\delta^2$ . To suppress this exponential accumulation of error the trace of  $D_1$  and  $\tilde{D}_1$  must be exactly equal.

The second step in the purification scheme involves the addition of an appropriate correction term to  $\tilde{D}_2$

$$D'_2 = \tilde{D}_2 + D_{\text{cor}}, \quad (2.118)$$

such that  $D'_2$  fulfills at least some of the  $N$ -representability conditions. The form of the correction matrix  $D_{\text{cor}}$  depends on the specific procedure employed. In a first step, by imposing the  $D$ -condition all negative eigenvalues  $\epsilon_i$  of the 2-RDM have to be removed from  $\tilde{D}_2$ . This can be achieved by subtracting the matrix  $\epsilon_i \nu_i \nu_i^\dagger = \epsilon_i A_i$  from the 2-RDM

$$D'_2 = \tilde{D}_2 + D_{\text{cor}} = \tilde{D}_2 - \sum_i \epsilon_i A_i, \quad (2.119)$$

where  $\nu_i$  are the eigenvectors corresponding to negative eigenvalues  $\epsilon_i$  and  $A_i$  denotes the dyadic product of the eigenvectors, i.e., the projector onto the corresponding eigenspace. The resulting



2-RDM is positive semidefinite, however, in general such a matrix will modify the trace as well as the 1-RDM which is in conflict with the purification of the first step. Therefore,  $D_{\text{cor}}$  has to vanish upon contraction into the one-particle subspace. Once again we employ the unitary decomposition for the matrix  $A_i = \nu_i \nu_i^\dagger$  to obtain the component  $A_{i;2}$ . Contrary to  $A_i$ , the addition of  $A_{i;2}$

$$D'_2 = \tilde{D}_2 + \sum_i \alpha_i A_{i;2} \quad (2.120)$$

does not alter the trace or the 1-RDM. The  $\alpha_i$  are determined through the system of linear equations

$$\text{Tr}(A_i D'_2) = 0. \quad (2.121)$$

This procedure creates a  $D'_2$  whose negative eigenvalues are smaller than those of  $\tilde{D}_2$  but, in general, do not vanish. Only after several iterations the resulting  $D'_2$  satisfies the  $D$ -condition without modifying the trace or the 1-RDM. However, enforcing the  $D$ -condition via [Equation 2.120](#), in general, enhances the violation of other conditions like the  $Q$ -condition. Fortunately it is possible to impose the  $D$  and the  $Q$ -condition at the same time. One can exploit the fact that altering the 2-RDM by  $D_{\text{cor}}$  with vanishing contraction into the one-particle space modifies 2-hole-RDM by exactly the same matrix and vice versa:

$$Q'_2 = \tilde{Q}_2 + D_{\text{cor}}. \quad (2.122)$$

This result follows from the formula

$$Q_2 = \delta^2 - 2\delta \wedge D_1 + D_2, \quad (2.123)$$

and can be used in order to impose simultaneously both the  $D$ -condition as well as the  $Q$ -condition

$$D'_2 = \tilde{D}_2 + \sum_i \alpha_i A_{i;2} + \sum_i \beta_i B_{i;2} \quad (2.124)$$

$$Q'_2 = \tilde{Q}_2 + \sum_i \alpha_i A_{i;2} + \sum_i \beta_i B_{i;2} \quad (2.125)$$

by solving the augmented system of linear equations

$$\text{Tr}(A_i D'_2) = 0 \quad (2.126)$$

$$\text{Tr}(B_i Q'_2) = 0, \quad (2.127)$$

where the matrix  $B_i = \mu_i \mu_i^\dagger$  corresponds to the negative eigenvalues  $Q_2$ . As previously, this purification leads to a reduction of the negative eigenvalues and after iterative application the resulting 2-RDM,  $D'_2$ , ultimately fulfills both the  $D$  and the  $Q$  condition.

We have extended Mazziotti's purification procedure by incorporating also the  $G$ -condition. Contrary to the 2-hole RDM the addition of a matrix with vanishing one-particle contraction to the 2-RDM does not modify the  $G$ -matrix simply by addition of  $D_{\text{cor}}$  but according to

$$G'_2 = G_2 + \bar{D}_{\text{cor}}. \quad (2.128)$$

Consequently, Equation 2.124 and Equation 2.120 can be extended by

$$D'_2 = D_2 + \sum_i \alpha_i A_{i;2} + \sum_i \beta_i B_{i;2} + \sum_i \gamma_i C_{i;2} \quad (2.129)$$

$$Q'_2 = Q_2 + \sum_i \alpha_i A_{i;2} + \sum_i \beta_i B_{i;2} + \sum_i \gamma_i C_{i;2} \quad (2.130)$$

$$G'_2 = G_2 + \sum_i \alpha_i \bar{A}_{i;2} + \sum_i \beta_i \bar{B}_{i;2} + \sum_i \gamma_i \bar{C}_{i;2}, \quad (2.131)$$

where  $C_{i;2}$  is obtained from  $C_i = \hat{\mathcal{A}}[\tilde{C}_i]$  which is the anti-symmetrized matrix  $\tilde{C}_i = \sigma_i \sigma_i^\dagger$  with  $\sigma_i$  being the negative eigenvectors of  $G$ . The anti-symmetrization is necessary because  $G_2$  and thereby  $\tilde{C}_i$  do not have any symmetry under index permutation since holes and particles are distinguishable. Therefore, the addition of  $\tilde{C}_{i;2}$  would violate the symmetry of the 2-RDM if not anti-symmetrized. The system of linear equations determining the coefficients  $\alpha_i, \beta_i$  and  $\gamma_i$  is

$$\text{Tr}(A_i D'_2) = 0 \quad (2.132)$$

$$\text{Tr}(B_i Q'_2) = 0 \quad (2.133)$$

$$\text{Tr}(\tilde{C}_i G'_2) = 0. \quad (2.134)$$

Despite the complicated form for the  $G$ -condition, Equations (2.132)-(2.134) converge after several iterations such that  $D'_2$  fulfills both the  $D$  and  $Q$ -condition, as well as the  $G$ -condition.

# 3. Results

In the first part of this chapter we review basic properties of one-dimensional (1D) multi-electron model systems, in particular, the lithium hydride (LiH) molecule. We calculate the ground state of LiH which serves as the initial state for the time propagation. For the ground state we show two-particle properties such as the probability distribution for the distance between two particles and we demonstrate the high quality of the reconstruction functional. In the second part we apply the time-dependent 2-RDM method to the laser driven electron dynamics of the 1D LiH molecule. We show that the accumulation of error in the 2-RDM leads to a strong violation of the  $N$ -representability creating instabilities in the time propagation. These instabilities can be suppressed by implementing a purification scheme to the propagation. Finally, we present challenges associated with a self-consistent propagation of 2-RDM elements and orbitals, and discuss in [chapter 4](#) how these difficulties might be overcome. Throughout this chapter we use atomic units ( $e = 1, m_e = 1, \hbar = 1$ ).

## 3.1. Basic properties of the 1D LiH

One-dimensional atoms and molecules serve as a numerically efficient testing ground for full three-dimensional (3D) calculations and have been used in the past to study various atomic properties like the double ionization of helium [40] and the response of lithium hydride in strong laser fields [32, 41]. Such 1D model calculations are capable of demonstrating advantages and limitations of the method under investigation but do not necessarily lead to agreement with full 3D calculations [42]. The Hamiltonian of 1D molecules consisting of  $M$  nuclei fixed at positions  $R_a$  and  $N$  electrons in the time-dependent external laser field  $E(t)$  within dipole approximation in length gauge is given by

$$H(z_1, \dots, z_N) = \sum_i^N \left[ -\frac{1}{2} \frac{\partial^2}{\partial z_i^2} - \sum_a^M \frac{Z_a}{\sqrt{(z_i - R_a)^2 + c}} - E(t)z_i \right] + \sum_{i < j}^N \frac{1}{\sqrt{(z_i - z_j)^2 + d}}, \quad (3.1)$$

where  $z_i$  are the spacial coordinates of electrons. The softening of the Coulomb interaction via the parameters  $c, d$  is necessary because in 1D the ground state energy does not converge for  $c = 0, d = 0$ . In general, these parameters are empirical quantities which can be chosen in such a way that the ground state energy and ionization energies correspond to the exact results in 3D.

For the numerical implementation, we solve the orbital equations of motion [Equation 2.64](#) on an equidistant grid with 2000 points and grid spacing  $\Delta z = 0.1$ . The second derivative in the kinetic term is evaluated in eight-order finite difference. We employ the Runge-Kutta propagator of fourth order to time propagation in real and imaginary time. These parameters are used throughout the thesis unless stated otherwise.

### 3.1.1. The ground state of LiH

The LiH molecule is one of the simplest multi-electron molecules and has been studied in the context of electron dynamics in strong laser fields (see, e.g., [32] and references therein). The bond length of LiH is given by  $a = 2.3$  and the nuclear charge of lithium and hydrogen is  $Z_{\text{Li}} = 3$  and  $Z_{\text{H}} = 1$ , respectively (see [Figure 3.1](#)).

The parameters  $c, d$  entering the soft Coulomb potential are determined by two basic conditions. First, the ground state energy within the 1D model has to be in agreement with the ground state energy obtained from 3D calculations. Second, the total energy consisting of electronic energy and configuration energy of the cores as a function of the bond length  $a$ ,

$$E(a) = \langle \Psi | H(a) | \Psi \rangle + \frac{3}{a}, \quad (3.2)$$

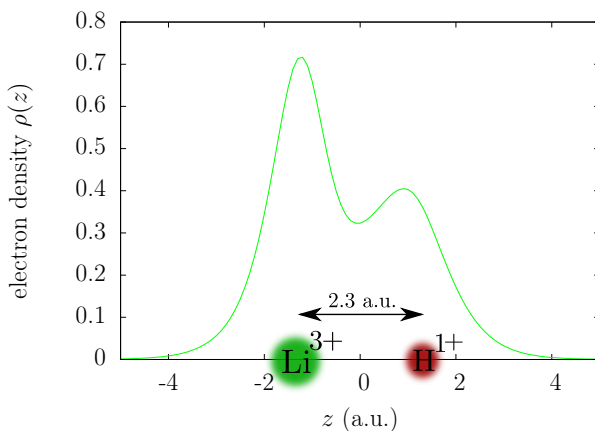
must have a minimum at the actual bond length of  $a = 2.3$ . These two conditions are fulfilled for  $c = 0.5$  and  $d = 1$  [32].

The ground state of LiH is determined by imaginary time propagation within the MCTDHF method incorporating eight spin orbitals (i.e., four spatial orbitals). The ground state of LiH is a spin singlet state. Since the Hamiltonian [Equation 3.1](#) does not couple to the spin of the electrons the spin singlet state is conserved during propagation.

A common observable to investigate the ground state properties is the spinless one-particle densities  $\rho(z_1)$

$$\rho(z_1) = D(z_1 \uparrow; z_1 \uparrow) + D(z_1 \downarrow; z_1 \downarrow). \quad (3.3)$$

The spinless one-particle density  $\rho(z_1)$ , or briefly the electron density, describes the average number of particles at the position  $z_1$  irrespective of their spin configuration. The electron density for the ground state shows a distinct maximum near the Li atom (see [Figure 3.1](#)) which originates from a deeply bound spatial core orbital occupied by two electrons at the lithium core. The remaining two electrons occupy the spatial valence orbital which is responsible for the chemical bond.



**Figure 3.1.:** Electron density for the 1D LiH molecule. The bond length  $a = 2.3$  between the lithium core and the hydrogen core is depicted. Most of the electrons are located near the lithium core, see the large peak in the electron density near  $z = -1.15$ .

### 3.1.2. Two-particle properties of the ground state

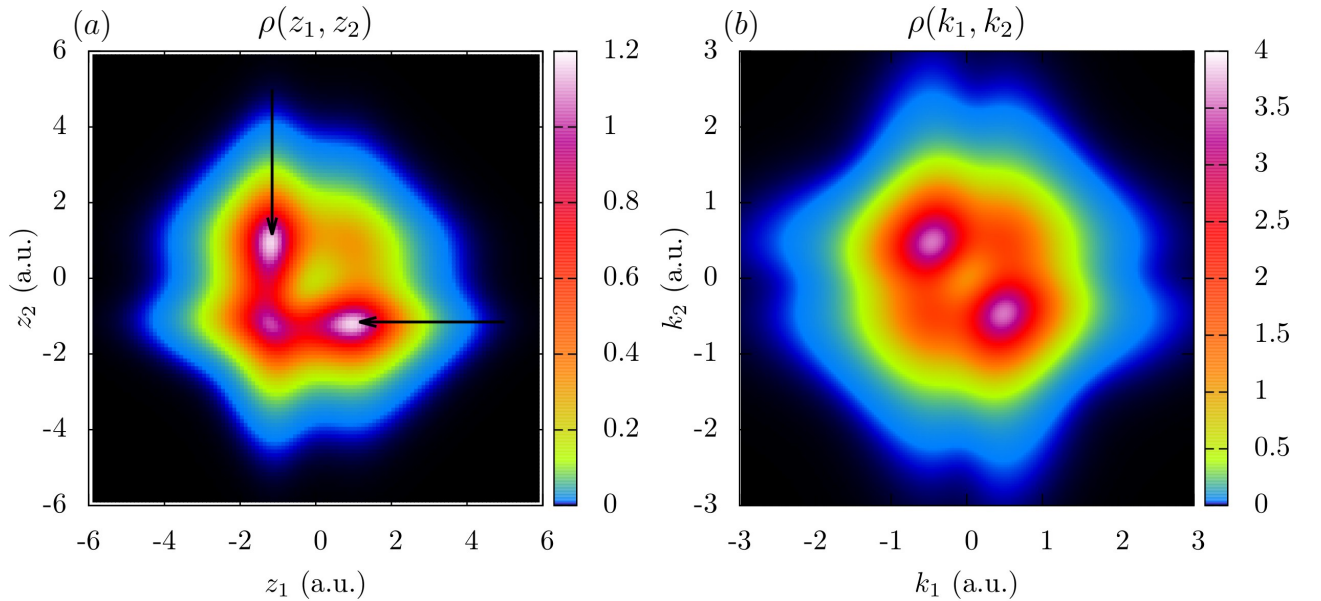
To investigate the two-particle ground state properties beyond those derivable from the electron density we consider the spinless two particle density  $\rho(z_1, z_2)$

$$\begin{aligned} \rho(z_1, z_2) = & D(z_1 \uparrow z_2 \uparrow; z_1 \uparrow z_2 \uparrow) + D(z_1 \uparrow z_2 \downarrow; z_1 \uparrow z_2 \downarrow) \\ & + D(z_1 \downarrow z_2 \uparrow; z_1 \uparrow z_2 \uparrow) + D(z_1 \downarrow z_2 \downarrow; z_1 \downarrow z_2 \downarrow). \end{aligned} \quad (3.4)$$

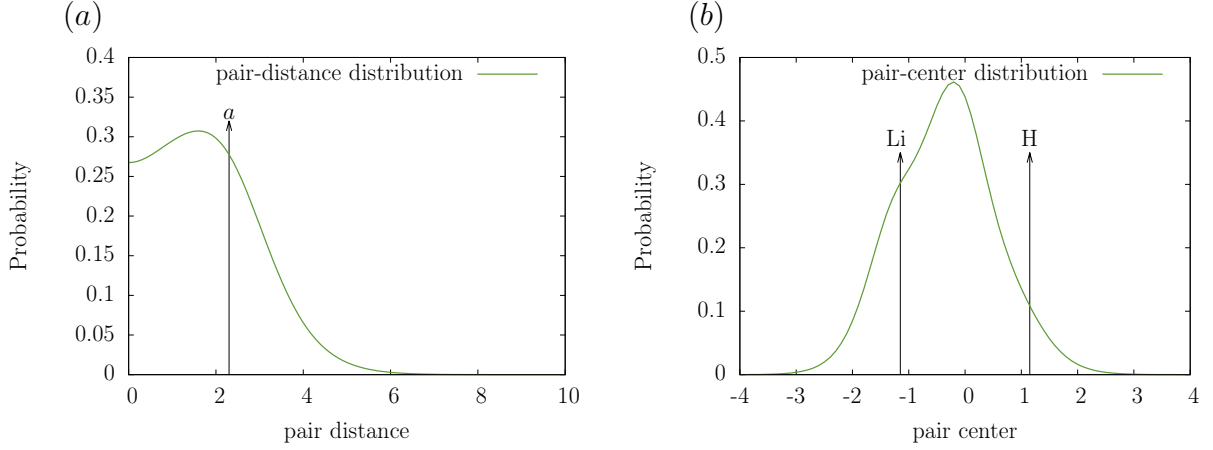
In general, the two-particle density  $\rho(z_1, z_2)$  contains significantly more information than the electron density since it reveals details on the pair distribution within the LiH molecule (see [Figure 3.2](#)). For the LiH molecule most of the pairs are distributed such that one electron is located near the lithium core and the other is located near the hydrogen core. We call these pairs inter-atomic pairs. This configuration is energetically favourable since the separation in space leads to a reduction of Coulomb repulsion. To study the average spacing between particles in more detail we introduce the pair-distance distribution, i.e., the probability distribution to find a pair with given distance  $l$ :

$$P_d(l) = \frac{2}{N(N-1)} \int \rho(z, z+l) dz. \quad (3.5)$$

This distribution has a pronounced peak near the bond length of LiH [see [Figure 3.3 \(a\)](#)]. The deviation of the maximum from the bond length is caused by the contribution of pairs located at the lithium core. We note that the reduced probability to find two particles close to each



**Figure 3.2.:** The pair-density distribution in (a) coordinate space and (b) momentum space for the ground state of the LiH molecule. The density distribution in coordinate space (a) shows distinct peaks for inter-atomic pairs where one electron is close to the lithium core while the other one is close to the hydrogen core (marked by arrows). The peaks in the momentum distribution (b) show that counter propagating pairs are most probable (see text).



**Figure 3.3.:** Probability distributions associated with pairs. Figure (a) shows the probability distribution to find a pair with a given distance. The peak of the distribution is shifted towards smaller distances compared to the bond length between lithium and hydrogen depicted by an arrow due to the contribution of strongly localized pairs at the site of the lithium. Figure (b) shows the distribution for the center of mass of the pairs. The dominant contribution is located approximately in the middle of the bond line between the lithium and the hydrogen core depicted by arrows. The asymmetry of the distribution is caused by the contribution of deeply bound pairs located at the lithium core.

other represented by the minimum at vanishing distance [see [Figure 3.3 \(a\)](#)] is a very general property of fermionic systems caused by the Pauli exclusion principle and the interaction and is referred to as the exchange-correlation hole. Another probability distribution that reveals the presence of inter-atomic pairs between lithium and hydrogen is the distribution of the pair center. The pair-center distribution which we define as

$$P_c(z_c) = \frac{2}{N(N-1)} \int \rho(z, z_c - z) dz, \quad (3.6)$$

determines the distribution of the center of mass averaged over all pairs regardless of their spin.  $P_c(z_c)$  has a maximum approximately in the middle between both cores [see [Figure 3.3 \(b\)](#)].

To gain more insight into the momentum configuration of the ground state we consider the two-particle momentum distribution

$$\begin{aligned} \rho(k_1, k_2) = & D(k_1 \uparrow k_2 \uparrow; k_1 \uparrow k_2 \uparrow) + D(k_1 \uparrow k_2 \downarrow; k_1 \downarrow k_2 \uparrow) \\ & + D(k_1 \downarrow k_2 \uparrow; k_1 \uparrow k_2 \downarrow) + D(k_1 \downarrow k_2 \downarrow; k_1 \downarrow k_2 \downarrow), \end{aligned} \quad (3.7)$$

where  $D(k_1 k_2; k_1 k_2)$  is defined as the Fourier transform of the 2-RDM. Note that  $\rho(k_1, k_2)$  is not the Fourier transform of  $\rho(z_1, z_2)$ . The symmetry of the pair momentum distribution under point reflection at the origin,  $(k_1, k_2) \rightarrow (-k_1, -k_2)$  [see [Figure 3.2 \(b\)](#)], follows from the fact that a non-degenerate ground state can always be described by a real wave function. As a consequence, the density matrix of the ground state and the RDMs are real quantities. Therefore, the Fourier transform of the RDMs for the ground state has the property

$$\begin{aligned} D(k_1 k_2; k'_1 k'_2) &= D^*(-k_1, -k_2; -k'_1, -k'_2) \\ &= D(-k'_1, -k'_2; -k_1, -k_2). \end{aligned} \quad (3.8)$$

For the ground state of LiH the pair-momentum distribution [Figure 3.2 \(b\)](#) shows that most of the pairs have opposite momenta, i.e., the largest contribution originates from pairs with vanishing total momentum and finite relative momentum. For LiH this effect can be explained in the Hartree-Fock limit whereas a similar but less pronounced effect in the pair momentum distribution of Helium relies on the correlation of the ground state [\[43\]](#). In the Hartree-Fock limit the wave function is a single determinant build up by two spatial orbitals  $\phi_1(z), \phi_2(z)$  each fully occupied with two electrons of opposite spin. The spinless 2-RDM of such a wave function is given by

$$\begin{aligned} D(z_1 z_2; z'_1 z'_2) &= \phi_1(z_1) \phi_1(z_2) \phi_1^*(z'_1) \phi_1^*(z'_2) + \phi_2(z_1) \phi_2(z_2) \phi_2^*(z'_1) \phi_2^*(z'_2) \\ &+ \phi_1(z_1) \phi_2(z_2) \phi_1^*(z'_1) \phi_2^*(z'_2) + \phi_2(z_1) \phi_1(z_2) \phi_2^*(z'_1) \phi_1^*(z'_2) \\ &+ \left( \phi_1(z_1) \phi_2(z_2) - \phi_2(z_1) \phi_1(z_2) \right) \left( \phi_1^*(z'_1) \phi_2^*(z'_2) - \phi_2^*(z'_1) \phi_1^*(z'_2) \right), \end{aligned} \quad (3.9)$$

which is obtained by employing [Equation A.3](#) in [Appendix A](#) and summing over the spin configuration. The corresponding momentum distribution is

$$\begin{aligned} \rho(k_1, k_2) &= |\phi_1(k_1)|^2 |\phi_1(k_2)|^2 + |\phi_2(k_1)|^2 |\phi_2(k_2)|^2 \\ &+ 2|\phi_1(k_1)|^2 |\phi_2(k_2)|^2 + 2|\phi_2(k_1)|^2 |\phi_1(k_2)|^2 \\ &- \phi_2(k_1) \phi_1(k_2) \phi_1^*(k_1) \phi_2^*(k_2) - \phi_1(k_1) \phi_2(k_2) \phi_2^*(k_1) \phi_1^*(k_2). \end{aligned} \quad (3.10)$$

In the Hartree-Fock approximation of the LiH ground state  $\phi_1(z)$  is the deeply bound spatial core orbital at the lithium core while  $\phi_2(z)$  is the spatial valence orbital that is responsible for the chemical bond. A direct calculation shows that  $\phi_1(z)$  has the form of a Gaussian located at the lithium core while  $\phi_2(z)$  resembles the first excited state of the harmonic oscillator with one node in between both cores (see [\[32\]](#)). Consequently,  $\phi_1(k)$  is symmetric and  $\phi_2(k)$  is antisymmetric. Thus, the last line in [Equation 3.10](#) gives a negative contribution for  $k_1 = k_2$

$$\begin{aligned} \rho(k_1 = k_2) &= |\phi_1(k_1)|^2 |\phi_1(k_1)|^2 + |\phi_2(k_1)|^2 |\phi_2(k_1)|^2 \\ &+ 2|\phi_1(k_1)|^2 |\phi_2(k_1)|^2 + 2|\phi_2(k_1)|^2 |\phi_1(k_1)|^2 \\ &- |\phi_1(k_1)|^2 |\phi_2(k_1)|^2 - |\phi_2(k_1)|^2 |\phi_1(k_1)|^2 \end{aligned} \quad (3.11)$$

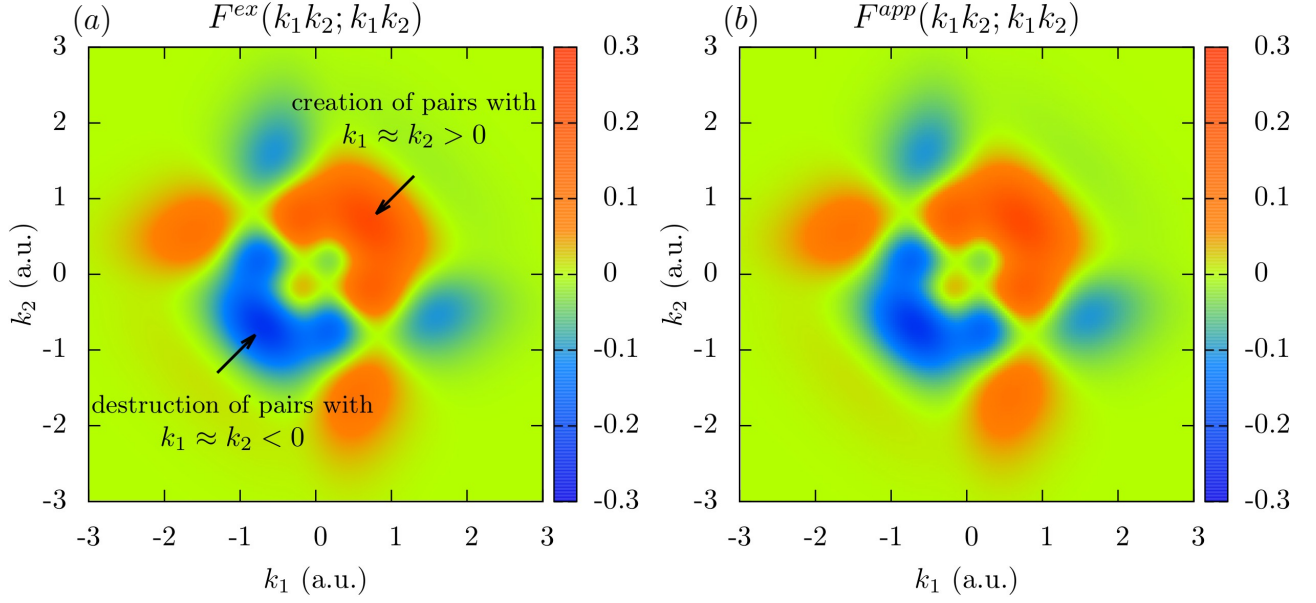
while it is positive for  $k_1 = -k_2$

$$\begin{aligned} \rho(k_1 = -k_2) &= |\phi_1(k_1)|^2 |\phi_1(k_1)|^2 + |\phi_2(k_1)|^2 |\phi_2(k_1)|^2 \\ &+ 2|\phi_1(k_1)|^2 |\phi_2(k_1)|^2 + 2|\phi_2(k_1)|^2 |\phi_1(k_1)|^2 \\ &+ |\phi_1(k_1)|^2 |\phi_2(k_1)|^2 + |\phi_2(k_1)|^2 |\phi_1(k_1)|^2. \end{aligned} \quad (3.12)$$

### 3.1.3. The $F$ -operator for the ground state

A crucial quantity of the 2-RDM method is the  $F$ -operator [Equation 2.41](#). The  $F$ -operator is an anti-hermitian operator. For the ground state the  $F$ -operator in coordinate space is a real quantity leading, in combination with anti-hermicity, to antisymmetric behaviour under point reflection at the origin in momentum space,  $(k_1, k_2) \rightarrow (-k_1, -k_2)$ , (see [Figure 3.4](#)):

$$\begin{aligned} F(k_1 k_2; k'_1 k'_2) &= F^*(-k_1, -k_2; -k'_1, -k'_2) \\ &= -F(-k'_1, -k'_2; -k_1, -k_2). \end{aligned} \quad (3.13)$$



**Figure 3.4.:** The imaginary diagonal elements of (a) the exact  $F$ -operator and (b) the approximated  $F$ -operator from the reconstructed 3-RDM Equation 2.62. The positive contribution for pairs with positive total momentum shows that the interactions with the surrounding particles create pairs moving collectively toward the hydrogen core.

In particular, for systems with reflection symmetry all physical quantities including the  $F$ -operator stay invariant under the replacement  $(k_1, k_2) \rightarrow (-k_1, -k_2)$  which requires the diagonal elements of the  $F$ -operator in momentum representation  $F(k_1 k_2; k_1 k_2)$  to vanish for the ground state of such systems, e.g. the beryllium atom. We note that in coordinate space the diagonal of the  $F$ -operator always vanishes, i.e.  $F(x_1 x_2; x_1 x_2) = 0$  because  $I(x_1 x_2; x_1 x_2)$  in Equation 2.41 is a real quantity. The fact that  $F(k_1 k_2; k_1 k_2)$  in Figure 3.4 does not vanish is, therefore, a direct consequence of the broken parity symmetry of the LiH molecule. This effect can be understood by an intuitive picture. Consider the equations of motion in momentum representation:

$$i\hbar\partial_t D(k_1 k_2; k_1 k_2; t) = [H, D_2](k_1 k_2; k_1 k_2; t) + 3F(k_1 k_2; k_1 k_2; t). \quad (3.14)$$

The stationarity of the 2-RDM in the ground state leads to the condition

$$[H, D_2](k_1 k_2; k_1 k_2; t) + 3F(k_1 k_2; k_1 k_2; t) = 0. \quad (3.15)$$

this condition can be interpreted as the interplay between two competing mechanisms. The commutator  $[H, D_2]$  describes the change in the momentum distribution of individual pairs in the Coulomb field of the cores without the influence of surrounding particles and it can be separated into the contribution of free electron pairs  $[H_{\text{free}}, D_2]$  and the potential generated by the lithium and the hydrogen core  $[V_{\text{core}}, D_2]$ :

$$[H, D_2] = [H_{\text{free}}, D_2] + [V_{\text{core}}, D_2]. \quad (3.16)$$

In a qualitative picture the term  $[H_{\text{free}}, D_2]$  describes the motion of free electron pairs while the contribution  $[V_{\text{core}}, D_2]$  attracts the pairs towards the lithium core creating pairs with negative



total momentum. This motion towards the lithium atom is compensated by  $F(k_1 k_2; k_1 k_2)$  which accounts for the collisions of the pairs with the surrounding particles. The interaction of the pair with the electron cloud at the Li atom repulses the pair into the opposite direction. This effect is visible in the momentum representation of the  $F$ -operator as a maximum for positive total momenta and minimum for negative total momenta (see [Figure 3.4](#)). In the ground state these two competing mechanisms are in equilibrium, i.e., for every pair that leaves the momentum configuration  $(k_1, k_2)$  due to the interaction with the environment the core potential creates such a pair.

The number of particle pairs that have exactly opposite momenta, i.e.,  $k_1 = -k_2$  are unaffected by collisions with the surrounding particles since the  $F$ -operator has a nodal line along  $k_1 = -k_2$ . To understand this effect consider that the replacement  $(k_1, k_2) \rightarrow (-k_2, -k_1)$  in momentum space can be interpreted as a combination of particle exchange and time reversal. Therefore, in the ground state every process leading to the formation of a pair with momentum configuration  $(k_1, -k_1)$  has by time reversal symmetry a compensating process with same probability.

The  $F$ -operator is crucially dependent on the 3-RDM via

$$F(x_1 x_2; x'_1 x'_2; t) = I(x_1 x_2; x'_1 x'_2; t) - I^*(x'_1 x'_2; x_1 x_2; t), \quad (3.17)$$

where

$$I(x_1 x_2; x'_1 x'_2; t) = \int (V_{\text{int}}(x_1, x_3) + V_{\text{int}}(x_2, x_3)) D(x_1 x_2 x_3; x'_1 x'_2 x_3; t) dx_3. \quad (3.18)$$

Central point for the propagation within the 2-RDM method is the reconstruction of the 3-RDM via [Equation 2.62](#). Replacing the 3-RDM in [Equation 3.18](#) by the reconstructed 3-RDM yields the approximated  $F$ -operator  $F^{\text{app}}$  which can be written as a functional of the 2-RDM  $F^{\text{app}}[D_2]$ . The comparison between  $F^{\text{app}}$  and the exact  $F$ -operator  $F^{\text{ex}}$  constructed with the exact 3-RDM shows that there is no visual difference between both quantities for the present system (see [Figure 3.4](#)). In [section 3.3](#) we will introduce a quantitative measure for the quality of the approximated  $F$ -operator and study its time evolution.

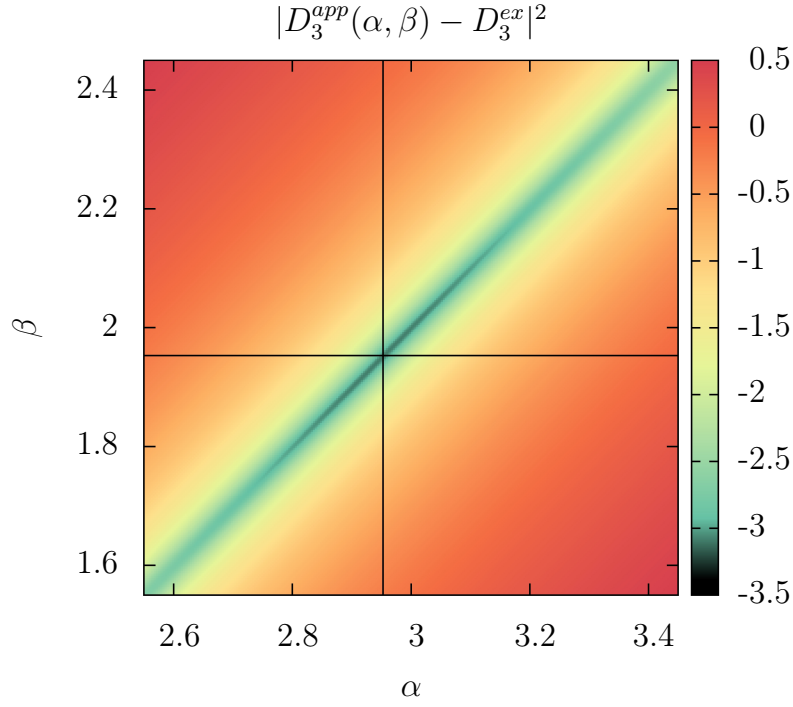
### 3.1.4. Quality of the 3-RDM reconstruction

In this subsection we study the quality of the 3-RDM reconstruction for the ground state in more detail. As a first step, we set the coefficients in the reconstruction [Equation 2.62](#) to arbitrary parameters  $\alpha, \beta$

$$D_3^{\text{app}} = \alpha D_2 \wedge D_1 - \beta D_1^3. \quad (3.19)$$

The derivation of the reconstruction functional based on cumulants suggests that the best reconstruction is found for the choice  $\alpha = 3, \beta = 2$ . To check this result we introduce the square distance

$$|D_3^{\text{app}}(\alpha, \beta) - D_3^{\text{ex}}|^2 = \sum_{i_1, i_2, i_3} \sum_{j_1, j_2, j_3} |D_3^{\text{app}}(\alpha, \beta)_{j_1, j_2, j_3}^{i_1, i_2, i_3} - D_3^{\text{ex}}_{j_1, j_2, j_3}^{i_1, i_2, i_3}|^2, \quad (3.20)$$



**Figure 3.5.:** The comparison between the reconstructed and the exact 3-RDM measured by the absolute square distance  $|D_3^{app}(\alpha, \beta) - D_3^{ex}|^2$  (see Equation 3.20).

as a measure for the accuracy of the reconstruction. Minimizing  $|D_3^{app}(\alpha, \beta) - D_3^{ex}|^2$  as a function of the coefficients  $\alpha, \beta$  for the ground state of LiH gives  $\alpha = 2.953, \beta = 1.953$  (see Figure 3.5). This result is in very good agreement with the result  $\alpha = 3, \beta = 2$  obtained from cumulant theory. Nonetheless, it is interesting to inquire the source of this deviation. We show in the following that the deviation can be understood by considering that for correlated states the reconstructed 3-RDM is not correctly normalized. The normalization condition on the 3-RDM leads to only one equation which is not sufficient to determine both  $\alpha$  and  $\beta$ , unless the terms  $D_2 \wedge D_1$  and  $D_1^3$  are normalized separately

$$\begin{aligned} D_3^{app} &= \alpha D_2 \wedge D_1 - \beta D_1^3 \\ &= 3 \frac{\binom{N}{3}}{\text{Tr}(D_2 \wedge D_1)} D_2 \wedge D_1 - 2 \frac{\binom{N}{3}}{\text{Tr}(D_1^3)} D_1^3. \end{aligned} \quad (3.21)$$

We find that this renormalization is in excellent agreement with the minimum of the square distance Equation 3.20 with numerical values

$$\alpha = 3 \frac{\binom{N}{3}}{\text{Tr}(D_2 \wedge D_1)} = 2.953 \quad \beta = 2 \frac{\binom{N}{3}}{\text{Tr}(D_1^3)} = 1.953. \quad (3.22)$$

From a computational point of view the improvement obtained by renormalization has no effect on the propagation and since it is computationally more demanding we employ the reconstruction with  $\alpha = 3, \beta = 2$  for the time-propagation of the 2-RDM. Note that the

normalization of  $D_3$  is not required in order to conserve the norm of the 2-RDM during time propagation. The conservation of the norm of the 2-RDM is built in by construction since the  $F$ -operator is traceless for any normalization of  $D_3$  (see Equation 2.41).

The minimum along the line  $\alpha - \beta = 1$  in Figure 3.5 originates from the fact that the Hartree-Fock solution for the ground state of LiH is in good agreement with the actual wave function. For the Hartree-Fock solution, where the wave function is approximated by a single Slater determinant, the reconstruction of the 3-RDM reduces to  $D_3 = D_1^3$  which has the correct norm if  $D_1$  is normalized. Taking into account that  $D_2 = D_1^2$ , the Hartree-Fock 3-RDM is obtained for all parameters satisfying the condition  $\alpha - \beta = 1$ . The correlation of the ground state, however, creates the minimum along  $\alpha - \beta = 1$  (see Figure 3.5).

## 3.2. LiH in intense laser fields

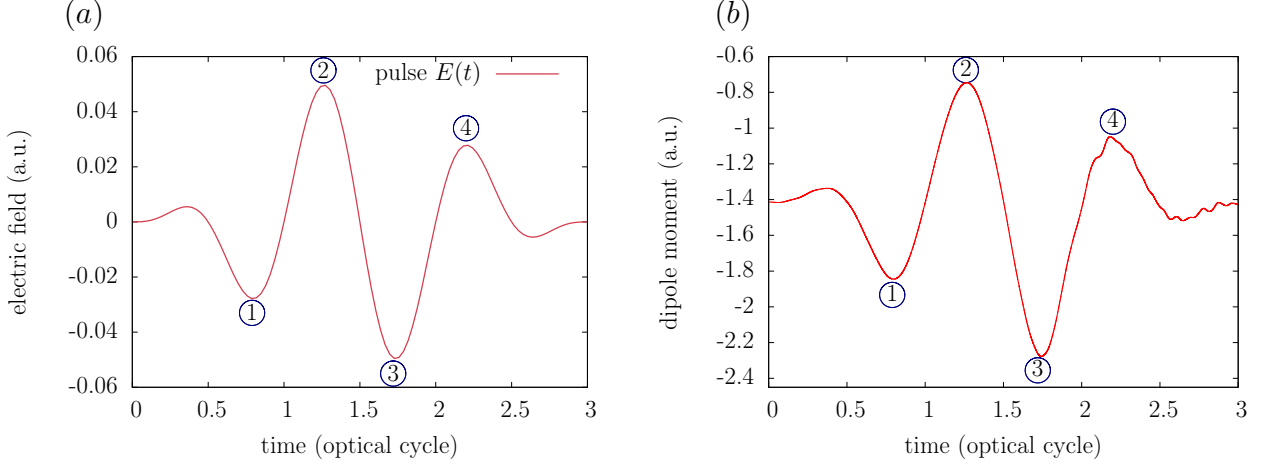
In this section we apply the time-dependent 2-RDM method to the electron dynamics of 1D LiH in strong field laser pulses and compare the results to the full MCTDHF method. A typical pulse shape for laser pulses is given by

$$E(t) = E_0 \sin(\omega t) \sin^2\left(\frac{\omega}{N_c} t\right) \quad 0 \leq t \leq N_c \frac{2\pi}{\omega} \quad (3.23)$$

where  $E_0$  is the amplitude of the electric field,  $\omega$  is the angular frequency, and  $N_c$  is the number of cycles. We use from now on  $\tau = t \frac{2\pi}{\omega}$  as a unit of time which varies between  $0 \leq \tau \leq N_c$ . A characteristic observable for the response of the many-body system to the laser pulse is the induced dipole moment

$$d(t) = d_0 - \int z \rho(z, t) dz, \quad (3.24)$$

which consists of the static dipole  $d_0 = 1 \times 1.15 - 3 \times 1.15$  arising from the strongly polar bond, and the time-dependent contribution depending on the electronic density. For weak light fields the electric field of the electromagnetic wave is much smaller than the electric field strength inside the molecule causing a linear relation between the induced dipole moment and the external field. In this regime the induced dipole moment follows the form of the laser pulse adiabatically and the system remains in the ground state after the pulse. To go beyond this linear regime we use a high-intense laser pulses defined by the parameters  $E_0 = 0.0534$ ,  $\lambda = 2\pi c/\omega = 750$  nm,  $N_c = 3$  [see Figure 3.6 (a)]. For this high intensity the system is excited such that additional Fourier components appear in the dipole moment originating from the interference between the ground state and excited states. These additional frequencies in the dipole moment are the source for electromagnetic waves of higher frequency than the incoming radiation, an effect termed high-harmonic generation [44]. This non-linear effect is visible in the dipole moment of LiH for the given pulse parameters starting at  $\tau \approx 2$  and becomes clearly apparent at the end of the pulse [see Figure 3.6 (b)]. The fluctuations with high frequency are very small such that the average energy is almost unchanged after the pulse. The pulse is strong enough to induce non-linear response but too weak for tunnel ionization.



**Figure 3.6.:** The laser pulse according to Equation 3.23 for the parameters  $E_0 = 0.0534$ ,  $\lambda = 2\pi c/\omega = 750$  nm,  $N_c = 3$ . The local extrema of the pulse are labeled by (1)-(4). (b) The induced dipole moment as a function of time.

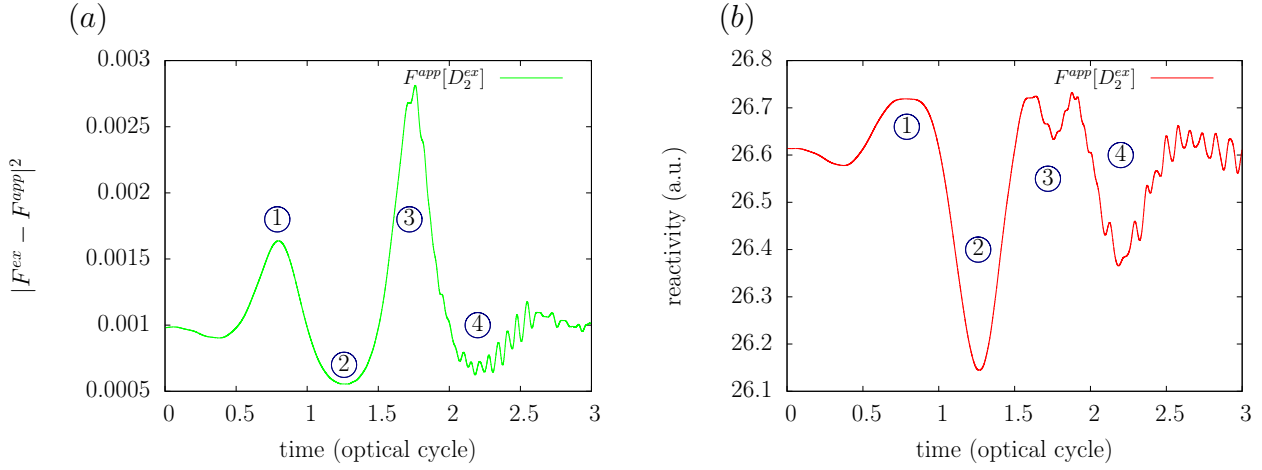
### 3.3. Results of the 2-RDM propagation

The dynamics of the 2-RDM is governed by the coupled set of equations, Equation 2.79 and Equation 2.71, which we reproduce here for convenience

$$i\partial_t D_2 = [H[\phi_i], D_2] + 3F[D_2] \quad (3.25)$$

$$\partial_t \phi_i = f^{\text{MC}}[\phi_i, D_2], \quad (3.26)$$

where from now on  $D_2$  denotes the orbital representation of the 2-RDM and the notation  $H[\phi_i]$  indicates that the Hamiltonian in orbital representation depends on the explicit form of the orbitals. In all calculations presented in this section we use 8 spin orbitals. As shown in [32] this is sufficient for accurate results for all observables discussed in this thesis. We approach the solution of Equation 3.25 and Equation 3.26 such that we stepwise depart from the MCTDHF method with the ultimate goal to solve the above equations self-consistently. We term all objects derived from the MCTDHF calculation as exact. When the  $F$ -operator is calculated from the exact 3-RDM the propagation according to the coupled equations Equation 3.25 and Equation 3.26 is exact. On the first level of approximation, we use the exact propagation of the orbitals obtained from the MCTDHF calculation and approximate the  $F$ -operator according to the reconstruction functional Equation 2.62 where we insert the exact 2-RDM,  $D_2^{\text{ex}}$ . We denote this object as  $F^{\text{app}}[D_2^{\text{ex}}]$ . In this way we estimate the error that arises in the propagation solely due to the inevitable error in the reconstruction functional. On the second level of approximation, we still use the exact propagation of the orbitals but now the approximated 2-RDM,  $D_2^{\text{app}}$ , obtained from the propagation of Equation 3.25, is used to approximate the  $F$ -operator at each time step. We denote the corresponding  $F$ -operator by  $F^{\text{app}}[D_2^{\text{app}}]$ . At this point we investigate the influence of the accumulated error in the 2-RDM on the propagation. On the third level of approximation we couple Equation 3.25 and Equation 3.26 by solving both equations self-consistently. At this level the 2-RDM method is self-consistent and independent from results of the MCTDHF method.



**Figure 3.7.:** (a) The time evolution of the absolute square distance between  $F^{app}$  and  $F^{ex}$  defined in Equation 3.27. The local maxima can be associated with maxima in the reactivity defined in Equation 3.31 and depicted in (b). The numbers (1)-(4) label extreme values of the pulse [see Figure 3.6 (a)]. The fluctuations appearing in (a) as well as in (b) at the time  $\tau \approx 2$  arise from excited states and appear also in the dipole moment [see Figure 3.6 (b)].

### 3.3.1. The first level of approximation

On the first level of approximation, we identify the error in the propagation that arises by the reconstruction of the 3-RDM via Equation 2.62. To measure the error in the approximated  $F$ -operator we employ the square distance

$$|F^{app} - F^{ex}|^2 = \sum_{i_1, i_2} \sum_{j_1, j_2} |F^{app i_1, i_2}_{j_1, j_2} - F^{ex i_1, i_2}_{j_1, j_2}|^2, \quad (3.27)$$

where  $F^{ex}$  is calculated from the exact 3-RDM and  $F^{app}$  is calculated from the 3-RDM reconstructed from the exact 2-RDM. Note that Equation 3.27 is a coordinate independent measure. It turns out that the quality of the reconstruction as measured by Equation 3.27 is very good but not uniform during the laser pulse [see Figure 3.7 (a)]. The approximation is better when the electric field is oriented towards the hydrogen core and worse when the direction is reversed [see Figure 3.7 (a)]. To understand this effect we employ the mean energy  $E_{\text{int}}^{\text{pair}}$  of a pair due to interactions with surrounding particles as a measure for the mean interaction of pairs with their environment. Considering that the expectation values for the interaction energy between two particles is given by

$$\langle \hat{V}_{\text{int}} \rangle = \int V_{\text{int}}(x_1, x_2) D(x_1 x_2; x_1 x_2) dx_1 dx_2, \quad (3.28)$$

and that both electrons of a pair interact with  $(N-2)$  surrounding particles the mean interaction energy between a pair and the surrounding particles can be written as

$$E_{\text{int}}^{\text{pair}} = 2(N-2) \langle \hat{V}_{\text{int}} \rangle. \quad (3.29)$$

In the following we will show that  $E_{\text{int}}^{\text{pair}}$  in atomic units is equivalent to the scattering rate between the pair and the surrounding particles. From subsection 2.3.1 we know that the

scattering rate for the formation of pairs with momentum configuration  $(k_1, k_2)$  is given by  $3I(k_1k_2; k_1k_2)$ . Integrating over all configurations yields the total number of scattering events per time interval between a pair and the surrounding particles. From Equation 2.42 we see that

$$\begin{aligned} 3 \int I(k_1k_2; k_1k_2)dk_1dk_2 &= 3 \int \left( V_{\text{int}}(x_1, x_3) + V_{\text{int}}(x_2, x_3) \right) D(x_1x_2x_3; x_1x_2x_3) dx_1dx_2dx_3 \\ &= 2(N-2) \int V_{\text{int}}(x_1, x_2) D(x_1x_2; x_1x_2) dx_1dx_2 \\ &= 2(N-2) \langle \hat{V}_{\text{int}} \rangle = E_{\text{int}}^{\text{pair}}, \end{aligned} \quad (3.30)$$

where we have used

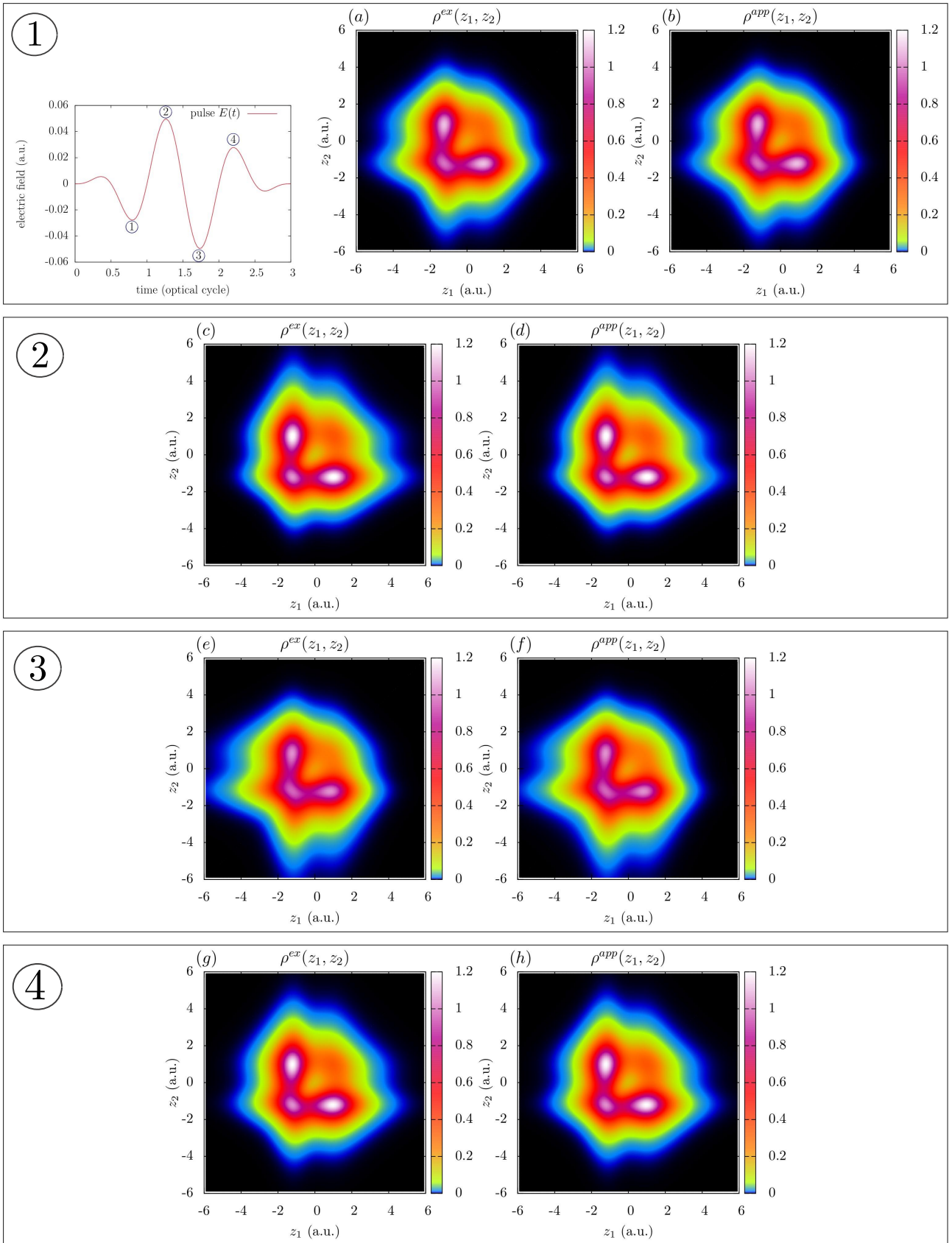
$$\int D(x_1x_2x_3; x_1x_2x_3) dx_3 = \frac{\binom{N}{3}}{\binom{N}{2}} D(x_1x_2; x_1x_2) = \frac{(N-2)}{3} D(x_1x_2; x_1x_2). \quad (3.31)$$

Since  $E_{\text{int}}^{\text{pair}}$  in atomic units can be interpreted as a scattering rate we call this quantity the reactivity. The reactivity is a non-negative quantity that is zero if and only if none of the pairs is influenced by other particles. If the interaction potential  $V_{\text{int}}(|x_1 - x_2|)$  is only dependent on the absolute distance between  $x_1$  and  $x_2$  the expression for the reactivity can be further simplified by using the particle distance distribution  $P(l)$  (see Equation 3.6):

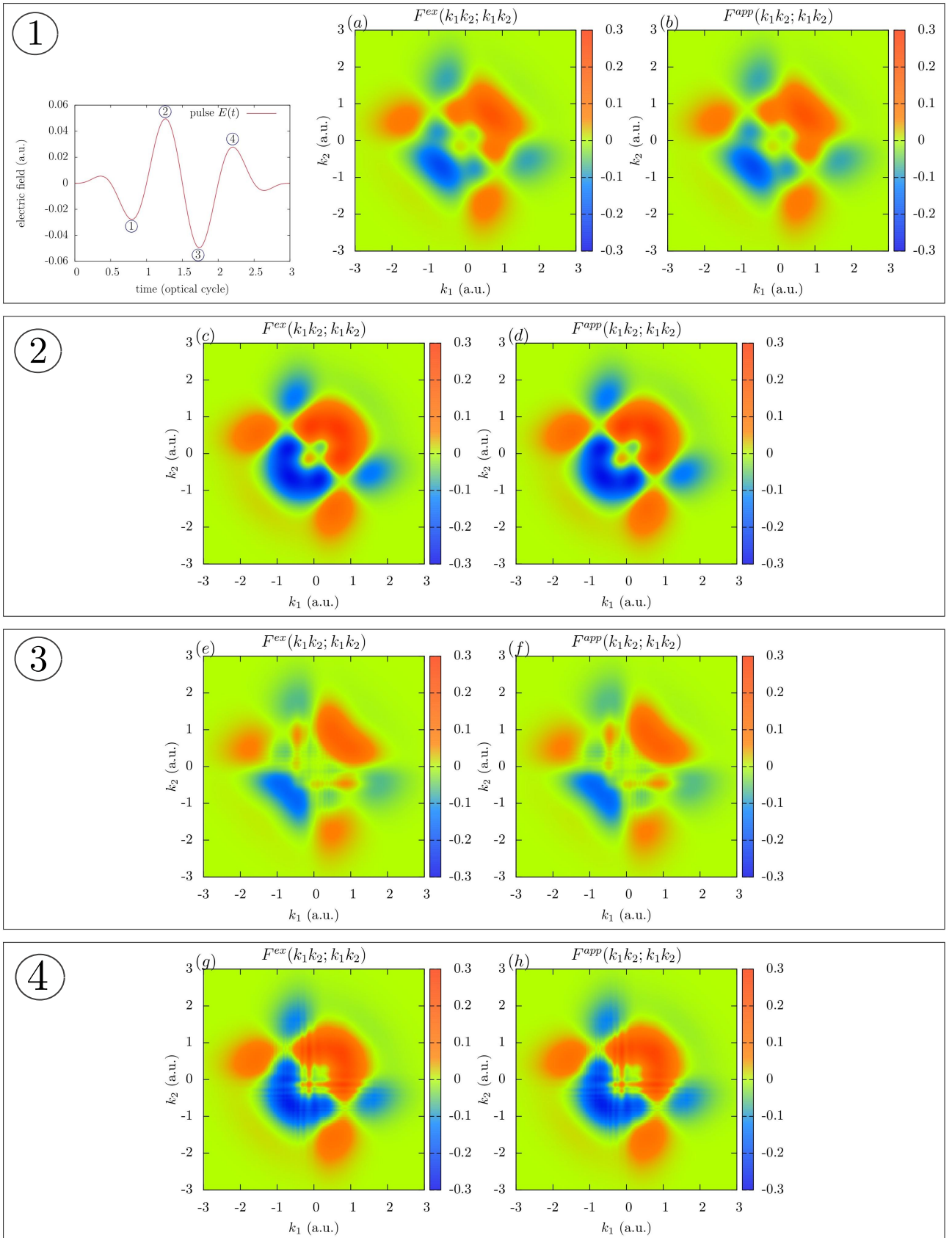
$$E_{\text{int}}^{\text{pair}} = N(N-1)(N-2) \int V_{\text{int}}(l) P(l) dl. \quad (3.32)$$

In case of long-range Coulomb interactions the reactivity is non-zero since every pair is influenced by other particles. The interaction between the particles is the source for the error in the reconstruction such that the reactivity is also a qualitative measure for the accuracy of the approximated  $F$ -operator. This result can be understood by considering the dynamics of the electron cloud. At times (1) and (3) (see Figure 3.8) the electron cloud is shifted towards the lithium core. The particles come closer to each other making the approximation of non-interacting pairs worse. At times (2) and (4) the laser field shifts the electron cloud towards the hydrogen core leading to a more dilute electron distribution and reducing the number of scattering events between the particles. The two deeply bound electrons at the lithium core do not participate in the oscillatory motion induced by the laser pulse. The shift of the valence electrons toward the hydrogen core is visible in Figure 3.8 through a stronger population of inter-atomic pairs with one electron at the lithium core and the other at the hydrogen core. The larger population of inter-atomic pairs at times (2) and (4) leads to a broadening of the pair-distance distribution as compared to (1) and (3) and, according to Equation 3.32, to a reduction of reactivity. Note that the reactivity does not contain any information on the magnitude  $|F|$  of the  $F$ -operator defined as the integral over the absolute value

$$|F| = \int |F(k_1k_2, k_1k_2)| dk_1dk_2. \quad (3.33)$$

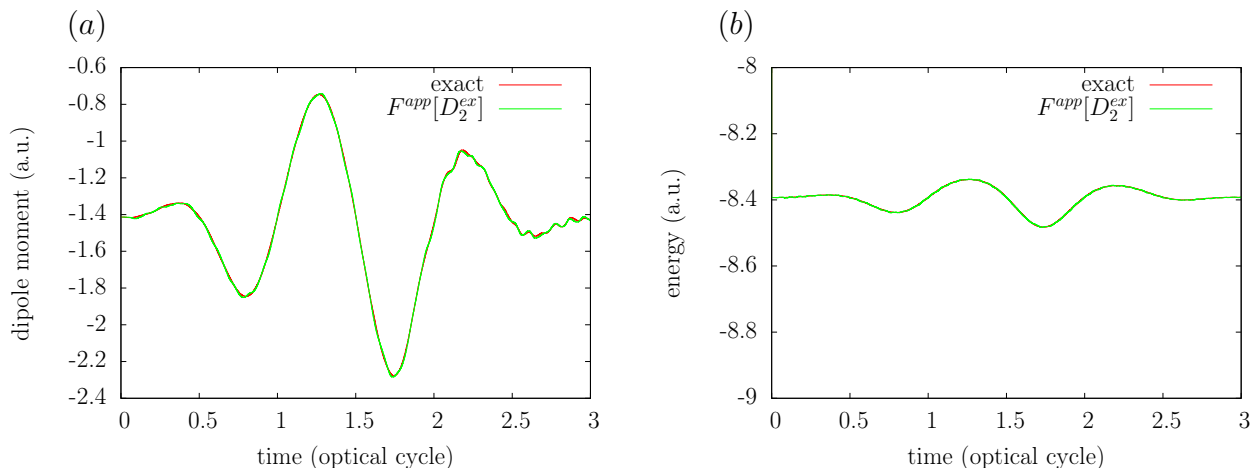


**Figure 3.8.:** The exact (a)-(d) and the approximated (e)-(h) pair-density distribution on the first level of approximation in coordinate space at four instances of times (1)-(4), defined for the electric field in Figure 3.6 which is replotted for convenience. The approximated pair density is obtained by propagation Equation 3.25 with  $F^{app}[D_2^{ex}]$ .



**Figure 3.9.:** The imaginary diagonal elements of the  $F$ -operator in momentum space for both the exact calculation (a)-(d) and the approximation (e)-(h) on the first level of approximation at different time steps (1)-(4) defined for the electric field in Figure 3.6 which is replotted for convenience.. The approximated  $F$ -operator corresponds to  $F^{app}[D_2^{ex}]$ .





**Figure 3.10.:** (a) The dipole moment and (b) the electronic energy  $E = \langle \Psi | H | \Psi \rangle$  with  $H$  defined in Equation 3.1 for LiH in the laser pulse Figure 3.6 on the first level of approximation. The high-frequency fluctuations near  $\tau = 3$  originate from superpositions between the ground state and excited states. The total energy (b) takes on almost the same value as before the pulse showing that excitations have only a very small amplitude.

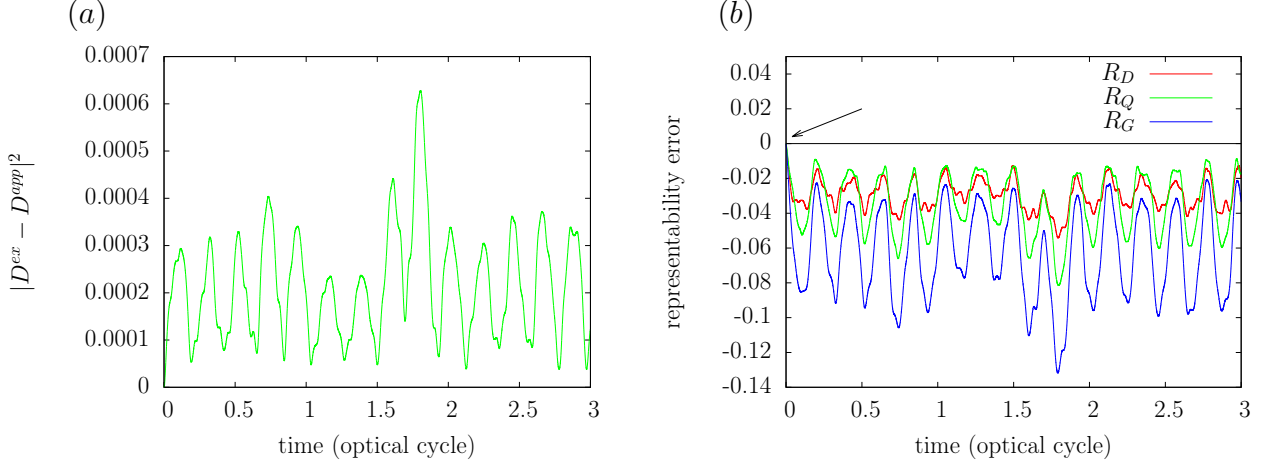
Indeed the magnitude of the  $F$ -operator is smaller for times (1) and (3) than for (2) and (4) although the reactivity of the system is larger at times (1) and (3) and smaller at (2) and (4) (see Figure 3.9). This is not a contradiction.  $|F(k_1 k_2, k_1 k_2)|$  measures the total change in the number of pairs with momentum configuration  $(k_1, k_2)$ , i.e., the sum over all created and annihilated pairs with momentum configuration  $(k_1, k_2)$ . If many positive and negative contributions balance each other out the magnitude of the  $F$ -operator is reduced even though a large number of scattering events take place (see Figure 3.9).

The dipole moment as well as the energy within the first level of approximation show excellent agreement with the full MCTDHF calculation (see Figure 3.10). In the dipole moment even small amplitude oscillations at the end of the pulse are reproduced with high accuracy [Figure 3.10 (a)]. These oscillations arise from the superposition of the ground state with excited states. The contribution of the excited states is very small such that the dominant part of the time evolution of the dipole moment comes from the linear response to the external field which manifests itself also in the behaviour of the electronic energy which remains almost unchanged after the pulse [see Figure 3.10 (b)]. Overall Figure 3.10 demonstrates that the error arising from the replacement of the exact 3-RDM by the reconstructed 3-RDM is small enough to obtain accurate results.

A direct measure for the quality of the approximated 2-RDM is the square distance  $|D_2^{app} - D_2^{ex}|^2$  defined in analogy to Equation 3.27

$$|D^{app} - D^{ex}|^2 = \sum_{i_1, i_2} \sum_{j_1, j_2} |D_{j_1, j_2}^{app, i_1, i_2} - D_{j_1, j_2}^{ex, i_1, i_2}|^2. \quad (3.34)$$

For the propagation on the first level of approximation where  $F^{app}[D_2^{ex}]$  is used in Equation 3.25 the square distance  $|D_2^{app} - D_2^{ex}|^2$  is very small demonstrating that the error of the reconstruction allows an accurate propagation of the 2-RDM [see Figure 3.11 (a)]. The influence of the error in the reconstruction of the 3-RDM on the  $N$ -representability of the 2-RDM can be measured

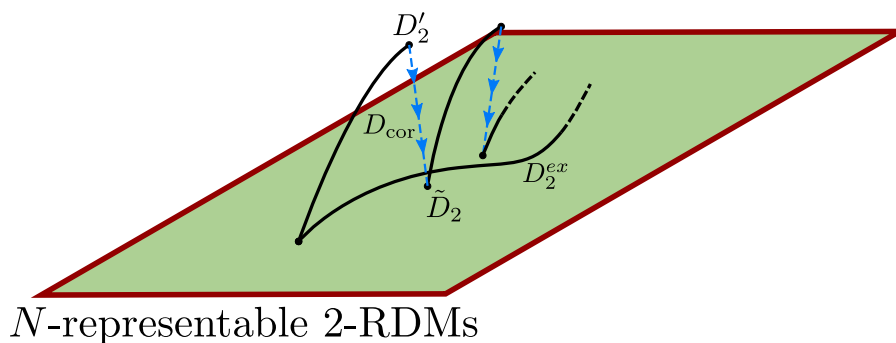


**Figure 3.11.:** (a) The error in the 2-RDM for the propagation on the first level of approximation. The oscillatory behaviour originates from breaking  $N$ -representability as shown in (b) where the representability errors defined in Equation 3.35 are plotted. Note that since the initial 2-RDM is  $N$ -representable the representability errors are zero at the beginning,  $R_D(t=0) = R_Q(t=0) = R_G(t=0) = 0$  (marked by an arrow). As a guide for the eye we plot the line corresponding to  $R = 0$ .

via the violation of the  $D$ -condition. For this purpose we sum over all negative eigenvalues  $\epsilon_i^D < 0$

$$R_D = \sum_{i: \epsilon_i^D < 0} \epsilon_i^D. \quad (3.35)$$

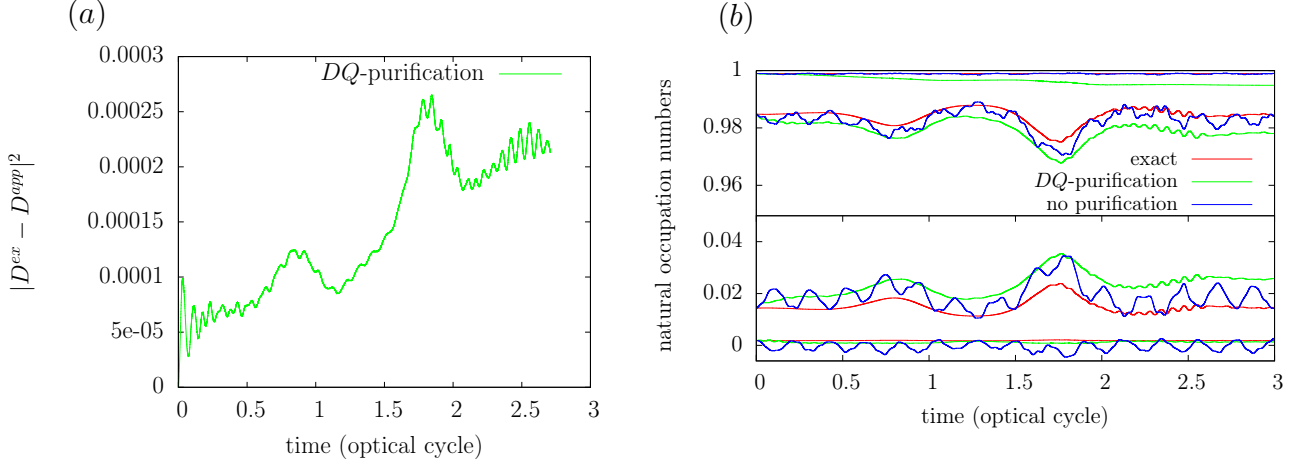
We call the above quantity the  $D$ -representability error. Likewise, the representability errors  $R_Q$  and  $R_G$  defined in analogy to  $R_D$  measure the violation of the  $Q$ -condition and the  $G$ -condition, respectively. Despite the fact that the propagation of the 2-RDM is very accurate as measured by the dipole moment and the electronic energy (see Figure 3.10), the  $N$ -representability of the 2-RDM is violated almost immediately [see Figure 3.11 (b)]. Approximately at  $\tau = 0.1$  the representability recovers again initializing an oscillatory behaviour with a period of  $T \approx 0.2$ . The same oscillations can be found in  $|D_2^{app} - D_2^{ex}|^2$  suggesting that this error in the 2-RDM originates from by the violation of the  $N$ -representability. Therefore, a way to further improve the result of the propagation is the application of a purification scheme which ensure that the 2-RDM stays  $N$ -representable during the propagation. In subsection 2.5.2 we discussed the  $DQ$ -purification which takes into account the  $D$ -condition and the  $Q$ -condition. The purification is an iterative procedure and the number of iterations is chosen such that the magnitude of the smallest eigenvalue of both the 2-RDM and the 2-hole-RDM is smaller than a given threshold  $\chi$ . We found empirically that the threshold parameter of  $\chi = -10^{-4}$  for the smallest eigenvalue is a reasonable choice. The purification procedure does not allow to set  $\chi$  to arbitrarily small values. Too many iterations within the purification lead at some point to further increase in the violation of  $N$ -representability. Indeed, the enforcement of the  $D$ -condition and the  $Q$ -condition via the  $DQ$ -purification improves the agreement between the exact 2-RDM and the approximated 2-RDM [see Figure 3.13 (a)]. In particular, the large amplitude fluctuations



$N$ -representable 2-RDMs

**Figure 3.12.:** The purification step  $D_{\text{cor}}$  that projects the 2-RDM into the set of  $N$ -representable 2-RDMs and contains an uncontrollable part which leads to deviations from the exact propagation.

arising from the violation of the  $N$ -representability disappear. The purification is employed after each time step. Unfortunately, the purification has a major drawback which can be observed already at this level of approximation although its overall effect is small. The error in the  $F$ -operator creates at each time step a small error in  $N$ -representability. By applying the purification, we project the 2-RDM back into the set of matrices that fulfill the  $N$ -representability conditions at hand. This projection, however, amounts to an additional effective propagation step that is uncontrollable [see [Figure 3.12](#)]. Therefore, it is of great interest to understand how the purification modifies the propagation. For this purpose we investigate the dynamics of the natural occupation numbers. Due to the spin symmetry of the system the natural occupation numbers for spin up orbitals are equal to the natural occupation numbers for spin down orbitals, i.e., the number of spin up electron in one spatial orbital is equal to the number of spin down electrons causing the natural occupation numbers to be doubly degenerate. The four electrons inside the LiH molecule can be divided into two core electrons deeply bound to the lithium nucleus and two valence electrons responsible for the molecular bond. The core orbital remains fully occupied during the pulse [see [Figure 3.13 \(b\)](#)]. Without purification and with  $F^{\text{app}}[D_2^{\text{ex}}]$  the occupation of the core orbitals is well reproduced [see [Figure 3.13 \(b\)](#)]. Note, however that the smallest occupation number is negative. Purification, on one hand, removes negative occupation numbers. On the other hand, the occupation numbers of all other orbitals is significantly altered as well [see [Figure 3.13 \(b\)](#)]. This artificial effect of the purification yields an error  $|D^{\text{app}} - D^{\text{ex}}|^2$  that is in this case of propagation with  $F^{\text{app}}[D_2^{\text{ex}}]$  very small and the actual form of the curve resembles  $|F^{\text{app}} - F^{\text{ex}}|^2$  in [Figure 3.7 \(a\)](#). Note that the fourth spatial orbital in [Figure 3.13 \(b\)](#) remains unoccupied throughout the whole laser pulse period indicating that the result is converged within four spatial orbitals.

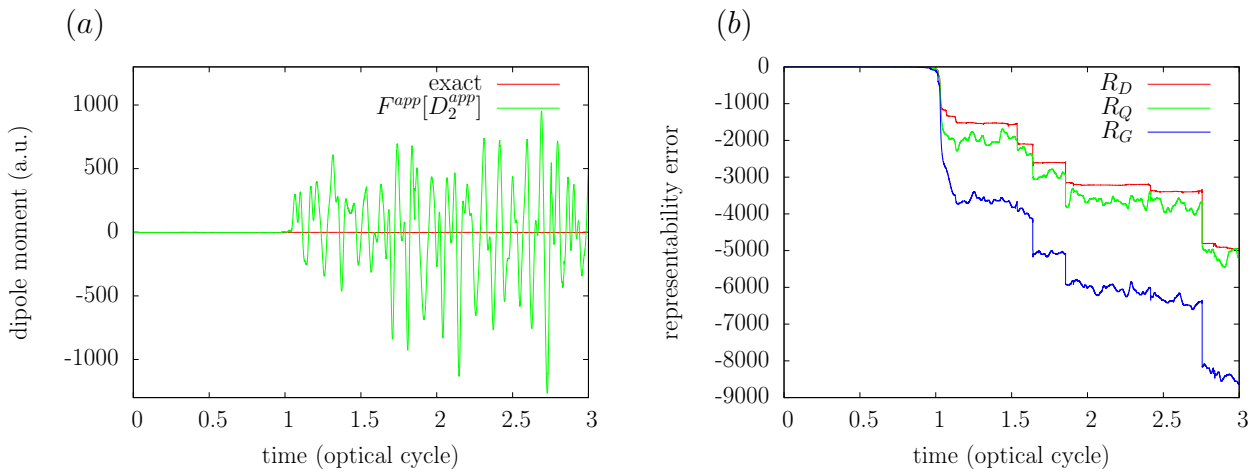


**Figure 3.13.:** (a) The error in the 2-RDM for the propagation on the first level of approximation with  $DQ$ -purification. (b) The time evolution of the natural occupation numbers for the exact propagation as well as the propagation with  $F^{app}[D_2^{ex}]$  both with and without purification. Note that the ordinate is split for graphical reasons.

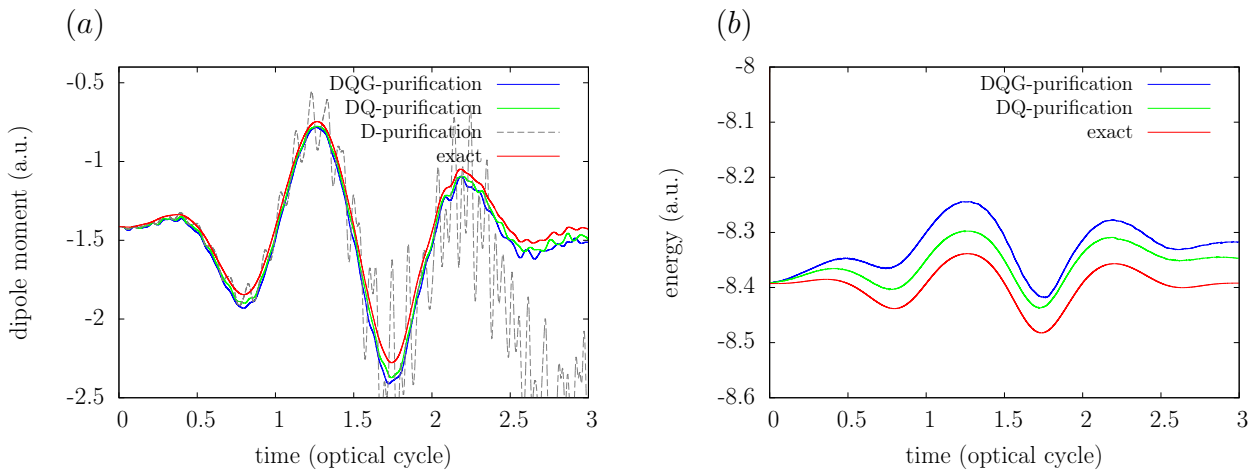
### 3.3.2. The second level of approximation

On the second level of approximation, we solve [Equation 3.25](#) self-consistently, i.e.,  $D_2^{app}(t)$  propagated by [Equation 3.25](#) is used to reconstruct the  $F$ -operator in order to determine the next time step  $D_2^{app}(t + \Delta t)$ . We denote this level of approximation as  $F^{app}[D_2^{app}]$ . The orbital equations of motion for the orbitals are still propagated within the MCTDHF. The decisive difference to the first level of approximation is that in the present case the accumulated error in the propagated 2-RDM affects the quality of the approximated  $F$ -operator and in turn the error in the  $F$ -operator affects the propagated 2-RDM. This feedback loop magnifies the error in the 2-RDM. In particular, violation of  $N$ -representability strongly accumulates and leads to instabilities within  $\tau \approx 1$  [see [Figure 3.14 \(a\)](#)]. At this time the representabilities  $R_D, R_Q, R_G$  fall to values below  $-1000$  [see [Figure 3.14 \(b\)](#)]. The purification is able to suppress this feedback loop and leads to reasonable results for the time evolution of the dipole moment  $d(t)$  and the energy (see [Figure 3.15](#)). However, the interplay between the error in the approximated  $F$ -operator and the error in the 2-RDM limits the accuracy of the propagation. Compared to the error of the in the  $F$ -operator on the first level of approximation [Figure 3.7](#) the error in the  $F$ -operator on the second level is increased by a factor of 10. This shows that for the second level of approximation the error of the  $F$ -operator originates primarily from the accumulated error in the 2-RDM. Consequently,  $|F_2^{app} - F_2^{ex}|^2$  closely resembles  $|D_2^{app} - D_2^{ex}|^2$  (see [Figure 3.16](#)). This shows that reducing the accumulation of error in the 2-RDM is the crucial point for an improvement of the method. The present purification schemes itself introduces a considerable error into the propagation due to the unphysical mixing of occupation numbers (see [Figure 3.13](#)).

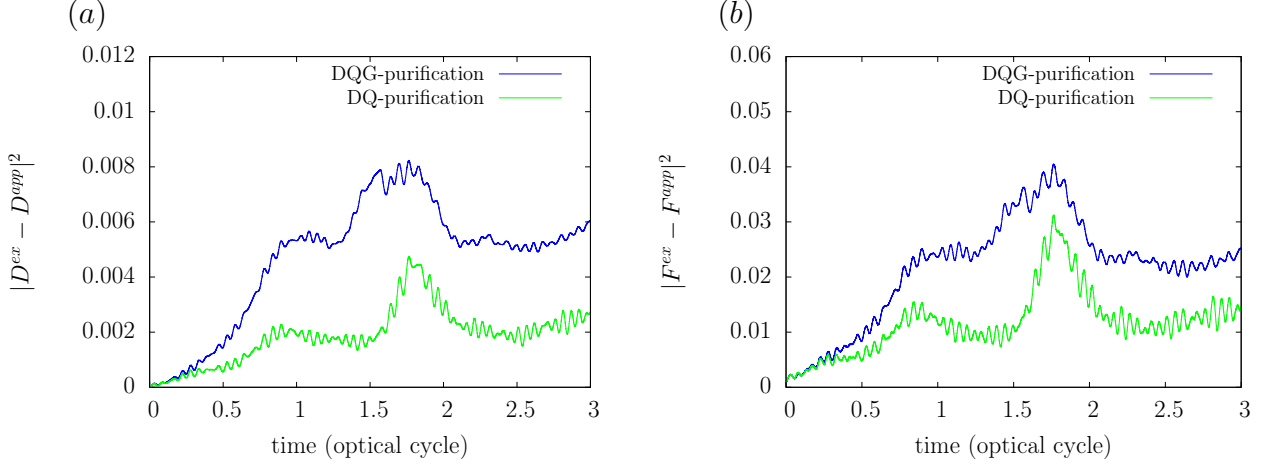
We observe that  $D$ -purification alone is able to avoid strong instabilities but the agreement with the MCTDHF result is very poor (see [Figure 3.15](#)). Better results are obtained by employing the  $DQ$ -purification which enforces, per constructionem, the  $D$ -representability condition and the  $Q$ -condition up to a specific accuracy  $\chi$  while the  $G$ -condition is not enforced and thus violated during the propagation [see [Figure 3.17 \(a\)](#)]. Nonetheless a rapid increase in the



**Figure 3.14.:** The time evolution of (a) the dipole moment and (b) the representability error for propagation with the  $F$ -operator constructed from the approximated 2-RDM at each time step, i.e. on the second level of approximation. The blow-up of the equations of motion for the 2-RDM at  $\tau \approx 1$  is clearly visible in the dipole moment and is caused by the dramatic loss of representability depicted in (b).



**Figure 3.15.:** The time evolution of (a) the dipole moment and (b) the electronic energy for the propagation on the second level of approximation including the  $D$ -purification, the  $DQ$ -purification as well as the  $DQG$ -purification.



**Figure 3.16.:** The absolute square error in (a) the 2-RDM and (b) the  $F$ -operator for the propagation with  $F^{app}[D_2^{app}]$  and several different purification schemes.

violation of the  $G$ -condition as it happens without  $DQ$ -purification [see Figure 3.14 (b)] is not observed. This shows that the inclusion of the  $DQ$ -purification leads to a stabilization of the  $G$ -condition as well.

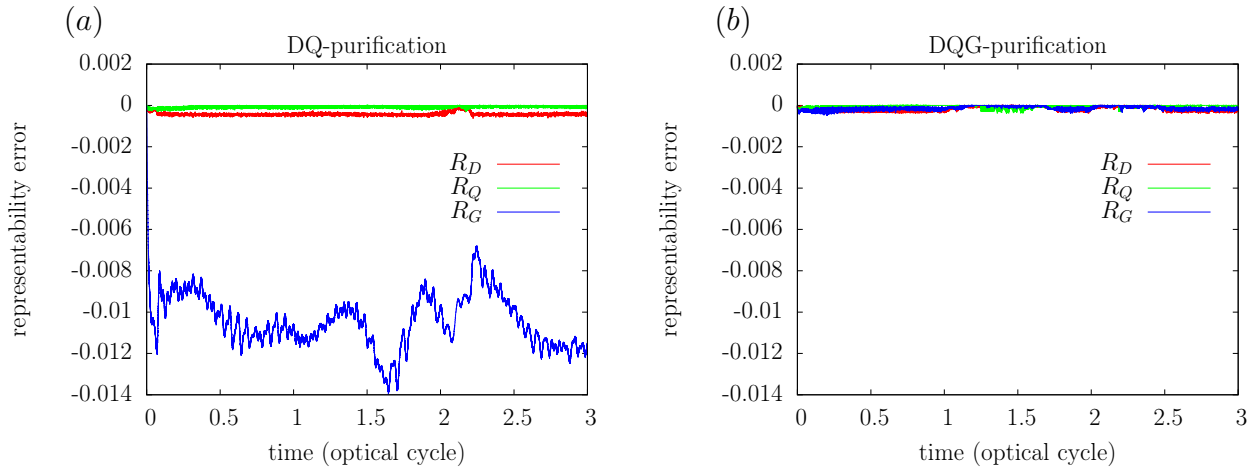
In addition to the  $DQ$ -purification we also investigated the results for the  $DQG$ -purification introduced in subsection 2.5.2. We find that the  $DQG$ -purification is capable of correctly restoring  $N$ -representability within the conditions at hand [see Figure 3.17 (b)]. However, additional implementation of the  $G$ -condition does not yield any improvement over the  $DQ$ -purification. Indeed the  $DQG$ -purification seems to have a stronger destructive effect on the propagation than the  $DQ$ -purification alone as measured by  $|D_2^{app} - D_2^{ex}|^2$  [see Figure 3.16 (a)]. This originates from the fact that since the  $DQG$ -purification enforces more conditions than the  $DQ$ -purification the number of iterations to reach the threshold  $\chi = 10^{-4}$  is enlarged leading to a stronger distortion of the 2-RDM and thus a larger uncontrollable part that ultimately increases the error in the 2-RDM. Therefore, to identify and separate the part of the purification that leads to an unphysical manipulation of occupation numbers without improving representability will be an essential step towards increasing the numerical accuracy of the time-dependent 2-RDM method.

### 3.3.3. The selfconsistent propagation

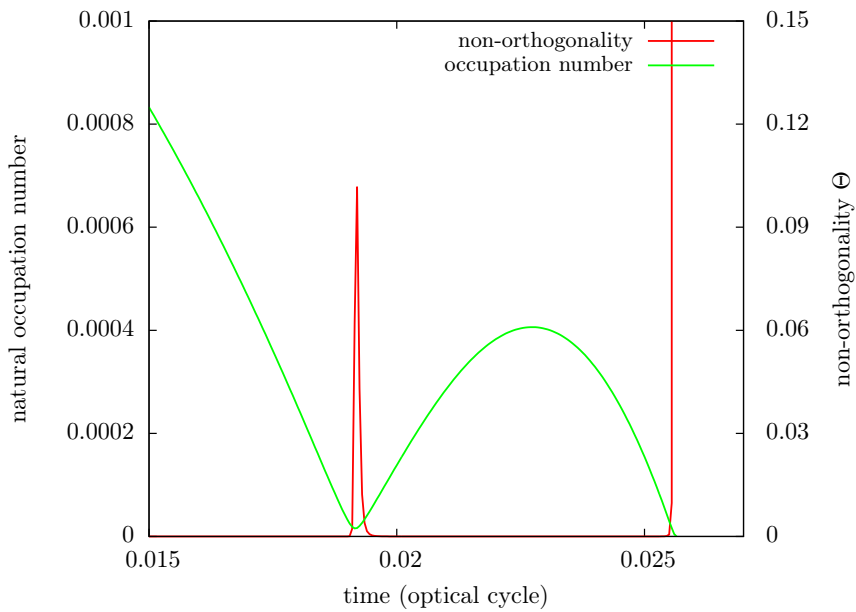
In the previous sections the equation of motion for the orbitals was solved using the exact 2-RDM from a simultaneous MCTDHF propagation at each time step. In this section we will approach the ultimate goal to propagate Equation 3.25 and Equation 3.26 fully self-consistently. The challenge in the self-consistent propagation of the orbitals is the dependence of the orbital equations of motion on the inverse 1-RDM. We reproduce Equation 2.71 for convenience

$$i\partial_t\phi_i(x,t) = \hat{Q} \left( h(x)\phi_i(x,t) + \hat{\Gamma}_u(x,t)(D^{-1})_i^u \right). \quad (3.36)$$

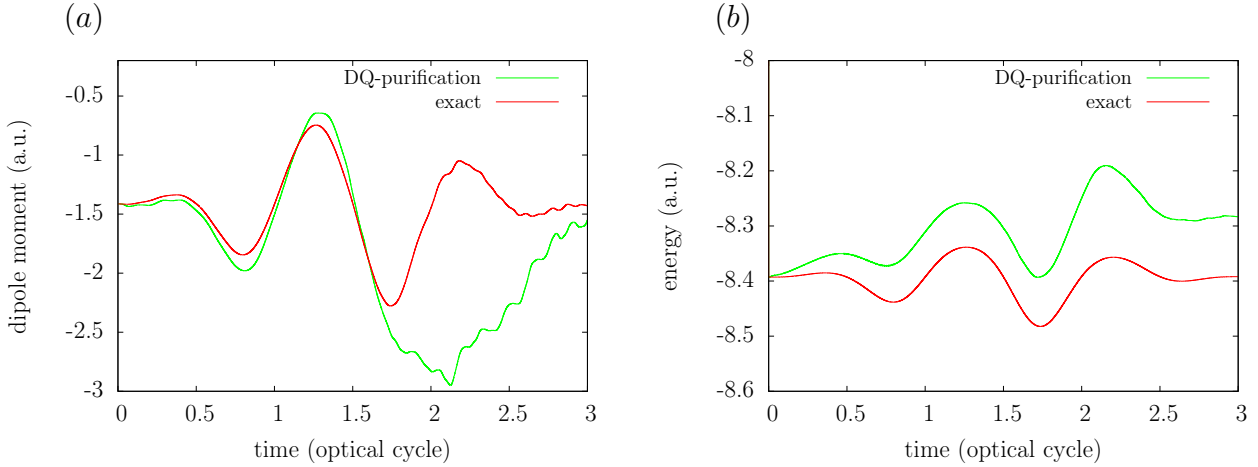
The dependence on the inverse 1-RDM makes the propagation of the orbitals extremely sensitive to small occupation numbers. In the presence of occupation numbers approaching zero



**Figure 3.17.:** The time evolution of the representability errors  $R_D, R_Q$ , and  $R_G$  for the propagation with  $F^{app}[D_2^{app}]$ . (a) DQ-purification, (b) DQG-purification.



**Figure 3.18.:** The time evolution of the non-orthogonality measure  $\Theta$  (see Equation 3.37) and the smallest natural occupation number for the self-consistent propagation of orbitals and coefficients Equation 3.25, Equation 3.26. At time  $\tau = 0.027$  the non-orthogonality peaks to a value of  $\Theta = 10^{50}$  before the propagation breaks down.



**Figure 3.19.:** The time evolution of (a) the dipole moment and (b) the energy for the selfconsistent propagation according to Equation 3.25 and Equation 3.26 including the  $DQ$ -purification.

the contribution  $\hat{\Gamma}_u(x, t)(D^{-1})_i^u$  diverges. The divergence of the inverse 1-RDM for orbitals with occupation numbers equal to zero can be suppressed by introducing a regularized inverse whose eigenvalues  $\frac{1}{n_i}$  are replaced by  $\frac{n_i}{n_i^2 + 10^{-12}}$ . This regularization truncates all occupation numbers below  $n_i < 10^{-6}$  and stabilizes the propagation in the presence of unoccupied virtual orbitals. Nonetheless we find that the self-consistent solution of the coupled set of equations Equation 3.25 and Equation 3.26 without purification diverges at  $\tau = 0.0257$ . This divergence originates from the fact that  $\hat{\Gamma}_u(x, t)(D^{-1})_i^u$  becomes very large for almost vanishing occupation numbers leading to numerical errors in the application of the projection operator  $\hat{Q}$  which ultimately leads to a non-unitary time propagation. As a measure for the non-orthogonality of the basis we introduce

$$\Theta = \sum_{i \neq j} |\langle \phi_i | \phi_j \rangle|^2. \quad (3.37)$$

The basis is orthogonal if and only if  $\Theta = 0$ . Indeed the non-orthogonality diverges at  $\tau = 0.0257$  for a self-consistent propagation without purification making a further propagation impossible (see Figure 3.18). A detailed investigation of orthogonality and the behaviour of the smallest eigenvalue reveals that both quantities are closely related. After only a short time of  $\tau = 0.019$  the smallest natural occupation number reaches a minimum of  $n = 1.4 \times 10^{-5}$ . At this point the orthogonality measure has reached  $\Theta = 0.1$ . For later times the natural occupation number increases again and simultaneously the orthogonality improves. At  $\tau = 0.0257$  the smallest occupation number approaches zero a second time and at this point the propagation breaks down. The same effect appears also in the MCTDHF calculation if the time step of the propagator is too large or the type of the propagator is not appropriate such as the Euler propagator. In this case the decay of the smallest natural occupation number towards zero is initiated by the error arising from the numerical errors of the propagation. The sensibility of the orbital propagation on the smallest natural occupation numbers is, therefore, a general problem that is intrinsically contained in the equations of motions. The error in the MCTDHF propagation, however, can be reduced by a smaller step size or a better propagator whereas the error in the reconstruction functional is an integral component of the time-dependent 2-RDM method. A



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self-consistent propagation of the 2-RDM, therefore, essentially depends on a well suited purification scheme. The procedures available at present, however, do not restore  $N$ -representability without introducing artificial errors. In particular within the self-consistent propagation these additional errors in the smallest occupation numbers lead to large errors in the inverse 1-RDM causing large errors in the propagation of the orbitals (see [Figure 3.19](#)). To improve this results there are two convenient ways to follow. The first is an advanced purification scheme that consists of the iterative procedure extended by an infinitesimal rotation that accounts for the unphysical change in the fully occupied orbitals. The second is to implement the propagation of the two-particle basis into the 2-RDM method. Both and further alternatives will be discussed in [chapter 4](#).



## 4. Summary and conclusions

In the present thesis we have investigated a theoretical method to propagate the 2-RDM without the knowledge of the  $N$ -particle wave function. The underlying idea is to reduce the overwhelming information contained in the wave function required to solve the time-dependent Schrödinger equation to the amount of information that is sufficient to correctly describe physical properties such as the total energy. We have derived the equations of motion for the 2-RDM and have provided an intuitive interpretation in terms of the interaction between particle pairs and the environment. The exact equations of motion for the 2-RDM crucially depend on the 3-RDM. We obtain a closed form of the equations of motion for the 2-RDM by approximating the 3-RDM in terms of the 2-RDM and the 1-RDM according to the cumulant theory of RDMs. At this point the time evolution of the 2-RDM is completely decoupled from the wave function such that the 2-RDM may get distorted in such a way that it cannot be derived from an actual many-body wave function anymore. This violation of  $N$ -representability is a crucial problem of the 2-RDM method and requires the restoration of  $N$ -representability via a procedure called purification. In our calculations we have incorporated purification methods known in the literature and in addition developed a purification scheme that takes into account the  $D$ -condition, the  $Q$ -condition, as well as the  $G$ -condition.

To test the accuracy of the new method we have calculated the dynamics of a lithium hydrogen (LiH) molecule in 1D subject to high-intense laser fields. We have studied the electron dynamics induced by the laser pulse on three levels of approximation. On the first level of approximation we have used the exact 2-RDM obtained from a simultaneous MCTDHF calculation for propagation of the orbitals and for the reconstruction of the 3-RDM. We have found on the first level of approximation near perfect agreement with full MCTDHF calculations. We conclude that the error in the reconstruction functional allows, in principle, a very accurate propagation for such systems. As an indicator for the quality of the reconstruction functional we have introduced the reactivity which is a measure for the number of scattering events between a pair and the surrounding particles. We have found that the error in the 2-RDM is very small and dominated by the violation of  $N$ -representability showing oscillations as a function of time. Employing purification, the 2-RDM can be brought to even better agreement with MCTDHF.

Purification becomes particularly important on the second level of approximation where the propagated 2-RDM is used to reconstruct the 3-RDM. In this case the error in the 2-RDM is imprinted on the reconstruction functional and accumulates leading eventually to instabilities in the propagation. The application of purification prevents instabilities and leads to results that are in good agreement with full MCTDHF calculations. However, the purification procedure unfortunately causes an unphysical mixing of natural occupation numbers. In particular, the natural occupation numbers of core orbitals are artificially decreased due to the purification while MCTDHF calculations show that they should be constant. This unphysical effect

of the purification is an additional source of error for the propagation. We have tested different purification schemes including the  $DQ$ -purification based on the  $D$ -condition and the  $Q$ -condition, as well as the  $DQG$ -purification including also the  $G$ -condition. We find that the  $DQ$ -purification yields slightly better results than the  $DQG$ -purification. This is due to the fact that the  $DQG$ -condition requires more iterations to converge thus further increasing the uncontrollable effect on the propagation.

Finally, we have studied the self-consistent propagation of the 2-RDM method where both the equations of motion for the orbitals and the 2-RDM are solved self-consistently. At this point the 2-RDM method does not rely on any input from a simultaneous MCTDHF calculation. We find that the inverse 1-RDM entering the equation of motion for the orbitals is very sensitive to small natural occupation numbers and diverges if the natural occupation numbers approach to zero. Without purification the self-consistent propagation of the orbitals is practically impossible. Only by including the purification into the propagation the equations are stabilized leading to reasonable results. Nonetheless, due to the strong sensitivity on small natural occupation numbers errors in the 1-RDM have a large impact on the orbital propagation. This poses a challenge for a selfconsistent propagation of both the orbitals and the 2-RDM coefficients. We find that the purification schemes tested in this thesis are not yet able to provide an accurate solution for the self-consistent 2-RDM equations of motion.

To overcome these difficulties two conceptually different approaches can be followed. The first approach circumvents the instabilities of the orbital equations of motion arising from the inverse 1-RDM by replacing the one-particle basis by a two-particle basis which intrinsically accounts for pair interaction. Such a time-dependent method based on a two-particle basis was sketched in [subsection 2.4.2](#) and will be subject of further studies. The second approach focuses on the improvement of the purification scheme. It has been observed previously [45] that the purification schemes employed in this thesis do not strictly conserve the spin singlet state of the wave function, i.e., the 2-RDM after the purification does not exactly correspond to a spin singlet state anymore. Recently, a new purification scheme was presented that takes into account the  $D$ -condition, the  $Q$ -condition, and the  $G$ -condition as well as the conservation of the spin singlet state [45]. We will employ this purification scheme in further studies.

Conceptually, the purification schemes available today are designed for the iterative solution of the contracted Schrödinger equation. In this iterative procedure the purification has the single purpose of restoring  $N$ -representability after each iteration step. In the application to time-dependent problems, however, the purification faces new challenges. It has to restore  $N$ -representability after each propagation step but should not artificially modify the occupation numbers. The major drawback of the present purification schemes in the context of time-dependent problems is that purification and propagation steps are applied independently. At present the input for the purification step is given by the 2-RDM of the last propagation step and, consequently, the purification contains an uncontrollable part that is not adapted to the actual propagation step. We observe that this uncontrollable part leads to an unphysical redistribution of natural occupation numbers. A convenient approach to correct this part of the purification is the implementation of a subsequent correction step

$$D'_2 = D_2 + i[H_{\text{eff}}, D_2], \quad (4.1)$$

with an appropriately chosen effective Hamiltonian  $H_{\text{eff}}$  that ensures conservation of occupation

numbers associated with highly occupied orbitals. In particular, for systems featuring deeply bound core orbitals it is convenient to fix the natural occupation numbers associated with core orbitals during the propagation following the recently developed TD-CASSCF method [32].

A convenient alternative to the purification of the 2-RDM is a purification scheme that acts on the time derivative of the 2-RDM in order to keep  $N$ -representability from the start. The purification of the time derivative has the advantage that the purification is correlated to the propagation step. An ambitious goal is the development of a purification scheme that acts on the approximated  $F$ -operator such that  $N$ -representability at least on the level of  $DQ$ -conditions is preserved during time-propagation. Further progress along these lines relies essentially on a deeper understanding of the  $F$ -operator.

From a conceptual point of view the question arises whether the  $N$ -representability of the 3-RDM entering the  $F$ -operator is sufficient to guarantee  $N$ -representability of the 2-RDM during propagation. If this is the case purification of the reconstructed 3-RDM may be a convenient approach to enforce  $N$ -representability in combination with an increased accuracy of the reconstruction. However, the enforcement of 3-positivity conditions on the basis of the 3-RDM is numerically very demanding.

Finally, the correlation between the accuracy of the approximated  $F$ -operator and the reactivity described in [subsection 3.3.1](#) suggests to search for systems with a dilute electron distribution as a testing ground for the propagation within the time-dependent 2-RDM method.



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# A. Reduced density matrices of Slater determinants

In this appendix we show that in the special case of a  $N$ -particle wave function equal to a single Slater determinant consisting of  $N$  orbitals  $\phi_i$  the RDMs have a simple form in terms of the orbitals  $\phi_i$ . In particular the  $p$ -RDM has exactly  $\binom{N}{p}$  non-vanishing eigenvalues which are all equal to one and the corresponding eigenfunctions are  $p$ -particle Slater determinants. To prove this we start with the  $N$ -particle density matrix

$$D(x_1 \dots x_N; x'_1 \dots x'_N) = \frac{1}{N!} \begin{vmatrix} \phi_1(x_1) & \phi_2(x_1) & \dots & \phi_N(x_1) \\ \phi_1(x_2) & \phi_2(x_2) & \dots & \phi_N(x_2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1(x_N) & \phi_2(x_N) & \dots & \phi_N(x_N) \end{vmatrix} \begin{vmatrix} \phi_1^*(x'_1) & \phi_2^*(x'_1) & \dots & \phi_N^*(x'_1) \\ \phi_1^*(x'_2) & \phi_2^*(x'_2) & \dots & \phi_N^*(x'_2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1^*(x'_N) & \phi_2^*(x'_N) & \dots & \phi_N^*(x'_N) \end{vmatrix}, \quad (\text{A.1})$$

and gradually reduce the number of variables by performing a partial trace over just one variable. In the first step we obtain the  $(N-1)$ -RDM by tracing out  $x_N$

$$\begin{aligned} & \int \begin{vmatrix} \phi_1(x_1) & \phi_2(x_1) & \dots & \phi_N(x_1) \\ \phi_1(x_2) & \phi_2(x_2) & \dots & \phi_N(x_2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1(x_N) & \phi_2(x_N) & \dots & \phi_N(x_N) \end{vmatrix} \begin{vmatrix} \phi_1^*(x'_1) & \phi_2^*(x'_1) & \dots & \phi_N^*(x'_1) \\ \phi_1^*(x'_2) & \phi_2^*(x'_2) & \dots & \phi_N^*(x'_2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1^*(x'_N) & \phi_2^*(x'_N) & \dots & \phi_N^*(x'_N) \end{vmatrix} dx_N = \\ & = \begin{vmatrix} \phi_2(x_1) & \phi_3(x_1) & \dots & \phi_N(x_1) \\ \phi_2(x_2) & \phi_3(x_2) & \dots & \phi_N(x_2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_2(x_{N-1}) & \phi_3(x_{N-1}) & \dots & \phi_N(x_{N-1}) \end{vmatrix} \begin{vmatrix} \phi_2^*(x'_1) & \phi_3^*(x'_1) & \dots & \phi_N^*(x'_1) \\ \phi_2^*(x'_2) & \phi_3^*(x'_2) & \dots & \phi_N^*(x'_2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_2^*(x'_{N-1}) & \phi_3^*(x'_{N-1}) & \dots & \phi_N^*(x'_{N-1}) \end{vmatrix} \\ & + \begin{vmatrix} \phi_1(x_1) & \phi_3(x_1) & \dots & \phi_N(x_1) \\ \phi_1(x_2) & \phi_3(x_2) & \dots & \phi_N(x_2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1(x_{N-1}) & \phi_3(x_{N-1}) & \dots & \phi_N(x_{N-1}) \end{vmatrix} \begin{vmatrix} \phi_1^*(x'_1) & \phi_3^*(x'_1) & \dots & \phi_N^*(x'_1) \\ \phi_1^*(x'_2) & \phi_3^*(x'_2) & \dots & \phi_N^*(x'_2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1^*(x'_{N-1}) & \phi_3^*(x'_{N-1}) & \dots & \phi_N^*(x'_{N-1}) \end{vmatrix} \\ & \quad \vdots \\ & + \begin{vmatrix} \phi_1(x_1) & \phi_2(x_1) & \dots & \phi_{N-1}(x_1) \\ \phi_1(x_2) & \phi_2(x_2) & \dots & \phi_{N-1}(x_2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1(x_{N-1}) & \phi_2(x_{N-1}) & \dots & \phi_{N-1}(x_{N-1}) \end{vmatrix} \begin{vmatrix} \phi_1^*(x'_1) & \phi_2^*(x'_1) & \dots & \phi_{N-1}^*(x'_1) \\ \phi_1^*(x'_2) & \phi_2^*(x'_2) & \dots & \phi_{N-1}^*(x'_2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1^*(x'_{N-1}) & \phi_2^*(x'_{N-1}) & \dots & \phi_{N-1}^*(x'_{N-1}) \end{vmatrix}. \quad (\text{A.2}) \end{aligned}$$

This relation is obtained by a Laplace expansion along the last row of the determinants inside the integral. The terms in the resulting expression are proportional to  $\int \phi_i(x_k)\phi_j(x_k)dx_k$  such that by orthonormality of the orbitals we arrive at the right hand side of [Equation A.2](#). To obtain the lower-order RDMs this relation for the partial trace of Slater determinants can be applied iteratively leading to

$$\begin{aligned}
& D(x_1 \dots x_p; x'_1 \dots x'_p) = \\
& = \frac{1}{p!} \sum_{\sigma \in S_n} \begin{vmatrix} \phi_{\sigma(1)}(x_1) & \phi_{\sigma(2)}(x_1) & \dots & \phi_{\sigma(p)}(x_1) \\ \phi_{\sigma(1)}(x_2) & \phi_{\sigma(2)}(x_2) & \dots & \phi_{\sigma(p)}(x_2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_{\sigma(1)}(x_p) & \phi_{\sigma(2)}(x_p) & \dots & \phi_{\sigma(p)}(x_p) \end{vmatrix} \begin{vmatrix} \phi_{\sigma(1)}^*(x'_1) & \phi_{\sigma(2)}^*(x'_1) & \dots & \phi_{\sigma(p)}^*(x'_1) \\ \phi_{\sigma(1)}^*(x'_2) & \phi_{\sigma(2)}^*(x'_2) & \dots & \phi_{\sigma(p)}^*(x'_2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_{\sigma(1)}^*(x'_p) & \phi_{\sigma(2)}^*(x'_p) & \dots & \phi_{\sigma(p)}^*(x'_p) \end{vmatrix}, \quad (\text{A.3})
\end{aligned}$$

where  $\sigma$  is a permutation within the symmetric group  $S_n$ . The factor  $\frac{1}{p!} = \frac{1}{N!} \binom{N}{p} (N-p)!$  is obtained by considering that each determinant can be obtained in  $(N-p)!$  different ways. The resulting  $p$ -RDM has the form of a spectral representation from which two important properties can be extracted. First, all eigenvalues of the RDMs are zero or one. This is the necessary and sufficient condition for the matrix to be idempotent, i.e.,  $D_p^2 = D_p$ . Contrary to density matrices normalized to one where idempotence is the condition for the system to be in a pure state, the idempotence of  $p$ -RDMs is a necessary condition for the many-body wave function to be in the form of a single Slater determinant. While for arbitrary  $p$  this is just a necessary condition it is also sufficient in the case of  $p = 1$ , i.e., the wave function has the form of a Slater determinant if and only if  $D_1$  is idempotent [\[23\]](#). The 2-RDM, for example, can be idempotent but if the eigenfunctions do not have the form of Slater determinants the corresponding  $N$ -particle wave function does not have this property neither.

## B. $p$ -RDM diagonal elements and $p$ -tuple expectation values

In [section 2.2](#) we showed that the average number of pairs with coordinates  $(x_1, x_2)$  is given by  $D(x_1 x_2; x_1 x_2)$ . In this appendix we generalize this result and demonstrate that the diagonal elements of the  $p$ -RDM can be interpreted in terms of expectation values of particle tuples, where a particle tuple is the generalization of pairs and triples to  $p$ -particle configurations. In particular we show that the average number  $\langle T_s \rangle$  of  $s$ -particle tuples inside the volume  $V$  is given by the integral over the  $p$ -RDM diagonal

$$\langle T_s \rangle = \int_V D(x_1 \dots x_s; x_1 \dots x_s) dx_1 \dots dx_s. \quad (\text{B.1})$$

This is in accordance with the normalization

$$\int D(x_1 \dots x_s; x_1 \dots x_s) dx_1 \dots dx_s = \binom{N}{s}, \quad (\text{B.2})$$

which gives the total number of  $s$ -particle tuples for a system of  $N$ -particles.

For the sake of simplicity we use the following notation

$$\left( \int_V \right)^p = \underbrace{\int_V \int_V \dots \int_V}_{p \text{ times}}. \quad (\text{B.3})$$

The probability  $P_V(p)$  to find exactly  $p$  particles inside the volume  $V$  while the other  $(N - p)$  particles are in the complementary volume denoted by  $V^c$  is

$$P_V(p) = \binom{N}{p} \left( \int_V \right)^p \left( \int_{V^c} \right)^{N-p} |\Psi|^2 dx_1 \dots dx_N. \quad (\text{B.4})$$

Due to particle conservation these probabilities have to add up to one which is in agreement with the normalization of  $\Psi$ :

$$\sum_{p=0}^N P_V(p) = \left( \int_{V+V^c} \right)^N |\Psi|^2 dx_1 \dots dx_N = 1. \quad (\text{B.5})$$

As a first step toward the general result we consider the particle number expectation value in

the volume  $V$

$$\begin{aligned}
\langle N \rangle &= \sum_{p=1}^N p P_V(p) = \sum_{p=1}^N p \binom{N}{p} \left( \int_V \right)^p \left( \int_{V^c} \right)^{N-p} |\Psi|^2 dx_1 \dots dx_N \\
&= \sum_{p=1}^N N \binom{N-1}{p-1} \left( \int_V \right)^p \left( \int_{V^c} \right)^{N-p} |\Psi|^2 dx_1 \dots dx_N \\
&= N \int_V \left( \int_{V+V^c} \right)^{N-1} |\Psi|^2 dx_1 \dots dx_N = \int_V D(x_1; x_1) dx_1.
\end{aligned} \tag{B.6}$$

We can generalize this result by using the relation

$$\binom{N-s}{p-s} \binom{N}{s} = \binom{N}{p} \binom{p}{s} \tag{B.7}$$

to the general expectation number of  $s$ -particle tuples inside the volume  $V$

$$\begin{aligned}
\langle T_s \rangle &= \sum_{p=s}^N \binom{p}{s} P_V(p) = \sum_{p=s}^N \binom{p}{s} \binom{N}{p} \left( \int_V \right)^p \left( \int_{V^c} \right)^{N-p} |\Psi|^2 dx_1 \dots dx_N \\
&= \sum_{p=s}^N \binom{N-s}{p-s} \binom{N}{s} \left( \int_V \right)^p \left( \int_{V^c} \right)^{N-p} |\Psi|^2 dx_1 \dots dx_N \\
&= \left( \int_V \right)^s D(x_1 \dots x_s; x_1 \dots x_s) dx_1 \dots dx_s.
\end{aligned} \tag{B.8}$$

# C. Valdemoro's reconstruction functionals derived from particle-hole-duality

The first important step towards the reconstruction of RDMs by lower-order ones was achieved by Valdemoro and co-workers in 1993 [26]. They used the fact that any  $N$ -body quantum system can also be expressed in terms of holes instead of particles by interpreting the annihilation operator  $\hat{a}_i$  as the creation operator  $\hat{b}_i^\dagger$  of holes, a concept that is very similar to antiparticles in elementary particle physics.

## C.1. Relation between particle-RDMs and hole RDMs

In general, holes can be defined for fermions as well as bosons. However, in the bosonic case the fundamental commutator relation  $\hat{a}_i \hat{a}_j^\dagger - \hat{a}_j^\dagger \hat{a}_i = \delta_i^j$  is not invariant under the replacement of the annihilation operator for particles  $\hat{a}_i$  by the creation operator for holes  $\hat{b}_i^\dagger$ . Therefore, holes in the bosonic case are not equivalent to particles. Nevertheless, in both cases we can define the  $p$ -particle density operator  $\Gamma_{j_1, \dots, j_p}^{i_1, \dots, i_p}$  and the  $p$ -hole density operator  $\tilde{\Gamma}_{j_1, \dots, j_p}^{i_1, \dots, i_p}$  as

$$\Gamma_{j_1, \dots, j_p}^{i_1, \dots, i_p} = \hat{a}_{i_1}^\dagger \dots \hat{a}_{i_p}^\dagger \hat{a}_{j_p} \dots \hat{a}_{j_1} \quad (\text{C.1})$$

$$\tilde{\Gamma}_{j_1, \dots, j_p}^{i_1, \dots, i_p} = \hat{a}_{j_1} \dots \hat{a}_{j_p} \hat{a}_{i_p}^\dagger \dots \hat{a}_{i_1}^\dagger, \quad (\text{C.2})$$

which are closely related to the  $p$ -RDM,  $D_p$ , and the  $p$ -hole RDM,  $Q_p$ , via

$$D_{j_1, \dots, j_p}^{i_1, \dots, i_p} = \frac{1}{p!} \langle \Psi | \Gamma_{j_1, \dots, j_p}^{i_1, \dots, i_p} | \Psi \rangle \quad (\text{C.3})$$

$$Q_{j_1, \dots, j_p}^{i_1, \dots, i_p} = \frac{1}{p!} \langle \Psi | \tilde{\Gamma}_{j_1, \dots, j_p}^{i_1, \dots, i_p} | \Psi \rangle. \quad (\text{C.4})$$

To express the hole-RDMs in terms of particle-RDMs we rearrange the creation and annihilation operators using  $[\hat{a}_i \hat{a}_j^\dagger]_{\pm} = \delta_i^j$ . This leads for the bosonic commutation relation  $\hat{a}_i \hat{a}_j^\dagger = \hat{a}_i^\dagger \hat{a}_j + \delta_i^j$

to the following equation

$$\begin{aligned}
\tilde{\Gamma}_{j_1, \dots, j_p}^{i_1, \dots, i_p} &= \Gamma_{j_1, \dots, j_p}^{i_1, \dots, i_p} \\
&+ \sum_{\substack{r_1 \\ t_1}} \delta_{j_{t_1}}^{i_{r_1}} \Gamma_{j_1, \dots, j_p \setminus \{j_{t_1}\}}^{i_1, \dots, i_p \setminus \{i_{r_1}\}} \\
&+ \sum_{\substack{r_1 < r_2 \\ t_1 \neq t_2}} \delta_{j_{t_1}}^{i_{r_1}} \delta_{j_{t_2}}^{i_{r_2}} \Gamma_{j_1, \dots, j_p \setminus \{j_{t_1}, j_{t_2}\}}^{i_1, \dots, i_p \setminus \{i_{r_1}, i_{r_2}\}} \\
&+ \sum_{\substack{r_1 < r_2 < r_3 \\ t_1 \neq t_2 \neq t_3}} \delta_{j_{t_1}}^{i_{r_1}} \delta_{j_{t_2}}^{i_{r_2}} \delta_{j_{t_3}}^{i_{r_3}} \Gamma_{j_1, \dots, j_p \setminus \{j_{t_1}, j_{t_2}, j_{t_3}\}}^{i_1, \dots, i_p \setminus \{i_{r_1}, i_{r_2}, i_{r_3}\}} \\
&\vdots \\
&+ \sum_{\substack{r_1 < r_2 < \dots < r_p \\ t_1 \neq t_2 \neq \dots \neq t_p}} \delta_{j_{t_1}}^{i_{r_1}} \delta_{j_{t_2}}^{i_{r_2}} \dots \delta_{j_{t_p}}^{i_{r_p}}, \tag{C.5}
\end{aligned}$$

where  $i_1, \dots, i_p \setminus \{i_{r_1}, i_{r_2}, i_{r_3}\}$  denotes the index set  $i_1, \dots, i_p$  reduced by the three indices  $i_{r_1}, i_{r_2}, i_{r_3}$ . A descriptive explanation for this formula is given by the interpretation of each term with  $s$  Kronecker deltas as the term created by the extinction of  $s$  annihilation operators  $\hat{a}_{j_{t_1}} \dots \hat{a}_{j_{t_s}}$  with  $s$  creation operators  $\hat{a}_{j_{r_1}}^\dagger \dots \hat{a}_{j_{r_s}}^\dagger$ . To prove this relation with mathematical rigour we use complete induction over the integer  $p$ . For  $p = 1$  the formula reduces to the canonical commutation relation. To prove the induction step from  $p$  to  $p + 1$  we use the following equation

$$\begin{aligned}
\tilde{\Gamma}_{j_1, \dots, j_p}^{i_1, \dots, i_p} &= \hat{a}_{i_p}^\dagger \tilde{\Gamma}_{j_1, \dots, j_{p-1}}^{i_1, \dots, i_{p-1}} \hat{a}_{j_p} + \sum_{k=1}^{p-1} \delta_{j_p}^{i_k} \tilde{\Gamma}_{j_1, \dots, j_{p-1}}^{i_1, \dots, i_p \setminus \{i_k\}} + \sum_{k=1}^{p-1} \delta_{j_k}^{i_p} \tilde{\Gamma}_{j_1, \dots, j_p \setminus \{j_k\}}^{i_1, \dots, i_{p-1}} + \delta_{j_p}^{i_p} \tilde{\Gamma}_{j_1, \dots, j_{p-1}}^{i_1, \dots, i_{p-1}} \\
&+ \sum_{k=1}^{p-1} \sum_{l=1}^{p-1} \delta_{j_p}^{i_k} \delta_{j_l}^{i_p} \tilde{\Gamma}_{j_1, \dots, j_{p-1} \setminus \{i_k\}}^{i_1, \dots, i_{p-1} \setminus \{i_l\}}, \tag{C.6}
\end{aligned}$$

which is obtained by rearranging the expression  $\tilde{\Gamma}_{j_1, \dots, j_p}^{i_1, \dots, i_p} = \hat{a}_{j_1} \dots \hat{a}_{j_p} \hat{a}_{i_p}^\dagger \dots \hat{a}_{i_1}^\dagger$  into the form  $\hat{a}_{i_p}^\dagger \hat{a}_{j_1} \dots \hat{a}_{i_1}^\dagger \hat{a}_{j_p} = \hat{a}_{i_p}^\dagger \tilde{\Gamma}_{j_1, \dots, j_{p-1}}^{i_1, \dots, i_{p-1}} \hat{a}_{j_p}$  which generates the additional terms. To treat the upper and the lower indices on the same footing we rewrite [Equation C.5](#) as

$$\begin{aligned}
\tilde{\Gamma}_{j_1, \dots, j_p}^{i_1, \dots, i_p} &= \Gamma_{j_1, \dots, j_p}^{i_1, \dots, i_p} \\
&+ \sum_{r_1} \sum_{t_1} \delta_{j_{t_1}}^{i_{r_1}} \Gamma_{j_1, \dots, j_p \setminus \{j_{t_1}\}}^{i_1, \dots, i_p \setminus \{i_{r_1}\}} \\
&+ \frac{1}{2!} \sum_{r_1 \neq r_2} \sum_{t_1 \neq t_2} \delta_{j_{t_1}}^{i_{r_1}} \delta_{j_{t_2}}^{i_{r_2}} \Gamma_{j_1, \dots, j_p \setminus \{j_{t_1}, j_{t_2}\}}^{i_1, \dots, i_p \setminus \{i_{r_1}, i_{r_2}\}} \\
&+ \frac{1}{3!} \sum_{r_1 \neq r_2 \neq r_3} \sum_{t_1 \neq t_2 \neq t_3} \delta_{j_{t_1}}^{i_{r_1}} \delta_{j_{t_2}}^{i_{r_2}} \delta_{j_{t_3}}^{i_{r_3}} \Gamma_{j_1, \dots, j_p \setminus \{j_{t_1}, j_{t_2}, j_{t_3}\}}^{i_1, \dots, i_p \setminus \{i_{r_1}, i_{r_2}, i_{r_3}\}} \\
&\vdots
\end{aligned} \tag{C.7}$$

$$+ \frac{1}{p!} \sum_{r_1 \neq r_2 \neq \dots \neq r_p} \sum_{t_1 \neq t_2 \neq \dots \neq t_p} \delta_{j_{t_1}}^{i_{r_1}} \delta_{j_{t_2}}^{i_{r_2}} \dots \delta_{j_{t_p}}^{i_{r_p}}. \tag{C.8}$$

In the next step we show that each term on the right hand side of [Equation C.7](#) for  $\tilde{\Gamma}_p$  can be decomposed into five sums:

$$\begin{aligned}
& \frac{1}{s!} \sum_{r_1 \neq r_2 \dots \neq r_s} \sum_{t_1 \neq t_2 \dots \neq t_s} \delta_{j_{t_1}}^{i_{r_1}} \delta_{j_{t_2}}^{i_{r_2}} \dots \delta_{j_{t_s}}^{i_{r_s}} \Gamma_{j_1, \dots, j_p \setminus \{j_{t_1}, j_{t_2}, \dots, j_{t_s}\}}^{i_1, \dots, i_p \setminus \{i_{r_1}, i_{r_2}, \dots, i_{r_s}\}} \\
&= \frac{1}{s!} \sum_{r_1 \neq r_2 \dots \neq r_s} \sum_{t_1 \neq t_2 \dots \neq t_s}^{p-1} \delta_{j_{t_1}}^{i_{r_1}} \delta_{j_{t_2}}^{i_{r_2}} \dots \delta_{j_{t_s}}^{i_{r_s}} \Gamma_{j_1, \dots, j_p \setminus \{j_{t_1}, j_{t_2}, \dots, j_{t_s}\}}^{i_1, \dots, i_p \setminus \{i_{r_1}, i_{r_2}, \dots, i_{r_s}\}} \\
&+ \frac{1}{(s-1)!} \sum_{t_s}^{p-1} \delta_{j_{t_s}}^{i_{r_s}} \sum_{r_1 \neq r_2 \dots \neq r_{s-1}}^{p-1} \sum_{t_1 \neq t_2 \dots \neq t_{s-1}}^p \delta_{j_{t_1}}^{i_{r_1}} \delta_{j_{t_2}}^{i_{r_2}} \dots \delta_{j_{t_{s-1}}}^{i_{r_{s-1}}} \Gamma_{j_1, \dots, j_p \setminus \{j_{t_1}, j_{t_2}, \dots, j_{t_s}\}}^{i_1, \dots, i_p \setminus \{i_{r_1}, \dots, i_{r_{s-1}}\}} \\
&+ \frac{1}{(s-1)!} \sum_{r_s}^{p-1} \delta_{j_p}^{i_{r_s}} \sum_{r_1 \neq r_2 \dots \neq r_s}^p \sum_{t_1 \neq t_2 \dots \neq t_{s-1}}^{p-1} \delta_{j_{t_1}}^{i_{r_1}} \delta_{j_{t_2}}^{i_{r_2}} \dots \delta_{j_{t_{s-1}}}^{i_{r_{s-1}}} \Gamma_{j_1, \dots, j_{p-1} \setminus \{j_{t_1}, \dots, j_{t_{s-1}}\}}^{i_1, \dots, i_p \setminus \{i_{r_1}, i_{r_2}, \dots, i_{r_s}\}} \\
&+ \frac{1}{(s-1)!} \sum_{r_1 \neq r_2 \dots \neq r_{s-1}}^{p-1} \sum_{t_1 \neq t_2 \dots \neq t_{s-1}}^{p-1} \delta_{j_{t_1}}^{i_{r_1}} \delta_{j_{t_2}}^{i_{r_2}} \dots \delta_{j_p}^{i_{r_p}} \Gamma_{j_1, \dots, j_{p-1} \setminus \{j_{t_1}, \dots, j_{t_{s-1}}\}}^{i_1, \dots, i_p \setminus \{i_{r_1}, \dots, i_{r_{s-1}}\}} \\
&- \frac{1}{(s-2)!} \sum_{r_1 \neq r_2 \dots \neq r_{s-1}}^{p-1} \sum_{t_1 \neq t_2 \dots \neq t_{s-1}}^{p-1} \delta_{j_{t_1}}^{i_{r_1}} \delta_{j_{t_2}}^{i_{r_2}} \dots \delta_{j_{t_{s-1}}}^{i_{r_{s-1}}} \delta_{j_p}^{i_{r_p}} \Gamma_{j_1, \dots, j_{p-1} \setminus \{j_{t_1}, \dots, j_{t_{s-1}}\}}^{i_1, \dots, i_p \setminus \{i_{r_1}, \dots, i_{r_{s-1}}\}}. \tag{C.9}
\end{aligned}$$

To illustrate this decomposition we apply it to the special case  $s = 2, p = 3$ :

$$\begin{aligned}
& \sum_{r_1 \neq r_2} \sum_{t_1 \neq t_2} \delta_{j_{t_1}}^{i_{r_1}} \delta_{j_{t_2}}^{i_{r_2}} \Gamma_{j_1, j_2, j_3 \setminus \{j_{t_1}, j_{t_2}\}}^{i_1, i_2, i_3 \setminus \{i_{r_1}, i_{r_2}\}} = \\
& \left( \delta_{j_1}^{i_1} \delta_{j_2}^{i_2} \Gamma_{j_3}^{i_3} + \delta_{j_2}^{i_1} \delta_{j_1}^{i_2} \Gamma_{j_3}^{i_3} + \delta_{j_1}^{i_2} \delta_{j_2}^{i_1} \Gamma_{j_3}^{i_3} + \delta_{j_2}^{i_2} \delta_{j_1}^{i_1} \Gamma_{j_3}^{i_3} \right) \\
& + 2\delta_{j_1}^{i_3} \left( \delta_{j_2}^{i_2} \Gamma_{j_3}^{i_1} + \delta_{j_3}^{i_2} \Gamma_{j_2}^{i_1} + \delta_{j_2}^{i_1} \Gamma_{j_3}^{i_2} + \delta_{j_3}^{i_1} \Gamma_{j_2}^{i_2} \right) \\
& + 2\delta_{j_2}^{i_3} \left( \delta_{j_1}^{i_2} \Gamma_{j_3}^{i_1} + \delta_{j_3}^{i_2} \Gamma_{j_1}^{i_1} + \delta_{j_1}^{i_1} \Gamma_{j_3}^{i_2} + \delta_{j_3}^{i_1} \Gamma_{j_1}^{i_2} \right) \\
& + 2\delta_{j_3}^{i_1} \left( \delta_{j_2}^{i_2} \Gamma_{j_1}^{i_3} + \delta_{j_1}^{i_2} \Gamma_{j_2}^{i_3} + \delta_{j_2}^{i_3} \Gamma_{j_1}^{i_2} + \delta_{j_1}^{i_3} \Gamma_{j_2}^{i_2} \right) \\
& + 2\delta_{j_3}^{i_2} \left( \delta_{j_2}^{i_1} \Gamma_{j_1}^{i_3} + \delta_{j_1}^{i_1} \Gamma_{j_2}^{i_3} + \delta_{j_2}^{i_3} \Gamma_{j_1}^{i_1} + \delta_{j_1}^{i_3} \Gamma_{j_2}^{i_1} \right) \\
& + 2\delta_{j_3}^{i_3} \left( \delta_{j_1}^{i_1} \Gamma_{j_2}^{i_2} + \delta_{j_2}^{i_1} \Gamma_{j_1}^{i_2} + \delta_{j_2}^{i_2} \Gamma_{j_1}^{i_1} + \delta_{j_1}^{i_2} \Gamma_{j_2}^{i_1} \right) \\
& - 2 \left( \delta_{j_1}^{i_3} \delta_{j_3}^{i_1} \Gamma_{j_2}^{i_2} + \delta_{j_2}^{i_3} \delta_{j_3}^{i_1} \Gamma_{j_1}^{i_2} + \delta_{j_1}^{i_3} \delta_{j_3}^{i_2} \Gamma_{j_2}^{i_1} + \delta_{j_2}^{i_3} \delta_{j_3}^{i_2} \Gamma_{j_1}^{i_1} \right). \tag{C.10}
\end{aligned}$$

By the induction assumption we have assumed [Equation C.7](#) to be correct up to  $p - 1$ . In the next step we show that each term in [Equation C.7](#) for  $\tilde{\Gamma}_p$  can be obtained from  $\tilde{\Gamma}_{p-1}$  and  $\tilde{\Gamma}_{p-2}$

via Equation C.6.

$$\begin{aligned}
\hat{a}_i^\dagger \tilde{\Gamma}_{j_1, \dots, j_{p-1}}^{i_1, \dots, i_{p-1}} \hat{a}_{j_p} &\rightarrow \frac{1}{s!} \sum_{r_1 \neq r_2 \dots \neq r_s}^{p-1} \sum_{t_1 \neq t_2 \dots \neq t_s}^{p-1} \delta_{j_{t_1}}^{i_{r_1}} \delta_{j_{t_2}}^{i_{r_2}} \dots \delta_{j_{t_s}}^{i_{r_s}} \Gamma_{j_1, \dots, j_p \setminus \{j_{t_1}, j_{t_2}, \dots, j_{t_s}\}}^{i_1, \dots, i_p \setminus \{i_{r_1}, i_{r_2}, \dots, i_{r_s}\}} \\
\sum_{k=1}^{p-1} \delta_{j_p}^{i_k} \tilde{\Gamma}_{j_1, \dots, j_{p-1}}^{i_1, \dots, i_p \setminus \{i_k\}} &\rightarrow \frac{1}{(s-1)!} \sum_{k=1}^{p-1} \delta_{j_p}^{i_k} \sum_{r_1 \neq r_2 \dots \neq r_{s-1} \neq k}^{p-1} \sum_{t_1 \neq t_2 \dots \neq t_{s-1}}^{p-1} \delta_{j_{t_1}}^{i_{r_1}} \delta_{j_{t_2}}^{i_{r_2}} \dots \delta_{j_{t_{s-1}}}^{i_{r_{s-1}}} \Gamma_{j_1, \dots, j_{p-1} \setminus \{j_{t_1}, j_{t_2}, \dots, j_{t_{s-1}}\}}^{i_1, \dots, i_p \setminus \{i_{r_1}, i_{r_2}, \dots, i_{r_{s-1}}, i_k\}} \\
\sum_{k=1}^{p-1} \delta_{j_k}^{i_p} \tilde{\Gamma}_{j_1, \dots, j_p \setminus \{j_k\}}^{i_1, \dots, i_{p-1}} &\rightarrow \frac{1}{(s-1)!} \sum_{k=1}^{p-1} \delta_{j_k}^{i_p} \sum_{r_1 \neq r_2 \dots \neq r_{s-1}}^{p-1} \sum_{t_1 \neq t_2 \dots \neq t_{s-1} \neq k}^p \delta_{j_{t_1}}^{i_{r_1}} \delta_{j_{t_2}}^{i_{r_2}} \dots \delta_{j_{t_{s-1}}}^{i_{r_{s-1}}} \Gamma_{j_1, \dots, j_p \setminus \{j_{t_1}, j_{t_2}, \dots, j_{t_{s-1}}, j_k\}}^{i_1, \dots, i_{p-1} \setminus \{i_{r_1}, \dots, i_{r_{s-1}}\}} \\
\delta_{j_p}^{i_p} \tilde{\Gamma}_{j_1, \dots, j_{p-1}}^{i_1, \dots, i_{p-1}} &\rightarrow \frac{1}{(s-1)!} \sum_{r_1 \neq r_2 \dots \neq r_{s-1}}^{p-1} \sum_{t_1 \neq t_2 \dots \neq t_{s-1}}^{p-1} \delta_{j_{t_1}}^{i_{r_1}} \delta_{j_{t_2}}^{i_{r_2}} \dots \delta_{j_p}^{i_p} \Gamma_{j_1, \dots, j_{p-1} \setminus \{j_{t_1}, \dots, j_{t_{s-1}}\}}^{i_1, \dots, i_{p-1} \setminus \{i_{r_1}, \dots, i_{r_{s-1}}\}} \\
\sum_{k=1}^{p-1} \sum_{l=1}^{p-1} \delta_{j_p}^{i_k} \delta_{j_l}^{i_p} \tilde{\Gamma}_{j_1, \dots, j_{p-1} \setminus \{i_l\}}^{i_1, \dots, i_{p-1} \setminus \{i_k\}} &\rightarrow \frac{1}{(s-2)!} \sum_{r_1 \neq r_2 \dots \neq r_{s-1}}^{p-1} \sum_{t_1 \neq t_2 \dots \neq t_{s-1}}^{p-1} \delta_{j_{t_1}}^{i_{r_1}} \delta_{j_{t_2}}^{i_{r_2}} \dots \delta_{j_{t_{s-1}}}^{i_{r_{s-1}}} \delta_{j_p}^{i_p} \Gamma_{j_1, \dots, j_{p-1} \setminus \{j_{t_1}, \dots, j_{t_{s-1}}\}}^{i_1, \dots, i_{p-1} \setminus \{i_{r_1}, \dots, i_{r_{s-1}}\}}.
\end{aligned} \tag{C.11}$$

On a similar line of reasoning the corresponding relation between hole-RDMs and particle-RDMs in the fermionic case can be constructed by applying the commutation relation  $\hat{a}_i \hat{a}_j^\dagger = -\hat{a}_i^\dagger \hat{a}_j + \delta_i^j$  to get the equation

$$\begin{aligned}
\tilde{\Gamma}_{j_1, \dots, j_p}^{i_1, \dots, i_p} &= (-1)^p \Gamma_{j_1, \dots, j_p}^{i_1, \dots, i_p} \\
&+ (-1)^{p-1} \sum_{\substack{r_1 \\ t_1}} \text{sgn}(\pi_i) \text{sgn}(\pi_j) \delta_{j_{t_1}}^{i_{r_1}} \Gamma_{j_1, \dots, j_p \setminus \{j_{t_1}\}}^{i_1, \dots, i_p \setminus \{i_{r_1}\}} \\
&+ (-1)^{p-2} \sum_{\substack{r_1 < r_2 \\ t_1 \neq t_2}} \text{sgn}(\pi_i) \text{sgn}(\pi_j) \delta_{j_{t_1}}^{i_{r_1}} \delta_{j_{t_2}}^{i_{r_2}} \Gamma_{j_1, \dots, j_p \setminus \{j_{t_1}, j_{t_2}\}}^{i_1, \dots, i_p \setminus \{i_{r_1}, i_{r_2}\}} \\
&+ (-1)^{p-3} \sum_{\substack{r_1 < r_2 < r_3 \\ t_1 \neq t_2 \neq t_3}} \text{sgn}(\pi_i) \text{sgn}(\pi_j) \delta_{j_{t_1}}^{i_{r_1}} \delta_{j_{t_2}}^{i_{r_2}} \delta_{j_{t_3}}^{i_{r_3}} \Gamma_{j_1, \dots, j_p \setminus \{j_{t_1}, j_{t_2}, j_{t_3}\}}^{i_1, \dots, i_p \setminus \{i_{r_1}, i_{r_2}, i_{r_3}\}} \\
&\vdots \\
&+ \sum_{\substack{r_1 < r_2 < \dots < r_p \\ t_1 \neq t_2 \neq \dots \neq t_p}} \text{sgn}(\pi_i) \text{sgn}(\pi_j) \delta_{j_{t_1}}^{i_{r_1}} \delta_{j_{t_2}}^{i_{r_2}} \dots \delta_{j_{t_p}}^{i_{r_p}},
\end{aligned} \tag{C.12}$$

where  $\text{sgn}(\pi_i)$  is the sign of one permutation of  $i_{r_1}, i_{r_2}, i_{r_3}, i_1, \dots, i_p \setminus \{i_{r_1}, i_{r_2}, i_{r_3}\}$ . Using Equation C.3 the relation between hole-RDMs and particle-RDMs for bosons becomes

$$\tilde{D}_{j_1, \dots, j_p}^{i_1, \dots, i_p} = \sum_{s=0}^p \frac{1}{p!} (p-s)! \sum_{\substack{r_1 < r_2 < \dots < r_s \\ t_1 \neq t_2 \neq \dots \neq t_s}} \delta_{j_{t_1}}^{i_{r_1}} \delta_{j_{t_2}}^{i_{r_2}} \dots \delta_{j_{t_s}}^{i_{r_s}} D_{j_1, \dots, j_p \setminus \{j_{t_1}, j_{t_2}, \dots, j_{t_s}\}}^{i_1, \dots, i_p \setminus \{i_{r_1}, i_{r_2}, \dots, i_{r_s}\}} \tag{C.13}$$

$$= \sum_{s=0}^p \frac{1}{p!} (p-s)! \frac{1}{(p-s)!^2} \frac{1}{s!} \sum_{\sigma, \pi} \delta_{j_{\pi(1)}}^{i_{\sigma(1)}} \delta_{j_{\pi(2)}}^{i_{\sigma(2)}} \dots \delta_{j_{\pi(s)}}^{i_{\sigma(s)}} D_{j_{\pi(s+1)} j_{\pi(s+2)} \dots j_{\pi(p)}}^{i_{\sigma(s+1)} i_{\sigma(s+2)} \dots i_{\sigma(p)}}, \tag{C.14}$$



and for fermions

$$\tilde{D}_{j_1, \dots, j_p}^{i_1, \dots, i_p} = \sum_{s=0}^p (-1)^{p-s} \frac{1}{p!} (p-s)! \sum_{\substack{r_1 < r_2 < \dots < r_s \\ t_1 \neq t_2 \neq \dots \neq t_s}} \text{sgn}(\pi_i) \text{sgn}(\pi_j) \delta_{j_{t_1}}^{i_{r_1}} \delta_{j_{t_2}}^{i_{r_2}} \dots \delta_{j_{t_s}}^{i_{r_s}} D_{j_1, \dots, j_p \setminus \{j_{t_1}, j_{t_2}, \dots, j_{t_s}\}}^{i_1, \dots, i_p \setminus \{i_{r_1}, i_{r_2}, \dots, i_{r_s}\}} \quad (\text{C.15})$$

$$= \sum_{s=0}^p (-1)^{p-s} \frac{1}{p!} (p-s)! \frac{1}{(p-s)!^2} \frac{1}{s!} \sum_{\sigma, \tau} \text{sgn}(\sigma) \text{sgn}(\tau) \delta_{j_{\tau(1)}}^{i_{\sigma(1)}} \delta_{j_{\tau(2)}}^{i_{\sigma(2)}} \dots \delta_{j_{\tau(s)}}^{i_{\sigma(s)}} D_{j_{\tau(s+1)}, j_{\tau(s+2)}, \dots, j_{\tau(p)}}^{i_{\sigma(s+1)}, i_{\sigma(s+2)}, \dots, i_{\sigma(p)}}. \quad (\text{C.16})$$

With the definition of the antisymmetric wedge product  $\wedge$  for fermions and the symmetric product  $\odot$  for bosons

$$A_{j_1, \dots, j_s}^{i_1, \dots, i_s} \odot B_{j_{s+1}, \dots, j_p}^{i_{s+1}, \dots, i_p} = \frac{1}{p!^2} \sum_{\sigma, \tau} A_{j_{\tau(1)}, \dots, j_{\tau(s)}}^{i_{\sigma(1)}, \dots, i_{\sigma(s)}} B_{j_{\tau(s+1)}, \dots, j_{\tau(p)}}^{i_{\sigma(s+1)}, \dots, i_{\sigma(p)}} \quad (\text{C.17})$$

$$A_{j_1, \dots, j_s}^{i_1, \dots, i_s} \wedge B_{j_{s+1}, \dots, j_p}^{i_{s+1}, \dots, i_p} = \frac{1}{p!^2} \sum_{\sigma, \tau} \text{sgn}(\sigma) \text{sgn}(\tau) A_{j_{\tau(1)}, \dots, j_{\tau(s)}}^{i_{\sigma(1)}, \dots, i_{\sigma(s)}} B_{j_{\tau(s+1)}, \dots, j_{\tau(p)}}^{i_{\sigma(s+1)}, \dots, i_{\sigma(p)}}, \quad (\text{C.18})$$

we can write [Equation C.3](#) and [Equation C.12](#) in a compact way

$$\text{Fermions: } \tilde{D}_p = (-1)^p D_p + \sum_{s=1}^p (-1)^{p-s} \binom{p}{s} \delta^s \wedge D_{p-s} \quad (\text{C.19})$$

$$\text{Bosons: } \tilde{D}_p = D_p + \sum_{s=1}^p \binom{p}{s} \delta^s \odot D_{p-s}. \quad (\text{C.20})$$

## C.2. Reconstruction

The key point in the derivation of the reconstruction functionals is the observation that the difference between hole-RDM and particle-RDM can be written as a sum of two contributions that have the same functional form for both [\[26\]](#)

$$\tilde{D}_p - (-1)^p D_p = \sum_{s=1}^p (-1)^{p-s} \binom{p}{s} \delta^s \wedge D_{p-s} = f(D_1, \dots, D_{p-1}) - (-1)^p f(\tilde{D}_1, \dots, \tilde{D}_{p-1}) \quad (\text{C.21})$$

$$\tilde{D}_p - D_p = \sum_{s=1}^p \binom{p}{s} \delta^s \odot D_{p-s} = f(D_1, \dots, D_{p-1}) - f(\tilde{D}_1, \dots, \tilde{D}_{p-1}). \quad (\text{C.22})$$

For fermions the functional  $f(D_1, \dots, D_{p-1})$  can be determined by considering a system with as many orbitals as particles. In this case there are no holes and therefore all hole RDMs have to vanish  $\tilde{D}_1 = 0, \dots, \tilde{D}_p = 0$ . Due to the universality of [Equation C.21](#) this leads in the fermionic case to

$$\delta = \tilde{D}_1 + D_1 = D_1, \quad (\text{C.23})$$

and thus

$$D_p = \sum_{s=1}^p (-1)^{s+1} \binom{p}{s} D_1^s \wedge D_{p-s}. \quad (\text{C.24})$$

This argument cannot be applied for bosons because each orbital can be occupied by an arbitrary number of particles. In fact it turns out that the reconstruction functional for bosons is not correctly normalized even for the case of single permanent wave functions (see [Appendix H](#)). Nonetheless with the appropriate normalization the same procedure as for fermions

$$\delta = \tilde{D}_1 - D_1 = -D_1 \quad (\text{C.25})$$

leads to

$$D'_p = \sum_{s=1}^p (-1)^{s+1} \binom{p}{s} D_1^s \odot D_{p-s} \quad (\text{C.26})$$

$$(\text{C.27})$$

and after normalization

$$D_p = \frac{\binom{N}{p}}{\text{Tr}(D'_p)} D'_p. \quad (\text{C.28})$$

It is surprising that both reconstruction functionals have, except for the normalization and the type of product, the same functional. In particular for  $p = 3$  we obtain for the fermionic case

$$D_3 = 3D_1 \wedge D_2 - 3D_1^2 \wedge D_1 + D_1^3 \quad (\text{C.29})$$

$$= 3D_1 \wedge D_2 - 2D_1^3. \quad (\text{C.30})$$

This derivation based on the particle-hole duality has the large disadvantage that correction terms that are symmetric under particle-hole exchange do not appear in the reconstruction. Such terms are obtained in the more general derivation using cumulants (see [Appendix F](#)).

## D. General structure of $N$ -representability conditions

In a search for further conditions Erdahl [37] imposed conditions which can be traced back to 3-positivity conditions. In general the 3-positivity conditions are given by the positivity of the four matrices:

$$D_{j_1, j_2, j_3}^{i_1, i_2, i_3} = \langle \Psi | \hat{a}_{i_1}^\dagger \hat{a}_{i_2}^\dagger \hat{a}_{i_3}^\dagger \hat{a}_{j_3} \hat{a}_{j_2} \hat{a}_{j_1} | \Psi \rangle \quad (\text{D.1})$$

$$Q_{j_1, j_2, j_3}^{i_1, i_2, i_3} = \langle \Psi | \hat{a}_{j_1} \hat{a}_{j_2} \hat{a}_{j_3} \hat{a}_{i_3}^\dagger \hat{a}_{i_2}^\dagger \hat{a}_{i_1}^\dagger | \Psi \rangle \quad (\text{D.2})$$

$$E_{j_1, j_2, j_3}^{i_1, i_2, i_3} = \langle \Psi | \hat{a}_{j_1} \hat{a}_{i_2}^\dagger \hat{a}_{i_3}^\dagger \hat{a}_{j_3} \hat{a}_{i_2}^\dagger \hat{a}_{i_1}^\dagger | \Psi \rangle \quad (\text{D.3})$$

$$G_{j_1, j_2, j_3}^{i_1, i_2, i_3} = \langle \Psi | \hat{a}_{i_1}^\dagger \hat{a}_{i_2}^\dagger \hat{a}_{j_3} \hat{a}_{i_3}^\dagger \hat{a}_{j_2} \hat{a}_{j_1} | \Psi \rangle. \quad (\text{D.4})$$

Each of these four conditions separately represent  $N$ -representability conditions for the 3-RDM and cannot be used directly as additional conditions on the 2-RDM. However, taking the sum

$$D_{j_1, j_2, j_3}^{i_1, i_2, i_3} + Q_{j_1, j_2, j_3}^{i_1, i_2, i_3} = \langle \Psi | \hat{a}_{i_1}^\dagger \hat{a}_{i_2}^\dagger \hat{a}_{i_3}^\dagger \hat{a}_{j_3} \hat{a}_{j_2} \hat{a}_{j_1} + \hat{a}_{j_1} \hat{a}_{j_2} \hat{a}_{j_3} \hat{a}_{i_3}^\dagger \hat{a}_{i_2}^\dagger \hat{a}_{i_1}^\dagger | \Psi \rangle \quad (\text{D.5})$$

and rearranging the creation/annihilation operators shows that the sum of the 3-particle and 3-hole RDM is actually a 2-particle operator and, therefore, completely determined by elements of the 2-RDM (see Equation C.19 in Appendix C). The same argument can be applied to the sum

$$E_{j_1, j_2, j_3}^{i_1, i_2, i_3} + G_{j_1, j_2, j_3}^{i_1, i_2, i_3}. \quad (\text{D.6})$$

This leads to new conditions on the 2-RDM

$$D_3 + Q_3 \geq 0 \quad (\text{D.7})$$

$$E_3 + G_3 \geq 0, \quad (\text{D.8})$$

which are referred to as  $T_1$  and  $T_2$  conditions [24]. Since these conditions on the 2-RDM arise from the 3-positivity conditions they are classified as (2, 3)-conditions. In this notation the ordinary 2-positivity condition may be denoted as (2, 2)-conditions [36].

Recently, a constructive approach was found which, in principle, characterizes all (2,  $q$ )-conditions for any integer  $q$  and shows that the sum of all (2,  $q$ )-conditions forms a complete set of  $N$ -representability conditions for the 2-RDM [36]. Since for a system consisting of  $r$  orbitals all  $p$ -particle operators with  $p > r$  are equal to zero and the (2,  $q$ )-conditions implicate (2,  $p$ )-conditions if  $p < q$ , the (2,  $r$ )-conditions contain all (2,  $q$ )-conditions for any integer  $q$ . Therefore, the (2,  $r$ )-conditions form a complete set of conditions.

To understand this result consider that the set of  $N$ -representable  $p$ -RDMs forms a convex set  $P_p$ . The convex sum of two  $N$ -representable  $p$ -RDMs is again a  $N$ -representable  $p$ -RDM. This convex set is used to define the convex set  $P_p^*$  of  $p$ -particle operators

$$\hat{O}_p = \frac{1}{p!} O_{i_1, \dots, i_p}^{j_1, \dots, j_p} \hat{a}_{i_1}^\dagger \dots \hat{a}_{i_p}^\dagger \hat{a}_{j_1} \dots \hat{a}_{j_p}, \quad (\text{D.9})$$

which fulfill

$$P_p^* = \{ \hat{O}_p | \langle \Psi | \hat{O}_p | \Psi \rangle = O_{i_1, \dots, i_p}^{j_1, \dots, j_p} D_{j_1, \dots, j_p}^{i_1, \dots, i_p} \geq 0 \quad \forall D_p \in P_p \}. \quad (\text{D.10})$$

The set  $P_p^*$  is a generalization of the set of operators  $M_p = \langle \Psi | \hat{C}_p^\dagger \hat{C}_p | \Psi \rangle$  we have already introduced in [Equation 2.98](#). It contains also  $p$ -particle operators  $M_p$ , i.e., operators calculated from  $p$ -RDM elements, whose  $\hat{C}$  are polynomials of higher degree than  $p$  and all convex combinations of such operators. For example,  $P_2^*$  contains  $D_2, Q_2, G_2$  but also  $\frac{1}{2}(D_3 + Q_3)$  and  $\frac{1}{2}(E_3 + F_3)$  which can be written as

$$\frac{1}{2}(D_3 + Q_3) = \langle \Psi | \hat{C}^\dagger \hat{C} | \Psi \rangle \quad \text{with} \quad \hat{C} = \frac{1}{\sqrt{2}}(\hat{a}_{j_3} \hat{a}_{j_2} \hat{a}_{j_1} + \hat{a}_{i_3}^\dagger \hat{a}_{i_2}^\dagger \hat{a}_{i_1}^\dagger) \quad (\text{D.11})$$

$$\frac{1}{2}(E_3 + F_3) = \langle \Psi | \hat{C}^\dagger \hat{C} | \Psi \rangle \quad \text{with} \quad \hat{C} = \frac{1}{\sqrt{2}}(\hat{a}_{j_3} \hat{a}_{i_2}^\dagger \hat{a}_{i_1}^\dagger + \hat{a}_{i_3}^\dagger \hat{a}_{j_2} \hat{a}_{j_1}), \quad (\text{D.12})$$

as well as further  $p$ -particle operators that involve  $\hat{C}_q$  with  $q < r$  as long as they reduce to  $p$ -particle operators in the end. The crucial point is that by the bipolar theorem [\[46\]](#) the set  $P_p^*$  is sufficient to define the set of  $N$ -representable  $p$ -RDMs:

$$P_p = \{ D_p | \langle \Psi | \hat{O}_p | \Psi \rangle = O_{j_1, \dots, j_p}^{i_1, \dots, i_p} D_{j_1, \dots, j_p}^{i_1, \dots, i_p} \geq 0 \quad \forall \hat{O}_p \in P_p^* \}. \quad (\text{D.13})$$

In particular, due to the convexity of the set  $P_p^*$  the conditions can be reduced to a finite set of conditions arising from the extreme elements in  $P_p^*$  where an element is called extreme if it cannot be expressed as the convex sum of other elements. This is a remarkable result indeed since the set of extreme conditions in  $P_p^*$  defines a complete set of conditions for  $N$ -representability of a  $p$ -RDM. The extreme conditions can be constructed from  $p$ -particle operators that are convex combinations of appropriated matrices  $M_p = \langle \Psi | \hat{C}_r^\dagger \hat{C}_r | \Psi \rangle$  where all terms with more than  $2p$ -creation/annihilation operators vanish. Such a construction has lead to the discovery of (2, 4)-, (2, 5)- and even (2, 6)-conditions for the  $N$ -representability of the 2-RDM [\[47\]](#). An explicit list of all necessary and sufficient conditions, however, is still missing.

## E. Equations of motion for $p$ -RDMs in second quantization

In this appendix we derive the equations of motion for RDMs of arbitrary order in second quantization. The formulation in second quantization is very elegant because the explicit calculation of partial traces does not show up. Nevertheless the derivation requires considerable manipulation of expressions containing creation/annihilation operators. To simplify notation we use Einstein's sum convention. Starting point of the derivation is the Heisenberg equation of motion for the reduced density operator  $\Gamma_{j_1, \dots, j_p}^{i_1, \dots, i_p} = \hat{a}_{i_1}^\dagger \dots \hat{a}_{i_p}^\dagger \hat{a}_{j_p} \dots \hat{a}_{j_1}$ :

$$\begin{aligned}
i\partial_t \Gamma_{j_1, \dots, j_p}^{i_1, \dots, i_p} &= [\Gamma_{j_1, \dots, j_p}^{i_1, \dots, i_p}, \hat{H}] = h_\mu^\sigma \hat{a}_{i_1}^\dagger \dots \hat{a}_{i_p}^\dagger \hat{a}_{j_p} \dots \hat{a}_{j_1} \hat{a}_\mu^\dagger \hat{a}_\sigma - h_\mu^\sigma \hat{a}_\mu^\dagger \hat{a}_\sigma \hat{a}_{i_1}^\dagger \dots \hat{a}_{i_p}^\dagger \hat{a}_{j_p} \dots \hat{a}_{j_1} \\
&+ \frac{1}{2} V_{\mu, \nu}^{\sigma, \tau} \hat{a}_{i_1}^\dagger \dots \hat{a}_{i_p}^\dagger \hat{a}_{j_p} \dots \hat{a}_{j_1} \hat{a}_\mu^\dagger \hat{a}_\nu^\dagger \hat{a}_\tau \hat{a}_\sigma - \frac{1}{2} V_{\mu, \nu}^{\sigma, \tau} \hat{a}_\mu^\dagger \hat{a}_\nu^\dagger \hat{a}_\tau \hat{a}_\sigma \hat{a}_{i_1}^\dagger \dots \hat{a}_{i_p}^\dagger \hat{a}_{j_p} \dots \hat{a}_{j_1} \\
&= h_\mu^\sigma \hat{a}_{i_1}^\dagger \dots \hat{a}_{i_p}^\dagger \hat{a}_{j_p} \dots \hat{a}_{j_1} \hat{a}_\mu^\dagger \hat{a}_\sigma - \left( h_\mu^\sigma \hat{a}_{j_1}^\dagger \dots \hat{a}_{j_p}^\dagger \hat{a}_{i_p} \dots \hat{a}_{i_1} \hat{a}_\sigma \hat{a}_\mu \right)^\dagger \\
&+ \frac{1}{2} V_{\mu, \nu}^{\sigma, \tau} \hat{a}_{i_1}^\dagger \dots \hat{a}_{i_p}^\dagger \hat{a}_{j_p} \dots \hat{a}_{j_1} \hat{a}_\mu^\dagger \hat{a}_\nu^\dagger \hat{a}_\tau \hat{a}_\sigma - \left( \frac{1}{2} V_{\mu, \nu}^{\sigma, \tau} \hat{a}_{j_1}^\dagger \dots \hat{a}_{j_p}^\dagger \hat{a}_{i_p} \dots \hat{a}_{i_1} \hat{a}_\sigma \hat{a}_\tau \hat{a}_\nu \hat{a}_\mu \right)^\dagger, \quad (\text{E.1})
\end{aligned}$$

where we have used the Hamilton operator in second quantization

$$\hat{H} = h_\mu^\sigma \hat{a}_\mu^\dagger \hat{a}_\sigma + \frac{1}{2} V_{\mu, \nu}^{\sigma, \tau} \hat{a}_\mu^\dagger \hat{a}_\nu^\dagger \hat{a}_\tau \hat{a}_\sigma. \quad (\text{E.2})$$

**Equation E.1** shows that the second term in the commutator is the adjoint operator of the first one. Therefore, it is sufficient to evaluate the first terms of the commutator:

$$\begin{aligned}
h_\mu^\sigma \hat{a}_{i_1}^\dagger \dots \hat{a}_{i_p}^\dagger \hat{a}_{j_p} \dots \hat{a}_{j_1} \hat{a}_\mu^\dagger \hat{a}_\sigma &= h_\mu^\sigma \hat{a}_{i_1}^\dagger \dots \hat{a}_{i_p}^\dagger \hat{a}_\mu^\dagger \hat{a}_\sigma \hat{a}_{j_p} \dots \hat{a}_{j_1} + \sum_{n=1}^p h_{j_n}^\sigma \hat{a}_{i_1}^\dagger \dots \hat{a}_{i_p}^\dagger \hat{a}_{j_p} \dots \hat{a}_{j_{n+1}} \hat{a}_\sigma \hat{a}_{j_{n-1}} \dots \hat{a}_{j_1} \\
&= h_\mu^\sigma \Gamma_{j_1, \dots, j_p, \sigma}^{i_1, \dots, i_p, \mu} + \sum_{n=1}^p h_{j_n}^\sigma \Gamma_{j_1, \dots, j_{n+1}, \sigma, j_{n+1}, \dots, j_p}^{i_1, \dots, i_p} \quad (\text{E.3})
\end{aligned}$$

$$\begin{aligned}
& V_{\mu,\nu}^{\sigma,\tau} \hat{a}_{i_1}^\dagger \dots \hat{a}_{i_p}^\dagger \hat{a}_{j_p} \dots \hat{a}_{j_1} \hat{a}_\mu^\dagger \hat{a}_\nu^\dagger \hat{a}_\sigma \hat{a}_\tau = V_{\mu,\nu}^{\sigma,\tau} \hat{a}_{i_1}^\dagger \dots \hat{a}_{i_p}^\dagger \hat{a}_\mu^\dagger \hat{a}_\nu^\dagger \hat{a}_\sigma \hat{a}_\tau \hat{a}_{j_p} \dots \hat{a}_{j_1} \\
& + \sum_{n=1}^p V_{j_n, j_m}^{\sigma,\tau} \hat{a}_{i_1}^\dagger \dots \hat{a}_{i_p}^\dagger \hat{a}_\nu^\dagger \hat{a}_\tau \hat{a}_{j_p} \dots \hat{a}_{j_{n+1}} \hat{a}_\sigma \hat{a}_{j_{n-1}} \dots \hat{a}_{j_1} + \sum_{n=1}^p V_{\mu, j_n}^{\sigma,\tau} \hat{a}_{i_1}^\dagger \dots \hat{a}_{i_p}^\dagger \hat{a}_\mu^\dagger \hat{a}_\sigma \hat{a}_{j_p} \dots \hat{a}_{j_{n+1}} \hat{a}_\tau \hat{a}_{j_{n-1}} \dots \hat{a}_{j_1} \\
& + \sum_{n \neq m}^p V_{j_n, j_m}^{\sigma,\tau} \hat{a}_{i_1}^\dagger \dots \hat{a}_{i_p}^\dagger \hat{a}_{j_p} \dots \hat{a}_{j_{n+1}} \hat{a}_\tau \hat{a}_{j_{n-1}} \dots \hat{a}_{j_{m+1}} \hat{a}_\sigma \hat{a}_{j_{m-1}} \dots \hat{a}_{j_1} \\
& = V_{\mu,\nu}^{\sigma,\tau} \Gamma_{j_1, \dots, j_p, \sigma, \tau}^{i_1, \dots, i_p, \mu, \nu} + 2 \sum_{n=1}^p V_{\mu, j_n}^{\sigma,\tau} \Gamma_{j_1, \dots, j_{n+1}, \tau, j_{n+1}, \dots, j_p, \sigma}^{i_1, \dots, i_p, \mu} + \sum_{n \neq m}^p V_{j_n, j_m}^{\sigma,\tau} \Gamma_{j_1, \dots, j_{n+1}, \tau, j_{n+1}, \dots, j_{m+1}, \sigma, j_{m+1}, \dots, j_p}^{i_1, \dots, i_p}.
\end{aligned} \tag{E.4}$$

The equations of motion for the reduced density operator  $\Gamma_{j_1, \dots, j_p}^{i_1, \dots, i_p}$  can be used to derive the equations of motion for the  $p$ -RDM by taking the expectation value of [Equation E.1](#):

$$i \partial_t D_{j_1, \dots, j_p}^{i_1, \dots, i_p} = \frac{1}{p!} \langle \Psi | [\Gamma_{j_1, \dots, j_p}^{i_1, \dots, i_p}, \hat{H}] | \Psi \rangle. \tag{E.5}$$

Using the results in [Equation E.3](#) and [Equation E.4](#) we get the following equations of motion for the  $p$ -RDM

$$\begin{aligned}
i \partial_t D_{j_1, \dots, j_p}^{i_1, \dots, i_p} &= \sum_{n=1}^p \left( h_{j_n}^\sigma D_{j_1, \dots, j_{n+1}, \sigma, j_{n+1}, \dots, j_p}^{i_1, \dots, i_p} - h_\mu^{i_n} D_{j_1, \dots, j_p}^{i_1, \dots, i_{n+1}, \mu, i_{n+1}, \dots, i_p} \right) \\
&+ \frac{1}{2} \sum_{n \neq m}^p \left( V_{j_n, j_m}^{\sigma, \tau} D_{j_1, \dots, j_{n+1}, \sigma, j_{n+1}, \dots, j_{m+1}, \tau, j_{m+1}, \dots, j_p}^{i_1, \dots, i_p} - V_{\mu, \nu}^{i_n, i_m} D_{j_1, \dots, j_p}^{i_1, \dots, i_{n+1}, \mu, i_{n+1}, \dots, i_{m+1}, \nu, i_{m+1}, \dots, i_p} \right) \\
&+ (p+1) \sum_{n=1}^p \left( V_{\mu, j_n}^{\sigma, \tau} D_{j_1, \dots, j_{n+1}, \tau, j_{n+1}, \dots, j_p, \sigma}^{i_1, \dots, i_p, \mu} - V_{\mu, \nu}^{\sigma, i_n} D_{j_1, \dots, j_p, \sigma}^{i_1, \dots, i_{n+1}, \nu, i_{n+1}, \dots, i_p, \mu} \right).
\end{aligned} \tag{E.6}$$

In the special case  $p = 2$  this equation reads

$$i \partial_t D_{j_1, j_2}^{i_1, i_2} = \left( h_{j_1}^\sigma \delta_{j_2}^\tau + \delta_{j_1}^\sigma h_{j_2}^\tau + V_{j_1, j_2}^{\sigma, \tau} \right) D_{\sigma, \tau}^{i_1, i_2} - \left( h_\mu^{i_1} \delta_\nu^{i_2} + \delta_\mu^{i_1} h_\nu^{i_2} + V_{\mu, \nu}^{i_1, i_2} \right) D_{j_1, j_2}^{\mu, \nu} \tag{E.7}$$

$$+ 3 \left( V_{\mu, j_2}^{\sigma, \tau} D_{j_1, \tau, \sigma}^{i_1, i_2, \mu} + V_{j_1, \nu}^{\sigma, \tau} D_{\sigma, j_2, \tau}^{i_1, i_2, \nu} - V_{\mu, \nu}^{\sigma, i_2} D_{j_1, j_2, \sigma}^{i_1, \nu, \mu} - V_{\mu, \nu}^{i_1, \tau} D_{j_1, j_2, \tau}^{\mu, i_2, \nu} \right). \tag{E.8}$$

## F. Reconstruction of the 3-RDM based on the cumulant expansion

In this appendix we show how to derive the reconstruction functional for the 3-RDM from the cumulant generating functional. We use an arbitrary orbital basis and the associated creation and annihilation operators  $\hat{a}_i^\dagger, \hat{a}_i$ . Considering the action of the normal ordering operator  $\hat{O}$ , the RDM generating functional can be expressed as

$$\begin{aligned}
\Gamma(J_i, J_i^\dagger) &= \langle \Psi | \hat{O} \exp \left( \hat{a}_i^\dagger J_i + \hat{a}_i J_i^\dagger \right) | \Psi \rangle \\
&= \langle \exp \left( \hat{a}_i^\dagger J_i \right) \exp \left( \hat{a}_i J_i^\dagger \right) \rangle \\
&= 1 + \sum_{p=1}^{\infty} \frac{1}{p!^2} \langle \hat{a}_{i_1}^\dagger J_{i_1} \dots \hat{a}_{i_p}^\dagger J_{i_p} \hat{a}_{j_p} J_{j_p}^\dagger \dots \hat{a}_{j_1} J_{j_1}^\dagger \rangle \\
&= 1 + \sum_{p=1}^{\infty} \frac{1}{p!} J_{i_1} \dots J_{i_p} J_{j_p}^\dagger \dots J_{j_1}^\dagger D_{j_1, \dots, j_p}^{i_1, \dots, i_p},
\end{aligned} \tag{F.1}$$

where the Einstein index summation convention was applied to sum over probe variables and creation/annihilation operators. The last line of [Equation F.1](#) corresponds to the multidimensional Taylor expansion of  $\Gamma(J_i, J_i^\dagger)$  and shows that the RDMs appear as the coefficients of this expansion. Note, however, that a detailed calculation of the RDM elements via [Equation 2.49](#) gives an additional anti-symmetrization (symmetrization) for fermions (bosons)

$$\frac{1}{p!} \lim_{J, J^\dagger \rightarrow 0} \frac{\partial^p \Gamma}{\partial J_{j_1}^\dagger \dots \partial J_{j_p}^\dagger \partial J_{i_1} \dots \partial J_{i_p}} = \frac{1}{p!^2} \sum_{\sigma, \tau \in \mathbb{S}_p} D_{j_{\sigma(1)}, \dots, j_{\sigma(p)}}^{i_{\tau(1)}, \dots, i_{\tau(p)}} = D_{j_1, \dots, j_p}^{i_1, \dots, i_p}. \tag{F.2}$$

Since the  $p$ -RDMs are already anti-symmetric (symmetric) the application of the anti-symmetrization (symmetrization) leaves the RDM unchanged but it is essential in the formula for cumulants as will be shown below.

The Taylor expansion of the cumulant generating functional  $W(J_i, J_i^\dagger) = \ln \left( \Gamma(J_i, J_i^\dagger) \right)$  can be determined from the Mac-Laurin Formula of the logarithmic function

$$\ln(1+x) = \sum_{i=1}^{\infty} \frac{(-1)^{i+1}}{i} x^i, \tag{F.3}$$

leading to the following form of the cumulant generating functional

$$W(J_i, J_i^\dagger) = \sum_{i=1}^{\infty} \frac{(-1)^{i+1}}{i} \left( \sum_{p=1}^{\infty} \frac{1}{p!} J_{i_1} \dots J_{i_p} J_{j_p}^\dagger \dots J_{j_1}^\dagger D_{j_1, \dots, j_p}^{i_1, \dots, i_p} \right)^i. \tag{F.4}$$

To derive the cumulants  $\Delta_p$  in terms of the  $p$ -RDMs we expand the two sums and order the terms by the number of probe variables

$$\begin{aligned}
W(J_i, J_i^\dagger) &= J_{i_1} J_{j_1}^\dagger D_{j_1}^{i_1} \\
&+ (1/2) J_{i_1} J_{i_2} J_{j_2}^\dagger J_{j_1}^\dagger D_{j_1, j_2}^{i_1, i_2} \\
&- (1/2) J_{i_1} J_{j_1}^\dagger J_{i_2} J_{j_2}^\dagger D_{j_1}^{i_1} D_{j_2}^{i_2} \\
&+ (1/6) J_{i_1} J_{i_2} J_{i_3} J_{j_3}^\dagger J_{j_2}^\dagger J_{j_1}^\dagger D_{j_1, j_2, j_3}^{i_1, i_2, i_3} \\
&- (1/2) J_{i_1} J_{i_2} J_{j_2}^\dagger J_{j_1}^\dagger J_{i_3} J_{j_3}^\dagger D_{j_1, j_2}^{i_1, i_2} D_{j_3}^{i_3} \\
&+ (1/3) J_{i_1} J_{j_1}^\dagger J_{i_2} J_{j_2}^\dagger J_{i_3} J_{j_3}^\dagger D_{j_1}^{i_1} D_{j_2}^{i_2} D_{j_3}^{i_3} \\
&\vdots \\
&= J_{i_1} J_{j_1}^\dagger D_{j_1}^{i_1} \\
&+ (1/2) J_{i_1} J_{i_2} J_{j_2}^\dagger J_{j_1}^\dagger (D_{j_1, j_2}^{i_1, i_2} - D_{j_1}^{i_1} D_{j_2}^{i_2}) \\
&+ (1/3!) J_{i_1} J_{i_2} J_{i_3} J_{j_3}^\dagger J_{j_2}^\dagger J_{j_1}^\dagger (D_{j_1, j_2, j_3}^{i_1, i_2, i_3} - 3D_{j_1, j_2}^{i_1, i_2} D_{j_3}^{i_3} + 2D_{j_1}^{i_1} D_{j_2}^{i_2} D_{j_3}^{i_3}) \\
&+ (1/4!) J_{i_1} J_{i_2} J_{i_3} J_{i_4} J_{j_4}^\dagger J_{j_3}^\dagger J_{j_2}^\dagger J_{j_1}^\dagger \\
&\times (D_{j_1, j_2, j_3, j_4}^{i_1, i_2, i_3, i_4} - 4D_{j_1, j_2, j_3}^{i_1, i_2, i_3} D_{j_4}^{i_4} - 3D_{j_1, j_2}^{i_1, i_2} D_{j_3, j_4}^{i_3, i_4} + 12D_{j_1, j_2}^{i_1, i_2} D_{j_3}^{i_3} D_{j_4}^{i_4} - 6D_{j_1}^{i_1} D_{j_2}^{i_2} D_{j_3}^{i_3} D_{j_4}^{i_4}) \\
&\vdots
\end{aligned} \tag{F.5}$$

Using the formula for the cumulants

$$\Delta_{j_1, \dots, j_p}^{i_1, \dots, i_p} = \lim_{J, J^\dagger \rightarrow 0} \frac{1}{p!} \frac{\partial^p W}{\partial J_{j_1}^\dagger \dots \partial J_{j_p}^\dagger \partial J_{i_1} \dots \partial J_{i_p}}, \tag{F.6}$$

this leads to the decomposition of the  $p$ -RDM into a connected (cumulant) and an unconnected part  $\Delta_p$ :

$$D_1 = \Delta_1 \tag{F.7}$$

$$D_2 = (D_1 \wedge D_1) + \Delta_2 \tag{F.8}$$

$$D_3 = (3D_2 \wedge D_1 - 2D_1^3) + \Delta_3 \tag{F.9}$$

$$D_4 = (4D_3 \wedge D_1 + 3D_2^2 \wedge D_2^2 - 12D_2 \wedge D_1^2 + 6D_1^4) + \Delta_4 \tag{F.10}$$

$$\vdots \tag{F.11}$$

The unconnected part for the  $p$ -RDM yields the best approximation in terms of wedge products of lower-order RDMs. For the  $p$ -RDM with  $p < 4$  the connected part of the  $p$ -RDM is in agreement with the reconstruction obtained by exploiting the particle-hole duality (see [Appendix C](#)):

$$D_p \approx \sum_{s=1}^p (-1)^{s+1} \binom{p}{s} D_1^s \wedge D_{p-s}. \tag{F.12}$$



For  $p = 4$ , however, Valdemoro's reconstruction functional reads

$$D_4 \approx 4D_1 \wedge D_3 - 6D_1^2 \wedge D_2 + 4D_1^4, \quad (\text{F.13})$$

which is not in agreement with the connected part of  $D_4$ . The difference between both reconstructions is given by the term  $3\Delta_2 \wedge \Delta_2$  and originates from the fact that the cumulant  $\Delta_2$  is invariant under particle-hole exchange and, therefore, cancels in [Equation C.21](#).



## G. The $\gamma, \kappa$ coefficients for bosons with short range interaction

The major drawback of the time-dependent 2-RDM method within a two-particle basis is the time consuming evaluation of the coefficients  $\gamma, \kappa$  entering the  $F$ -operator

$$F_j^i = I_j^i - I_i^{*j} \quad (\text{G.1})$$

$$I_j^i = \gamma_{j,i_1,i_2}^{i,j_1,j_2} \lambda_{j_1}^{i_1} \lambda_{j_2}^{i_2} - \kappa_{j,i_1,i_2,i_3}^{i,j_1,j_2,j_3} \lambda_{j_1}^{i_1} \lambda_{j_2}^{i_2} \lambda_{j_3}^{i_3}. \quad (\text{G.2})$$

The calculation of  $\gamma, \kappa$  simplifies in the case of a system consisting of bosons with short-range interaction that can be approximated by a delta function

$$V_{\text{int}}(x_1, x_2) = g_s \delta(x_1 - x_2). \quad (\text{G.3})$$

Such a system for example is realized by ultra-cold atoms whose interaction can be reduced to s-wave scattering. In this case the parameter  $g_s$  contains the s-wave scattering length. Starting with the  $F$ -operator in coordinate space ([Equation 2.42](#)) the integral over the delta function can be evaluated and leads to

$$F(x_1 x_2; x'_1 x'_2) = I(x_1 x_2; x'_1 x'_2) - I^*(x'_1 x'_2; x_1 x_2) \quad (\text{G.4})$$

$$I(x_1 x_2; x'_1 x'_2) = a_s D(x_1 x_2 x_1; x'_1 x'_2 x_1) + a_s D(x_1 x_2 x_2; x'_1 x'_2 x_2). \quad (\text{G.5})$$

The two-particle basis representation of the  $F$ -operator is determined by the projection onto the basis functions  $\psi_i(x_1, x_2)$ :

$$F_j^i = I_j^i - I_i^{*j} \quad (\text{G.6})$$

$$I_j^i = a_s \int [D(x_1 x_2 x_1; x'_1 x'_2 x_1) + D(x_1 x_2 x_2; x'_1 x'_2 x_2)] \psi_i^*(x_1, x_2) \psi_j(x'_1, x'_2) dx_1 dx_2 dx'_1 dx'_2 \quad (\text{G.7})$$

$$= 2a_s \int D(x_1 x_2 x_1; x'_1 x'_2 x_1) \psi_i^*(x_1, x_2) \psi_j(x'_1, x'_2) dx_1 dx_2 dx'_1 dx'_2. \quad (\text{G.8})$$

In the next step we use the reconstruction functional in [Equation 2.62](#) to approximate the 3-RDM in terms of  $D_2$  and  $D_1$ :

$$D(x_1 x_2 x_3; x'_1 x'_2 x'_3) \approx 3D_2 \wedge D_1 - 2D_1^3 \quad (\text{G.9})$$

$$\approx \frac{3}{3!^2} \sum_{\sigma, \pi} D(x_{\sigma(1)} x_{\sigma(2)}; x'_{\tau(1)} x'_{\tau(2)}) D(x_{\sigma(3)}; x'_{\tau(3)}) \quad (\text{G.10})$$

$$- \frac{2}{3!^2} \sum_{\sigma, \pi} D(x_{\sigma(1)}; x'_{\tau(1)}) D(x_{\sigma(2)}; x'_{\tau(2)}) D(x_{\sigma(3)}; x'_{\tau(3)}). \quad (\text{G.11})$$

This expression can be further simplified by taking into account the symmetry of the 2-RDM and by commuting the three terms in  $D_1^3$ :

$$\begin{aligned}
D(x_1x_2x_3; x'_1x'_2x'_3) \approx & 1/3 \left[ D(x_1x_2; x'_1x'_2)D(x_3; x'_3) + D(x_3x_1; x'_1x'_2)D(x_2; x'_3) + D(x_2x_3; x'_1x'_2)D(x_1; x'_3) \right. \\
& + D(x_1x_2; x'_3x'_1)D(x_3; x'_2) + D(x_3x_1; x'_3x'_1)D(x_2; x'_2) + D(x_2x_3; x'_3x'_1)D(x_1; x'_2) \\
& \left. + D(x_1x_2; x'_2x'_3)D(x_3; x'_1) + D(x_3x_1; x'_2x'_3)D(x_2; x'_1) + D(x_2x_3; x'_2x'_3)D(x_1; x'_1) \right] \\
& - 1/3 \left[ D(x_1; x'_1)D(x_2; x'_2)D(x_3; x'_3) + D(x_1; x'_1)D(x_3; x'_2)D(x_2; x'_3) \right. \\
& + D(x_2; x'_1)D(x_1; x'_2)D(x_3; x'_3) + D(x_2; x'_1)D(x_3; x'_2)D(x_1; x'_3) \\
& \left. + D(x_3; x'_1)D(x_1; x'_2)D(x_2; x'_3) + D(x_3; x'_1)D(x_2; x'_2)D(x_1; x'_3) \right].
\end{aligned} \tag{G.12}$$

Inserting this approximation into [Equation G.6](#) gives an expression that can be further simplified by using the fact that the replacement  $x_1 \leftrightarrow x'_1, x_2 \leftrightarrow x'_2$  is merely a change in the integration variables. Therefore, terms that differ solely by this replacement can be considered equal

$$\begin{aligned}
I_j^i = \frac{2a_s}{3} \int & \left[ 2D(x_1x_2; x'_1x'_2)D(x_1; x_1) + D(x_1x_1; x'_1x'_2)D(x_2; x_1) \right. \\
& + 4D(x_1x_2; x'_1x_1)D(x_1; x'_2) + 2D(x_1x_1; x'_1x_1)D(x_2; x'_2) \\
& - 4D(x_1; x'_1)D(x_2; x'_2)D(x_1; x_1) \\
& \left. + 2D(x_1; x'_1)D(x_2; x_1)D(x_1; x'_2) \right] \psi_i^*(x_1, x_2)\psi_j(x'_1, x'_2)dx_1dx_2dx'_1dx'_2.
\end{aligned} \tag{G.13}$$

Inserting the expression for the 1-RDM

$$D(x_1; x'_1) = \int D(x_1x_2; x'_1x_2)dx_2 = \lambda_j^i \int \psi_i(x_1, x_2)\psi_j^*(x'_1, x_2)dx_2, \tag{G.14}$$

into [Equation G.13](#) and comparing the result with [Equation G.1](#) yields the reconstruction coefficients

$$\begin{aligned}
\gamma_{j, i_1, i_2}^{i, j_1, j_2} = \frac{2a_s}{3} \int & \left[ 2\psi_{i_1}(x_1, x_2)\psi_{j_1}^*(x'_1, x'_2)\psi_{i_2}(x_1, x_3)\psi_{j_2}^*(x_1, x_3) \right. \\
& + \psi_{i_1}(x_1, x_1)\psi_{j_1}^*(x'_1, x'_2)\psi_{i_2}(x_2, x_3)\psi_{j_2}^*(x_1, x_3) \\
& + 4\psi_{i_1}(x_1, x_2)\psi_{j_1}^*(x'_1, x_1)\psi_{i_2}(x_1, x_3)\psi_{j_2}^*(x'_2, x_3) \\
& \left. + 2\psi_{i_1}(x_1, x_1)\psi_{j_1}^*(x'_1, x_1)\psi_{i_2}(x_2, x_3)\psi_{j_2}^*(x'_2, x_3) \right] \\
& \times \psi_i^*(x_1, x_2)\psi_j(x'_1, x'_2)dx_1dx_2dx'_1dx'_2dx_3
\end{aligned} \tag{G.15}$$

$$\begin{aligned}
\kappa_{j, i_1, i_2, i_3}^{i, j_1, j_2, j_3} = \frac{2a_s}{3} \int & \left[ 4\psi_{i_1}(x_1, x_3)\psi_{j_1}^*(x'_1, x_3)\psi_{i_2}(x_2, x_4)\psi_{j_2}^*(x'_2, x_4)\psi_{i_3}(x_1, x_5)\psi_{j_3}^*(x_1, x_5) \right. \\
& \left. + 2\psi_{i_1}(x_1, x_3)\psi_{j_1}^*(x'_1, x_3)\psi_{i_2}(x_2, x_4)\psi_{j_2}^*(x_1, x_4)\psi_{i_3}(x_1, x_5)\psi_{j_3}^*(x'_2, x_5) \right] \\
& \times \psi_i^*(x_1, x_2)\psi_j(x'_1, x'_2)dx_1dx_2dx'_1dx'_2dx_3dx_4dx_5.
\end{aligned} \tag{G.16}$$

In the case of a one-particle basis these integrations can be simplified significantly using the orthonormality of orbitals. In the two-particle basis this is not possible due to the complicated intertwining of the integration variables within the two-particle basis functions. Nonetheless, some simplification can be achieved using the definitions

$$T_i^j(x_1; x'_1) = \int \psi_i(x_1, x_2) \psi_j^*(x'_1, x_2) dx_2 \quad (\text{G.17})$$

$$T_{i_1}^{j_1, j_2}(x_1; x'_1) = \int \psi_{j_1}^*(x_1, x_2) \psi_{i_1}(x_2, x_3) \psi_{j_2}^*(x'_1, x_3) dx_2 dx_3 \quad (\text{G.18})$$

and rewriting the expressions for  $\gamma, \kappa$  in the following way

$$\begin{aligned} \gamma_{j, i_1, i_2}^{i, j_1, j_2} &= \frac{2a_s}{3} \delta_j^{j_1} \int \left[ 2T_{i_1}^i(x_1; x_1) T_{i_2}^{j_2}(x_1; x_1) + \psi_{i_1}(x_1, x_1) T_{i_2}^{j, j_2}(x_1; x_1) \right] dx_1 \\ &\quad + \frac{2a_s}{3} \int \left[ 4T_{i_1}^1(x_1; x_1) T_j^{j_1}(x'_2; x_1) T_{i_2}^{j_2}(x_1; x'_2) \right. \\ &\quad \left. + 2\psi_{i_1}(x_1, x_1) T_j^{j_1}(x'_2; x_1) T_{i_2}^{i, j_2}(x_1; x'_2) \right] dx_1 dx'_2 \end{aligned}$$

$$\begin{aligned} \kappa_{j, i_1, i_2, i_3}^{i, j_1, j_2, j_3} &= \frac{2a_s}{3} \int \left[ 4(T_{j_1}^{i_1, j}(x_1; x'_2))^* T_{i_2}^{i, j_2}(x_1; x'_2) T_{i_3}^{j_3}(x_1; x_1) \right. \\ &\quad \left. + 2(T_{j_1}^{i_1, j}(x_1; x'_2))^* T_{i_2}^{i, j_2}(x_1; x_1) T_{i_3}^{j_3}(x_1; x'_2) \right] dx_1 x'_2. \end{aligned}$$



## H. Reconstruction functionals for Slater determinants

A necessary and sufficient condition for a fermionic many-body wave function to be a single Slater determinant is given by the idempotence of the 1-RDM (see [Appendix A](#)). In this case the 1-RDM contains enough information to reconstruct all  $p$ -RDMs according to

$$D_p = \underbrace{D_1 \wedge D_1 \dots \wedge D_1}_{p \text{ times}} = D_1^p. \quad (\text{H.1})$$

This reconstruction is obtained by setting  $\Delta_p$  to zero for all  $p > 1$  which is equivalent to the condition for independent particles (see [subsection 2.3.2](#)). In the following we will show that in this case the reconstructed RDMs are appropriately normalized to

$$\text{Tr}(D_p) = \text{Tr}(D_1^p) = \binom{N}{p}. \quad (\text{H.2})$$

In general, if  $\Delta_2 \neq 0$  the approximation of the  $p$ -RDM in terms of lower-order RDMs is not correctly normalized and requires renormalization. To proof [Equation H.2](#) we use complete induction with respect to the integer  $p$ . For  $p = 1$  the relation reduces to the normalization of the 1-RDM  $D_1 = N$ . For the induction step from  $p$  to  $p + 1$  we use the following theorem

$$\begin{aligned} \text{Tr}(D_p \wedge D_1) &= \frac{1}{p!^2} \sum_{\sigma, \tau} \text{sgn}(\sigma) \text{sgn}(\tau) D_{i_{\sigma(1)}, \dots, i_{\sigma(p)}}^{i_{\sigma(1)}, \dots, i_{\sigma(p)}} D_{i_{\tau(1)}, \dots, i_{\tau(p+1)}}^{i_{\tau(1)}, \dots, i_{\tau(p+1)}} \\ &= \frac{1}{(p+1)!} \left[ p! D_{i_1, \dots, i_p}^{i_1, \dots, i_p} D_{i_{p+1}}^{i_{p+1}} - p! p \left( D_{i_1, \dots, i_p}^{i_1, \dots, i_p} D_{i_p}^{i_p} \right) \right] \\ &= \frac{1}{(p+1)} \left[ \text{Tr}(D_p) \text{Tr}(D_1) - p \left( D_{i_1, \dots, i_p}^{i_1, \dots, i_p} D_{i_p}^{i_p} \right) \right]. \end{aligned} \quad (\text{H.3})$$

Using the idempotence of the 1-RDM and the fact that the  $p$ -RDM decomposes into the product of 1-RDMs [Equation H.3](#) can be written as

$$\begin{aligned} \text{Tr}(D_1^{p+1}) = \text{Tr}(D_1^p \wedge D_1) &= \frac{1}{(p+1)} [\text{Tr}(D_1^p) N - p \text{Tr}(D_1^p)] \\ &= \frac{N-p}{p+1} \text{Tr}(D_1^p) \\ &= \frac{N-p}{p+1} \binom{N}{p} = \binom{N}{p+1}, \end{aligned} \quad (\text{H.4})$$

which proves the assumption. In the case of a bosonic wave function having the form of a single permanent whose occupation numbers are limited by one the corresponding formula gives

$$\mathrm{Tr}(D_1^{p+1}) = \frac{N+p}{p+1} \mathrm{Tr}(D_1^p) \rightarrow \mathrm{Tr}(D_1^p) = \binom{N+p-1}{p}, \quad (\text{H.5})$$

which is not in agreement with the normalization to  $\binom{N}{p}$ . This shows that even for non-interacting bosons the reconstruction functional is exact only after the appropriate renormalization.



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