



DISSERTATION

# Time-dependent two-particle reduced density matrix theory: application to multi-electron atoms and molecules in strong laser pulses

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# Deutsche Kurzfassung

Es scheint in der Natur der Sache zu liegen, dass Systeme dann besonders komplex werden, wenn viele Teile desselben miteinander interagieren und sich wechselseitig beeinflussen. Dies trifft im Besonderen auf physikalische Systeme zu, die aus einer Vielzahl an wechselwirkenden Teilchen bestehen. Während es in vielen Bereichen der Physik um die Suche nach den unbekanntem Gesetzmäßigkeiten unter immer extremeren Bedingungen geht, so geht es in der Vielteilchenphysik um neue Approximationen zur Beschreibung wohlbekannter Naturgesetze. Im Besonderen die nicht-relativistischen quantenmechanischen Vielteilchensysteme, beschrieben durch die Schrödinger-Gleichung, verwehren sich einer direkten Lösung bereits für mehr als zwei Teilchen. Eine Vielzahl an Approximationen wurde entwickelt, um diese Limitation zu überwinden. Dies trifft insbesondere auf die Berechnung der stationären elektronischen Struktur von komplexen Atomen und Molekülen zu, wie sie im Rahmen der Quantenchemie von großer Bedeutung ist. Quantenchemische Berechnungen basieren im Wesentlichen auf zwei unterschiedlichen Herangehensweisen. Einerseits werden Ansätze für die Vielteilchenwellenfunktion verwendet und diese mittels Variationsrechnung optimiert oder durch störungstheoretische Methoden verbessert, andererseits wird im Rahmen der Dichtefunktionaltheorie die Wellenfunktion durch die Elektronendichte als fundamentale Größe ersetzt. Beide Zugänge haben sich für zeitunabhängige Systeme als sehr fruchtbar erwiesen.

Die Übertragung dieser beiden theoretischen Methoden auf die Beschreibung der zeitabhängigen Dynamik von Vielteilchensystemen steckt allerdings noch in den Kinderschuhen. Zwar gibt es zeitabhängige Erweiterungen sowohl wellenfunktionsbasierter Methoden als auch der Dichtefunktionaltheorie, jedoch ist deren Anwendbarkeit beschränkt, da eine starke Nichtgleichgewichtsdynamik oft auch stärkere elektronische Korrelation bedingt. Die korrekte Beschreibung dieser Korrelationen erfordert einen hohen numerischen Aufwand bei wellenfunktionsbasierten Methoden und resultiert in einer verringerten Genauigkeit der zeitabhängigen Dichtefunktionaltheorie aufgrund der Approximation des Austauschkorrelationspotentials. Um das Beste aus beiden Ansätzen zu vereinen, untersuchen wir in dieser Dissertation die zeitabhängige Zweiteilchendichtematrix als fundamentale Größe. Als Anwendung wählen wir die Simulation der Elektronendynamik in Atomen und Molekülen, wie sie unter Bestrahlung mit starken Femtosekundenlaserpulsen in Gang gesetzt wird. Die dadurch produzierten höheren Harmonischen der Laserfrequenz sind von großer technologischer Bedeutung in kompakten Röntgenquellen und der Erzeugung von Attosekundenpulsen.

Die Zweiteilchendichtematrix kann als eine Verallgemeinerung der Elektronendichte auf zwei Teilchen verstanden werden. Damit beinhaltet die Zweiteilchendichtematrix nicht nur Infor-

mation über die Verteilung der Elektronen im Atom bzw. Molekül, sondern auch über deren paarweise Wechselwirkung. Um die Propagation der Zweiteilchendichtematrix zu bewerkstelligen, ist es notwendig die Bewegungsgleichung durch eine Rekonstruktion der Dreiteilchendichtematrix zu schließen. Daher legen wir besonderes Augenmerk auf ein möglichst genaues Rekonstruktionsfunktional. Hierfür verwenden wir eine neue Technik um sicherzustellen, dass Symmetrien der Bewegungsgleichung erhalten bleiben. Um die Genauigkeit der Methode zu überprüfen, vergleichen wir mit einer "state of the art" zeitabhängigen wellenfunktionsbasierten Methode als Referenz sowie mit Dichtefunktionaltheorie. Wir finden eine sehr gute Übereinstimmung der Propagation der Zweiteilchendichtematrix mit der Referenzrechnung, wohingegen die Dichtefunktionaltheorie eine deutliche Diskrepanz aufweist. Wir präsentieren hier die ersten Ergebnisse der erfolgreichen und stabilen Propagation der Zweiteilchendichtematrix zur Beschreibung laserinduzierter Elektronendynamik in Vielelektronensystemen.



# Abstract

The accurate simulation of time-dependent many-body systems is among the most challenging topics in modern theoretical physics. For many-body systems the number of degrees of freedom is large and conservation laws are rare making the numerical solution very demanding. Quantum mechanics adds further complications. It requires the collective description of the system in terms of the many-body wavefunction whose time evolution is governed by the Schrödinger equation. The collective nature of the description forbids to decompose the system into individual entities and makes the calculation of a quantum many-body system particularly complicated. In fact, the direct solution of the Schrödinger equation is not a viable option for atomic and molecular systems consisting of more than two electrons. To overcome this limitation a variety of approaches have been developed for the calculation of ground state properties of multi-electron systems relevant for the kinetics of chemical reactions. These methods of quantum chemistry can be roughly divided into two groups: methods that are based on the wavefunction as the fundamental object, such as multiconfigurational Hartree-Fock, and methods based on reduced quantities, such as density functional theory. While wavefunction-based methods are very accurate their applicability is limited to small systems due to the exponential scaling with particle number. Density functional theory, on the other hand, can treat large and extended systems, however, at the price of introducing the exchange-correlation functional whose exact form is unknown and whose approximations are hard to improve systematically.

Time-dependent formulations have been achieved for both of the aforementioned approaches. The multiconfigurational time-dependent Hartree-Fock method is among the most accurate approaches to simulate dynamical many-body systems. Time-dependent density functional theory is regularly employed to simulate time-dependent large-scale systems. In this thesis, we aim for a method that combines the best of both worlds, the accuracy of wavefunction-based approaches with the efficiency of polynomial scaling as in density functional theory. To this end we propagate the time-dependent two-particle reduced density matrix. As a hybrid between the electron density and the many-body wavefunction the two-particle reduced density matrix fully includes two-particle correlations which is a prerequisite to accurately capture effects that arise from electron-electron interactions. Further observables such as kinetic energy spectra, ionization probabilities or the total energy can be expressed directly without invoking approximate read-out functionals as required in density functional theory. We develop a closed equation of motion for the two-particle reduced density matrix by constructing a novel reconstruction functional for the three-particle reduced density matrix that preserves norm, energy, and spin symmetries during time propagation. Further, we show how to avoid instabilities associated with the violation of  $N$ -representability that have been

a considerable limitation in previous approaches.

We have implemented the time-dependent two-particle reduced density matrix method to describe high-harmonic generation from fully three-dimensional multi-electron atoms as well as from one-dimensional molecules. We benchmark the performance of the time-dependent two-particle reduced density matrix method by comparing it to a state of the art multiconfigurational time-dependent Hartree-Fock calculation as well as to time-dependent density functional theory. We find very good agreement between the time-dependent two-particle reduced density matrix method and the multiconfigurational time-dependent Hartree-Fock method while time-dependent density functional theory within the local density approximation shows clear deviations indicating that the correct treatment of two-particle correlations is essential to obtain accurate high-harmonic spectra.

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# List of Acronyms

The most frequently used acronyms are listed.

<b>1D</b>	One-dimension(al)
<b>3D</b>	Three-dimension(al)
<b>ATI</b>	Above-threshold ionization
<b>BBGKY</b>	Bogoliubov–Born–Green–Kirkwood–Yvon
<b>CI</b>	Configuration interaction
<b>DFT</b>	Density functional theory
<b>DMRG</b>	Density matrix renormalization group
<b>FCIQMC</b>	Full configuration interaction quantum Monte Carlo
<b>FEDVR</b>	Finite-element discrete variable representation
<b>HHG</b>	High-harmonic generation
<b>HOMO</b>	Highest occupied molecular orbital
<b>LDA</b>	Local density approximation
<b>LOPT</b>	Lowest order perturbation theory
<b>MCTDHF</b>	Multiconfigurational time-dependent Hartree-Fock
<b>NSDI</b>	Non-sequential double ionization
<b>NY</b>	Nakatsuji-Yasuda
<b>RDM</b>	Reduced density matrix
<b>SAE</b>	Single-active electron
<b>SFA</b>	Strong-field approximation
<b>TDCI</b>	Time-dependent configuration interaction
<b>TDDFT</b>	Time-dependent density functional theory
<b>TDHF</b>	Time-dependent Hartree-Fock
<b>TD-2RDM</b>	Time-dependent two-particle reduced density matrix
<i>p</i> RDM	<i>p</i> -particle reduced density matrix
<i>p</i> HRDM	<i>p</i> -hole reduced density matrix



# 1. Introduction

The description of many-body systems within the framework of quantum mechanics is among the computationally most intensive fields of science. This complexity originates from the failure to describe quantum many-body systems as an ensemble of individual entities. Quantum mechanics requires to describe the collective system as a whole within the many-body wavefunction. However, such a description is challenging because of the inherently large amount of information stored in the wavefunction.

Considerable effort has been dedicated to the accurate description of stationary electronic properties of large atoms and molecules within the framework of quantum chemistry. Ground state properties of large systems involving tens to hundreds of particles can routinely be calculated employing sophisticated methods such as configuration interaction methods, coupled cluster methods, perturbative methods, and density functional theory (DFT) (see e.g. [1, 2]). Apart from these well-known methods alternative methods have been developed such as the two-particle reduced density matrix theory. This method which uses the two-particle reduced density matrix (2RDM) as the fundamental object has matured to accuracies that often outperform those of coupled-cluster singles-doubles with perturbative triples [CCSD(T)] at similar or smaller numerical cost (see e.g. [3–7]). Similar to DFT, the 2RDM method bypasses the need for the  $N$ -particle wavefunction but employs the 2-RDM rather than the one-particle density as the fundamental quantity. Unlike DFT, however, the energy and all two-particle observables can be expressed exactly in terms of the 2-RDM without invoking an approximate exchange-correlation functional or read-out functional. Proposed methods for calculating the ground state 2-RDM include variational minimization of the energy as a functional of the 2-RDM [3, 8, 9], solution of the contracted Schrödinger equation [10, 11], and solution of the antihermitian part of the contracted Schrödinger equation [7] (for a review see [12]). A major challenge in applying the 2-RDM method is to enforce  $N$ -representability conditions, i.e. to constrain the trial 2-RDMs to those that represent reductions of either pure or ensembles of fermionic  $N$ -particle states [8, 13, 14]. Despite recent progress [15], a complete set of (pure state)  $N$ -representability conditions is not known and one is limited to few necessary but not sufficient  $N$ -representability conditions in numerical implementations. An analogous development of methods for time-dependent systems and systems far from the ground state is still in its infancy. The time-dependent extension of DFT, the time-dependent density functional theory (TDDFT) (for a review see [16]) features a favorable linear scaling with  $N$  and allows the approximate treatment of atomic [17–20], and molecular [21, 22] systems, as well as nanostructures [23–26] and extended systems [27–30]. The efficiency of TDDFT, however, comes at the price of introducing exchange-correlation functionals which are only known approximately and hard to improve systematically. Further, exchange-

correlation functionals within the time-dependent setting contain memory effects which are known to play an important role in the proper description of doubly-excited states [31], charge transfer [32, 33] and Rabi oscillations [34–37]. The majority of TDDFT applications employs ground state functionals within the adiabatic approximation. Exchange-correlation functionals beyond the adiabatic limit are rare and hard to construct [38–43]. Alternatively, the so-called time-dependent current-density functional theory (TDCDFT) has been proposed (for a review see [16]) for which, up to now, however only few approximations for the exchange-correlation vector potential have become available [38]. Moreover, even if an accurate time-dependent density would become available only physical observables that are explicit functionals of the one-particle density can be easily determined from TDDFT. Read-out functionals of  $N$ -particle observables are still largely unknown [44–47].

Extension to the direct solution of the  $N$ -electron Schrödinger equation beyond the two-particle problem employs the multiconfigurational time-dependent Hartree-Fock (MCTDHF) method ([48–51]). In principle, the MCTDHF method converges to the numerically exact solution if a sufficient number of orbitals is used. However, the exponential scaling with the number of particles limits its applicability. A recently proposed variant, the time-dependent complete active space self-consistent field (TD-CASSCF) method [52, 53] which, in analogy to its ground-state counterpart, decomposes the state space into frozen, dynamically polarized, and dynamically active orbitals can considerably reduce the numerical effort yet eventually still leads to a exponential scaling with the number of active electrons  $N^*$  ( $N^* < N$ ). Further reduction of the numerical effort and, consequently, extension to larger systems appears possible, e.g., by applying the time-dependent occupation restricted multiple active space method [54].

The time-dependent two-particle reduced density matrix (TD-2RDM) method intends to bridge the gap between full wavefunction-based  $N$ -electron descriptions such as MCTDHF and the time-dependent reduced one-particle density  $\rho(\mathbf{r}, t)$  based TDDFT. The underlying idea is to strike a compromise between accuracy of electron-electron correlations achieved by wavefunction-based methods and the ease to treat larger and, eventually, extended systems afforded by density-based approximations [55]. The original idea goes back to Bogoliubov [56, 57] who proposed to close the equation of motion for the time-dependent 2RDM,  $D(\mathbf{r}_1\mathbf{r}_2; \mathbf{r}'_1\mathbf{r}'_2; t)$ , to construct a self-contained theory that relies solely on the TD-2RDM as the working variable. This closure requires the reconstruction of the three-particle reduced density matrix (3RDM) in terms of the 2RDM. Initially, such reconstructions were motivated by closure schemes of the (related) Martin-Schwinger hierarchy [58] (see e.g. [59]). More advanced reconstructions are based on the cluster expansion [60–63] which was rediscovered by Valdemoro in the attempt to solve the contracted Schrödinger equation [64]. Application of the cluster-expansion (or Valdemoro reconstruction) have been performed to evaluate ground state and excited state properties of the Lipkin and Hubbard model [65–68] as well as time-dependent simulations of nuclear dynamics (within the Lipkin model) [69], strong non-equilibrium dynamics in the Hubbard model [70] and one-dimensional (1D) beryllium in ultra short laser pulses [71]. All of these calculations encountered severe instabilities that, eventually, lead to divergences. These instabilities are due to the intrinsic nonlinearity of



the equation of motion for the 2-RDM resulting in the violation of positive definiteness.

In this thesis we take several steps overcoming the hurdles that have previously limited the applicability of the TD-2RDM theory. We develop a novel reconstruction functional that allows closure of the equation of motion for the 2-RDM without introducing uncontrolled violations of norm, spin, and energy conservation. Further we include three-particle correlations by using a reconstruction functional originally inspired by Nakatsuji and Yasuda [10] that has not been implemented for the propagation of the 2RDM. These improvements lead to an accurate and sophisticated reconstruction functional. For moderate excitations of the system beyond the ground state these improvements already render the propagation of the 2RDM stable. For stronger perturbations we impose two necessary  $N$ -representability constraints “on the fly” during the time evolution thereby controlling and bypassing the dynamical instabilities observed previously [62, 66, 69–71].

We apply the TD-2RDM method to the nonlinear response of many-electron atoms and molecules in strong few cycle laser pulses. As a stringent test for the accuracy of the TD-2RDM method we investigate high-harmonic generation (HHG) which is one of the fundamental strong-field processes whose applications range from attosecond metrology [72], tunable table-top XUV/Soft X-ray sources [73] to high precision spectroscopy [74] and orbital imaging [75]. We simulate the HHG from beryllium and neon targets in full three-dimensional (3D) space and with all electrons active. We benchmark the resulting HHG against accurate spectra obtained by MCTDHF [53]. Qualitatively, the structure of the high-harmonic spectrum can be well captured by the so called three-step model [76, 77] in which an electron is first tunnel-ionized by the strong field, then accelerated in the laser field, and finally radiatively recombines with the parent ion emitting an energetic photon. For an accurate quantitative description it is, however, crucial to explore and include correlations and many-electron effects neglected by such a one-electron model. In particular, the collective polarization response of the residual  $(N - 1)$ -electron system to the external field and the emitted electron as well as the relaxation of the excitonic electron-hole pair are expected to be sensitive to correlation effects. We show that the TD-2RDM method is well suited to account for these subtle many-body effects whereas time-dependent mean-field or effective field descriptions such as the time-dependent Hartree-Fock (TDHF) method or time-dependent density functional theory (TDDFT) show deviations from the MCTDHF reference calculations.

Further, we investigate molecular HHG from LiH within the aligned electron approximation in which the 3D molecule is replaced with a 1D model system. HHG from molecular systems has been shown experimentally [78, 79] and theoretically [80] to contain interference effects from recombination at different nuclear centres. We identify the two-center interference between high-harmonic radiation emitted from the lithium and the hydrogen core. We find very good agreement between the TD-2RDM method and MCTDHF reference calculations. Additionally we compare with TDHF and TDDFT calculations and find that the TD-2RDM method performs better than these theories.

The thesis is structured as follows: In Chapter 2 we briefly review existing time-dependent wavefunction-based many-body methods and their application to strong field processes. In

Chapter 3 we lay the theoretical foundation of the TD-2RDM method introducing RDMs, their equations of motion, and their diagrammatic expansion. In Chapter 4 we give a short review of approaches that propagate one-particle objects before we introduce the basic elements of the TD-2RDM method in Chapter 5. These include reconstruction functionals of the 3RDM in terms of the 2RDM, conservation laws associated with particle number energy and spin as well as purification to ensure stable and physical results. Chapter 6 is devoted to the numerical implementation of the TD-2RDM method and the orbital equations of motion in strong field applications. A short introduction to strong field physics with emphasis on HHG, to which we apply our TD-2RDM method in the following, is given in Chapter 7. Numerical results of high-harmonic spectra and ionization probabilities for the atomic targets beryllium and neon subject to ultra-short laser pulses are discussed in Chapter 8. Results for molecular HHG from LiH calculated within a 1D model is presented in Chapter 9. We summarize the results of this thesis in Chapter 10. Some of the results of this thesis are contained in the publications [53, 81–83]. Throughout this thesis we use atomic units ( $e = \hbar = m = 1$ )

## 2. Time-dependent wavefunction-based many-body theories

Quantum many-body systems are at the core of current research in physics including atomic, molecular, and solid state physics, ultra-cold atoms, nuclear physics, plasma physics and many more. While these systems are governed by very different time and length scales their non-relativistic time-dependent behaviour can be described by the time-dependent Schrödinger equation [84]

$$i\partial_t|\Psi(t)\rangle = H_{12\dots N}|\Psi(t)\rangle, \quad (2.1)$$

where the many-body Hamiltonian

$$H_{12\dots N} = \sum_n^N h_n + \sum_{n<m}^N W_{nm}, \quad (2.2)$$

contains the one-body operator  $h_n$  and the interaction between the particles  $W_{nm}$ , and the wavefunction  $|\Psi(t)\rangle$  is a time-dependent element of a complex Hilbert space  $\mathcal{H}$ . It is the central tenet of quantum theory that the solution of the Schrödinger equation

$$\Psi(\mathbf{x}_1, \dots, \mathbf{x}_N, t) = \langle \mathbf{x}_1 \dots \mathbf{x}_N | \Psi(t) \rangle \quad (2.3)$$

contains all information on the physical system, where  $\mathbf{x}_n$  is the coordinate of the  $n$ th particle. Whatever we can say about the system under investigation can be extracted from this function and whatever we can extract from this wavefunction is all we can say about the system. This fundamental proposition of quantum mechanics holds for one-particle as well as many-body problems. The direct solution of the Schrödinger equation, therefore, fully determines the dynamics of the system under investigation.

While the method presented in this thesis is very general and can be applied to various different many-body systems we will focus in the following on the description of multi-electron atoms and molecules in strong fields. For electrons the coordinate  $\mathbf{x} = (\mathbf{r}, \sigma)$  comprises the 3D space coordinate  $\mathbf{r}$  and the spin coordinate  $\sigma \in \{\uparrow, \downarrow\}$ . With the advent of intense ultra-short laser pulses the time-dependent simulation of atoms and molecules has become the essential theoretical tool to understand strong-field phenomena [85, 86]. For atomic and molecular targets subject to strong-field pulses the one-body operator

$$h_n = -\frac{\nabla_n^2}{2} + V(\mathbf{r}_n) + V^{\text{ext}}(\mathbf{r}_n, t), \quad (2.4)$$

contains the kinetic energy, the electrostatic potential  $V(\mathbf{r})$  created by atomic nuclei, and the time-dependent external laser potential  $V^{\text{ext}}(\mathbf{r}, t)$ . The two-body operator

$$W_{nm} = \frac{1}{|\mathbf{r}_n - \mathbf{r}_m|} \quad (2.5)$$

describes the Coulomb interaction between the electrons. In the regime where the external potential  $V^{\text{ext}}(\mathbf{r}, t)$  competes in magnitude with the nuclear potential  $V(\mathbf{r})$  a variety of interesting effects (see Chapter 7) can be observed. The proper theoretical description of these strong-field effects requires non-perturbative methods for the solution of the time-dependent Schrödinger equation.

Simulations of one-electron atoms in strong laser fields are routinely performed by direct solution of the underlying Schrödinger equation (see e.g. [87–90]). The direct solution of the Schrödinger equation for multi-electron systems is currently only possible for two-electron systems. Computations of the full electron dynamics in helium, especially for near-infrared pulses, require the use of state-of-the-art supercomputers with parallelized codes employing thousands of cores [91–94]. The reason for this numerical complexity is the large memory consumption of the two-particle wavefunction  $\Psi(\mathbf{x}_1, \mathbf{x}_2, t)$ . While in the numerical implementation the central symmetric atomic potential can be exploited to save computational time and memory by expanding the angular part of the two-electron wavefunction in a coupled set of spherical harmonics the direct determination of the time-dependent two-particle wavefunction is still highly non-trivial. Extensions of this direct approach to the solution of the many-body Schrödinger equation beyond two-particle systems turns out to be unfeasible due to the exponential growth of the Hilbert space dimension  $\dim(\mathcal{H})$  that accommodates the wavefunction. For the neon atom in a box with 100 grid points per axis the dimension of the subspace of  $\mathcal{H}$  thus generated has dimension  $\dim(\mathcal{H}) = \binom{100^3}{10} \approx 10^{53}$  (neglecting spin), far larger than what can be stored on present day computational systems. This conceptual limitation is the fundamental difficulty in the solution of quantum many-body problems. Accurate approximations are needed to solve the Schrödinger equation for systems consisting of more than two particles.

From a broader perspective these approaches can be divided into wavefunction-based methods and methods based on the time propagation of reduced objects. In the class of wavefunction-based methods the most frequently employed method is the single-active electron (SAE) approximation (see e.g. [95–97]) which treats only one single electron actively and the interaction between the active electron and the remaining electrons is modelled by a mean-field approximation that modifies the nuclear potential into a model potential. This model potential can be tuned, e.g., to reproduce the measured ionization potential [98]. One of the apparent short comings of the SAE is the missing possibility of a rescattered electron to excite or ionize further electrons. The latter process is the basis of non-sequential double ionization (NSDI) [99–102]. Further, the single-electron approximation misses the dynamic polarization of the remaining ion. Conceptually a hybrid between SAE and the full  $N$ -particle solution of the Schrödinger equation is the time-dependent R-Matrix theory. In the original approach the configuration space is divided into an inner region where the full

many-body wavefunction is expanded in states of the field-free Hamiltonian and an outer region where a single active electron is propagated [103–106]. Modern versions of the time-dependent R-Matrix theory go beyond the single-active-electron approximation in the outer region by including a two-electron continuum [107].

In the next two sections we will briefly review approximate wavefunction-based theories that permit to treat more than two active particles by employing an explicit ansatz for the wavefunction. They are used in the context of strong-field physics. The MCTDHF presented in Chapter 2.2 can be, in principle, brought to agreement with the exact solution of the Schrödinger equation and will therefore serve as a benchmark for comparisons with the TD-2RDM method. The TDHF method presented in the following section will be used to assess the role of correlations.

## 2.1. Time-dependent Hartree-Fock

Wavefunction-based methods to the solution of the Schrödinger equation build on the idea to reduce the full Hilbert space to a subspace spanned by wavefunctions of a specific form. One of the simplest and earliest approaches in this direction is the TDHF method [108, 109]. Originally proposed as a method to calculate the ground state energy of atoms and molecules by Hartree [110] and later generalized to fermions by Fock [111] the time-independent Hartree-Fock method asks for the best possible representation of the wavefunction in terms of a single Slater determinant such that the energy deviation to the exact ground state energy is minimal. A Slater determinant is a specific type of a many-body wavefunction

$$|\mathcal{I}\rangle = |\phi_1\phi_2\dots\phi_N\rangle, \quad (2.6)$$

where each one-particle state in the orthonormal set  $\{|\phi_i\rangle\}_{i\in\{1\dots N\}}$  is occupied by exactly one particle and the state is fully antisymmetric, i.e.  $|\phi_1\phi_2\dots\phi_N\rangle = -|\phi_2\phi_1\dots\phi_N\rangle$ . In coordinate space this wavefunction can be represented as

$$\mathcal{I}(\mathbf{x}_1 \dots \mathbf{x}_N) = \sum_{\tau} (-1)^{\tau} \phi_1(\mathbf{x}_{\tau(1)}) \dots \phi_N(\mathbf{x}_{\tau(N)}), \quad (2.7)$$

where  $\tau \in \mathcal{S}_N$  is an  $N$ -particle permutation and  $(-1)^{\tau}$  is the sign of the permutation.

Minimizing the energy within the set of Slater determinants gives the Hartree-Fock approximation for the ground state energy [1]. More specifically, employing the Rayleigh–Ritz method by minimizing the energy functional

$$E[\phi_1\dots\phi_N] = \langle \mathcal{I} | H_{1\dots N} | \mathcal{I} \rangle, \quad (2.8)$$

while conserving orbital orthonormality gives the Hartree-Fock orbitals  $\{|\epsilon_i\rangle\}$  satisfying the Hartree-Fock equations

$$h_1^{\text{HF}} |\epsilon_i\rangle = \epsilon_i |\epsilon_i\rangle. \quad (2.9)$$

The Hartree-Fock operator

$$h_1^{\text{HF}} = h_1 + V_1^{\text{HF}} \quad (2.10)$$

is a one-body operator that includes the mean-field

$$\langle \mathbf{x} | V_1^{\text{HF}} | \phi_i \rangle = \sum_{j=1}^N \int \frac{\phi_j(\mathbf{x}') \phi_j^*(\mathbf{x}') \phi_i(\mathbf{x})}{|\mathbf{x} - \mathbf{x}'|} d\mathbf{x}' - \sum_{j=1}^N \int \frac{\phi_j(\mathbf{x}) \phi_j^*(\mathbf{x}') \phi_i(\mathbf{x}')}{|\mathbf{x} - \mathbf{x}'|} d\mathbf{x}', \quad (2.11)$$

where the first term on the r.h.s. describes the electrostatic field created by all electrons and the second term accounts for the exchange interaction. Solving Eq. 2.9 requires a self-consistent procedure ensuring that the Hartree-Fock orbitals are eigenfunction to the Hartree-Fock operator generated from them.

In the application to strong-field processes in multi-electron atoms the ground state generated in such a way serves as the initial state for time propagation. The extension of the Hartree-Fock method to time-dependent systems was derived by Dirac [108] based on the time-dependent variational principle nowadays called Dirac-Frenkel variational principle. It states that the exact propagation of the wavefunction  $|\Psi(t)\rangle$  can be derived from the stationarity of the Dirac-Frenkel action functional

$$\mathcal{L} = \int \langle \Psi | H_{1\dots N} - i\partial_t | \Psi \rangle dt. \quad (2.12)$$

While variation within the full Hilbert space  $\mathcal{H}$  gives the original Schrödinger equation (Eq. 2.1) variation within the set of all Slater determinants gives the best possible approximation in terms of a single time-dependent Slater determinant  $|\mathcal{I}(t)\rangle$ . Carrying out the variational calculation gives for the equation of motion of the TDHF method

$$i\partial_t |\epsilon_i\rangle = h_1^{\text{HF}} |\epsilon_i\rangle. \quad (2.13)$$

The TDHF method takes into account the electron-electron interaction as a mean-field but neglects correlations between the particles arising from their interaction. To speed up calculations the exchange term (second term in on the r.h.s on Eq. 2.11) is often approximated within exchange functionals in terms of the density.

In the context of strong-field processes the TDHF method was first employed by Kulander [95, 112] for helium and xenon. Already the first studies revealed the weak points of the TDHF approximation. Due to the single determinant ansatz for the wavefunction Eq. 2.7 the single and double ionization process becomes intertwined and are not properly separated from each other. This artificial coupling between single and double ionization leads to significant errors in the ionization rate of multi-electron atoms as discussed in Chapter 8. By Brillouin's theorem (see e.g. [1]) the Hartree-Fock result is the first-order approximation to the exact dynamics of the many-body system. Higher orders must account for effects arising from particle-particle correlation.

## 2.2. Time-dependent post-Hartree-Fock methods

Restricting the dynamics of the wavefunction to the set of single determinants leads to the equation of motion of TDHF as discussed. Extending this ansatz to superpositions of many determinants is the general strategy in time-dependent post-Hartree-Fock methods. In the most general case given any complete one-particle basis  $\{|\phi_i\rangle\}$  the expansion of the wavefunction reads

$$\begin{aligned} |\Psi(t)\rangle &= \sum_{i_1 < i_2 < \dots < i_N} \langle \phi_{i_1} \phi_{i_2} \dots \phi_{i_N} | \Psi(t) \rangle |\phi_{i_1} \phi_{i_2} \dots \phi_{i_N}\rangle \\ &= \sum_{i_1 < i_2 < \dots < i_N} C_{i_1 i_2 \dots i_N}(t) |\phi_{i_1} \phi_{i_2} \dots \phi_{i_N}\rangle \\ &= \sum_{\mathcal{I}} C_{\mathcal{I}}(t) |\mathcal{I}\rangle, \end{aligned} \quad (2.14)$$

where  $|\mathcal{I}\rangle$  is any Slater determinant build from  $N$  orbitals within the spin orbital basis  $\{|\phi_i\rangle\}$  and the orbital index  $i$  comprises also the spin coordinate  $\sigma \in \{\uparrow, \downarrow\}$ . For a complete basis  $\{|\phi_i\rangle\}$  this so called configuration interaction (CI) expansion (Eq. 2.14) is exact. Numerical implementation requires to separate the basis into  $2I$  occupied orbitals  $\{|\phi_i\rangle\}_{i \in \{1 \dots 2I\}}$  and remaining unoccupied orbitals  $\{|\phi_\nu\rangle\}_{\nu > 2I}$ . The set of all determinants that can be build from distributing  $N$  particles among  $2I$  (spin-dependent) working orbitals  $\{|\phi_i\rangle\}$  is denoted as  $\Pi$ .

The Schrödinger equation Eq. 2.1 gives the equations of motion for the CI-coefficients

$$i\partial_t C_{\mathcal{I}}(t) = \sum_{\mathcal{J} \in \Pi} C_{\mathcal{J}}(t) \langle \mathcal{I} | H_{1 \dots N} | \mathcal{J} \rangle, \quad (2.15)$$

which are the basis of the time-dependent configuration interaction (TDCI) method. In this approach the one-particle basis  $\{|\phi_i\rangle\}$  is set to be time-independent. Within the application of the TDCI method to strong-field processes the basis  $\{|\phi_i\rangle\}$  is often chosen as the basis of Hartree-Fock orbitals  $\{|\epsilon_i\rangle\}$  obtained from solving Eq. 2.9, where in addition to the  $N$  occupied Hartree-Fock orbitals additional  $(2I - N)$  virtual Hartree-Fock orbitals are calculated [113–119]. Attempts to improve TDCI results for strong field processes by employing optimized time-independent basis sets (e.g. from MCTDHF calculations) have not worked out so far [115].

The expansion in time-independent orbitals within TDCI faces a major difficulty when applied to strong-field processes. First, processes that involve ionization or highly excited states require a large number of orbitals for the proper description of the electron dynamics. For a large number of orbitals the number of determinants in case of closed shell atoms and molecules as given by the cardinality

$$|\Pi| = \binom{I}{N/2}^2 \quad (2.16)$$

becomes very large. Convergence with  $I$  is feasible only if the number of excitations from the Hartree-Fock reference is limited. Usually, excitations are limited to single or double

excitation [114–117]. However, methods based on a truncated CI expansion are known to violate size-consistency, a central property to describe larger systems, in particular molecules [1].

An alternative route is the MCTDHF method in which the orbitals as well as the CI-coefficients are time-dependent [50, 51, 120]

$$\begin{aligned} |\Psi\rangle &= \sum_{i_1 < i_2 < \dots < i_N} C_{i_1 i_2 \dots i_N}(t) |\phi_{i_1}(t) \phi_{i_2}(t) \dots \phi_{i_N}(t)\rangle \\ &= \sum_{\mathcal{I} \in \Pi} C_{\mathcal{I}}(t) |\mathcal{I}(t)\rangle. \end{aligned} \quad (2.17)$$

The time-dependence of the orbitals can be exploited to cover the exact dynamics of the wavefunction with as few orbitals as possible. To ensure the optimal representation of the wavefunction the orbital dynamics is determined by substituting Eq. 2.17 into the Dirac-Frenkel action functional. Variation with respect to the orbitals and the CI coefficients leads in addition to the equations of motion for the CI coefficients Eq. 2.15 the equations of motion for the working orbitals  $\{|\phi_i\rangle\}$

$$i\partial_t |\phi_i\rangle = \mathcal{Q}_1 (h_1^{\text{HF}} |\phi_i\rangle + \Gamma_1 |\phi_i\rangle), \quad (2.18)$$

where

$$\mathcal{Q}_1 = 1 - \sum_{i=1}^{2I} |\phi_i\rangle \langle \phi_i| \quad (2.19)$$

is the projection operator onto the subspace of unoccupied orbitals and  $\Gamma_1$  accounts for the correlation induced coupling between the working orbitals. More precisely  $\Gamma_1$  depends on the two-particle cumulant and the inverse of the 1RDM (see Eq. 6.21 below for the explicit form of  $\Gamma_1$ ). We note that the Dirac-Frenkel variational principle does not determine the dynamics of the occupied orbitals  $\{|\phi_i\rangle\}$  within the subspace of occupied orbitals since every orthonormal variation within the set of occupied orbitals

$$\delta |\phi_j\rangle = \sum_{i=1}^{2I} X_i^j |\phi_i\rangle \quad (2.20)$$

can be compensated by a corresponding variation of the CI-coefficients

$$\delta C_{\mathcal{I}} = \sum_{\mathcal{J} \in \Pi} C_{\mathcal{J}} \langle \mathcal{J} | X_{1\dots N} | \mathcal{I} \rangle, \quad (2.21)$$

with

$$X_{1\dots N} = \sum_{n=1}^N X_n \quad \text{and} \quad X_n = \sum_{i,j} X_i^j |\phi_i\rangle \langle \phi_j| \quad (2.22)$$



such that the total wavefunction remains invariant. The equations of motion Eq. 2.15 and Eq. 2.18 are the result of the particular choice  $\langle \phi_i | i\partial_t | \phi_j \rangle = 0$ . Other choices such as  $\langle \phi_i | i\partial_t | \phi_j \rangle = \langle \phi_i | h_1^{\text{HF}} | \phi_j \rangle$  are possible leading to the modified equations of motions

$$i\partial_t C_{\mathcal{I}}(t) = \sum_{J \in \Pi} C_{\mathcal{J}}(t) \langle \mathcal{I} | \bar{H}_{1\dots N} | \mathcal{J} \rangle \quad (2.23)$$

$$i\partial_t |\phi_i\rangle = h_1^{\text{HF}} |\phi_i\rangle + \mathcal{Q}_1 \Gamma_1 |\phi_i\rangle, \quad (2.24)$$

where

$$\bar{H}_{1\dots N} = H_{1\dots N} - \sum_{n=1}^N h_n^{\text{HF}}. \quad (2.25)$$

If the basis truncation is performed for  $I = N/2$  the subspace  $\Pi$  in Eq. 2.17 collapses to a single determinant and the correlation operator vanishes  $\Gamma_1 = 0$ . In this limit the MCTDHF method reduces to the TDHF method.

The application of MCTDHF to strong field processes has been performed for a variety of 1D model systems [48, 120–123] as well as full 3D calculations [124–131] and an generalization to non-Born-Oppenheimer dynamics of  $\text{H}_2$  [132]. The results obtained suggest that observables such as the dipole acceleration are converged for  $I \approx N$ . Accordingly, the number of configurations grows exponentially with increasing number of particles

$$|\Pi| \approx \binom{N}{N/2}^2 \approx 2^N \sqrt{\frac{2}{\pi N}} \quad (2.26)$$

limiting the applicability to relatively small systems. Recently, by adopting concepts from quantum chemistry new strategies have been developed to limit the number of configurations within the MCTDHF setting. The time-dependent version of the complete-active-space self-consistent-field method (TD-CASSCF) eliminates configurations that contain excitations from deeply bound core orbitals and has been applied to the ionization dynamics of 1D molecules [52] and HHG in full 3D calculations for atoms [53]. The core orbitals are often only spectators not participating in the electron dynamics initiated by near infrared laser pulses and their dynamics can be either frozen completely or included as a time-dependent field-induced polarization. The TD-CASSCF method is gauge invariant [51] and size-consistent [133]. A further possibility to reduce the number of configurations in the wavefunction ansatz is to truncate the number of possible excitations from the deepest bound  $N$  orbitals. This time-dependent restricted-active-space self-consistent-field (TD-RASSCF) method has been applied to 1D systems [54, 134–137] as well as 3D atoms [138] in strong laser pulses (see [51] for an overview).

In general, wavefunction based approaches to the solution of the Schrödinger equation aim at overcoming the exponential growth of the Hilbert space dimension by restricting the dynamics to a specific subspace of the full Hilbert space spanned by either a single or a multitude of determinants. While optimizing this subspace to capture the essential dynamics by introducing core orbitals (TD-CASSCF) or limiting the number of excitations (TD-RASSCF)

can enable calculations for small multi-electron atoms and molecules these methods are not suited to go to larger systems because in presence of strong correlation the proper resolution of the wavefunction within the Hilbert space requires an exponentially growing number of contributing determinants.

Several alternative approaches exist that go beyond Hartree-Fock calculations. One promising ansatz for the many-body wavefunction that goes beyond a single Slater determinant is the matrix product state which is the fundamental object of density matrix renormalization group theory (DMRG). The time-dependent extension of DMRG is based on the time propagation of matrix product states [139] and has recently been adapted to handle the long-range Coulomb interaction present in atomic and molecular systems [140]. However, the time-dependent multi-dimensional application of this method is still in its infancy.

Another method that works within the CI-space of Slater-determinants is full configuration interaction quantum Monte Carlo (FCIQMC). In this approach the CI-expansion of the wavefunction (Eq. 2.14) is represented by a large number of "walkers" that can occupy Slater determinants. The more walkers are present on a specific determinant the bigger its weight becomes corresponding to a large magnitude of the CI coefficient. Stationary as well as dynamical simulations are possible by permitting these walkers to span and die as well as change the occupied determinant in time. Within quantum chemistry the FCIQMC method is well established [141]. Recently a time-dependent version of FCIQMC has been proposed that holds the promise to become an efficient method for the time-dependent simulations of systems with ab-initio Hamiltonians [142].

Theories that go beyond the expansion of the many-body wavefunction into a superposition of determinants use explicitly correlated basis functions that explicitly depend on the inter-electronic distances. Such methods are in use for quantum chemistry calculations [143, 144] but no time-dependent extension of this approach has been achieved yet. Ultimately, much of the overwhelming amount of information contained in the wavefunction is not needed for most quantities of interest. It is therefore a long-sought dream of quantum physicists to replace the full wavefunction by a concise object that contains the relevant properties in a condensed form. Such objects will be the subject of the next chapter.

### 3. Reduced density matrices

Important objects employed in the study of quantum many-body systems are reduced density matrices (RDMs) (for books on the topic see [12, 145–150]). The approach within RDM theory, in general, is to abandon the wavefunction altogether and develop a self-contained theory for many-body quantum systems solely based on RDMs. The theoretical basis for RDMs was laid by von-Neumann [151] who showed that  $p$ -particle subsystems embedded in a larger environment require the description with density matrices

$$\tilde{D}_{1\dots p} = \sum_i P_i^{(p)} |\xi_i\rangle \langle \xi_i|, \quad (3.1)$$

i.e. ensembles of  $p$ -particle wavefunctions  $|\xi_i\rangle$  each appearing with probability  $P_i^{(p)}$ . These probabilities  $P_i^{(p)}$  express the incomplete knowledge about the microscopic state of the system. For subsystems decoupled from the environment the probabilities  $P_i^{(p)}(t)$  are constants of motion. In the simulation of time-dependent subsystems interacting with the environment both probabilities  $P_i^{(p)}(t)$  and eigenstates  $|\xi_i(t)\rangle$  become time-dependent objects.

The expectation value of any  $p$ -particle observable represented by the Hermitian operator  $\mathcal{O}_{1\dots p}$  can be calculated similarly as in classical statistical mechanics by

$$\langle \mathcal{O}_{1\dots p} \rangle = \sum_i P_i^{(p)}(t) \langle \xi_i | \mathcal{O}_{1\dots p} | \xi_i \rangle, \quad (3.2)$$

i.e., as the sum over the probability for the system to be in state  $|\xi_i\rangle$  times the expectation value of  $\langle \xi_i | \mathcal{O}_{1\dots p} | \xi_i \rangle$ . Interference between eigenstates of  $\tilde{D}_{1\dots p}$  are by construction (Eq. 3.1), absent.

The obvious question that arises in the context of the many-body problem is: What is the state of just a few particles in an  $N$ -body system described by the wavefunction  $|\Psi\rangle$ ? The answer is given by reduced density matrices. On the lowest level, the one-particle reduced density matrix (1RDM) and the two-particle reduced density matrix (2RDM) are sufficient to calculate properties most relevant for experiments. While the 1RDM suffices to calculate properties such as the dipole moment, momentum distributions, absorption spectra, the 2RDM gives additionally information on the interaction energy, excitation and ionization probabilities, the spin state, or pair correlation densities.

#### 3.1. One-particle reduced density matrix (1RDM)

The one-particle reduced density matrix (1RDM) is defined as

$$\tilde{D}_1 = \text{Tr}_{2\dots N} |\Psi\rangle \langle \Psi|, \quad (3.3)$$

which expresses the 1RDM as an operator in the one-particle subspace. The notation  $\text{Tr}_{2\dots N}$  expresses the fact that the partial trace extends over all but one particle of the  $N$ -particle system. We will adopt the ambiguity of terminology that is present in literature and use to term "density matrix" for the operator as well as the associated matrix. To actually calculate the matrix elements of the 1RDM we need to introduce a one-particle basis  $\{|i\rangle\}$  which can be an orbital basis  $\{|\phi_i\rangle\}$  or a continuous basis such as the coordinate basis  $\{|\mathbf{x}\rangle\}$  in which case summation has to be replaced by integration. The one-particle basis is essential to evaluate the partial trace in Eq. 3.3 according to

$$\langle i_1 | \tilde{D}_1 | j_1 \rangle = \sum_{i_2, i_3, \dots, i_N} \langle i_1 i_2 \dots i_N | \Psi \rangle \langle \Psi | j_1 i_2 \dots i_N \rangle, \quad (3.4)$$

where  $|i_1 i_2 \dots i_N\rangle$  represents the  $N$ -particle state where each one-particle state  $|i_n\rangle$  with  $n \in \{1 \dots N\}$  is occupied by exactly one particle (for details on the notation see Appendix A).

Here and in the following we will assume the particles to be indistinguishable fermions but the formalism can be equally applied to bosons and distinguishable particles as well. For fermions,  $|i_1 i_2 \dots i_N\rangle$  correspond to the Slater determinants introduced in Eq. 2.7. The analogy to the statistical ensemble discussed previously (Eq. 3.1) becomes obvious upon diagonalization

$$\tilde{D}_1 = \sum_i P_i^{(1)} |\eta_i\rangle \langle \eta_i|, \quad (3.5)$$

where the eigenstates  $|\eta_i\rangle$  of the 1RDM are called the natural orbitals. Therefore, a single particle in an interacting  $N$ -particle system can be described by an ensemble of one-particle states  $|\eta_i\rangle$  each appearing with probability  $P_i^{(1)}$ . The expectation value of any one-particle operator, e.g. the one-body operator  $h_1$  of the Hamiltonian, is given by

$$\begin{aligned} \langle h_1 \rangle_{\text{single}} &= \sum_i P_i^{(1)} \langle \eta_i | h_1 | \eta_i \rangle \\ &= \text{Tr}_1(h_1 \tilde{D}_1). \end{aligned} \quad (3.6)$$

Adding the contribution from all particles the total expectation value is

$$\langle h_1 \rangle = \sum_{n=1}^N \langle h_n \rangle_{\text{single}} = N \langle h_1 \rangle_{\text{single}}. \quad (3.7)$$

For identical particles it is therefore convenient to introduce the 1RDM normalized to  $N$  rather than to 1,

$$D_1 = N \tilde{D}_1 = N \text{Tr}_{2\dots N} |\Psi\rangle \langle \Psi|, \quad (3.8)$$

to describe the set of particles collectively. With this normalization the eigenvalues of the 1RDM are no longer probabilities but occupation numbers referred to as the natural occupation numbers

$$n_i = N P_i^{(1)}. \quad (3.9)$$

The ensemble of natural orbitals gives the expectation values for all one-particle observables. In this respect, the natural orbitals are the best one-particle orbitals to describe the many-body system. In the following we give this handwaving argument a precise meaning which will be relevant later when we discuss the expansion of the 2RDM in a time-dependent orbital basis in Chapter 6.1.

### 3.1.1. Natural orbitals as optimal basis

The CI-expansion of many-body states (Eq. 2.14 reproduced here for convenience)

$$|\Psi\rangle = \sum_{i_1 < i_2 < \dots < i_N} C_{i_1 i_2 \dots i_N} |\phi_{i_1} \phi_{i_2} \dots \phi_{i_N}\rangle \quad (3.10)$$

in terms of the natural orbitals  $\{|\eta_i\rangle\}$  is optimal in the sense that a truncation of the basis representation  $\{|\phi_i\rangle\}$  at some  $i = 2I$  gives the least truncation error. The truncation error is measured by

$$\sigma_I[\phi_i] = 1 - \sum_{i_1 < i_2 < \dots < i_N \leq 2I} |C_{i_1 i_2 \dots i_N}|^2 = \sum_{i > 2I} \langle \phi_i | D_1 | \phi_i \rangle. \quad (3.11)$$

$\sigma_I$  is minimal if  $\{|\phi_i\rangle\}$  coincides with the natural orbitals  $\{|\eta_i\rangle\}$ . Intuitively,  $\sigma_I$  can be understood as the average number of electrons in the subspace spanned by the orbitals  $|\phi_\nu\rangle$  with  $\nu > 2I$ . An elegant proof of this property was found by Kobe [152]: In order for the basis  $|\phi_i\rangle$  to be optimal  $\delta\sigma_I$  should vanish

$$\delta\sigma_I = \sum_{i > 2I} \langle \delta\phi_i | D_1 | \phi_i \rangle + \sum_{i > 2I} \langle \phi_i | D_1 | \delta\phi_i \rangle = 0 \quad (3.12)$$

for all orthogonal variations  $\langle \phi_i | \delta\phi_i \rangle = 0$ . Since  $|\delta\phi_i\rangle$  and  $\langle \delta\phi_i|$  can be varied independently each term on the r.h.s. of Eq. 3.12 has to vanish independently. Therefore,  $D_1 |\phi_i\rangle \propto |\phi_i\rangle$  proving that the optimal expansion is given in natural orbitals,  $D_1 |\eta_i\rangle = n_i |\eta_i\rangle$ .

## 3.2. Two-particle reduced density matrix (2RDM)

The 2RDM has been studied extensively since its introduction in the 1950's [153, 154]. It was recognized early on that for pair-wise interacting systems the 2RDM contains the information for calculation of all (equal-time) two-particle observables, e.g. the total energy. The two-particle reduced density matrix (2RDM) is given by

$$\tilde{D}_{12} = \text{Tr}_{3\dots N} |\Psi\rangle\langle\Psi|, \quad (3.13)$$

describing the state of an arbitrary pair in the many-body state. The elements of the 2RDM in a particular basis  $\{|i\rangle\}$  can be calculated according to

$$\langle i_1 i_2 | \tilde{D}_{12} | j_1 j_2 \rangle = \sum_{i_3 \dots i_N} \langle i_1 i_2 i_3 \dots i_N | \Psi \rangle \langle \Psi | j_1 j_2 i_3 \dots i_N \rangle. \quad (3.14)$$

As for a single particle, a single pair in a many-body system is not associated with a single two-body wavefunction but rather with a whole ensemble given by the diagonalization of the 2RDM

$$\tilde{D}_{12} = \sum_i P_i^{(2)} |\gamma_i\rangle \langle \gamma_i|, \quad (3.15)$$

where the eigenstates are called geminals  $|\gamma_i\rangle$ . The calculation of expectation values of two-particle observables can be performed in the same way as described previously for one-particle observables. One important application is the calculation of the interaction energy which is the part of the total energy that cannot be determined from the 1RDM. A single pair in the many-body state has an average interaction energy of

$$\begin{aligned} \langle W_{12} \rangle_{\text{single}} &= \sum_i P_i^{(2)} \langle \gamma_i | W_{12} | \gamma_i \rangle \\ &= \text{Tr}_{12} W_{12} \tilde{D}_{12}, \end{aligned} \quad (3.16)$$

and the total interaction energy  $\langle W_{12} \rangle$  is obtained by multiplying by the number of pairs

$$\langle W_{12} \rangle = \frac{N(N-1)}{2} \langle W_{12} \rangle_{\text{single}}. \quad (3.17)$$

For the sake of simplicity the factor  $N(N-1)$  is usually absorbed into the definition of the 2RDM to describe the whole set of particle pairs as

$$D_{12} = N(N-1) \tilde{D}_{12} = N(N-1) \text{Tr}_{3\dots N} |\Psi\rangle \langle \Psi|, \quad (3.18)$$

and the renormalized probabilities  $P_i^{(2)}$  become the geminal occupation numbers

$$g_i = N(N-1) P_i^{(2)}. \quad (3.19)$$

### 3.2.1. 2RDM energy functional

With this definition of the 1RDM and the 2RDM the total energy of the many-body state can be expressed as

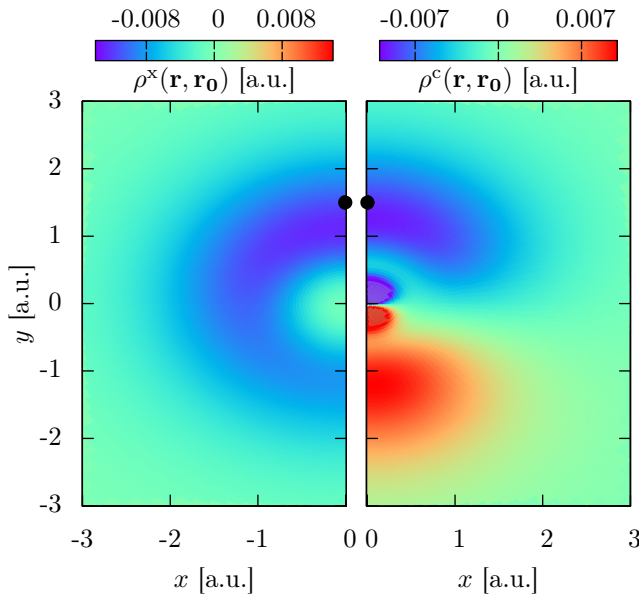
$$\begin{aligned} E &= \langle h_1 \rangle + \langle W_{12} \rangle \\ &= \text{Tr}_1 h_1 D_1 + \frac{1}{2} \text{Tr}_{12} W_{12} D_{12}. \end{aligned} \quad (3.20)$$

This expression for the total energy can be converted into a functional of the 2RDM alone by employing the trace relation

$$D_1 = \frac{1}{N-1} \text{Tr}_2 D_{12}. \quad (3.21)$$

Using this relation the total energy can be rewritten as

$$E = \frac{1}{2} \text{Tr}_{12} \tilde{H}_{12} D_{12} \quad (3.22)$$



**Figure 3.1.:** Exchange hole  $\rho^x(\mathbf{r}, \mathbf{r}_0)$  (left) and correlation hole  $\rho^c(\mathbf{r}, \mathbf{r}_0)$  (right) in the ground state of Be created by an electron located at the fixed position  $\mathbf{r}_0 = (0, 1.5, 0)$  (black dot). For a pure Slater determinant the exchange hole (Eq. 3.28) would be identical to the 2s orbital of the same spin. The asymmetry of the exchange hole originates from contributions beyond the single Slater determinant. The correlation hole accounting for the electron repulsion is given by the two-particle cumulant (Eq. 3.32) and reduces the probability to find the second electron near the first one repelling the second electron to the other side of the atom. (Calculation of the ground state has been performed within MCTDHF.)

with the modified two-electron Hamiltonian

$$\tilde{H}_{12} = \frac{h_1 + h_2}{N - 1} + W_{12}. \quad (3.23)$$

This equation is the basis of a variety of different variational techniques in the calculation of ground state energy [3, 5, 8, 9, 155–157]. Historically, the first calculations to find the ground state energy by minimizing the energy functional Eq. 3.22 with the 2RDM as the variational parameter were performed by Mayer [158]. Soon after this initial attempt it was recognized that the obtained result gives a lower bound for the exact ground state energy [159, 160]. Additional constraints, called  $N$ -representability conditions, that guarantee the existence of a wavefunction that is associated with the 2RDM via Eq. 3.18 are necessary to obtain correct results within the variational 2RDM method [13]. Contrary to the 2RDM, the  $N$ -representability conditions for the 1RDM are known exactly (see Section 5.3). In the variational 1RDM method the known  $N$ -representability conditions are traded for the unknown energy functional [161, 162].

### 3.2.2. Two-particle correlation

In general, the 2RDM contains the information on electron correlation at the two-particle level. Correlation is defined in analogy to statistics as the degree to which quantities are dependent from one another. An uncorrelated system of distinguishable particles has the property that the pair-probability density

$$\rho(\mathbf{r}_1, \mathbf{r}_2) = \sum_{\sigma_1 \sigma_2} \langle \mathbf{r}_1 \sigma_1 \mathbf{r}_2 \sigma_2 | D_{12} | \mathbf{r}_1 \sigma_1 \mathbf{r}_2 \sigma_2 \rangle, \quad (3.24)$$

measuring the probability to find one particle with coordinate  $\mathbf{r}_1$  and the other with  $\mathbf{r}_2$  can be expressed with the one-particle densities

$$\rho(\mathbf{r}_1) = \int \rho(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 \quad \text{and} \quad \rho(\mathbf{r}_2) = \int \rho(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 \quad (3.25)$$

as a simple product

$$\rho^{\text{H}}(\mathbf{r}_1, \mathbf{r}_2) = \rho(\mathbf{r}_1)\rho(\mathbf{r}_2). \quad (3.26)$$

For identical fermions the Pauli principle prohibits the coalescence of two particles with the same spin giving rise to a deviation from a simple product

$$\rho^{\text{HF}}(\mathbf{r}_1, \mathbf{r}_2) = \rho(\mathbf{r}_1)\rho(\mathbf{r}_2) + \rho^{\text{x}}(\mathbf{r}_1, \mathbf{r}_2) \quad (3.27)$$

with the exchange hole (see Fig. 3.1)

$$\rho^{\text{x}}(\mathbf{r}_1, \mathbf{r}_2) = - \sum_{\sigma} |\langle \mathbf{r}_1 \sigma | D_1 | \mathbf{r}_2 \sigma \rangle|^2. \quad (3.28)$$

This kind of exchange correlation is fully included in the Hartree-Fock method by making the antisymmetric ansatz Eq. 2.7 for the wavefunction. The Coulomb interaction leads to the appearance of an additional correlation  $\rho^{\text{c}}(\mathbf{r}_1, \mathbf{r}_2)$  in the pair density,

$$\rho(\mathbf{r}_1, \mathbf{r}_2) = \rho^{\text{HF}}(\mathbf{r}_1, \mathbf{r}_2) + \rho^{\text{c}}(\mathbf{r}_1, \mathbf{r}_2), \quad (3.29)$$

which is not included in the Hartree-Fock method. Post-Hartree Fock methods are necessary to take into account this correlation.

To quantify the amount of correlation,  $D_{12}$  is expanded into an uncorrelated tensor product  $\hat{A}D_1D_2$  describing independent identical particles and a proper correlation term  $\Delta_{12}$  that is referred to as the two-particle cumulant [163, 164] originating solely from the Coulomb interaction between the electrons

$$D_{12} = \hat{A}D_1D_2 + \Delta_{12} = D_{12}^{\text{HF}} + \Delta_{12}. \quad (3.30)$$

Explicitly, the Hartree-Fock approximation  $D_{12}^{\text{HF}} = \hat{A}D_1D_2$  is given by

$$\langle \mathbf{x}_1 \mathbf{x}_2 | D_{12}^{\text{HF}} | \mathbf{x}'_1 \mathbf{x}'_2 \rangle = \langle \mathbf{x}_1 | D_1 | \mathbf{x}'_1 \rangle \langle \mathbf{x}_2 | D_1 | \mathbf{x}'_2 \rangle - \langle \mathbf{x}_2 | D_1 | \mathbf{x}'_1 \rangle \langle \mathbf{x}_1 | D_1 | \mathbf{x}'_2 \rangle \quad (3.31)$$

where the antisymmetrization operator  $\hat{A}$  is defined such that only non-equivalent terms are summed weighted by the sign of the corresponding permutation. (Note that the used convention here is different from the one commonly used in literature. The latter has the disadvantage that it introduces unnecessary prefactors.) The two-particle cumulant  $\Delta_{12}$  is a sensitive measure for electron correlation [165] and vanishes if and only if the particles are uncorrelated [154]. The correlation in the pair density  $\rho^{\text{c}}(\mathbf{r}_1, \mathbf{r}_2)$  (see Fig. 3.1) is directly given by the two-particle cumulant

$$\rho^{\text{c}}(\mathbf{r}_1, \mathbf{r}_2) = \sum_{\sigma_1, \sigma_2} \langle \mathbf{r}_1 \sigma_1 \mathbf{r}_2 \sigma_2 | \Delta_{12} | \mathbf{r}_1 \sigma_1 \mathbf{r}_2 \sigma_2 \rangle \quad (3.32)$$



Using the decomposition, Eqs. (3.27) and (3.29), the exact total electron-electron interaction energy,

$$E^{\text{int}} = \frac{1}{2} \int \frac{\rho(\mathbf{r}_1, \mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2, \quad (3.33)$$

follows as a sum of Hartree, exchange, and correlation energy. With the help of the cumulant expansion (Eq. 3.30) the correlation contribution to other observables can be identified analogously.

### 3.3. Equation of motion of RDMs - the BBGKY hierarchy

A given isolated two-particle system represented by the density matrix

$$D_{12} = \sum_i g_i |\gamma_i\rangle \langle \gamma_i| \quad (3.34)$$

evolves in time under the two-particle Hamiltonian  $H_{12} = h_1 + h_2 + W_{12}$  according to the von-Neumann-Liouville equation

$$i\partial_t D_{12} = [H_{12}, D_{12}]. \quad (3.35)$$

This equation is equivalent to the propagation of each eigenfunction  $|\gamma_i\rangle$  of the ensemble  $D_{12}$  according to the Schrödinger equation

$$i\partial_t |\gamma_i\rangle = H_{12} |\gamma_i\rangle, \quad (3.36)$$

and the associated occupation numbers  $g_i$  are constants of motion. This means that all components of the ensemble propagate independently just influenced by their pair interaction. For a pair embedded in a many-body system, however, a very different behaviour is expected. In addition to the interaction between the constituents of the pair interactions with other particles are present that lead to an additional term in the equation of motion [166]

$$i\partial_t D_{12} = [H_{12}, D_{12}] + C_{12}[D_{123}], \quad (3.37)$$

with

$$C_{12}[D_{123}] = \text{Tr}_3 [W_{13} + W_{23}, D_{123}]. \quad (3.38)$$

The collision operator  $C_{12}[D_{123}]$  describes the interaction of pairs with their  $(N - 2)$  surrounding particles. Since this interaction depends on the three-particle configuration (the pair plus one additional surrounding particle) the collision operator depends on the 3RDM,

$$D_{123} = \frac{N!}{(N - 3)!} \text{Tr}_{4\dots N} |\Psi\rangle \langle \Psi|. \quad (3.39)$$

The collision operator can be derived by considering the equation of motion for the complete system described by the full density matrix  $D_{1\dots N} = |\Psi\rangle\langle\Psi|$

$$\begin{aligned} i\partial_t D_{1\dots N} &= [H_{1\dots N}, D_{1\dots N}] \\ &= [H_{12} + \sum_{n=3}^N h_n + \sum_{2 < m < n}^N W_{mn} + \sum_{m \leq 2 < n}^N W_{mn}, D_{1\dots N}], \end{aligned} \quad (3.40)$$

and tracing out all but two particles

$$\begin{aligned} i\partial_t D_{12} &= [H_{12}, D_{12}] + N(N-1) \overbrace{\text{Tr}_{3\dots N} \left[ \sum_{n=3}^N h_n + \sum_{2 < m < n}^N W_{mn}, D_{1\dots N} \right]}^{=0} \\ &\quad + N(N-1) \text{Tr}_{3\dots N} \sum_{m \leq 2 < n}^N [W_{mn}, D_{1\dots N}] \\ &= [H_{12}, D_{12}] + \text{Tr}_3 [W_{13} + W_{23}, D_{123}]. \end{aligned} \quad (3.41)$$

Naturally, the definition of RDMS can be generalized to arbitrary particle number  $p$  as

$$D_{1\dots p} = \frac{N!}{(N-p)!} \text{Tr}_{p+1\dots N} |\Psi\rangle\langle\Psi| \quad (3.42)$$

referred to as  $p$ RDM. Following the same derivation for the equations of motion gives the coupled set of equations known as the quantum Bogoliubov–Born–Green–Kirkwood–Yvon (BBGKY) hierarchy [56, 57]

$$\begin{aligned} i\partial_t D_{1\dots p} &= [H_{1\dots p}, D_{1\dots p}] + \frac{N!}{(N-p)!} \overbrace{\text{Tr}_{p+1\dots N} \left[ \sum_{n=p+1}^N h_n + \sum_{p < m < n}^N W_{mn}, D_{1\dots N} \right]}^{=0} \\ &\quad + \frac{N!}{(N-p)!} \text{Tr}_{p+1\dots N} \sum_{m \leq p < n}^N [W_{mn}, D_{1\dots N}] \\ &= [H_{1\dots p}, D_{1\dots p}] + \text{Tr}_{p+1} \left[ \sum_{m=1}^p W_{mp+1}, D_{1\dots p+1} \right]. \end{aligned} \quad (3.43)$$

The equation of motion for the 2RDM (Eq. 3.41) and the equation of motion for the 1RDM

$$i\partial_t D_1 = [h_1, D_1] + C_1[D_{12}] \quad (3.44)$$

with

$$C_1[D_{12}] = \text{Tr}_2 [W_{12}, D_{12}] \quad (3.45)$$

are the lowest two members of this hierarchy. It is an important feature of the BBGKY hierarchy that in the presence of pairwise interaction the equation of motion for the  $p$ RDM

depends on the  $(p + 1)$ RDM. It is clear that any application of the hierarchy would require to decouple the equations of motion at some level by expressing the  $(p + 1)$ RDM in terms of the  $p$ RDM. Closure on the second level requires an expression of the 3RDM in terms of the 2RDM. This "reconstruction" is the basis of the time-dependent 2RDM method discussed in Chapter 5.

While the BBGKY hierarchy couples the time-derivative of the  $p$ RDM to the  $(p + 1)$ RDM these two objects are further coupled via the trace relation

$$(N - p)D_{1\dots p} = \text{Tr}_{p+1}D_{1\dots p+1}. \quad (3.46)$$

Compatibility between trace relation (Eq. 3.46) and the BBGKY hierarchy (Eq. 3.43) will constitute an important point in the development of the TD-2RDM method in Chapter 5. Due to the presence of the collision operator in the equations of motion the geminals no longer propagate independently

$$i\partial_t|\gamma_i\rangle = H_{12}|\gamma_i\rangle + \sum_{j \neq i} \frac{\langle \gamma_j | C_{12} | \gamma_i \rangle}{g_i - g_j} |\gamma_j\rangle, \quad (3.47)$$

and pairs can be scattered from one geminal into another making the geminal occupation number time-dependent

$$i\partial_t g_i = \langle \gamma_i | C_{12} | \gamma_i \rangle. \quad (3.48)$$

In analogy, the natural orbitals of the 1RDM are dynamically coupled to each other

$$i\partial_t|\eta_i\rangle = h_1|\eta_i\rangle + \sum_{j \neq i} \frac{\langle \eta_j | C_1 | \eta_i \rangle}{n_i - n_j} |\eta_j\rangle, \quad (3.49)$$

and the natural occupation numbers become time dependent in general

$$i\partial_t n_i = \langle \eta_i | C_1 | \eta_i \rangle. \quad (3.50)$$

For completeness we mention that a convenient way to derive the equations of motion for general eigenfunctions of the  $p$ RDM is based on Rayleigh-Schrödinger perturbation theory to first order, e.g. by considering the infinitesimal change of a 1RDM via

$$D_1(t + dt) = D_1(t) + \partial_t D_1 dt. \quad (3.51)$$

In first order perturbation theory the natural occupation numbers and the natural orbitals change according to

$$n_i(t + dt) = n_i(t) + \langle \eta_i | \partial_t D_1 | \eta_i \rangle dt \quad (3.52)$$

$$|\eta_i(t + dt)\rangle = |\eta_i(t)\rangle + \sum_{j \neq i} \frac{\langle \eta_j | \partial_t D_1 | \eta_i \rangle}{n_i - n_j} |\eta_j\rangle dt. \quad (3.53)$$

Substituting the derivative of the 1RDM (Eq. 3.44) into the latter two equations and taking the corresponding differential quotient gives the equations of motion Eq. 3.49 and Eq. 3.50.

### 3.4. Diagrammatic analysis of RDMs

RDMs of complex interacting many-body systems can, in principle, be approached in two conceptually different ways. The first way is "top-down" and is relevant, e.g., in MCTDHF calculations. By calculating the many-body wavefunction  $|\Psi\rangle$  the 1RDM and the 2RDM can be constructed via the partial trace according to Eq. 3.3 and Eq. 3.13. This procedure of calculating the RDMs from the wavefunction, however, can be numerically very expensive. Indeed, if the CI coefficients  $C_I$  of an MCTDHF calculations are few enough to be stored in the available memory the evaluation of the 2RDM, necessary for the orbital propagation, turns out to be the bottleneck of the calculation. The second approach is "bottom-up". Departing from simple non-interacting systems for which the RDMs can be calculated directly, the RDMs of complex systems can be constructed by considering particle interactions as a perturbation. Consecutively taking into account the perturbation to higher order gives better and better approximations to the exact RDMs of the complex system eventually resulting in the exact RDMs if convergence is achieved. This "bottom-up" approach gives insight into where the dominant contributions to the RDM are coming from, it explains why some elements are small or large, and it reveals relations between parts of the RDMs that would be hidden otherwise. We give a review of many-body perturbation theory for RDMs in the following. This rather lengthy review is needed to understand the reconstruction theory presented in Chapter 5 which is one of the cornerstones of the TD-2RDM theory. The general idea behind many-body perturbation theory is to approximate the solution of the many-body system by decomposing the Hamiltonian (Eq. 2.2)

$$H_{12\dots N} = H_{12\dots N}^{(0)} + \mathcal{V}_{12\dots N} \quad (3.54)$$

into a (solvable) unperturbed part  $H_{12\dots N}^{(0)}$  and a perturbation  $\mathcal{V}_{12\dots N}$ . For the moment we will use the non-interacting system as the unperturbed system

$$H_{12\dots N}^{(0)} = \sum_n h_n, \quad (3.55)$$

and the particle interaction as the perturbation

$$\mathcal{V}_{12\dots N} = \sum_{m<n} W_{mn}. \quad (3.56)$$

Given the eigenfunctions  $\{|\chi_i\rangle\}$  of the single-particle operator,

$$h_1|\chi_i\rangle = e_i|\chi_i\rangle \quad (3.57)$$

ordered according to  $(e_1 < e_2 < e_3 < \dots)$  the ground state of the unperturbed Hamiltonian  $H_{12\dots N}^{(0)}$  is given by the Slater determinant

$$|\mathcal{I}\rangle = |\chi_1\chi_2\dots\chi_N\rangle. \quad (3.58)$$

As in Eq. 2.7 the many-body state  $|\chi_1\chi_2\dots\chi_N\rangle$  represents the antisymmetric state with one particle occupying  $|\chi_o\rangle$  where  $o \in \{1, 2, \dots, N\}$ . This clear separation between occupied orbitals  $|\chi_o\rangle$  with  $o \in \{1, 2, \dots, N\}$  and virtual orbitals  $|\chi_a\rangle$  with  $a \in \{N+1, N+2, \dots\}$  is a feature of systems whose Hamiltonian is a single-particle operator.

### 3.4.1. Second quantization

We use, for the convenience of bookkeeping, in the following the formulation of second quantization for the further description of the many-body system. There are three things we need to build up the structure of the many-body system: the vacuum state  $|\rangle$  containing no particle at all, the creation operator  $a_i^\dagger$  creating one particle in state  $|\chi_i\rangle = a_i^\dagger|\rangle$ , and the destruction operator  $a_i$  annihilating the particle  $a_i|\chi_i\rangle = |\rangle$ . In this formalism the Hamiltonian can be expressed as

$$H = \frac{1}{2} \sum_{i_1 i_2 j_1 j_2} \tilde{H}_{i_1 i_2}^{j_1 j_2} a_{i_1}^\dagger a_{i_2}^\dagger a_{j_2} a_{j_1}, \quad (3.59)$$

where

$$\tilde{H}_{i_1 i_2}^{j_1 j_2} = \langle \chi_{j_1} \chi_{j_2} | \tilde{H}_{12} | \chi_{i_1} \chi_{i_2} \rangle \quad (3.60)$$

are the matrix elements of the modified two-electron Hamiltonian  $\tilde{H}_{12}$  introduced in Eq. 3.23. Using Eq. 3.59 the total energy can be calculated from

$$E = \langle \Psi | H | \Psi \rangle = \frac{1}{2} \sum_{i_1 i_2 j_1 j_2} \tilde{H}_{i_1 i_2}^{j_1 j_2} \langle \Psi | a_{i_1}^\dagger a_{i_2}^\dagger a_{j_2} a_{j_1} | \Psi \rangle, \quad (3.61)$$

corresponding to the energy functional (Eq. 3.22)

$$E = \frac{1}{2} \text{Tr}_{12} \tilde{H}_{12} D_{12} = \frac{1}{2} \sum_{i_1 i_2 j_1 j_2} \tilde{H}_{i_1 i_2}^{j_1 j_2} D_{j_1 j_2}^{i_1 i_2}. \quad (3.62)$$

Equating both expressions, Eq. 3.61 and Eq. 3.62, gives the expression for the matrix elements of the 2RDM in terms of the creation and annihilation operators

$$D_{j_1 j_2}^{i_1 i_2} = \langle \chi_{i_1} \chi_{i_2} | D_{12} | \chi_{j_1} \chi_{j_2} \rangle = \langle \Psi | a_{i_1}^\dagger a_{i_2}^\dagger a_{j_2} a_{j_1} | \Psi \rangle. \quad (3.63)$$

In analogy, the matrix elements of the 1RDM

$$D_{j_1}^{i_1} = \langle \chi_{i_1} | D_1 | \chi_{j_1} \rangle = \langle \Psi | a_{i_1}^\dagger a_{j_1} | \Psi \rangle \quad (3.64)$$

and of all higher RDMs can be obtained accordingly.

### 3.4.2. The one-body propagator

A quantity that is closely related to the 1RDM (Eq. 3.64) is the single-particle propagator defined by the transition amplitude for an additionally created particle to go from state  $|\chi_{j_1}\rangle$  at time  $t'$  to state  $|\chi_{i_1}\rangle$  at time  $t$

$$i \langle \chi_{i_1} | \mathcal{G}_1^p(t, t') | \chi_{j_1} \rangle = \langle \Psi | a_{i_1}(t) a_{j_1}^\dagger(t') | \Psi \rangle, \quad \text{with } t > t', \quad (3.65)$$

where we have switched to creation and annihilation operators in Heisenberg picture (denoted by the time-dependency) whose equation of motion read

$$i\partial_t a_{i_1}^\dagger(t) = [H, a_{i_1}^\dagger(t)]. \quad (3.66)$$

In addition to the single-particle propagator  $\mathcal{G}_1^p$  there is another propagator, the single-hole operator  $\mathcal{G}_1^h$ , that turns out to be very handy when treating many-body systems. The single-hole operator describes the propagation of the hole from state  $|i_1\rangle$  at time  $t$  to state  $|j_1\rangle$  at time  $t'$

$$i\langle\chi_{i_1}|\mathcal{G}_1^h(t, t')|\chi_{j_1}\rangle = -\langle\Psi|a_{j_1}^\dagger(t')a_{i_1}(t)|\Psi\rangle, \quad \text{with } t' > t. \quad (3.67)$$

Both expressions can be elegantly combined by defining the one-body propagator

$$i\langle\chi_{i_1}|\mathcal{G}_1(t, t')|\chi_{j_1}\rangle = \langle\Psi|T[a_{i_1}(t)a_{j_1}^\dagger(t')]| \Psi\rangle, \quad (3.68)$$

by using the time-ordering operator  $T[A(t_2)B(t_1)...C(t_n)] = (-1)^\tau B(t_1)A(t_2)...C(t_n)$  with  $t_1 > t_2 > \dots > t_n$  that orders operators with increasing time from right to left, and  $\tau$  the number of transpositions. From this definition of the one-body propagator the close relation to the 1RDM (Eq. 3.64) becomes apparent. In particular, depending on the limit we perform

$$\lim_{\delta \rightarrow 0} i\mathcal{G}_1(t, t + \delta) = -D_1(t) \quad (3.69)$$

$$\lim_{\delta \rightarrow 0} i\mathcal{G}_1(t + \delta, t) = Q_1(t), \quad (3.70)$$

either the 1RDM,  $D_1(t)$ , or the corresponding one-hole reduced density matrix (1HRDM)

$$Q_1(t) = \mathbb{1}_1 - D_1(t) \quad (3.71)$$

is obtained, where  $\mathbb{1}_1$  is the identity in the one-particle subspace. The 1HRDM,  $Q_1$ , describes the system in terms of an ensemble of holes rather than of particles. Note that the equal-time limit of the single-hole propagator gives the negative 1RDM (Eq. 3.69) and the equal-time limit of the single-particle propagator gives the 1HRDM (Eq. 3.70). This subtle twist in the role of particles and holes has its origin in the fact that single-particle propagator probes the system by adding one additional particle above the Fermi-surface. The 1RDM on the other hand describes the particles below the Fermi-surface. Instead of following the motion of an additional particle (above the Fermi-surface) one could also follow the motion of an already existing particle below the Fermi-surface by removing it and watching the created hole move. The (time-reversed) motion of the hole corresponds to the motion of an internal particle of the system. In this sense the single-hole propagator (Eq. 3.67) describes the time-reversed propagation of particles below the Fermi-surface (in occupied states) and gives the 1RDM upon the equal-time limit.

In the non-interacting system, particles added in the eigenstates  $|\chi_i\rangle$  (Eq. 3.57) of the single-particle operator  $h_1$  remain in these eigenstates evolving in time merely by a phase  $e^{-ie_i(t-t')}$ .

Therefore, the one-body propagator of a non-interacting system is given by [167]

$$i\langle\chi_{i_1}|\mathcal{G}_1^{(0)}(t,t')|\chi_{j_1}\rangle = \begin{cases} e^{-ie_{i_1}(t-t')} & \text{if } t > t' \text{ and } i_1 = j_1 > N \\ -e^{ie_{i_1}(t'-t)} & \text{if } t' > t \text{ and } i_1 = j_1 \leq N \\ 0 & \text{else} \end{cases} \quad (3.72)$$

The requirement  $i_1 = j_1 > N$  ( $i_1 = j_1 \leq N$ ) is necessary since particles (holes) can only be added above (below) the Fermi surface due to the Pauli principle.

For the interacting system the one-body propagator is significantly more complicated. There are essentially two different ways for its calculation. One is the solution of the equations of motion given by the Martin-Schwinger hierarchy [58]. This approach suffers from the same coupling to higher-order propagators as the equations of motion for the RDMs (Eq. 3.43). Alternatively the known one-body propagator of the non-interacting system  $\mathcal{G}_1^{(0)}$  and the interaction operator  $W_{12}$  can be used to express the one-body propagator of the interacting system in terms of a perturbation expansion. This perturbation expansion can become very tedious with increasing perturbative order. To keep track of the individual terms in the perturbation expansion Feynman diagrams are a very helpful tool [168]. Here we only scratch the surface of this elaborate method as far as needed in the following.

### 3.4.3. Perturbation expansion

With the exact ground state of the many-body system  $|\Psi\rangle$  at hand the one-body operator  $\mathcal{G}_1(t,t')$  can be evaluated via Eq. 3.68. The known ground state of the non-interacting system  $|\Psi_0\rangle$  can be connected with the ground state of the interacting system  $|\Psi\rangle$  by adiabatically turning on interactions as described by the Gell-Mann and Low theorem [169, 170]. In order for this to work two requirements have to be met. First,  $|\Psi_0\rangle$  should not be orthogonal to  $|\Psi\rangle$ . This is generally the case except for exceptional situations in which the system undergoes some phase transition arising from the particle-particle interaction (such as superconducting systems [170]). Second, the switching has to be adiabatic, i.e. slow enough that no excitation takes place. Under this adiabatic condition the precise form with which the interaction is switched on does not enter the final expressions. In mathematical terms, the switching is described by the time-evolution operator  $U(t',t)$  that evolves the ground state of the unperturbed system  $|\Psi_0\rangle$  at time  $t \rightarrow -\infty$  into the state of the interacting system via

$$|\Psi(t)\rangle = U(t, -\infty)|\Psi_0\rangle. \quad (3.73)$$

Employing this relation we can write the one-body operator (Eq. 3.68) as

$$i\langle\chi_{i_1}|\mathcal{G}_1(t,t')|\chi_{j_1}\rangle = \frac{\langle\Psi_0|U(\infty,0)T[a_{i_1}(t)a_{j_1}^\dagger(t')]U(0,-\infty)|\Psi_0\rangle}{\langle\Psi_0|U(\infty,0)U(0,-\infty)|\Psi_0\rangle}. \quad (3.74)$$

The complexity of the interacting system is now hidden within the time-evolution operator  $U(t,t')$  whose Dyson expansion reads

$$U(t,t') = \sum_{k=0}^{\infty} \frac{(-i)^k}{k!} \int_{t_1=t'}^t \dots \int_{t_k=t'}^t T[H(t_1)\dots H(t_k)]dt_1\dots dt_k. \quad (3.75)$$

Perturbation theory is usually performed in the interaction picture of Dirac which transforms the operators as

$$\tilde{\mathcal{O}}(t) = e^{iH^{(0)}t} \mathcal{O}(0) e^{-iH^{(0)}t} \quad (3.76)$$

and the states according to

$$|\tilde{\Psi}\rangle = e^{iH^{(0)}t} |\Psi\rangle. \quad (3.77)$$

In this way the "trivial" dynamics is hidden within the operators and the "non-trivial" dynamics of the state  $|\tilde{\Psi}\rangle$  is solely influenced by the perturbation itself ensuring that the time-evolution operator  $\tilde{U}(t, t')$  reduces to the identity for vanishing perturbation.

Employing the adiabatic expression for the one-body propagator (Eq. 3.74) together with the the Dyson equation (Eq. 3.75) and transforming into the interaction picture gives the perturbation expansion of the one-body propagator as

$$i\langle\chi_{i_1}|\mathcal{G}_1(t, t')|\chi_{j_1}\rangle = \frac{\sum_{k=0}^{\infty} \frac{(-i)^k}{k!} \int_{-\infty}^{\infty} \dots \int_{-\infty}^{\infty} \langle\tilde{\Psi}_0|T[\tilde{W}(t_1)\dots\tilde{W}(t_k)\tilde{a}_{i_1}(t)\tilde{a}_{j_1}^\dagger(t')]| \tilde{\Psi}_0\rangle dt_1\dots dt_k}{\sum_{k=0}^{\infty} \frac{(-i)^k}{k!} \int_{t_1=-\infty}^{t=\infty} \dots \int_{t_k=-\infty}^{t=\infty} \langle\tilde{\Psi}_0|T[\tilde{W}(t_1)\dots\tilde{W}(t_k)]|\tilde{\Psi}_0\rangle dt_1\dots dt_k}. \quad (3.78)$$

The basic building blocks of the expression above are the creation and annihilation operators in the interaction picture  $\tilde{a}_{i_1}(t)$ , the interaction operator  $\tilde{W}(t)$ , and the unperturbed state  $|\tilde{\Phi}_0\rangle$ . Evaluating the terms in the expansion requires to evaluate the matrix elements  $\langle\tilde{\Psi}_0|T[\tilde{W}(t_1)\dots\tilde{W}(t_k)\tilde{a}_{i_1}(t)\tilde{a}_{j_1}^\dagger(t')]| \tilde{\Psi}_0\rangle$ . By employing Wick's theorem [171] each of these elements can be calculated based on the the interaction operator

$$W_{j_1 j_2}^{i_1 i_2} = \langle\chi_{i_1}\chi_{i_2}|W_{12}|\chi_{j_1}\chi_{j_2}\rangle \quad (3.79)$$

and the so called contraction

$$\overline{\tilde{a}_{i_1}(t)\tilde{a}_{j_1}^\dagger(t')} = \langle\tilde{\Phi}_0|T[\tilde{a}_{i_1}(t)\tilde{a}_{j_1}^\dagger(t')]| \tilde{\Phi}_0\rangle = i\langle\chi_{i_1}|\mathcal{G}_1^{(0)}(t, t')|\chi_{j_1}\rangle, \quad (3.80)$$

which is nothing but the unperturbed propagator given in Eq. 3.72 because the creation and annihilation operators are in the interaction picture (compare to Eq. 3.68). Thus, the one-body propagator of the interacting system is expressed in terms of basic ingredients: the unperturbed propagator and the interaction elements. This is the starting point of the diagrammatic expansion.

### 3.4.4. Diagrammatic expansion

In our convention we draw  $i\langle\chi_{i_1}|\mathcal{G}_1^{(0)}(t, t')|\chi_{j_1}\rangle$  as a dashed line and  $i\langle\chi_{i_1}|\mathcal{G}_1(t, t')|\chi_{j_1}\rangle$  as a double line with a lower and upper end point corresponding to the initial  $|\chi_{j_1}\rangle$  and final



$|\chi_{i_1}\rangle$  state of the propagation

$$\begin{array}{c} i_1 \\ \vdots \\ \uparrow \\ \vdots \\ j_1 \\ t' \end{array} = i \langle \chi_{i_1} | \mathcal{G}_1^{(0)}(t, t') | \chi_{j_1} \rangle \qquad \begin{array}{c} i_1 \\ \parallel \\ \uparrow \\ \parallel \\ j_1 \\ t' \end{array} = i \langle \chi_{i_1} | \mathcal{G}_1(t, t') | \chi_{j_1} \rangle. \quad (3.81)$$

The interaction between two particles is represented by a horizontal wiggly line at constant time with two vertices that have one incoming and one outgoing connection each corresponding to the lower and upper indices as

$$\begin{array}{c} i_1 \\ \nearrow \\ \text{---} \\ \searrow \\ j_1 \end{array} \begin{array}{c} i_2 \\ \nearrow \\ \text{---} \\ \searrow \\ j_2 \end{array} = -i W_{j_1 j_2}^{i_1 i_2}, \quad (3.82)$$

where the factor  $-i$  is a convenient convention to absorb the factor  $(-i)^k$  in Eq. 3.78 into the diagrammatic expansion. The set of all terms in  $n$ th order in the perturbation expansion can be generated by drawing all topologically different diagrams that connect the incoming state  $|\chi_{j_1}\rangle$  at time  $t'$  with the outgoing state  $|\chi_{i_1}\rangle$  at time  $t$  through the presence of  $n$  wiggly lines representing the interaction operator  $W_{j_1 j_2}^{i_1 i_2}$ . There are essentially two definitions of topological equivalence for diagrams. In the Feynman sense two diagrams are equivalent if they can be transformed into each other by a continuous transformation. In the Goldstone sense two diagrams are equivalent if they can be transformed into each other by a continuous transformation without changing the time order of the interaction wiggles. In other word Goldstone diagrams are time-ordered while Feynman diagrams are not [170]. We will stick to the Goldstone convention for the topological equivalence of diagrams.

### Diagrammatic expansion of the one-body propagator

The first few terms in the perturbation expansion of the one-body propagator (Eq. 3.78) can be represented by

$$\begin{array}{c} i_1 \\ \parallel \\ \uparrow \\ \parallel \\ j_1 \\ t' \end{array} = \begin{array}{c} i_1 \\ \vdots \\ \uparrow \\ \vdots \\ j_1 \\ t' \end{array} + \begin{array}{c} i_1 \\ \vdots \\ \uparrow \\ \text{---} \\ \vdots \\ j_1 \\ t' \end{array} + \begin{array}{c} i_1 \\ \vdots \\ \uparrow \\ \text{---} \\ \text{---} \\ \vdots \\ j_1 \\ t' \end{array} + \begin{array}{c} i_1 \\ \vdots \\ \uparrow \\ \text{---} \\ \text{---} \\ \text{---} \\ \vdots \\ j_1 \\ t' \end{array} + \begin{array}{c} i_1 \\ \vdots \\ \uparrow \\ \text{---} \\ \text{---} \\ \text{---} \\ \text{---} \\ \vdots \\ j_1 \\ t' \end{array} + \begin{array}{c} i_1 \\ \vdots \\ \uparrow \\ \text{---} \\ \text{---} \\ \text{---} \\ \text{---} \\ \text{---} \\ \vdots \\ j_1 \\ t' \end{array} + \dots \quad (3.83)$$

where each diagram corresponds to one term whose quantitative contribution can be precisely evaluated according to simple rules (see e.g. [170]). One important property known as the linked-cluster theorem [172, 173] states that the denominator in Eq. 3.78 exactly cancels all diagrams that consist of two or more unlinked parts. Only linked diagrams, i.e. diagrams where each vertex is linked through a sequence of propagator lines, appear in the perturbation expansion.

The derivation of the diagrammatic method is based on perturbation theory (Eq. 3.78), however, the diagrammatic approach does not have to remain a purely perturbative method. Whereas in perturbation theory usually the order of the perturbation expansion is truncated at some order in hope that higher order contributions are negligible this is not necessarily the case in the diagrammatic method. The diagrammatic method rather seeks to find important subsets of diagrams that have a large contribution and to sum them up to infinite order. One important subclass of diagrams that can be summed to infinite order are diagrams that contain contributions referred to as Hartree-Fock diagrams

$$(3.84)$$

These corrections to the propagation are localized in time and represent interactions with the mean field created by the many-body environment. In Section 2.1 we discussed this mean-field (Eq. 2.11) in connection with the TDHF approach. In an intuitive picture these contributions may be understood as a particle interacting with a spontaneously created particle-hole pair and its exchange partner. This interaction can occur repeatedly and, in fact, all such diagrams can be summed up to infinite order which correspond to the self-consistent solution of the Hartree-Fock equations (Eq. 2.9). The corresponding propagator is known as the Hartree-Fock propagator

$$(3.85)$$

It constitutes an early and well established approximation to the fully dressed propagator (Eq. 3.68). One particular property that can be traced back to the localized time structure of the Hartree-Fock diagrams is that the Hartree-Fock propagator Eq. 3.85 can be written similarly to the unperturbed propagator (Eq. 3.72) where the mean-field is accounted for by Hartree-Fock energy  $\varepsilon_{i_1}$  and Hartree-Fock orbitals  $|\epsilon_{i_1}\rangle$ .

Replacing the unperturbed propagator by the Hartree-Fock propagator corresponds to using the Hartree-Fock solution as the zeroth order of perturbation theory. This is the standard approach to many-body perturbation theory (Møller–Plesset perturbation theory [174, 175]). The lowest order correction to the single-particle propagator is thus given by diagrams such as

$$(3.86)$$

where the Hartree-Fock diagrams (Eq. 3.84) are absorbed into the Hartree-Fock propagator depicted by the (thicker) solid line (Eq. 3.85).

### Diagrammatic expansion of the 1RDM

Based on the diagrammatic expansion of the one-body propagator that we have reviewed here we make now just a small but important step in developing the diagrammatic expansion of RDMs. Remembering the 1RDM as the equal-time limit of the single-hole propagator (Eq. 3.69) the diagrams for the 1RDM can be generated by bending the outgoing line back to the equal-time line from which the incoming line emanates. The line emanating from the equal-time line (represented by a dashed line) starts in the orbital with the lower index and arrives at the equal-time line in the upper index

$$t \text{ --- } \overset{\curvearrowright}{\underset{j_1}{\bullet}} \text{ --- } \overset{\curvearrowleft}{\underset{i_1}{\bullet}} \text{ --- } = \langle \epsilon_{i_1} | D_1^{\text{HF}}(t) | \epsilon_{j_1} \rangle = \begin{cases} 1 & i_1 = j_1 \leq N \\ 0 & \text{else} \end{cases} \quad (3.87)$$

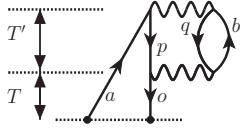
$$t \text{ --- } \overset{\curvearrowright}{\underset{j_1}{\bullet}} \text{ --- } \overset{\curvearrowright}{\underset{i_1}{\bullet}} \text{ --- } = \langle \epsilon_{i_1} | D_1(t) | \epsilon_{j_1} \rangle = D_{j_1}^{i_1}(t). \quad (3.88)$$

According to the equal-time limit (Eq. 3.69) each term in the expansion of the one-body propagator can be associated with a well defined diagram of the 1RDM. The corresponding diagrammatic expansion reads

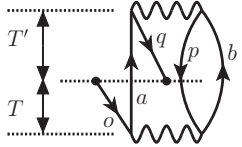
$$\text{---} \overset{\curvearrowright}{\bullet} \text{---} \overset{\curvearrowright}{\bullet} \text{---} = \text{---} \overset{\curvearrowright}{\bullet} \text{---} \overset{\curvearrowright}{\bullet} \text{---} + \text{---} \overset{\curvearrowright}{\bullet} \text{---} \overset{\curvearrowright}{\bullet} \text{---} \text{---} \text{---} \text{---} + \text{---} \overset{\curvearrowright}{\bullet} \text{---} \overset{\curvearrowright}{\bullet} \text{---} \text{---} \text{---} \text{---} \text{---} \text{---} + \text{---} \overset{\curvearrowright}{\bullet} \text{---} \overset{\curvearrowright}{\bullet} \text{---} \text{---} \text{---} \text{---} \text{---} \text{---} \text{---} \text{---} + \dots \quad (3.89)$$

As a representative example we will evaluate the second and third diagram of Eq. 3.89. For each internal line there is a summation over the associated orbital indices, and the time position of the interaction wiggly line is integrated over all configurations conserving the time ordering of the diagram. Note that the single-particle propagator requires the associated orbital to be unoccupied because particles can only be added above the Fermi surface while the single-hole propagator requires the associated orbital to be occupied. The values of the

second and third diagram of Eq. 3.89 are thus



$$\begin{aligned}
 &= - \sum_{pqb} \int_0^\infty \int_0^\infty e^{-i(\varepsilon_a - \varepsilon_o)T} e^{-i(\varepsilon_a + \varepsilon_b - \varepsilon_p - \varepsilon_q)T'} (-iW_{pq}^{ob}) (-iW_{ab}^{pq}) dT dT' \\
 &= - \sum_{pqb} \frac{W_{pq}^{ob} W_{ab}^{pq}}{(\varepsilon_o - \varepsilon_a)(\varepsilon_p + \varepsilon_q - \varepsilon_a - \varepsilon_b)}.
 \end{aligned} \tag{3.90}$$



$$= - \sum_{apb} \frac{W_{op}^{ab} W_{ab}^{qp}}{(\varepsilon_o + \varepsilon_p - \varepsilon_a - \varepsilon_b)(\varepsilon_q + \varepsilon_p - \varepsilon_a - \varepsilon_b)}, \tag{3.91}$$

where we have used the convention that occupied reference orbitals are denoted with indices starting from  $o$ , i.e.  $\{o, p, q, r, s, t\}$  and unoccupied reference orbitals are denoted with indices starting from  $a$ , i.e.  $\{a, b, c, d\}$ . The indices  $\{i_1, i_2, i_3, j_1, j_2, j_3\}$  continue to denote both occupied as well as unoccupied reference orbitals. Instead of evaluating the time-integrals explicitly there are simple rules that allow to translate each diagrams into its analytical expressions:

1. Draw auxiliary lines between two pairs of neighbouring wiggly lines, and between the equal-time line and its neighbouring wiggly lines. For the diagram in Eq. 3.90 there are two such auxiliary lines. Each auxiliary line corresponds to one time-integral extending from 0 to  $\infty$  and gives rise to an energy denominator  $1/(\varepsilon_o + \dots + \varepsilon_q - \varepsilon_a - \dots - \varepsilon_c)$  including the energies of the particle and hole propagator lines crossed by the auxiliary line.
2. The sign of the diagram is calculated by multiplication with  $(-1)$  for each hole-propagator (due to the sign in the definition of hole propagator Eq. 3.85) and for each loop that is contained in the diagram.
3. If there is an additional minus sign in the relation between the equal-time limit of the Green's function and the corresponding RDM this sign has to accounted as well. For the 1RDM there is such an additional global minus sign (Eq. 3.69).

Given these rules the perturbative correction to the Hartree-Fock result for the 1RDM can be calculated to arbitrary order (assuming convergence) resulting in the 1RDM calculated from the state  $|\Psi\rangle$  of the interacting system. These rules for evaluating RDM diagrams can be understood as an extension of the corresponding Goldstone rules for evaluating Goldstone diagrams [173].

### Diagrammatic expansion of the two-body propagator

In analogy to the one-body propagator (Eq. 3.68) using the Hartree-Fock orbitals as zeroth order the two-body propagator describes the transition amplitude of two bodies from initial

state  $|\epsilon_{j_1}\epsilon_{j_2}\rangle$  to final state  $|\epsilon_{i_1}\epsilon_{i_2}\rangle$ .

$$i^2\langle\epsilon_{i_1}\epsilon_{i_2}|\mathcal{G}_{12}(t_1, t_2, t'_1, t'_2)|\epsilon_{j_1}\epsilon_{j_2}\rangle = \langle\Psi|T[a_{i_1}(t_1)a_{i_2}(t_2)a_{j_2}^\dagger(t'_2)a_{j_1}^\dagger(t'_1)]|\Psi\rangle. \quad (3.92)$$

By choosing  $t_1, t_2, t'_1, t'_2$  in different time orders we obtain different types of two-body propagators; the particle-particle propagator ( $t_1 > t'_1, t_2 > t'_2$ ), the hole-hole propagator ( $t_1 < t'_1, t_2 < t'_2$ ) and the particle-hole propagator ( $t_1 < t'_1, t_2 > t'_2$ ). In analogy to the one-body propagator  $\mathcal{G}_1(t, t')$  (Eq. 3.69) the equal-time limit gives different representations of the two-body subspace

$$\lim_{\delta \rightarrow 0} i^2 \mathcal{G}_{12}(t, t, t + \delta, t + \delta) = D_{12}(t) \quad (3.93)$$

$$\lim_{\delta \rightarrow 0} i^2 \mathcal{G}_{12}(t + \delta, t + \delta, t, t) = Q_{12}(t) \quad (3.94)$$

$$\lim_{\delta \rightarrow 0} i^2 \mathcal{G}_{12}(t + \delta, t, t, t + \delta) = -G_{12}(t), \quad (3.95)$$

where the interrelation between the 2RDM,  $D_{12}$ , the two-hole reduced density matrix (2HRDM),  $Q_{12}$ , and the particle-hole reduced density matrix,  $G_{12}$ , is given by

$$Q_{12} = \hat{A}\mathbb{1}_1\mathbb{1}_2 + \hat{A}D_1\mathbb{1}_2 + D_{12} \quad (3.96)$$

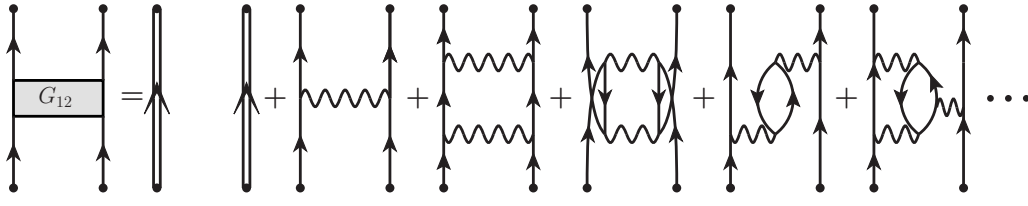
$$G_{12} = D_1\mathbb{1}_2 - D_{12}. \quad (3.97)$$

These matrices will later become important in connection with  $N$ -representability conditions defined in Section 5.3.

Employing the idea of adiabatic switching (in analogy to Eq. 3.78) leads to the perturbation expansion

$$\begin{aligned} i^2\langle\epsilon_{i_1}\epsilon_{i_2}|\mathcal{G}_{12}(t_1, t_2, t'_1, t'_2)|\epsilon_{j_1}\epsilon_{j_2}\rangle &= \\ &= \frac{\sum_{k=0}^{\infty} \frac{(-i)^k}{k!} \int_{-\infty}^{\infty} \dots \int_{-\infty}^{\infty} \langle\tilde{\Phi}_0|T[\tilde{W}(t_1)\dots\tilde{W}(t_k)\tilde{a}_{i_1}(t_1)\tilde{a}_{i_2}(t_2)\tilde{a}_{j_2}^\dagger(t'_2)\tilde{a}_{j_1}^\dagger(t'_1)]|\tilde{\Phi}_0\rangle dt_1\dots dt_k}{\sum_{k=0}^{\infty} \frac{(-i)^k}{k!} \int_{-\infty}^{\infty} \dots \int_{-\infty}^{\infty} \langle\tilde{\Phi}_0|T[\tilde{W}(t_1)\dots\tilde{W}(t_k)]|\tilde{\Phi}_0\rangle dt_1\dots dt_k}. \end{aligned} \quad (3.98)$$

Each term in this expression can be depicted as a diagram connecting the incoming state  $|\epsilon_{j_1}\epsilon_{j_2}\rangle$  with the outgoing state  $|\epsilon_{i_1}\epsilon_{i_2}\rangle$ . Unlinked diagrams, i.e. diagrams that contain parts that cannot be reached from either of the two incoming states, are cancelled by the denominator in Eq. 3.98. Note that in the diagrammatic expansion of two-particle propagators there is a difference between unlinked and unconnected diagrams. Unconnected diagrams represent uncorrelated propagation of two individual particles while all parts of the diagram can be reached from either of the two incoming states. They are present and do not cancel out. Employing the fully dressed propagator (Eq. 3.86) we can write the diagrams for the two-particle propagator as



$$(3.99)$$

where all unconnected diagrams are collected into the first term. Note that in addition to the first diagram there is another class of unconnected diagrams represented by



however, in the following we will use the convention that all diagrams that can be generated by permutation of upper or lower indices are represented by only one representative.

### Diagrammatic expansion of the 2RDM

With the corresponding equal-time limit of Eq. 3.99 we obtain the diagrams for the 2RDM as

$$(3.100)$$

where we have used the diagrammatic representation of the 2RDM

$$= \langle \epsilon_{i_1} \epsilon_{i_2} | D_{12} | \epsilon_{j_1} \epsilon_{j_2} \rangle = D_{j_1 j_2}^{i_1 i_2} \quad (3.101)$$

and of the antisymmetric product of 1RDMs

$$= \langle \epsilon_{i_1} \epsilon_{i_2} | \hat{\mathcal{A}} D_1 D_1 | \epsilon_{j_1} \epsilon_{j_2} \rangle = D_{j_1}^{i_1} D_{j_2}^{i_2} - D_{j_2}^{i_1} D_{j_1}^{i_2}. \quad (3.102)$$

As an example, we explicitly evaluate of the second and the 5th diagram of Eq. 3.100

$$= \int_0^\infty e^{-i(\epsilon_a + \epsilon_b - \epsilon_o - \epsilon_p)T} (-iW_{ab}^{op}) dT \quad (3.103)$$

$$= \frac{W_{ab}^{op}}{\epsilon_o + \epsilon_p - \epsilon_a - \epsilon_b}$$

$$= \sum_{ab} \frac{W_{op}^{ab} W_{ab}^{qs}}{(\epsilon_o + \epsilon_p - \epsilon_a - \epsilon_b)(\epsilon_q + \epsilon_s - \epsilon_a - \epsilon_b)}. \quad (3.104)$$

The diagrammatic expansion of the 2RDM (Eq. 3.100) suggests the decomposition into unconnected (Eq. 3.102) and connected diagrams corresponding to the two-particle cumulant (Eq. 3.30)

The diagram shows a shaded rectangular box with four external legs (two on the left, two on the right) and two internal arcs connecting the top and bottom lines. This is equal to the sum of two unconnected diagrams (two separate arcs) and one connected diagram (a shaded oval with four external legs).

$$(3.105)$$

From Eq. 3.103 and Eq. 3.104 we can read off two important observations for the two-particle cumulant. First, the lowest non-vanishing order in perturbation theory (LOPT) is different for different classes of the two-particle cumulant. While the LOPT of the classes  $\Delta_{op}^{ab}$  and  $\Delta_{ab}^{op}$  (correlated double excitation and deexcitation) is of first order in  $W_{12}$  the LOPT of the classes  $\Delta_{op}^{qs}$  is of second order in  $W_{12}$ . Evaluation of further diagrams reveals that elements such as  $\Delta_{op}^{aq}$  are in LOPT of third-order in  $W_{12}$ . Second, due to the energy denominator in the first-order correction (Eq. 3.103) the largest contribution to correlation comes from correlated two-particle transitions between the highest occupied and lowest unoccupied orbitals.

### Diagrammatic expansion of the 3RDM

In analogy to the one-body and the two-body propagator (Eq. 3.68 and Eq. 3.92) the three-body propagator is defined by

$$i^3 \langle \epsilon_{i_1} \epsilon_{i_2} \epsilon_{i_3} | \mathcal{G}_{123}(t_1, t_2, t_3, t'_1, t'_2, t'_3) | \epsilon_{j_1} \epsilon_{j_2} \epsilon_{j_3} \rangle = \langle \Psi | T [ a_{i_1}(t_1) a_{i_2}(t_2) a_{i_3}(t_3) a_{j_3}^\dagger(t'_3) a_{j_2}^\dagger(t'_2) a_{j_1}^\dagger(t'_1) ] | \Psi \rangle. \quad (3.106)$$

Depending on the time ordering of the equal-time limit four different representations of the three-particle subspace can be generated

$$\lim_{\delta \rightarrow 0} i^3 \mathcal{G}_{123}(t, t, t, t + \delta, t + \delta, t + \delta) = -D_{123}(t) \quad (3.107)$$

$$\lim_{\delta \rightarrow 0} i^3 \mathcal{G}_{123}(t + \delta, t + \delta, t + \delta, t, t, t) = Q_{123}(t) \quad (3.108)$$

$$\lim_{\delta \rightarrow 0} i^3 \mathcal{G}_{123}(t, t, t + \delta, t, t + \delta, t + \delta) = F_{123}(t) \quad (3.109)$$

$$\lim_{\delta \rightarrow 0} i^3 \mathcal{G}_{123}(t, t + \delta, t + \delta, t, t, t + \delta) = -E_{123}(t). \quad (3.110)$$

The perturbation expansion of the 3RDM

The diagram shows a shaded rectangular box with six external legs and two internal arcs. This is equal to a series of diagrams: two unconnected diagrams (two separate arcs), followed by a series of connected diagrams (shaded ovals with six external legs) of increasing complexity, ending with an ellipsis.

$$(3.111)$$

suggests the expansion of the 3RDM into unconnected and connected diagrams (in analogy to Eq. 3.100) as

The diagram shows a shaded rectangular box with six external legs and two internal arcs. This is equal to the sum of two unconnected diagrams (two separate arcs) and two connected diagrams (shaded ovals with six external legs).

$$(3.112)$$

where the first term on the r.h.s. consists of 6 topologically distinct diagrams

$$\begin{aligned}
\begin{array}{c} \text{---} \circlearrowleft \text{---} \circlearrowleft \text{---} \circlearrowleft \text{---} \\ j_1 \ i_1 \ j_2 \ i_2 \ j_3 \ i_3 \end{array} &= \hat{A}D_1D_2D_3 \\
&= D_{j_1}^{i_1}D_{j_2}^{i_2}D_{j_3}^{i_3} - D_{j_1}^{i_2}D_{j_2}^{i_1}D_{j_3}^{i_3} - D_{j_1}^{i_3}D_{j_2}^{i_2}D_{j_3}^{i_1} \\
&\quad - D_{j_1}^{i_1}D_{j_2}^{i_3}D_{j_3}^{i_2} + D_{j_1}^{i_2}D_{j_2}^{i_3}D_{j_3}^{i_1} + D_{j_1}^{i_3}D_{j_2}^{i_1}D_{j_3}^{i_2}
\end{aligned}$$

and the second term consists of 9 topologically distinct diagrams

$$\begin{aligned}
\begin{array}{c} \text{---} \circlearrowleft \text{---} \circlearrowleft \text{---} \circlearrowleft \text{---} \\ j_1 \ i_1 \ j_2 \ i_2 \ j_3 \ i_3 \end{array} &= \hat{A}\Delta_{12}D_3 \\
&= \Delta_{j_1j_2}^{i_1i_2}D_{j_3}^{i_3} + \Delta_{j_1j_2}^{i_3i_1}D_{j_3}^{i_2} + \Delta_{j_1j_2}^{i_2i_3}D_{j_3}^{i_1} \\
&\quad + \Delta_{j_3j_1}^{i_1i_2}D_{j_2}^{i_3} + \Delta_{j_3j_1}^{i_3i_1}D_{j_2}^{i_2} + \Delta_{j_3j_1}^{i_2i_3}D_{j_2}^{i_1} \\
&\quad + \Delta_{j_2j_3}^{i_1i_2}D_{j_1}^{i_3} + \Delta_{j_2j_3}^{i_3i_1}D_{j_1}^{i_2} + \Delta_{j_2j_3}^{i_2i_3}D_{j_1}^{i_1}.
\end{aligned}$$

The third term in the r.h.s. of Eq. 3.112 defines the three-particle cumulant

$$\Delta_{123} = D_{123} - \hat{A}D_1D_2D_3 - \hat{A}\Delta_{12}D_3 \quad (3.113)$$

consisting of all connected diagrams. The 4th, 5th, and 6th diagram in Eq. 3.111 are such connected diagrams and their contribution can be calculated according to

$$\begin{array}{c} \text{---} \text{---} \text{---} \text{---} \text{---} \text{---} \\ a \ o \ b \ p \ c \ q \ d \end{array} = \sum_p \frac{W_{ab}^{op}W_{pq}^{cd}}{(\varepsilon_o + \varepsilon_p - \varepsilon_a - \varepsilon_b)(\varepsilon_p + \varepsilon_q - \varepsilon_c - \varepsilon_d)} \quad (3.114)$$

$$\begin{array}{c} \text{---} \text{---} \text{---} \text{---} \text{---} \text{---} \\ a \ o \ p \ s \ b \ q \ d \end{array} = - \sum_b \frac{W_{ab}^{op}W_{sq}^{bd}}{(\varepsilon_o + \varepsilon_p - \varepsilon_a - \varepsilon_b)(\varepsilon_s + \varepsilon_q - \varepsilon_b - \varepsilon_d)} \quad (3.115)$$

$$\begin{array}{c} \text{---} \text{---} \text{---} \text{---} \text{---} \text{---} \\ c \ q \ d \ o \ a \ b \ p \end{array} = \sum_a \frac{W_{ab}^{op}W_{cd}^{qa}}{(\varepsilon_o + \varepsilon_p - \varepsilon_a - \varepsilon_b)(\varepsilon_q + \varepsilon_o + \varepsilon_p - \varepsilon_c - \varepsilon_d - \varepsilon_b)}. \quad (3.116)$$



## 4. Time-dependent many-body theories based on single-particle objects

The crucial advantage of MCTDHF and related methods (discussed in Section 2.2) is that, in principle, there is a systematic way to improve the result by increasing the number of orbitals (Eq. 2.17). If convergence is reached the exact solution of the Schrödinger equation (Eq. 2.1) is constructed. This possibility of systematic improvement allows to judge the accuracy and estimate the remaining error in the solution. If feasible, wavefunction-based approaches deliver the most "trustworthy" and accurate results. However, when going to large systems or strong excitation the number of required determinants in the expansion explodes making wavefunction-based methods unfeasible. The exponential increase in numerical complexity poses a conceptual limitation that forces the development of alternative approaches.

One strategy is to trade the known equations of motion for the wavefunction with equations of motion for reduced quantities whose closed form is only known approximately. Contrary to wavefunction-based methods these approximate equations of motion contain a finite error that cannot be eliminated completely. The gain, however, is the possibility to treat systems that are not in reach of wavefunction-based methods. Among the methods that avoid the wavefunction are the time-dependent density function theory (TDDFT) [16], and the time-dependent IRDM theory [176], or a special flavor thereof, the time-dependent renormalized natural orbital theory [177]. In the next two sections we give a brief review of those approaches, to be able to draw comparisons to the here developed TD-2RDM method.

### 4.1. Time-dependent density functional theory

The idea to formulate the many-body problem in terms of the electron density builds upon the theoretical foundation laid by Thomas and Fermi [178, 179] and the theorem by Hohenberg and Kohn [180]. Hohenberg and Kohn showed that for fixed kinetic and interaction term,  $T_1$  and  $W_{12}$  respectively, each ground state density  $\rho(\mathbf{r})$  has a uniquely defined pre-image in the set of  $N$ -particle wavefunctions  $\Psi[\rho, W_{12}, T_1]$ . Usually, the dependency on the interaction  $W_{12}$  and kinetic term  $T_1$  is dropped and the bijective map is written as  $\Psi[\rho]$  [2, 181]. One should keep in mind that this bijective map can only be established under the boundary condition of fixed  $W_{12}$  and fixed  $T_1$ . Exploiting this bijective map  $\Psi[\rho]$  the ground state energy can be calculated by minimizing the energy functional

$$E[\rho] = \langle \Psi[\rho] | H | \Psi[\rho] \rangle = T[\rho] + E^V[\rho] + E^H[\rho] + E^{xc}[\rho]. \quad (4.1)$$

From the individual terms in the Hamiltonian only the potential energy (in the present case the ionic potential)

$$E^V[\rho] = \int V(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} \quad (4.2)$$

and the Hartree energy

$$E^H[\rho] = \frac{1}{2} \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' \quad (4.3)$$

are known functionals of the density. The kinetic energy functional  $T[\rho]$  and the exchange-correlation functional  $E^{\text{xc}}[\rho]$  have to be approximated.

The simplest approximation for  $E^{\text{xc}}[\rho]$ , the local density approximation (LDA) is based on replacing the electron density locally by that of a homogenous electron gas (HEG) and summing all contributions via spatial integration. While the exchange energy of the HEG has been calculated long ago by Dirac [108] the exact correlation functional for the HEG is not known but several analytic approximations exist [182, 183]. Beyond the LDA approximation modern exchange-correlation functionals are constructed by taking into account the gradient of the density (GGA), derivatives of higher order (META-GGA), and the exact exchange energy of the Kohn-Sham orbitals [16] (see below).

Besides the exchange-correlation functional also the kinetic energy is an unknown functional of the electron density. The kinetic energy functional  $T[\rho]$  can be approximated within the Kohn-Sham method which is the basis for the majority applications of DFT [16, 184]. The idea behind the Kohn-Sham method is to define an auxiliary non-interacting system  $|\Psi^{\text{KS}}\rangle = |\psi_1 \dots \psi_N\rangle$  that gives the exact density of the interacting system

$$\rho(\mathbf{r}) = \sum_i \psi_i^*(\mathbf{r})\psi_i(\mathbf{r}). \quad (4.4)$$

The Kohn-Sham orbitals of the ground state are determined by

$$-\frac{\nabla_i^2}{2}\psi_i(\mathbf{r}) + V^{\text{KS}}(\mathbf{r})\psi_i(\mathbf{r}) = \varepsilon^{\text{KS}}\psi_i(\mathbf{r}), \quad (4.5)$$

where the Kohn-Sham potential is defined by

$$\begin{aligned} V^{\text{KS}}[\rho(\mathbf{r})] &= \frac{\delta}{\delta\rho} \left( E^V[\rho] + E^H[\rho] + E^{\text{xc}}[\rho] \right) \\ &= V(\mathbf{r}) + \int \frac{\rho(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + V^{\text{xc}}[\rho(\mathbf{r})], \end{aligned} \quad (4.6)$$

and the last term is the exchange-correlation potential

$$V^{\text{xc}}[\rho(\mathbf{r})] = \frac{\delta}{\delta\rho} \left( E^{\text{xc}}[\rho(\mathbf{r})] \right) \quad (4.7)$$

whose exact form is unknown. Approximations for the exchange-correlation potential can be calculated from approximate exchange-correlation functionals  $E^{\text{xc}}[\rho]$  via Eq. 4.7.

The time-dependent extension of DFT is based on the propagation of Kohn-Sham orbitals according to the equations of motion

$$i\partial_t\psi_i(\mathbf{r},t) = -\frac{\nabla_i^2}{2}\psi_i(\mathbf{r},t) + V^{\text{KS}}[\rho(\mathbf{r}',t')]\psi_i(\mathbf{r},t) + V^{\text{ext}}(\mathbf{r},t)\psi_i(\mathbf{r},t). \quad (4.8)$$

The existence of the auxiliary non-interacting Kohn-Sham system in the time-dependent setup is ensured by the van-Leeuwen theorem [185]. It states that for a time-dependent many-body system with fixed time-dependent external potential  $V^{\text{ext}}(\mathbf{r},t)$  and fixed interaction  $W(\mathbf{r}_1,\mathbf{r}_2)$  there exists for any other interaction  $\bar{W}(\mathbf{r}_1,\mathbf{r}_2)$  a uniquely determined time-dependent external potential  $\bar{V}^{\text{ext}}(\mathbf{r},t)$  such that the time-dependent densities match for all times  $\rho(\mathbf{r},t) = \bar{\rho}(\mathbf{r},t)$ . Two important corollaries for this theorem can be obtained: First, by choosing  $W(\mathbf{r}_1,\mathbf{r}_2) = \bar{W}(\mathbf{r}_1,\mathbf{r}_2)$  the Runge-Gross theorem [186] is recovered which is the time-dependent generalization of the Hohenberg-Kohn theorem. It states that given fixed interaction and kinetic operators the time-dependent potential uniquely determines the time-dependent density. Second, by choosing  $\bar{W}(\mathbf{r}_1,\mathbf{r}_2) = 0$  the existence of the auxiliary Kohn-Sham system with Kohn-Sham potential  $\bar{V}^{\text{ext}} = V^{\text{ext}} + V^{\text{KS}}$  is guaranteed. However, the theorem tells nothing about the form of this potential.

In general, the time-dependent Kohn-Sham potential  $V^{\text{KS}}([\rho(\mathbf{r}',t')])$  is non-local in space and time, i.e., it depends on the density at different positions in space and time. Effects that arise from the dependence of the time-dependent exchange-correlation functional on the history of the electron density are called memory effects. These effects are known to play an important role in the proper description of doubly-excited states [31], charge transfer [32, 33], Rabi oscillations [34–37]. Exchange-correlation functionals beyond the adiabatic limit, however, are rare [38–43] and the majority of TDDFT applications use the adiabatic approximation. If the variation of the external potential is slow enough to avoid excitation the system is in the ground state of the instantaneous Hamiltonian at every instance of time. In this case ground state functionals can be employed to approximately calculate the Kohn-Sham potential. Even though the adiabatic approximation is not justified for rapidly varying external potentials it is regularly employed to describe strong field processes due to the lack of reliable non-adiabatic functionals.

In the application to strong-field processes TDDFT has become a versatile tool that has been applied to a variety of atomic [17–20], and molecular [21, 22] systems, as well as nanostructures [23–26] and extended systems [27–30]. Structurally, TDDFT is similar to TDHF where the Kohn-Sham orbitals have taken the role of the Hartree-Fock orbitals. However, TDDFT is numerically more efficient because the non-local exchange potential is replaced by a local functional of the density. One conceptual limitation of TDDFT compared to TDHF is that even if the exact electron density is given at each point in time many observables such as ionization probabilities, photoelectron spectra, momentum distributions, interaction energies or pair distributions can only be extracted from the electron density via read out functionals whose exact form is mostly unknown and imply additional approximation errors [44, 47]. Often the determinant constructed from the Kohn-Sham orbitals is adopted to calculate quantities for which the read out functional is unknown. However, the validity of this approach has remained an open question [45, 46]. Beyond the limitations of the adiabatic

approximation TDDFT faces several other challenges. No calculation so far has been able to unambiguously identify NSDI [187]. The failure of TDDFT in NSDI can be related to the insufficient accuracy of read-out as well as exchange-correlation functionals available today [188, 189].

One of the known deficiencies of LDA is the presence of self interaction and consequently the failure to reproduce ionization and highly excited states (Rydberg states) [16]. Self-interaction free approximations can be constructed ensuring the proper asymptotic behaviour of the exchange-correlation potential [20]

$$V^{\text{xc}}(\mathbf{r}, t) \sim -\frac{1}{r} \quad (\text{as } r \rightarrow \infty). \quad (4.9)$$

The approximations for the exchange-correlation potential are hard to improve systematically and more and more empirical parameters are introduced as one is climbing up the (Jacob's) ladder of more accurate functionals. One way of overcoming these limitations is to propagate objects that contain more information than the electron density. Time-dependent current density functional theory adds to the electron density the current density as a fundamental variable [38]. A more general approach is to propagate reduced density matrices by closing the BBGKY-hierarchy.

## 4.2. Closing the BBGKY hierarchy on the first level

Closing the BBGKY hierarchy on the first level by employing a reconstruction functional that expresses the 2RDM in terms of the 1RDM

$$D_{12} \approx D_{12}^{\text{R}}\{D_1\}, \quad (4.10)$$

gives a self-contained time-dependent theory for the 1RDM. Such reconstruction functionals have been developed in the variational 1RDM method to express the energy functional, Eq. 3.22, in terms of the 1RDM and perform variational calculations of ground state energies [162]. In the time-dependent context such reconstruction functionals can be used to close the equation of motion for the 1RDM

$$i\partial_t D_1 = [h, D_1] + \text{Tr}_2[W_{12}, D_{12}^{\text{R}}\{D_1\}]. \quad (4.11)$$

Many of the reconstruction functionals  $D_{12}^{\text{R}}$  adopted from the variational 1RDM approach, however, lead to time-independent natural occupation numbers and thereby limit the applicability of the time-dependent 1RDM method [190].

For two-electron systems the natural occupation numbers are pairwise degenerate and the Carlson-Keller theorem [191] allows to express the 2RDM exactly in terms of the natural orbitals

$$|\Psi\rangle = \sum_i \sqrt{n_i} |\eta_i\rangle |\eta'_i\rangle, \quad (4.12)$$

where  $|\eta'_i\rangle$  and  $|\eta_i\rangle$  belong to the same degenerate pair with occupation number  $n_i$ . Recently, a variant of the time-dependent 1RDM method was developed [177, 192–194] based on the propagation of renormalized natural orbitals  $|\tilde{n}_i\rangle = \sqrt{n_i}|\eta_i\rangle$  which allow to express the 1RDM as

$$D_1 = \sum_i |\tilde{n}_i\rangle\langle\tilde{n}_i|. \quad (4.13)$$

The equations of motion for the renormalized natural orbitals combine the equations of motion for the natural orbitals, Eq. 3.49, and for the natural occupation numbers, Eq. 3.50. The performance of the time-dependent renormalized natural orbital theory was tested for a variety of different two-electron systems. Excellent agreement with TDSE reference calculations was found when employing the exact reconstruction. By employing the approximate reconstruction proposed by Müller [161] deviations from the exact result occur and become more dramatic if the number of propagated natural orbitals is increased [192]. Alternative closure schemes for the first level of the BBGKY hierarchy were proposed based on semi-classical approximations of electron correlations and TDHF [195].

From a theoretical point of view it is not clear whether an "universal" reconstruction function for the 2RDM in terms of the 1RDM independent of any properties of the underlying Hamiltonian exists. Gilbert was able to show that there is a one-to-one mapping between ground state 1RDMs and their corresponding ground state wavefunction [196]. However, this mapping  $\Psi[D_1, W_{12}]$  (in the spirit of the Hohenberg-Kohn theorem) depends also on the interaction operator. Therefore, reconstruction functionals for the 2RDM in terms of the 1RDM independent of the interaction operator are not guaranteed by Gilbert's theorem. This is different for the reconstruction of the 3RDM in terms of the 2RDM. For ground state 2RDMs the existence of a Hamiltonian-independent reconstruction is shown by Rosina's theorem [157]. The possibility to harvest the information from the 2RDM that defines its own propagation is the central assumption in the time-dependent 2RDM method.



## 5. Time-dependent 2RDM theory

The basic idea of the time-dependent 2RDM theory is to develop a self-contained propagation scheme for the 2RDM. This idea was first formulated by Bogoliubov [56, 57]. He proposed to close the quantum BBGKY hierarchy for the 2RDM by reconstructing the 3RDM in terms of the 2RDM

$$D_{123} \approx D_{123}^R\{D_{12}\}. \quad (5.1)$$

We will refer to this approximation as the reconstruction functional of the 3RDM. The equation of motion to be solved is thus

$$i\partial_t D_{12} = [H_{12}, D_{12}] + \text{Tr}_3[W_{13} + W_{23}, D_{123}^R\{D_{12}\}]. \quad (5.2)$$

Several approaches in this direction have been made. Initially the theoretical development was driven by the close relation to the Martin-Schwinger hierarchy [58] for Green's functions (see e.g. [59]). Further theoretical development led to the formulation of the cluster-expansion [60] and its employment to close the hierarchy [61–63]. Numerical calculations have been performed to evaluate ground state and excited state properties of the Lipkin and Hubbard model [65–68] as well as time-dependent simulations of nuclear dynamics (within the Lipkin model) [69], strong non-equilibrium dynamics in the Hubbard model [70] and 1D beryllium in ultra short laser pulses [71]. All of the time-dependent simulations encountered instabilities and the practical applications were limited.

In this thesis we report on three improvements with which previous limitations can be overcome. First, we use an accurate reconstruction functional that includes the approximation of the three-particle cumulant  $\Delta_{123}$  [197]. We show how to obtain this functional using the diagrammatic expansion of RDMs presented in Chapter 3.4. Accurate reconstruction functionals are essential to render this method applicable. Second, we show how to enforce conservation laws associated with symmetries of the Hamiltonian on any reconstructions functional [82]. Third, we introduce methods to control instabilities by applying a procedure termed "purification" [198] ensuring stable and accurate propagation [199]. These three elements allow to accurately propagate the 2RDM of atoms and molecules in strong laser pulses as presented in Chapter 8.

Since the reconstruction functional is the only approximation entering the TD-2RDM method an accurate reconstruction functional is paramount. The key issue to be explored in this work is whether the 2RDM not only contains the relevant information on statistical properties but even more importantly also enough information to determine its own propagation. Such a hypothesis is based on the underlying pair-wise interaction between particles. Since the 2RDM carries the information on single-particle propagation as well as particle-particle

interaction it may hold all necessary information on the building blocks that make up the dynamics of the many-body system. In this chapter we discuss the essentials of the TD-2RDM theory, i.e. the reconstruction, conservation laws and purification.

## 5.1. Reconstruction - closing the BBGKY hierarchy on the second level

Originally, the BBGKY hierarchy was formulated for classical distribution functions [200–202]. In their original paper [201] Green and Born formulated the idea to close the equation of motion for the classical two-particle distribution function by approximating the three-particle distribution function in terms of a product of one- and two-particle distribution functions. This reconstruction was further improved by Green in 1956 [203] employing the cluster expansion of the three-particle distribution function in terms of one and two-particle Ursel-Mayer functions [204]. These  $p$ -particle Ursel-Mayer functions can be understood as the classical analog of  $p$ -particle cumulants (introduced in Section 3.4) and, like cumulants, they measure the correlation between clusters of particles. The closure scheme devised by Green then amounts to neglecting proper three-particle correlations. The cluster expansion can be applied to the closure of the quantum BBGKY hierarchy as well. In this context it is also referred to as the cumulant expansion. However, it took almost 30 years before the cumulant expansion for the 3RDM was used to close the equation of motion for the 2RDM in the attempt to solve the nuclear many-body problem [60]. Before that the closure of the BBGKY hierarchy was primarily derived from closure schemes of the (closely related) Schwinger-Martin hierarchy for Green's functions [59].

On a theoretical level it is not clear whether a general reconstruction functional for the 3RDM in terms of the 2RDM exists. For ground state 2RDMs of a non-degenerate two-particle Hamiltonian Rosina showed that there exists a unique preimage within the set of wavefunctions and consequently a uniquely defined 3RDM. This one-to-one map between the 2RDM and the wavefunction is different from the one-to-one map between the density and the wavefunction from the Hohenberg-Kohn theorem. While in the Hohenberg-Kohn theorem uniqueness is only guaranteed for a specific kinetic and interaction term, the wavefunction preimage in Rosina's theorem can be constructed without reference to the explicit form of the Hamiltonian. At least for "ground state-representable" 2RDMs the existence of a 3RDM reconstruction functional with the 2RDM as the only input is guaranteed. It remains to be shown if, in correspondence to the Runge-Gross theorem, the time evolved 2RDM uniquely (up to a time-dependent constant) determines the time-dependent Hamiltonian and thereby the time-dependent wavefunction.

### 5.1.1. Cumulant expansion

The truncated cluster expansion

$$D_{123}^V = \hat{A}D_1D_2D_3 + \hat{A}\Delta_{12}D_3 \quad (5.3)$$



was one of the first closure schemes for the classical as well as the quantum BBGKY hierarchy and was later rediscovered by Valdemoro in search for the solution of the contracted Schrödinger equation [64]. This equation is an exact relation between the 2RDM, the 3RDM, and the 4RDM, and holds for every eigenstate of the Hamiltonian (see Eq. A.17). Reconstruction functionals are required to formulate the contracted Schrödinger equation as a self-contained equation for the 2RDM. We will refer to Eq. 5.3 as the Valdemoro reconstruction ( $D_{123}^V$ ). In terms of the diagrammatic expansion it constitutes the sum of all unconnected diagrams (for details see Section 3.4)

$$\text{Diagram} \approx \text{Diagram} + \text{Diagram} = D_{123}^V. \quad (5.4)$$

Mazziotti systematized the cumulant expansion for general  $p$ RDMs to a hierarchy [163]

$$D_1 = \Delta_1 \quad (5.5)$$

$$D_{12} = \hat{\mathcal{A}}\Delta_1\Delta_2 + \Delta_{12} \quad (5.6)$$

$$D_{123} = \hat{\mathcal{A}}\Delta_1\Delta_2\Delta_3 + \hat{\mathcal{A}}\Delta_{12}\Delta_3 + \Delta_{123} \quad (5.7)$$

$$D_{1234} = \hat{\mathcal{A}}\Delta_1\Delta_2\Delta_3\Delta_4 + \hat{\mathcal{A}}\Delta_{12}\Delta_3\Delta_4 + \hat{\mathcal{A}}\Delta_{12}\Delta_{34} + \hat{\mathcal{A}}\Delta_{123}\Delta_4 + \Delta_{1234}, \quad (5.8)$$

where  $\hat{\mathcal{A}}$  is again the antisymmetrization operator creating only permutations that give non-equivalent terms. By neglecting  $\Delta_{123}$  in Eq. 5.7 the Valdemoro reconstruction (Eq. 5.3) can be recovered. Mazziotti proposed to use the cumulant expansion to approximate the three-particle cumulant. His approximation for the three-particle cumulant  $\Delta_{123}^M$  is based on performing the contraction over the fourth particle in Eq. 5.8 and neglecting the contraction of the four-particle cumulant  $\text{Tr}_4\Delta_{1234}$  [205]. Collecting all terms that scale linearly with particle number  $N$  results in an implicit equation for  $\Delta_{123}^M$

$$3\Delta_{123}^M = \hat{\mathcal{A}}D_1\Delta_{123}^M + \hat{\mathcal{A}}\Delta_{123}^M D_1 + \hat{\mathcal{A}}\Delta_{12}\Delta_{23}, \quad (5.9)$$

which can be explicitly solved by transforming into the eigenbasis of the 1RDM. The final expression for the Mazziotti reconstruction is given by

$$D_{123}^M = D_{123}^V + \Delta_{123}^M. \quad (5.10)$$

### 5.1.2. Nakatsuji-Yasuda reconstruction

A different method to approximate  $\Delta_{123}$  directly exploits the diagrammatic expansion discussed in Section 3.4. This method is based on the work by Nakatsuji and Yasuda in the mid 90s. Their point of departure was to exploit the close relationship between RDMs and Green's functions. In analogy to the BBGKY hierarchy (Eq. 3.43) Green's functions satisfy a coupled set of differential equations called Martin-Schwinger hierarchy [58]. Analogously to the TD-2RDM method closure schemes for the equation of motion of the two-particle Green's function have been developed [206]. However, while RDMs are directly suited to

describe non-equilibrium situations, the description of non-equilibrium Green's functions requires additional theoretical considerations within the so called Keldysh formalism [207]. The missing part in the Valdemoro reconstruction, i.e. the three-particle cumulant  $\Delta_{123}$ , can be determined diagrammatically as first pointed out by Nakatsuji and Yasuda [197]. They managed to evaluate an additional class of 3RDM diagrams. This class consists of all diagrams that can be separated into two pieces by removing one line that crosses the equal time line. We refer to such diagrams as separable. The two most important separable diagrams are evaluated in Eq. 3.114 and Eq. 3.115 reproduced here for convenience

$$\begin{array}{c} \text{Diagram 1} \\ \text{Diagram 2} \end{array} = \sum_p \frac{W_{ab}^{op} W_{pq}^{cd}}{(\varepsilon_o + \varepsilon_p - \varepsilon_a - \varepsilon_b)(\varepsilon_p + \varepsilon_q - \varepsilon_c - \varepsilon_d)} \quad (5.11)$$

$$\begin{array}{c} \text{Diagram 3} \\ \text{Diagram 4} \end{array} = - \sum_b \frac{W_{ab}^{op} W_{sq}^{bd}}{(\varepsilon_o + \varepsilon_p - \varepsilon_a - \varepsilon_b)(\varepsilon_s + \varepsilon_q - \varepsilon_b - \varepsilon_d)} \quad (5.12)$$

While these two contributions are associated with particular diagrams in the diagrammatic expansion of the 3RDM (Eq. 3.111), it is possible to extend this evaluation to the infinite set of topologically equivalent diagrams by employing the following substitution

$$\frac{W_{op}^{ab}}{(\varepsilon_o + \varepsilon_p - \varepsilon_a - \varepsilon_b)} \rightarrow \Delta_{op}^{ab} \quad \frac{W_{ab}^{op}}{(\varepsilon_o + \varepsilon_p - \varepsilon_a - \varepsilon_b)} \rightarrow \Delta_{ab}^{op} \quad (5.13)$$

leading to

$$\begin{array}{c} \text{Diagram 5} \\ \text{Diagram 6} \end{array} = \sum_p \Delta_{ab}^{op} \Delta_{pq}^{cd} \approx \Delta_{abp}^{ocd} \quad (5.14)$$

$$\begin{array}{c} \text{Diagram 7} \\ \text{Diagram 8} \end{array} = - \sum_b \Delta_{ab}^{op} \Delta_{sq}^{bd} \approx \Delta_{asq}^{opd}. \quad (5.15)$$

The latter of the last two expressions allows to approximately calculate the elements  $\Delta_{asq}^{opd}$  and the former allows to calculate  $\Delta_{abp}^{ocd}$ . These elements contain the largest contribution within the class of separable diagrams. Evaluation of all separable diagrams gives the general expression

$$[\Delta^{\text{NY}}]_{j_1 j_2 j_3}^{i_1 i_2 i_3} = \hat{\mathcal{A}} \left[ \sum_p \Delta_{j_1 j_2}^{i_1 p} \Delta_{p j_3}^{i_2 i_3} - \sum_b \Delta_{j_1 b}^{i_1 i_2} \Delta_{j_2 j_3}^{b i_3} \right], \quad (5.16)$$

where the antisymmetrization operator  $\hat{\mathcal{A}}$  generates 9 non-equivalent terms with the appropriate sign. The complete Nakatsuji-Yasuda approximation can be diagrammatically

represented as

The diagram shows a sequence of terms on a horizontal line. The first term is a diagram with four vertical lines and a rectangular box at the top with four arrows pointing down to the lines. This is followed by an approximation symbol  $\approx$ . The next part is a sum of four diagrams: 1) three small circles on the line; 2) a circle with an arrow pointing up to the line; 3) a circle with an arrow pointing down to the line; 4) a circle with an arrow pointing up to the line and another pointing down to the line. This sum is followed by an equals sign and the expression  $D_{123}^{\text{NY}}$ .

## 5.2. Symmetries

The close relation between conserved quantities and symmetries of the Hamiltonian is one of the fundamental insights underlying classical as well as quantum mechanics. The associated conservation laws provide a powerful tool to reduce the degrees of freedom of a complex physical system and serve as control parameters whether a calculation still gives reasonable results. In the context of the time-dependent 2RDM theory symmetries and their conservation are important constraints on admissible reconstruction functionals [61, 70]. In particular, energy conservation is assured if the 3RDM reconstruction functional is contraction consistent (see Eq. 3.46)

$$(N - 2)D_{12} = \text{Tr}_3 D_{123}^{\text{R}} \{D_{12}\}. \quad (5.18)$$

Even though attempts to construct consistent reconstruction functionals have been made [63] these functionals were later shown to violate contraction consistency [69] so that, to the best of our knowledge, at present no fully contraction consistent reconstruction exists.

The conservation of energy without contraction consistency of the 3RDM reconstruction functional can be achieved by decoupling the propagation of the 1RDM from the 2RDM [70]. In this thesis we approach this problem another way. We ensure conservation laws by enforcing contraction consistency upon the 3RDM reconstruction functionals. To be precise we will refer to Eq. 5.18 as general contraction consistency. This general contraction consistency is sufficient for energy conservation (as shown in the following subsection) and compatibility between the 1RDM and 2RDM equation of motion, i.e. the 1RDM calculated from the propagated 2RDM via Eq. 3.21 satisfies Eq. 3.44. Beyond general contraction consistency there are additional more stringent spin contraction consistency conditions for individual spin blocks of the 3RDM if the system is in a well defined spin state. While spin contraction consistency implies general contraction consistency the converse is not true. We will discuss the spin contraction consistency conditions in Subsection 5.2.2.

### 5.2.1. Particle and energy conservation

Equation 5.2 must conserve invariants of the  $N$ -particle system. These include the norm (or particle number), the energy (for time-independent Hamilton operators), and spin (for spin-independent interactions). Conservation of particle number follows immediately from

$$i\partial_t \text{Tr}_{12} D_{12} = \text{Tr}_{12} [H_{12}, D_{12}] + \text{Tr}_{123} [W_{13} + W_{23}, D_{123}^{\text{R}}] = 0 \quad (5.19)$$

using the permutation symmetry of traces and the antisymmetry of the commutator. Equation 5.19, thus, does not provide any constraints on the reconstructed 3RDM  $D_{123}^R$ . The time evolution of the energy (Eq. 3.22),

$$i\partial_t E(t) = \frac{1}{2}\text{Tr}_{12} \left( i\partial_t \tilde{H}_{12} D_{12} \right) + \frac{1}{2}\text{Tr}_{12} \left( \tilde{H}_{12} i\partial_t D_{12} \right) \quad (5.20)$$

consists of two contributions. The first contribution on the r.h.s. of Eq. 5.20 describes the excitation within the external time-dependent field. The second term vanishes identically for the exact equation of motion (Eq. 3.41). This becomes apparent by transforming the 2RDM equation of motion into the equivalent form

$$i\partial_t D_{12} = [\tilde{H}_{12}, D_{12}] + \text{Tr}_3[\tilde{H}_{13} + \tilde{H}_{23}, D_{123}] \quad (5.21)$$

via the equivalence transformation of the Hamiltonian

$$h_1 \rightarrow 0 \quad (5.22)$$

$$W_{12} \rightarrow \tilde{H}_{12} = W_{12} + \frac{h_1 + h_2}{N-1}. \quad (5.23)$$

Under this transformation the Hamiltonian (Eq. 2.2) is invariant and, therefore, the equation of motion of the 2RDM should be invariant too. However, when employing approximate reconstruction functionals  $D_{123}^R$  the invariance of the 2RDM equations of motion is guaranteed only if

$$\text{Tr}_3 \left[ \frac{h_1 + h_3}{N-1} + \frac{h_2 + h_3}{N-1}, D_{123}^R \right] = \frac{N-2}{N-1} [h_1 + h_2, D_{12}], \quad (5.24)$$

which is equivalent to general contraction consistency (Eq. 5.18). From Eq. 5.21 conservation of energy is evident

$$\text{Tr}_{12} \left( \tilde{H}_{12} i\partial_t D_{12} \right) = \text{Tr}_{12} \tilde{H}_{12} [\tilde{H}_{12}, D_{12}] + \text{Tr}_{123} \tilde{H}_{12} [\tilde{H}_{13} + \tilde{H}_{23}, D_{123}^R] = 0, \quad (5.25)$$

where we have used  $\text{Tr}_{123} \tilde{H}_{13} \tilde{H}_{12} D_{123}^R = \text{Tr}_{123} \tilde{H}_{23} \tilde{H}_{12} D_{123}^R$ .

Beyond energy conservation general contraction consistency ensures consistency between the first and the second level of the BBGKY hierarchy. The time evolution of the 1RDM calculated via (Eq. 3.21) from the propagated 2RDM (Eq. 5.2) follows as

$$\begin{aligned} i\partial_t \text{Tr}_2 D_{12} &= \text{Tr}_2 [H_{12}, D_{12}] + \text{Tr}_{23} [W_{13} + W_{23}, D_{123}^R] \\ &= (N-1)[h_1, D_1] + \text{Tr}_2 [W_{12}, D_{12} + \text{Tr}_3 D_{123}^R], \end{aligned} \quad (5.26)$$

which reduces to the correct equation of motion for  $D_1$ , Eq. 3.44, provided general contraction consistency (Eq. 5.18) is fulfilled.

### 5.2.2. Conserving spin symmetries

Additional constraints on the 3RDM follow from spin conservation. The conservation of spin symmetries is an important factor ensuring stability and accuracy of the propagation. Exploiting the spin symmetry in fermionic systems is, furthermore, a convenient way to speed up calculations. Since the non-relativistic Hamiltonian for atoms and molecules is spin independent, i.e.  $[H, S^2] = [H, S_z] = 0$ , with

$$S_z = \frac{1}{2} \sum_i (a_{i\uparrow}^\dagger a_{i\uparrow} - a_{i\downarrow}^\dagger a_{i\downarrow}) \quad (5.27)$$

$$S^2 = S_z^2 + S_- S_+ \quad (5.28)$$

and

$$S_+ = \sum_i a_{i\uparrow}^\dagger a_{i\downarrow} \quad \text{and} \quad S_- = \sum_i a_{i\downarrow}^\dagger a_{i\uparrow}, \quad (5.29)$$

the ground state (initial state) of the system is an eigenstate of both  $S_z$  and  $S^2$  and remains in this spin state during time evolution of  $\Psi(t)$  for spin-independent interactions, e.g., in the present case of a laser field in dipole approximation. In particular, for closed-shell systems with an equal number of electrons in spin up  $N_\uparrow = N/2$  and spin down  $N_\downarrow = N/2$  the wavefunction satisfies

$$S_z |\Psi(t)\rangle = 0 \quad (5.30)$$

$$S_+ |\Psi(t)\rangle = 0, \quad (5.31)$$

where Eq. 5.30 together with Eq. 5.31 is equivalent to  $S^2 |\Psi(t)\rangle = 0$ . These spin symmetries enforce specific symmetries on the 2RDM that must be conserved during time propagation. The most obvious symmetry originating from Eq. 5.30 is that the 2RDM contains only two independent non-vanishing blocks given by

$$D_{j_1\uparrow j_2\uparrow}^{i_1\uparrow i_2\uparrow} = \langle \Psi | a_{i_1\uparrow}^\dagger a_{i_2\uparrow}^\dagger a_{j_2\uparrow} a_{j_1\uparrow} | \Psi \rangle \quad (5.32)$$

$$D_{j_1\uparrow j_2\downarrow}^{i_1\uparrow i_2\downarrow} = \langle \Psi | a_{i_1\uparrow}^\dagger a_{i_2\downarrow}^\dagger a_{j_2\downarrow} a_{j_1\uparrow} | \Psi \rangle \quad (5.33)$$

with  $i_1, i_2, j_1, j_2 \in \{1, \dots, I\}$ . All other spin blocks either vanish if the net spin of the upper indices and lower indices differs, e.g.

$$D_{j_1\uparrow j_2\downarrow}^{i_1\uparrow i_2\uparrow} = 0, \quad (5.34)$$

or can be expressed in terms of  $D_{12}^{\uparrow\uparrow}$  and  $D_{12}^{\uparrow\downarrow}$  (a compact notation for Eq. 5.32 and Eq. 5.33)

$$D_{j_1\uparrow j_2\downarrow}^{i_2\downarrow i_1\uparrow} = -D_{j_1\uparrow j_2\downarrow}^{i_1\uparrow i_2\downarrow} \quad D_{j_1\downarrow j_2\downarrow}^{i_1\downarrow i_2\downarrow} = D_{j_1\uparrow j_2\uparrow}^{i_1\uparrow i_2\uparrow}. \quad (5.35)$$

Further symmetries based on Eq. 5.30 pose constraints on the contractions of the 2RDM spin blocks. The vanishing norm of the vector  $S_z |\Psi\rangle$  gives

$$0 = \langle \Psi | S_z S_z | \Psi \rangle = \frac{1}{2} \sum_{i,m} \left( D_{i\uparrow m\uparrow}^{i\uparrow m\uparrow} - D_{i\uparrow m\downarrow}^{i\uparrow m\downarrow} \right) + \frac{1}{2} \sum_i D_{i\uparrow}^{i\uparrow} = \frac{N^2}{4} - \sum_{i,m} D_{i\uparrow m\downarrow}^{i\uparrow m\downarrow}, \quad (5.36)$$

where we have used the interrelation between the 2RDM and the 1RDM (Eq. 3.21)

$$\sum_m \left( D_{j\uparrow m\uparrow}^{i\uparrow m\uparrow} + D_{j\uparrow m\downarrow}^{i\uparrow m\downarrow} \right) = (N-1)D_{j\uparrow}^{i\uparrow}, \quad \text{and} \quad \sum_i D_{i\uparrow}^{i\uparrow} = \frac{N}{2}. \quad (5.37)$$

Similarly,  $S_z|\Psi\rangle = 0$  implies

$$0 = \langle \Psi | a_{i\uparrow}^\dagger a_{j\uparrow} S_z | \Psi \rangle = \frac{N}{2} D_{j\uparrow}^{i\uparrow} - \sum_m D_{j\uparrow m\downarrow}^{i\uparrow m\downarrow}. \quad (5.38)$$

We note that Eq. 5.38 reduces to Eq. 5.36 by tracing out the non-contracted indices. While for the  $N$ -particle state  $\Psi(t)$  the conditions  $\langle \Psi | \hat{S}_z \hat{S}_z | \Psi \rangle = 0$  and  $\hat{S}_z |\Psi\rangle = 0$  are equivalent, this is not the case for the (in general, non  $N$ -representable) 2RDM within a truncated BBGKY hierarchy. For the latter, Eq. 5.38 imposes additional constraints not implied by Eq. 5.36.

Further spin symmetries of the 2RDM can be derived from  $\hat{S}_+ |\Psi\rangle = 0$ . The vanishing norm of the vector  $\hat{S}_+ |\Psi\rangle$  implies

$$0 = \langle \Psi | S_- S_+ | \Psi \rangle = \sum_i D_{i\uparrow}^{i\uparrow} - \sum_{i,m} D_{i\uparrow m\downarrow}^{m\uparrow i\downarrow} = \frac{N}{2} - \sum_{i,m} D_{i\uparrow m\downarrow}^{m\uparrow i\downarrow}, \quad (5.39)$$

and the stronger condition

$$0 = \langle \Psi | a_{i\downarrow}^\dagger a_{j\uparrow} S_+ | \Psi \rangle = D_{j\uparrow}^{i\uparrow} - \sum_m D_{j\uparrow m\downarrow}^{m\uparrow i\downarrow}. \quad (5.40)$$

In compact notation Eq. 5.38 and Eq. 5.40 can be written as

$$\text{Tr}_2 D_{12}^{\uparrow\downarrow} = \frac{N}{2} D_1^\uparrow \quad (5.41)$$

$$\text{Tr}_2 \Lambda_{12} D_{12}^{\uparrow\downarrow} = D_1^\uparrow, \quad (5.42)$$

where  $\Lambda_{12}$  is the particle exchange operator defined by

$$\Lambda_{12} |\phi_{1\sigma} \phi_{2\sigma'}\rangle = |\phi_{2\sigma} \phi_{1\sigma'}\rangle, \quad (5.43)$$

for more detail on the notation see Appendix A.

We, furthermore, derive an interrelation between blocks of the 2RDM. Projecting the vector  $\hat{S}_+ |\Psi\rangle$  onto two-particle-two-hole excitations we find

$$\begin{aligned} 0 &= \langle \Psi | a_{i_1\uparrow}^\dagger a_{i_2\downarrow}^\dagger a_{j_2\uparrow} a_{j_1\uparrow} S_+ | \Psi \rangle = \sum_k \langle \Psi | a_{i_1\uparrow}^\dagger a_{i_2\downarrow}^\dagger a_{j_2\uparrow} a_{k\uparrow}^\dagger a_{k\downarrow} a_{j_1\uparrow} | \Psi \rangle - D_{j_2\uparrow j_1\downarrow}^{i_1\uparrow i_2\downarrow} \\ &= \sum_k \langle \Psi | a_{i_1\uparrow}^\dagger a_{i_2\downarrow}^\dagger a_{k\uparrow}^\dagger a_{k\downarrow} a_{j_2\uparrow} a_{j_1\uparrow} | \Psi \rangle - D_{j_2\uparrow j_1\downarrow}^{i_1\uparrow i_2\downarrow} + D_{j_1\uparrow j_2\downarrow}^{i_1\uparrow i_2\downarrow} \\ &= \langle \Psi | \hat{S}_+ a_{i_1\uparrow}^\dagger a_{i_2\downarrow}^\dagger a_{j_2\uparrow} a_{j_1\uparrow} | \Psi \rangle - D_{j_1\uparrow j_2\uparrow}^{i_1\uparrow i_2\uparrow} + D_{j_1\uparrow j_2\downarrow}^{i_1\uparrow i_2\downarrow} - D_{j_2\uparrow j_1\downarrow}^{i_1\uparrow i_2\downarrow} \\ &= -D_{j_1\uparrow j_2\uparrow}^{i_1\uparrow i_2\uparrow} + D_{j_1\uparrow j_2\downarrow}^{i_1\uparrow i_2\downarrow} - D_{j_2\uparrow j_1\downarrow}^{i_1\uparrow i_2\downarrow}. \end{aligned} \quad (5.44)$$

Consequently, we arrive at the important interrelation written in compact notation

$$D_{12}^{\uparrow\uparrow} = D_{12}^{\uparrow\downarrow} - \Lambda_{12} D_{12}^{\downarrow\downarrow}, \quad (5.45)$$

which has been derived previously employing the Wigner-Eckhart theorem [208]. This relation is important for numerical efficiency. Since the 2RDM can be reconstructed completely from the  $(\uparrow\downarrow)$ -block, it is sufficient to propagate only the  $(\uparrow\downarrow)$ -block. The origin of Eq. 5.45 becomes more apparent by going from the individual spin basis into the total spin basis of both fermions. Corresponding to the coupling of two spin- $\frac{1}{2}$  particles the irreducible components in the total spin basis can be separated into a fully symmetric singlet component

$$D_{12}^{0,0} = D_{12}^{\uparrow\downarrow} + \Lambda_{12} D_{12}^{\downarrow\uparrow} \quad (5.46)$$

and three fully antisymmetric triplet components

$$D_{12}^{1,1} = D_{12}^{\uparrow\uparrow} \quad (5.47)$$

$$D_{12}^{1,0} = D_{12}^{\uparrow\downarrow} - \Lambda_{12} D_{12}^{\downarrow\uparrow} \quad (5.48)$$

$$D_{12}^{1,-1} = D_{12}^{\downarrow\downarrow}. \quad (5.49)$$

In this representation Eq. 5.45 has the simple interpretation as  $D_{12}^{1,1} = D_{12}^{1,0} = D_{12}^{1,-1}$ , i.e. the spin-triplet subspace is degenerate.

Beyond the general trace relation (Eq. 5.18) ensuring the conservation of energy, conservation of the singlet state constraints Eq. 5.41 and Eq. 5.42 calls for additional trace relations between individual spin blocks of the 3RDM and the 2RDM. We focus in the following on spin trace relations of the  $(\uparrow\uparrow\downarrow)$ -block of the 3RDM. For singlet states it is the only non-redundant block. All other elements of the full 3RDM can be constructed from this spin block. The  $(\uparrow\uparrow\downarrow)$ -block of the 3RDM has four distinct one-fold contractions. From the time derivative of Eq. 5.41 we obtain conditions for two of these

$$\text{Tr}_2 D_{123}^{\uparrow\uparrow\downarrow} = \left(\frac{N}{2} - 1\right) D_{12}^{\uparrow\downarrow} \quad \text{Tr}_3 D_{123}^{\uparrow\uparrow\downarrow} = \frac{N}{2} D_{12}^{\uparrow\uparrow} \quad (5.50)$$

and by taking the time derivative of Eq. 5.42 the two remaining ones

$$\text{Tr}_2 \Lambda_{23} D_{123}^{\uparrow\uparrow\downarrow} = D_{12}^{\uparrow\uparrow} \quad \text{Tr}_3 D_{123}^{\uparrow\uparrow\downarrow} \Lambda_{23} = \frac{N}{2} D_{12}^{\uparrow\uparrow}. \quad (5.51)$$

In analogy to energy conservation, we find that conservation of spin requires the reconstructed 3RDM spin-blocks to correctly contract in all diagonal and off-diagonal partial traces into the two-particle subspace.

### 5.2.3. Contraction consistency

The general contraction consistency (Eq. 5.18) as well as the more stringent spin contraction consistency (Eq. 5.50 and Eq. 5.51) are important constraints on the reconstruction functionals of the 3RDM,  $D_{123}^R$ , that are not fulfilled by reconstruction functionals discussed

in Section 5.1. The reconstruction functionals discussed there are based on a truncation of the diagrammatic expansion. The truncation of diagrams, however, changes the norm of the 3RDM and more generally violates (general and spin) contraction consistency essential for the consistent closure of the BBGKY-hierarchy. To overcome this deficiency we will present in the following a general procedure to enforce contraction consistency on any given reconstruction functional.

### Contraction consistent reconstruction of one individual 2RDM diagram

As an introductory example we will first consider the trace relation between the 1RDM and the 2RDM, Eq. 3.21. Since the trace is a linear operator the sum of all diagrams for the 2RDM results in the sum of all 1RDM diagrams upon performing the contraction of the last index pair. The individual contribution of some diagrams to this contraction is zero, e.g. the diagram evaluated in Eq. 3.103, other diagrams give a non-zero contribution, e.g. the diagram evaluated in Eq. 3.104 whose contribution is denoted as

$$\text{Diagram} = K_{12}. \quad (5.52)$$

The contraction of this diagram  $\text{Tr}_2 K_{12} = K_1$  gives the 1RDM diagram evaluated in Eq. 3.91

$$\text{Diagram} = K_1 \quad (5.53)$$

If the (approximate) expansion of the 2RDM truncates the contribution of the diagram  $K_{12}$  the corresponding contribution will be missing in the diagrammatic expansion of the 1RDM and this error will show up as the violation of the trace relation Eq. 3.21. As a correction of this truncation error we can approximate the diagram as

$$\text{Diagram} = \frac{1}{N} \text{Diagram}_1 + \frac{1}{N} \text{Diagram}_2 - \frac{1}{N^2} \text{Diagram}_3 \quad (5.54)$$

or in algebraic notation

$$K_{12} \approx K_{12}^{\text{CC}} = \frac{1}{N} K_1 D_2^{\text{HF}} + \frac{1}{N} D_1^{\text{HF}} K_2 - \frac{(\text{Tr}_1 K_1)}{N^2} D_1^{\text{HF}} D_2^{\text{HF}}, \quad (5.55)$$

where we have used the undressed propagator, Eq. 3.87, whose trace is  $\text{Tr}_1 D_1^{\text{HF}} = N$ . By contraction we find

$$\text{Tr}_2 K_{12}^{\text{CC}} = K_1. \quad (5.56)$$

In this way we accomplished to approximate the contribution of diagram  $K_{12}$  with the correct contribution to the 1RDM expansion. This technique can be generalized to enforce contraction consistency on the 3RDM reconstruction functional.



### Contraction consistent 3RDM reconstruction

The basic tool for constructing a contraction consistent 3RDM reconstruction is the unitary decomposition. The concept of the unitary decomposition is very general. Any  $p$ -particle matrix  $M_{j_1 \dots j_p}^{i_1 \dots i_p}$  irrespective of whether it features any symmetry upon particle exchange can be uniquely decomposed [209, 210] into coordinate independent components

$$M_{12 \dots p} = M_{12 \dots p; \perp} + M_{12 \dots p; K}, \quad (5.57)$$

where the (kernel) component  $M_{12 \dots p; K}$  vanishes upon all contractions. The remaining component  $M_{12 \dots p; \perp}$  is perpendicular to the kernel component with respect to the Frobenius norm and contains all the information of the contraction into lower-dimensional subspaces. The important property shown in the following is that the perpendicular component  $M_{12 \dots p; \perp}$  can be expressed in terms of contractions.

First consider a fully antisymmetric matrix  $M_{12 \dots p}$ , e.g. the full 3RDM not restricted to a specific spin-block expanded in a total number of  $2I$  basis orbitals. We make the following ansatz for the perpendicular component

$$M_{123; \perp} = \alpha M \hat{A} \mathbb{1}_1 \mathbb{1}_2 \mathbb{1}_3 + \beta \hat{A} M_1 \mathbb{1}_2 \mathbb{1}_3 + \gamma \hat{A} M_{12} \mathbb{1}_3 \quad (5.58)$$

with the real coefficients  $\alpha$ ,  $\beta$  and  $\gamma$  are determined by

$$M_{12} = \text{Tr}_3 M_{123; \perp} \quad M_1 = \text{Tr}_2 M_{12} \quad M = \text{Tr}_1 M_1 \quad (5.59)$$

The contraction into the two-particle subspace gives for the individual terms

$$\text{Tr}_3 \hat{A} M_{12} \mathbb{1}_3 = \hat{A} M_1 \mathbb{1}_2 + (2I - 4) M_{12} \quad (5.60)$$

$$\text{Tr}_3 \hat{A} M_1 \mathbb{1}_2 \mathbb{1}_3 = M \hat{A} \mathbb{1}_1 \mathbb{1}_2 + (2I - 3) \hat{A} M_1 \mathbb{1}_2 \quad (5.61)$$

$$\text{Tr}_3 M \hat{A} \mathbb{1}_1 \mathbb{1}_2 \mathbb{1}_3 = (2I - 2) M \hat{A} \mathbb{1}_1 \mathbb{1}_2 \quad (5.62)$$

leading to the implicit equation

$$M_{12} = (2I\alpha - 2\alpha + M\beta) \hat{A} \mathbb{1}_1 \mathbb{1}_2 + (2I\beta - 3\beta + \gamma) \hat{A} M_1 \mathbb{1}_2 + (2I\gamma - 4\gamma) M_{12}. \quad (5.63)$$

Equivalence of the left and right hand side of Eq. 5.63 gives for the values of the coefficients

$$a = \frac{1}{(2I - 4)(2I - 3)(2I - 2)} \quad b = -\frac{1}{(2I - 4)(2I - 3)} \quad c = \frac{1}{2I - 4}. \quad (5.64)$$

The idea to restore the contraction consistency of the reconstruction functional is now to calculate the contribution of all 2RDM diagrams that cannot be recovered by contracting the reconstructed 3RDM

$$D_{12}^d = D_{12} - \text{Tr}_3 D_{123}^R. \quad (5.65)$$

From this defect  $D_{12}^d$  we calculate the perpendicular component  $D_{123; \perp}^d$  and add it to the reconstruction functional

$$D_{123}^{\text{CC}} = D_{123}^R + D_{123; \perp}^d. \quad (5.66)$$

One possibility is to directly use the unitary decomposition for antisymmetric matrices

$$D_{123;\perp}^d = \frac{(\text{Tr}_{12} D_{12}^d) \hat{\mathcal{A}} \mathbb{1}_1 \mathbb{1}_2 \mathbb{1}_3}{(2I-4)(2I-3)(2I-2)} + \frac{\hat{\mathcal{A}} (\text{Tr}_2 D_{12}^d) \mathbb{1}_2 \mathbb{1}_3}{(2I-4)(2I-3)} + \frac{\hat{\mathcal{A}} D_{12}^d \mathbb{1}_3}{(2I-4)} \quad (5.67)$$

to enforce general contraction consistency and therefore (as discussed in Section 5.2.1) energy conservation as well as the compatibility of the first and the second members of the BBGKY hierarchy.

The conservation of spin symmetries requires the more stringent contraction consistency of the  $(\uparrow\uparrow\downarrow)$ -Block of the 3RDM according to Eq. 5.50 and Eq. 5.51. This spin block of the 3RDM does no longer feature full antisymmetry and the simple unitary decomposition in Eq. 5.58 cannot be applied. We have generalized the unitary decomposition to matrices without any symmetry by a corresponding ansatz for the perpendicular component (see Appendix C). For matrices with arbitrary symmetry this ansatz requires a larger number of coefficients (instead of just  $\alpha$ ,  $\beta$  and  $\gamma$  for the fully antisymmetric case Eq. 5.58). Requiring the correct contraction of this ansatz into the two-particle subspace gives a highly nontrivial linear set of coupled equations whose unique solution is given in Appendix C.

### 5.3. $N$ -representability

In Section 3.2 we have presented the intriguing picture to replace the  $N$ -particle wavefunction with an ensemble of two-particle states (described by the 2RDM) that gives the same result for the evaluation of two-particle observables such as the energy. While this picture is appropriate to understand the evaluation of expectation values at fixed times it breaks down if we consider the dynamical evolution. An ensemble of two-particle states allows, in principle for unitary time-evolution  $D'_{12}(t') = U_{12}^\dagger D_{12}(t) U_{12}$  with every unitary matrix  $U_{12}^\dagger U_{12} = \mathbb{1}_1 \mathbb{1}_2$ . The variation of reduced density matrices on the other hand is subject to further constraints. Indeed there are normalized, hermitian, positive 2RDMs that cannot be calculated from any  $N$ -particle wavefunction. These 2RDMs are unphysical and their appearance leads to unphysical results such as instabilities and divergences. The constraints that any admissible 2RDM has to fulfill are known by the name of  $N$ -representability conditions [13].

The intrinsic complexity of  $N$ -representability conditions cooled down the initial euphoria to solve the many-body problem easily within the two-body subspace [159]. Since then the search for a complete set of conditions for the 2RDM is an ongoing effort [5, 8, 14, 211]. A systematic classification of  $N$ -representability conditions has been developed [15] for ensemble representable RDMs, i.e., matrices that are derivable from a mixed quantum state. A complete set of conditions for pure states has remained undetermined. Moreover, numerical calculations allow to implement only few  $N$ -representability conditions. There exist several explicit necessary conditions for  $N$ -representability in the form of positivity conditions. The two most important positivity conditions for the 2RDM are called the  $D$  and the  $Q$ -positivity condition [8, 12]. They guarantee that the 2RDM

$$D_{12} = \sum_i g_i |\gamma_i\rangle \langle \gamma_i| \quad (5.68)$$

and the 2HRDM (Eq. 3.96)

$$Q_{12} = \sum_i \tilde{g}_i |\tilde{\gamma}_i\rangle \langle \tilde{\gamma}_i| \quad (5.69)$$

are positive semidefinite (i.e. have non-negative eigenvalues  $g_i \geq 0$  and  $\tilde{g}_i \geq 0$ ). These positivity conditions imply that the occupation numbers of particle pairs or hole pairs in any two-particle state are always non-negative. Although 2RDM and the 2HRDM are interconvertible by a rearrangement of the creation and annihilation operators (Eq. 3.96) the positive conditions  $g_i \geq 0$  and  $\tilde{g}_i \geq 0$  represents independent conditions. A further positivity condition, the G-condition, guarantees that the  $G$ -matrix (Eq. 3.97) is positive semidefinite ensuring the occupation of particle-hole pairs to be non-negative [12]. For the calculations presented here, the G-condition turned out to be much less important than the  $D$  and  $Q$ -condition. In fact, the G-condition was found to be well conserved whenever the  $D$  and  $Q$ -condition were fulfilled.

The positivity conditions are conveniently implemented since they can be formulated solely in terms of the 2RDM. Beyond these  $D$ ,  $Q$  and  $G$ -positivity conditions referred to as 2-positivity conditions there are 3-positivity conditions that are inherited from the three-particle space [5]. The  $T^1$ -condition is based on the positivity of the  $T^1_{123}$ -matrix

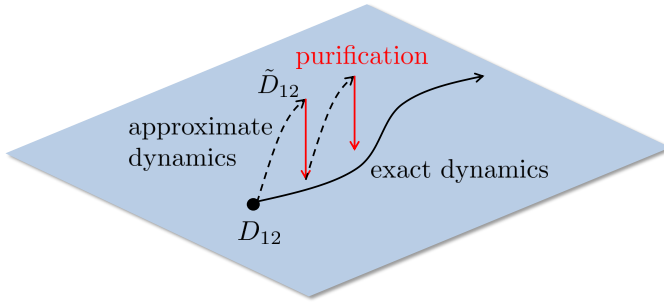
$$T^1_{123} = D_{123} + Q_{123} \quad (5.70)$$

and the  $T^2$ -condition is based on the positivity of the  $T^2_{123}$ -matrix

$$T^2_{123} = E_{123} + F_{123} \quad (5.71)$$

(see Eq. 3.107-Eq. 3.110 for the definition of the involved matrices). Although these are objects on the three-particle subspace the  $T^1_{123}$  matrix as well as the  $T^2_{123}$  can be evaluated in terms of the 2RDM. However, since these conditions require to work in the three-particle subspace they are computationally much more demanding to enforce. Going to even higher orders is possible and the set of all  $p$ -positivity conditions with  $p \leq N$  gives a necessary and sufficient set of constraints [15], however the computational effort rises quickly severely limiting the applicability. In the purification scheme presented below we focus only on the  $D$  and  $Q$ -conditions.

While a compact and feasible solution of the 2RDM  $N$ -representability has not been and will, possibly, never be achieved [212], the ensemble  $N$ -representability problem for the 1RDM was solved long ago by Coleman [13]. A given 1RDM is  $N$ -representable if and only if its eigenvalues (the natural occupation numbers) are between zero and one, i.e.  $n_i \in [0, 1]$ . Beyond the ensemble  $N$ -representability also the pure-state  $N$ -representability has been recently solved restricting the occupation numbers from the hypercube  $n_i \in [0, 1]$  to an inscribed convex polytope [213]. The solution of the  $N$ -representability problem for the 1RDM is significantly easier than for the 2RDM. The reason for this can be understood by an intuitive picture. Consider a three-particle system. Instead of describing the system in terms of three particles this system can also be described in terms of three pairs. However, these



**Figure 5.1.: Schematic illustration of the purification scheme.** The dynamical purification is applied after each time step to project the propagated 2RDM,  $\tilde{D}_{12}(t + dt)$ , back onto the set of 2RDMs that satisfy certain  $N$ -representability conditions (in the present case the  $D$  and  $Q$ -condition).

three pairs are not allowed to be varied in an arbitrary fashion. In fact each pair is coupled to the other pairs by one shared particle. By varying the state of the pairs in an arbitrary way the consistency of the three-particle system breaks down. In analogy the geminals of the 2RDM cannot be varied by an arbitrary unitary rotation without, eventually, breaking the consistency of the  $N$ -particle state. Describing the aforementioned three-particle system in terms of three individual particles on the other hand does not feature constraints in the way the single particle states can be varied. Any unitary variation of the natural orbitals results in a consistent  $N$ -particle state. Consequently the  $N$ -representability conditions on the 1RDM can be written solely in terms of the natural occupation numbers and do not depend on the natural orbitals.

Due to the presence of the  $N$ -representability problem the realization of the goal to replace the propagation of the  $N$ -particle wavefunction by that of the 2RDM faces, in addition to the reconstruction (or closure) problem, a second and closely intertwined conceptual hurdle. While the many-body wavefunction  $\Psi(t)$  itself is not needed to propagate the 2RDM via the closed equations of motion (Eq. 5.2) it should be existent at any time such that the solution of  $D_{12}(t)$  retains  $N$ -representability. If the exact form of  $D_{123}$  were to be used in Eq. 5.2, this would be trivially the case. However, as soon as approximations to  $D_{123}$  are employed, the time evolved  $D_{12}(t)$  may leave the subspace of  $N$ -representable 2RDMs. Even when the 2RDM associated with the initial state satisfies the  $D$  and the  $Q$ -positivity condition initially, the  $N$ -representability conditions may be violated during time evolution calculated according to Eq. 5.2 due to the residual errors in the reconstruction functional. Correction of such errors is referred to as purification.

### 5.3.1. Purification

Several types of purifications have been discussed in literature for the time-independent 2RDM and are used primarily to enhance convergence in the iterative solution of the second-order contracted Schrödinger equation [198, 214]. We have adopted and modified the known purification schemes for application in the time-dependent setting. Since the purification is applied after each time propagation step an efficient and effective purification is paramount. For this reason the purification schemes adopted from literature are further improved by exploiting spin-symmetries and reducing the numerically demanding procedures as far as possible. In the following we give a short review of the purification schemes known from

literature.

During time-evolution the 2RDM  $D_{12}(t)$  will, in general, depart from the subspace of  $N$ -representable 2RDMs after each propagation step (Fig. 5.1). To correct the error from the violation of  $N$ -representability the evolved  $\tilde{D}_{12}(t+dt)$  is projected back onto (or rather close to) the subspace of  $N$ -representable 2RDMs,

$$D_{12}(t+dt) = \tilde{D}_{12}(t+dt) + D_{12}^{\text{cor}}(t+dt), \quad (5.72)$$

where the correction  $D_{12}^{\text{cor}}$  enforces a set of preselected  $N$ -representability conditions. A purification scheme which accounts for the  $D$  and the  $Q$ -condition and employs the unitary decomposition was presented by Mazziotti [198]. Briefly, the 2RDM,  $\tilde{D}_{12}(t)$ , and the 2HRDM,  $\tilde{Q}_{12}(t)$ , are corrected via

$$D_{12} = \tilde{D}_{12} + D_{12}^{\text{cor}} \quad (5.73)$$

$$Q_{12} = \tilde{Q}_{12} + D_{12}^{\text{cor}} \quad (5.74)$$

where the ansatz for the correction is given by

$$D_{12}^{\text{cor}} = \sum_i (\alpha_i A_{12;K}^i + \beta_i B_{12;K}^i), \quad (5.75)$$

with  $A_{12;K}^i$  and  $B_{12;K}^i$  the contraction free components (see Eq. C.1) of

$$A_{12}^i = |\gamma_i^< \rangle \langle \gamma_i^< | \quad (5.76)$$

$$B_{12}^i = |\tilde{\gamma}_i^< \rangle \langle \tilde{\gamma}_i^< |. \quad (5.77)$$

We denote by  $\gamma_i^<$  and  $\tilde{\gamma}_i^<$  the eigenstates of the 2RDM and 2HRDM with negative occupation number. In order to preserve the  $D$  and  $Q$ -positivity condition the coefficients  $\alpha_i$  and  $\beta_i$  are determined by the set of linear equations

$$\text{Tr}_{12}(A_{12}^i D_{12}) = 0 \quad (5.78)$$

$$\text{Tr}_{12}(B_{12}^i Q_{12}) = 0. \quad (5.79)$$

Correcting the 2RDM via Eq. 5.75 creates a new  $D_{12}$  whose norm and 1RDM is preserved, and whose negative eigenvalues are smaller than those of  $\tilde{D}_{12}$ . Repeating this process iteratively yields the purified  $D_{12}(t)$ . We note that this iterative procedure converges only if the underlying 1RDM is  $N$ -representable, i.e. has eigenvalues between 0 and 1. We find that the time-dependent 1RDM remains  $N$ -representable during the evolution when the  $D$  and  $Q$ -condition on  $D_{12}$  and  $Q_{12}$  are enforced.

We have found that this purification according to Mazziotti can be simplified in a way that reduces the numerical effort and enhances the convergence. To isolate the defective part of the 2RDM we decompose the 2RDM into components with negative eigenvalues  $D_{12}^<$  and positive eigenvalues  $D_{12}^>$ ,

$$D_{12}^< = \sum_{g_i < 0} g_i |\gamma_i \rangle \langle \gamma_i |, \quad (5.80)$$

$$D_{12}^> = \sum_{g_i > 0} g_i |\gamma_i \rangle \langle \gamma_i |, \quad (5.81)$$

where  $g_i$  are the eigenvalues of the 2RDM. Simply neglecting  $D_{12}^<$  in the decomposition of the 2RDM is not a viable option as it would lead to uncontrolled errors in the normalization as well as the associated 1RDM. Instead we employ the unitary decomposition of the 2RDM (Eq. C.1)

$$D_{12}^< = D_{12;\perp}^< + D_{12;K}^<. \quad (5.82)$$

As above, the kernel  $D_{12;K}^<$  is by definition fully contraction free. Therefore, subtracting the kernel component from the 2RDM,

$$D_{12} = \tilde{D}_{12} - D_{12;K}^<, \quad (5.83)$$

leaves the norm and the 1RDM invariant. After a single purification step  $D_{12}$  has significantly reduced negative eigenvalues. The same unitary decomposition can be applied to simultaneously enforce the approximate positivity of the 2HRDM

$$D_{12} = \tilde{D}_{12} - D_{12;K}^< - Q_{12;K}^<. \quad (5.84)$$

Compared to the Mazziotti ansatz for the correction (Eq. 5.75) it is not necessary to solve a linear set of equations simplifying and speeding up the purification process. Since the negative eigenvalues of the 2HRDM have dominant contributions in the high occupation numbers of the 2RDM the two matrices  $D_{12;K}^<, Q_{12;K}^<$  act on different subspaces and, therefore, do not destroy the purifying effect of each other but lead to a simultaneous enforcement of the  $D$ - and  $Q$ -condition. Due to the simplicity and the numerical effectiveness we will apply the new purification scheme (Eq. 5.84) when applying the TD-2RDM method to atom-laser interactions in Chapter 8.

### 5.3.2. Spin-conserving purification

The purification processes outlined above requires extension when spin symmetries are to be conserved simultaneously. We first note that it is sufficient to only purify the  $(\uparrow\downarrow)$ -block because in the singlet spin state this block contains all the information of the full 2RDM and has the same eigenvalues (except of a factor two) as the full 2RDM. The  $D$  and  $Q$ -condition are then equivalent to the positivity of the  $(\uparrow\downarrow)$ -block of the 2RDM and the 2HRDM. We separate the  $(\uparrow\downarrow)$ -block further into the symmetric (Eq. 5.46) and the antisymmetric (Eq. 5.48) irreducible spin components

$$D_{12}^{\uparrow\downarrow} = D_{12}^{0,0} + D_{12}^{0,1} \quad (5.85)$$

$$Q_{12}^{\uparrow\downarrow} = Q_{12}^{0,0} + Q_{12}^{0,1} \quad (5.86)$$

While for the antisymmetric triplet-spin block  $D_{12}^{0,1}$  we can directly apply the purification procedures described above, the purification of the symmetric singlet-spin block  $D_{12}^{0,0}$  employs the unitary decomposition for symmetric matrices (see Eq. C.5 in the Appendix). This purification does not alter the one-particle traces of the  $(\uparrow\downarrow)$ -block such that the conditions

Eq. 5.36, Eq. 5.38, Eq. 5.39, and Eq. 5.40 remain conserved. The convergence is strongly dependent on the positive semidefiniteness of the one-particle traces of the singlet and triplet-spin block:

$$\begin{aligned} \text{Tr}_2 D_{12}^{0,0} &\geq 0 & \text{Tr}_2 Q_{12}^{0,0} &\geq 0 \\ \text{Tr}_2 D_{12}^{0,1} &\geq 0 & \text{Tr}_2 Q_{12}^{0,1} &\geq 0. \end{aligned} \quad (5.87)$$

If conditions Eq. 5.38 and Eq. 5.40 are met these matrices are proportional to the 1RDM and, therefore, positive semidefinite.

### 5.3.3. $N$ -representability in the BBGKY-hierarchy

We close this section on  $N$ -representability with an interesting observation. As mentioned previously the violation of  $N$ -representability of the 2RDM is caused by errors in the reconstruction functional. It is, therefore, natural to attempt to conserve  $N$ -representability of the 2RDM by improving the reconstruction functional rather than correcting the 2RDM in an *a posteriori* purification step. While such an  $N$ -representability conserving reconstruction is still missing we have found one interesting relation that connects the conservation of the positivity of the 1RDM with a particular positivity condition of the 3RDM:

Given a 1RDM that has a certain number of occupied natural orbitals  $|\eta_i\rangle$  we can always add one orbital  $|\eta_\nu\rangle$  that has zero occupation and is orthogonal to all other natural orbitals

$$D_i^\nu = (D_\nu^i)^* = \langle n_\nu | D_1 | \eta_i \rangle = 0 \quad D_\nu^\nu = \langle n_\nu | D_1 | \eta_\nu \rangle = 0, \quad (5.88)$$

without changing the 1RDM. This one (virtual) orbital can be used as a "probe". Its occupation cannot become negative due to the positivity condition of the 1RDM. Therefore we get the condition

$$0 \leq \partial_t D_\nu^\nu = -i \sum_{i_2 j_1 j_2} (\tilde{H}_{\nu i_2}^{j_1 j_2} D_{j_1 j_2}^{\nu i_2} - D_{\nu i_2}^{j_1 j_2} \tilde{H}_{j_1 j_2}^{\nu i_2}) = 0, \quad (5.89)$$

which is always fulfilled since  $D_{\nu j_1}^{i_1 i_2} = 0$  for an unoccupied (virtual) orbital  $|\eta_\nu\rangle$ . While the time derivative of the occupation of a virtual orbital is always zero this is not necessarily the case for the second derivative:

$$\begin{aligned} 0 \leq \partial_t^2 D_\nu^\nu &= \sum_{i_2 j_1 j_2} (\tilde{H}_{\nu i_2}^{j_1 j_2} \partial_t D_{j_1 j_2}^{\nu i_2} - \partial_t D_{\nu i_2}^{j_1 j_2} \tilde{H}_{j_1 j_2}^{\nu i_2}) \\ &= \sum_{i_2 n_1 n_2 m_2 j_1 j_2} 2\tilde{H}_{\nu m_2}^{n_1 n_2} \left( D_{n_1 n_2}^{j_1 j_2} \delta_{i_2}^{m_2} - D_{n_1 n_2 i_2}^{j_1 j_2 m_2} \right) \tilde{H}_{j_1 j_2}^{\nu i_2}, \end{aligned} \quad (5.90)$$

where we have used the equation of motion for the 2RDM and some algebraic manipulation from the first to the second line. Since the second derivative of the occupation of a virtual orbital has to be non-negative for an arbitrary Hamiltonian the last line of Eq. 5.90 is actually a positivity condition for the  $E_{123}$  matrix (see Eq. 3.110)

$$E_{n_1 n_2 i_2}^{j_1 j_2 m_2} = D_{n_1 n_2}^{j_1 j_2} \delta_{i_2}^{m_2} - D_{n_1 n_2 i_2}^{j_1 j_2 m_2}. \quad (5.91)$$

that can be expressed as

$$E_{n_1 n_2 i_2}^{j_1 j_2 m_2} = \langle \Psi | a_{j_1}^\dagger a_{j_2}^\dagger a_{i_2} a_{m_2}^\dagger a_{n_1} a_{n_2} | \Psi \rangle. \quad (5.92)$$

In this form the second time derivative of  $D_v^v$  can be compactly expressed as

$$0 \leq \partial_t^2 D_\nu^\nu = \langle \Phi_\nu | \Phi_\nu \rangle \quad \text{with} \quad |\Phi_\nu\rangle = \sum_{i_1 j_1 j_2} \tilde{H}_{\nu m_2}^{n_1 n_2} a_{m_2}^\dagger a_{n_1} a_{n_2} | \Psi \rangle \quad (5.93)$$

which is fulfilled due to the positivity of the norm. In this way we succeeded in relating the positivity of the 3RDM to the conservation of the positivity of the 1RDM.

From the latter result we can conclude that the BBGKY hierarchy does not only couple the time-evolution of the RDMs of different orders but also relates the positivity conditions of different orders with each other. The full consequences of this observation are still to be investigated. One obvious conclusion is that if the reconstructed 3RDM violates positivity conditions, violation of positivity of the 1RDM and thus the break-down of the propagation of the 2RDM is ultimately to be expected.



## 6. Implementation of TD-2RDM for atomic and molecular systems

The 2RDM in spatial representation is given by

$$\langle \mathbf{x}_1 \mathbf{x}_2 | D_{12} | \mathbf{x}'_1 \mathbf{x}'_2 \rangle = D(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}'_1, \mathbf{x}'_2; t). \quad (6.1)$$

The application to strong field processes in atomic and molecular systems requires large box sizes to describe electrons with a large excursion radius and at the same time fine spatial discretizations to resolve the small wavelengths electrons can acquire upon rescattering at the nuclear core. To fulfill both requirements the numerical implementation of the TD-2RDM method for strong field processes uses the expansion of the 2RDM within a suited set of  $2I$  time-dependent spin orbitals  $\{|\phi_i\rangle\}$

$$D(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}'_1, \mathbf{x}'_2; t) = \sum_{i_1, i_2, j_1, j_2} D_{j_1 j_2}^{i_1 i_2}(t) \phi_{i_1}(\mathbf{x}_1, t), \phi_{i_2}(\mathbf{x}_2, t) \phi_{j_1}^*(\mathbf{x}'_1, t) \phi_{j_2}^*(\mathbf{x}'_2, t), \quad (6.2)$$

where the orbital index  $i \in \{1 \dots 2I\}$  comprises also the spin coordinate  $\sigma \in \{\uparrow, \downarrow\}$ . Conceptually, there is no predetermined choice for the dynamics of the orbitals. Any choice

$$i\partial_t \phi_i(\mathbf{x}_1, t) = F[\phi_j(\mathbf{x}_1, t)] \quad (6.3)$$

is permitted and leads to equations of motion for the 2RDM expansion coefficients of the form

$$i\partial_t D_{j_1 j_2}^{i_1 i_2} = \sum_{k_1, k_2} (\bar{H}_{j_1 j_2}^{k_1 k_2} D_{k_1 k_2}^{i_1 i_2} - D_{j_1 j_2}^{k_1 k_2} \bar{H}_{k_1 k_2}^{i_1 i_2}) + C_{j_1 j_2}^{i_1 i_2}, \quad (6.4)$$

with

$$\bar{H}_{j_1 j_2}^{i_1 i_2}(t) = \langle \phi_{i_1} \phi_{i_1} | \bar{h}_1 \delta_1 + \delta_1 \bar{h}_2 + W_{12} | \phi_{j_1} \phi_{j_2} \rangle \quad \text{and} \quad C_{j_1 j_2}^{i_1 i_2} = \langle \phi_{i_1} \phi_{i_1} | C_{12} | \phi_{j_1} \phi_{j_2} \rangle, \quad (6.5)$$

where the one-particle Hamiltonian is modified by the time dependence of the orbital basis

$$\bar{h}_{j_1}^{i_1} = \langle \phi_{i_1} | h_1 - i\partial_t | \phi_{j_1} \rangle. \quad (6.6)$$

## 6.1. Orbital dynamics

In principle, the expansion of the 2RDM can be performed within a time-independent basis. For weak perturbations this is a good choice. For strong laser pulses, however, the strong response induced by the laser field would require a very large basis set of time-independent orbitals. To keep the number of orbitals and, therefore, the numerical effort to a minimum a time-dependent adaption of the orbitals is necessary. Conceptually, the natural orbitals would be the optimal choice to minimize the number of active orbitals. This property of natural orbitals was proven in Section 3.1. As such it would be natural to expand the 2RDM in the set of time-dependent natural orbitals  $\eta_i(\mathbf{x}, t) = \langle \mathbf{x} | \eta_i(t) \rangle$  whose dynamics is given by Eq. 3.49 reproduced here for convenience

$$i\partial_t |\eta_i\rangle = h_1 |\eta_i\rangle + \sum_{j \neq i} \frac{\langle \eta_j | C_1 | \eta_i \rangle}{n_i - n_j} |\eta_j\rangle. \quad (6.7)$$

Expanding the 2RDM directly in the basis of time-dependent natural orbitals, however, faces a practical difficulty. In general, there is an infinite number of natural orbitals and in order to exactly calculate their dynamics it is necessary to know all natural orbitals. From a computational point of view this is of course unfeasible. In the numerical implementation only a finite number of orbitals can have a non-zero occupation. The optimization property (see Section 3.1) for natural orbitals, however, assures a rapid decay of their (natural) occupation numbers. Therefore, it is a good approximation to assume  $n_\nu = 0$  if  $\nu > 2I$  for a reasonable choice of  $I$ .

Under the approximation  $n_\nu = 0$  for  $\nu > 2I$  the natural orbitals  $\eta_i(\mathbf{x}, t)$  are approximated by the working orbitals  $\phi_i(\mathbf{x}, t)$ . The dynamics of the working orbitals  $\phi_i(\mathbf{x}, t)$  is slightly altered compared to the dynamics of the natural orbitals  $\eta_i(\mathbf{x}, t)$  (Eq. 6.7). However, assuming small natural occupation  $n_\nu$  for  $\nu > 2I$  the expansion within the time-dependent working orbitals  $\phi_i(\mathbf{x}, t)$  will be the optimal expansion within a total number of  $2I$  occupied (active) orbitals. Employing the projection operators  $\mathcal{Q}_1$  (see Eq. 2.19) and

$$\mathcal{P}_1 = \sum_{i=1}^{2I} |\phi_i\rangle \langle \phi_i| = 1 - \mathcal{Q}_1 \quad (6.8)$$

the dynamics of the working orbitals can be decomposed

$$i\partial_t |\phi_i\rangle = \mathcal{P}_1 i\partial_t |\phi_i\rangle + \mathcal{Q}_1 i\partial_t |\phi_i\rangle \quad (6.9)$$

into a component within the occupied subspace

$$\mathcal{P}_1 i\partial_t |\phi_i\rangle = \mathcal{P}_1 h_1 |\phi_i\rangle + \sum_{j \neq i} \frac{\langle \phi_j | C_1 | \phi_i \rangle}{n_i - n_j} |\phi_j\rangle, \quad (6.10)$$

and a component within the unoccupied (virtual) subspace

$$\begin{aligned}
\mathcal{Q}_1 i\partial_t |\phi_i\rangle &= \mathcal{Q}_1 h_1 |\phi_i\rangle + \sum_{\nu=2I}^{\infty} |\phi_\nu\rangle \langle \phi_\nu | \sum_{k \neq i}^{\infty} \frac{\langle \phi_k | C_1 | \phi_i \rangle}{n_i - n_k} |\phi_k\rangle \\
&= \mathcal{Q}_1 h_1 |\phi_i\rangle + \mathcal{Q}_1 \frac{C_1 |\phi_i\rangle}{n_i} \\
&= \mathcal{Q}_1 h_1 |\phi_i\rangle + \mathcal{Q}_1 C_1 D_1^{-1} |\phi_i\rangle,
\end{aligned} \tag{6.11}$$

where we have employed the inverse of the 1RDM  $D_1^{-1} |\phi_i\rangle = (1/n_i) |\phi_i\rangle$  and we have assumed that  $n_\nu = 0$  for  $\nu > 2I$ . From the last line in Eq. 6.11 we see that the time derivative of the working orbitals within the unoccupied subspace can be calculated solely by employing the orbitals of the occupied subspace. This is an important property that allows to propagate the occupied working orbitals without having to co-propagate the virtual subspace.

The propagation within the occupied subspace  $\mathcal{P}_1 \partial_t |\phi_i\rangle$  is redundant in the sense that it describes only the internal orbital dynamics within the occupied subspace and does not influence the rotation of the orbitals out of the occupied subspace. Any choice for the internal propagation  $\mathcal{P}_1 \partial_t |\phi_i\rangle$  can be compensated by a suitable transformation of the one-particle Hamiltonian (Eq. 6.6)

$$\bar{h}_j^i = h_j^i - \langle \phi_i | i\partial_t | \phi_j \rangle. \tag{6.12}$$

This freedom to choose for  $\langle \phi_i | i\partial_t | \phi_j \rangle$  an arbitrary hermitian matrix is closely related to the variational freedom in MCTDHF discussed in Section 2.2 (compare with Eq. 2.20 and Eq. 2.21). For convenience three choices seem most natural. Either Eq. 6.10 can be adopted as it is. In this case the propagation within the occupied subspace is directly modelled according to the time dependence of the natural orbitals. However, the drawback of this approach is that the denominator of the last term on the r.h.s. in Eq. 6.10 can become quite small causing numerical stability problems if not appropriately regularized [123]. A better choice from the perspective of numerical stability is to choose

$$\langle \phi_i | i\partial_t | \phi_j \rangle = 0. \tag{6.13}$$

In this case the modified Hamiltonian reduces to  $\bar{h}_j^i = h_j^i$ . This choice has the advantage that the propagation of the orbitals within the occupied subspace becomes trivial.

Both approaches Eq. 6.10 and Eq. 6.13 represent two extreme cases of how much dynamics is contained in the orbitals themselves and how much dynamics is left in the expansion coefficients of the 2RDM (Eq. 6.4). Using Eq. 6.10 for the internal dynamics the orbitals account for a large portion of the dynamics and the dynamics of the 1RDM expansion coefficients reduces to

$$i\partial_t D_j^i = \delta_j^i C_i^i, \tag{6.14}$$

where  $\delta_j^i$  denotes the Kronecker delta. Using Eq. 6.13, on the other hand, eliminates the internal dynamics of the orbitals completely while the 1RDM expansion coefficients account

for the full dynamics

$$i\partial_t D_j^i = [h_1, D_1]_j^i + C_j^i. \quad (6.15)$$

A third choice is given by

$$\langle \phi_i | i\partial_t | \phi_j \rangle = h_j^i. \quad (6.16)$$

This choice is somewhat in between the two extreme cases Eq. 6.10 and Eq. 6.13, respectively. The equation of motion for the orbitals within the occupied subspace Eq. 6.16 avoids the numerically challenging denominator compared to Eq. 6.10 while the dynamics within the 1RDM is given by

$$i\partial_t D_j^i = C_j^i. \quad (6.17)$$

We find this choice to be the numerically most favourable one. The final equation for the dynamics of the working orbitals can be compactly written as

$$\begin{aligned} i\partial_t |\phi_i\rangle &= \mathcal{P}_1 i\partial_t |\phi_i\rangle + \mathcal{Q}_1 i\partial_t |\phi_i\rangle \\ &= h_1 |\phi_i\rangle + \mathcal{Q}_1 C_1 D_1^{-1} |\phi_i\rangle. \end{aligned} \quad (6.18)$$

On first sight the expression involving the inverse  $D_1^{-1}$  appears to be divergent for orbitals whose occupation is close to zero. Such a divergence cannot be physical and therefore corresponds to a removable singularity. To show this explicitly we employ the cumulant expansion Eq. 3.30 which gives for the last term on the r.h.s. of Eq. 6.18

$$\begin{aligned} \mathcal{Q}_1 C_1 D_1^{-1} |\phi_i\rangle &= \mathcal{Q}_1 \text{Tr}_2 [W_{12}, D_{12}] D_1^{-1} |\phi_i\rangle = \mathcal{Q}_1 \text{Tr}_2 W_{12} D_{12} D_1^{-1} |\phi_i\rangle \\ &= \mathcal{Q}_1 \text{Tr}_2 W_{12} (\hat{\mathcal{A}} D_1 D_2 + \Delta_{12}) D_1^{-1} |\phi_i\rangle \\ &= \mathcal{Q}_1 V_1^{\text{HF}} |\phi_i\rangle + \mathcal{Q}_1 \text{Tr}_2 W_{12} \Delta_{12} D_1^{-1} |\phi_i\rangle, \end{aligned} \quad (6.19)$$

where we have used  $\mathcal{Q}_1 D_{12} = 0$  due to the vanishing occupation of virtual orbitals and

$$V_1^{\text{HF}} = \text{Tr}_2 D_2 W_{12} - \text{Tr}_2 D_2 \Lambda_{12} W_{12} \quad (6.20)$$

is the mean field of the Hartree-Fock Hamiltonian defined in Eq. 2.10. Therefore, the second term in the equation of motion for the working orbitals can be decomposed into a mean-field part  $V_1^{\text{HF}} |\phi_i\rangle$  and a correction

$$\mathcal{Q}_1 \Gamma_1 |\phi_i\rangle = \mathcal{Q}_1 \text{Tr}_2 W_{12} \Delta_{12} D_1^{-1} |\phi_i\rangle, \quad (6.21)$$

originating from two-particle correlation. The essential observation is that the two-particle cumulant vanishes if at least one of its indices corresponds to either a fully occupied or a completely empty orbital [164]. Therefore the combined expression  $\Delta_{j_1 j_2}^{i_1 i_2} / n_{i_1}$  and consequently  $\Gamma_1$  remains regular in the limit  $n_{i_1} \rightarrow 0$ .

## 6.2. Numerical implementation

The equations of motion for the orbitals (Eq. 6.18) in the last section are given in general form. The specific numerical implementation for the 3D simulation of atoms in strong laser pulses (Chapter 8) is based on the spherical-FEDVR basis functions [215],

$$\langle r, \theta, \phi | \chi_{qlm} \rangle = \frac{1}{r} f_q(r) Y_{lm}(\theta, \phi), \quad (6.22)$$

where  $(r, \theta, \phi)$  are the spherical coordinates of  $\mathbf{r}$ ,  $Y_{lm}(\theta, \phi)$  are spherical harmonics, and  $f_q(r)$  are radial-FEDVR functions parametrized by the integer  $q$  that runs from 1 to  $K_{\text{rad}}$ , i.e. the radial coordinate is discretized into a grid with a total number of  $K_{\text{rad}}$  grid points. Specifically this discretization consists of  $K_{\text{FE}}$  finite elements with  $K_{\text{DVR}}$  basis functions each. The spherical-FEDVR basis is well suited to describe atomic systems that feature central symmetry [215].

With this basis the expansion of the working orbitals can be written as

$$\langle \chi_{qlm} | \phi_i(t) \rangle = \phi_{im}^{ql}(t). \quad (6.23)$$

One important observation that saves a lot of computational work is that the magnetic quantum number  $m$  is conserved for each orbital individually during the interaction with linearly polarized electric fields (within dipole approximation). This conservation of  $m$  is not obvious because of the second term in Eq. 6.18. The conservation of  $m$  is related to the fact that the total magnetic quantum number  $M$  is conserved. If the system under investigation has a well defined total magnetic quantum number  $M$  the RDMs have a block structure with respect to the magnetic quantum number

$$\langle \chi_{q_1 l_1 m_1} \dots \chi_{q_p l_p m_p} | D_{1\dots p} | \chi_{q'_1 l'_1 m'_1} \dots \chi_{q'_p l'_p m'_p} \rangle \propto \delta_{m'_1 + \dots + m'_p}^{m_1 + \dots + m_p}, \quad (6.24)$$

i.e. the RDMs vanish unless the sum of the magnetic quantum numbers of upper and lower indices is equal. This relation translates into

$$\langle \chi_{q_1 l_1 m_1} | C_1 D_1^{-1} | \chi_{q'_1 l'_1 m'_1} \rangle \propto \delta_{m'_1}^{m_1} \quad (6.25)$$

showing that orbitals with different magnetic quantum number are not coupled. Consequently, we can assume the working orbitals to have fixed magnetic quantum numbers set by the initial state.

For simplicity of notation we absorb the magnetic quantum number into the orbital index and write the working orbitals in vector form  $\phi_i(t) := \phi_{im}^{ql}(t)$ . Thus, the equation of motion to be solved within the spherical-FEDVR representation is give by

$$i\partial_t \phi_i(t) = \mathbf{h} \phi_i(t) + \mathbf{Q} \mathbf{F}_i[\phi_j], \quad (6.26)$$

where the detailed expression for the matrices  $\mathbf{h}$  and  $\mathbf{F}_i$  can be found in Appendix E.

For closed shell systems the initial singlet state is conserved during propagation in which

case the  $(\uparrow\downarrow)$ -block of the 2RDM contains all information on the full 2RDM (Eq. 5.45). The corresponding equation of motion for the  $(\uparrow\downarrow)$ -block reduces to

$$i\partial_t D_{j_1\uparrow j_2\downarrow}^{i_1\uparrow i_2\downarrow} = \sum_{k_1, k_2} (\bar{H}_{j_1 j_2}^{k_1 k_2} D_{k_1\uparrow k_2\downarrow}^{i_1\uparrow i_2\downarrow} - D_{j_1\uparrow j_2\downarrow}^{k_1\uparrow k_2\downarrow} \bar{H}_{k_1 k_2}^{i_1 i_2}) + C_{j_1\uparrow j_2\downarrow}^{i_1\uparrow i_2\downarrow}, \quad (6.27)$$

where  $C_{12}^{\uparrow\downarrow}$  can be written solely in terms of the  $(\uparrow\uparrow\downarrow)$ -block of the 3RDM

$$\begin{aligned} C_{12}^{\uparrow\downarrow} &= \text{Tr}_3[W_{13}^{\uparrow\downarrow} + W_{23}^{\downarrow\downarrow}, D_{123}^{\uparrow\downarrow\downarrow}] + \text{Tr}_3[W_{13}^{\uparrow\uparrow} + W_{23}^{\downarrow\uparrow}, D_{123}^{\uparrow\downarrow\uparrow}] \\ &= \text{Tr}_3[W_{13} + W_{23}, D_{123}^{\uparrow\downarrow\downarrow} + D_{123}^{\uparrow\downarrow\uparrow}]. \end{aligned} \quad (6.28)$$

Further, due to the block structure with respect to the total magnetic quantum number the evaluation of the reconstruction can be restricted to non-zero matrix elements  $D_{j_1\uparrow j_2\uparrow j_3\downarrow}^{i_1\uparrow i_2\uparrow i_3\downarrow}$  with  $m_{i_1} + m_{i_2} + m_{i_3} = m_{j_1} + m_{j_2} + m_{j_3}$  which reduces the numerical effort significantly. For propagating the orbitals in time it is necessary to take into account the stiffness of the spatial-derivative operators. For that reason it is beneficial to use a split-step method that separately treats the stiff and non-stiff parts of the equation of motion on a different footing. We use a second-order split step procedure as follows: First, the linear equation

$$\partial_t \phi_i(t) = -i\mathbf{h}(t)\phi_i(t) \quad (6.29)$$

is solved for  $[t, t + 0.5\delta t]$ . Then the nonlinear part

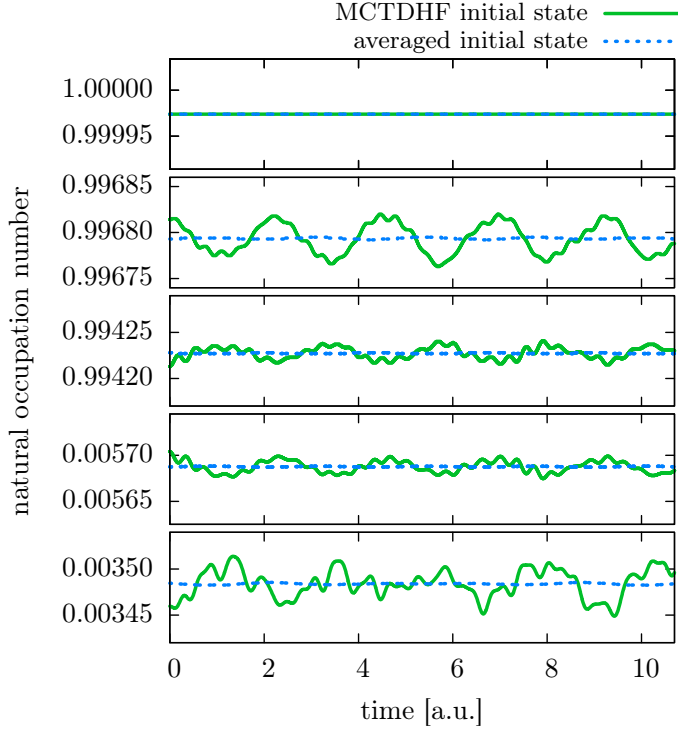
$$\partial_t \phi_i(t) = -i\mathbf{QF}_i[\phi_j] \quad (6.30)$$

and the 2RDM coefficients are propagated (Eq. 6.27) within the time-interval  $[t, t + \delta t]$ . Finally, the orbitals are propagated for  $[t + 0.5\delta t, t + \delta t]$  according to equation Eq. 6.29. The linear equation Eq. 6.29 contains the stiff kinetic operator, the Coulomb potential of the atomic nucleus, and the laser potential that is also stiff in velocity gauge. For handling stiff equations of motion special techniques are necessary. An efficient choice is the Crank-Nicolson method [216],

$$\phi_i(t + 0.5\delta t) = \frac{1 - i\mathbf{h}(t + 0.25\delta t)0.25\delta t}{1 + i\mathbf{h}(t + 0.25\delta t)0.25\delta t} \phi_i(t), \quad (6.31)$$

which is a unitary propagator with good stability conditions. The orbital propagation according to Eq. 6.30 and the propagation of the 2RDM matrix elements (Eq. 6.27) is performed by employing the explicit Runge-Kutta propagator of fourth order [217]. An absorbing boundary is implemented by a mask function of  $\cos^{\frac{1}{4}}$  shape.

Compared to wavefunction-based methods which scale factorially with the number of particles the computational cost of the TD-2RDM method is independent of the particle number  $N$  and depends only on the total number of basis functions  $2I$ . The most time consuming operation within Eq. 6.27 is the evaluation of the collision operator  $C_{12}$  where a partial trace over the interaction operator  $W_{12}$  and the 3RDM has to be evaluated. This calculation scales as  $\mathcal{O}(I^5)$  with the number of spatial basis functions  $I$  if the interaction potential is diagonal



**Figure 6.1.: Approximating the ground state of the TD-2RDM method.** Oscillating natural occupation numbers of the 2RDM propagated without external field using the exact 2RDM from an MCTDHF ground state calculation as the initial condition (green solid line). If the averaged 2RDM (Eq. 6.34) is used as the initial condition (blue dashed line) the oscillations are almost absent. The orbitals are fixed during the propagation. The y-axis is cut into segments to enlarge the individual oscillations.

in the basis (as, e.g., in spatial representation), or as  $\mathcal{O}(I^7)$  for the expansion in orbitals. The implementation for the 1D simulation of LiH discussed in Chapter 9 is less demanding in terms of the numerical stability. The equations of motion (Eq. 6.11) for the 1D orbitals  $\phi_i(z, t)$  are given by

$$i\partial_t\phi_i(z, t) = \mathcal{Q}_1 \left( h(z)\phi_i(z, t) + \sum_{uvws} W_w^s(z, t) D_{su}^{wv} [D^{-1}]_i^u \phi_v(z, t) \right), \quad (6.32)$$

where  $[D^{-1}]_i^u$  is the inverse of the 1-RDM in the orbital representation, and

$$W_w^s(z, t) = \int \phi_w(z', t) \phi_s^*(z', t) W_{12}(z, z') dz' \quad (6.33)$$

is the mean field operator. We observe that the stiffness of the kinetic part in the orbital equations of motion is in the 1D case not as problematic as in the 3D implementation. Therefore, we choose  $\langle \phi_i | i\partial_t | \phi_j \rangle = 0$  (compare Eq. 6.15) and propagate the linear as well as the nonlinear part of the orbital equation of motion with the explicit Runge-Kutta propagator of fourth order. The second derivative of the kinetic energy operator is evaluated within the eighth-order finite difference representation.

### 6.3. Ground state preparation for the TD-2RDM method

The 2RDM of the MCTDHF ground state is equal to the ground state of the TD-2RDM method only if the exact 3RDM could be used in the equation of motion for the 2RDM. By

employing approximate reconstruction functionals  $D_{123}^R$  the 2RDM of the MCTDHF ground state is, in general, not a stationary solution of closed equation of motion for the 2RDM (Eq. 5.2). Consequently, the admixture of excitations relative to the stationary ground state of Eq. (5.2) leads to oscillations in the natural occupation numbers that show up as artificial frequency components in the result of the calculation (Fig. 6.1). These oscillations are stable and evolves around a mean value. The mean values are the natural occupation numbers of the proper ground state of the TD-2RDM method. To approximate the proper ground state of the TD-2RDM method we perform a time average

$$\bar{D}_{12} = \frac{1}{T} \int_0^T D_{12}(t) dt \quad (6.34)$$

over a period  $T$  sufficiently long compared to the dominant characteristic inverse frequency for a field-free simulation with the initial 2RDM adopted from the MCTDHF ground state calculation. Propagation employing this averaged 2RDM as the initial condition leads to improved results for dynamical observables. Alternatively, one could employ established algorithms to directly solve the anti-hermitian contracted Schrödinger equation [7] to directly calculate the exact ground state of the TD-2RDM method.



## 7. Strong-field physics of atoms and molecules

Strong field physics studies the response of matter to electromagnetic fields whose field strengths are comparable to the internal field of the material under investigation. In these strong fields the reaction of matter is highly nonlinear and requires non-perturbative methods for a proper description. The effects that arise under such extreme conditions are often quite different from what is observed within the perturbative regime. Of particular importance within the last 30 years have become studies of atoms and molecules subject to strong laser pulses. In the strong field regime the energy that binds the electron to the atom (the ionization potential  $I_p$ ) becomes comparable to or smaller than the laser field induced energy of the electron. The laser induced energy is measured by the ponderomotive energy<sup>1</sup>

$$U_p = \frac{F_0^2}{4\omega^2}, \quad (7.1)$$

which is the average energy of a free electron in an oscillating external field with strength  $F_0$ , intensity  $I = cF_0^2/4\pi$  and wavelength  $\lambda = 2\pi c/\omega$ . To be precise, the motion of a free classical particle in an oscillating external field is a superposition of a constant drift motion (depending of the initial condition) and an oscillatory (quiver) motion. Assuming the initial velocity is zero the average kinetic energy of the oscillatory motion is  $U_p$  while the maximal kinetic energy of the induced drift motion is  $2U_p$  [86]. In total the maximum kinetic energy a particle can gain from the oscillating electric field is

$$E_{\max}^{\text{kin}} = 3.17U_p. \quad (7.2)$$

The strong field regime is characterized by a Keldysh parameter

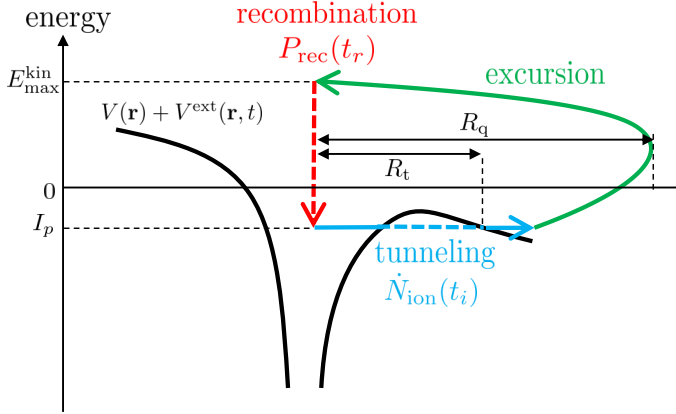
$$\gamma = \sqrt{\frac{I_p}{2U_p}} \quad (7.3)$$

that is smaller than one  $\gamma < 1$ . In this case the maximal drift energy the electron can gain in the field ( $2U_p$ ) is larger than the first ionization potential of the atom ( $I_p$ ).

Entering the strong field regime of atoms and molecules was enabled by technological improvements in laser physics that allowed to drastically increase the intensity, decrease the pulse length and increase the repetition rate. Today the workhorse in the generation of

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<sup>1</sup> A convenient way to calculate the ponderomotive energy in electron volt is  $U_p[\text{eV}] = 9.337 \times I[10^{14}\text{W/cm}^2](\lambda[\mu\text{m}])^2$



**Figure 7.1.: The three-step model.**

In the first step the electron is liberated from the atom via tunnel ionization followed by acceleration in the laser field before recombining with the parent atom and release of its excess energy (Eq. 7.4) in form of high-harmonics. The intensity of the harmonics is proportional to the ionization rate  $\dot{N}_{\text{ion}}$  and the recombination probability  $P_{\text{rec}}$ . Additionally, the tunnel ionization radius (Eq. 7.5) as well as the quiver radius (Eq. 7.6) are depicted.

ultra-short high-intense laser pulses with high repetition rates are Ti:sapphire lasers with a central wavelength of  $\lambda = 800\text{nm}$  ( $\omega = 0.057$  a.u.). The Ti:sapphire lasers in combination with chirped pulse amplification allows the production of pulses with focused intensities of  $10^{14} - 10^{19}\text{W/cm}^2$  and pulse lengths of below 10 fs at a repetition rate of several kHz. The nonlinear reaction of the atoms and molecules radiated with such laser pulses of high-intensity and short duration can be studied by measuring the photons, the electrons or the ions. Each of these reaction products carries information on the underlying strong-field process. While the photon spectrum shows HHG, i.e. a plateau of harmonics ranging to high energy, the photoelectron spectrum shows above-threshold ionization (ATI) characterized by discrete peaks and a plateau in the kinetic energy spectrum. The ionic products can be used to detect dissociation and (multiple) ionization including sequential and NSDI.

## 7.1. High-harmonic generation

High-harmonic generation is one of the fundamental processes in strong field physics. It was first observed in the end of the 80s [218–220]. While the generation of low harmonics in the perturbative regime has been observed much earlier [221] the availability of high-intense laser sources revealed the presence of a plateau of harmonics with almost constant intensity extending to very high energies. The cut-off energy of these high-harmonics is given by

$$E_{\max} \approx I_p + E_{\max}^{\text{kin}}, \quad (7.4)$$

which can be explained by the three-step model [76, 77].

### 7.1.1. The (semi)classical three-step model

The first term in Eq. 7.4 originates from the atomic force and the second term  $E_{\max}^{\text{kin}}$  is the maximum kinetic energy a free particle can gain in the presence of an external oscillating field (Eq. 7.2). In strong near-infrared pulses with  $I \approx 10^{14}\text{W/cm}^2$  both contributions are of comparable magnitude and are combined within the three-step model (Fig. 7.1). In the first

step the initially bound electron tunnels out and leaves the atom at the tunnelling radius

$$R_t = \frac{I_p}{F_0}. \quad (7.5)$$

In the second step the laser field dominates and drives the electron to a maximal quiver radius of

$$R_q = \frac{F_0}{\omega^2} \quad (7.6)$$

before accelerating it back towards to parent atom with a kinetic energy of up to  $E_{\max}^{\text{kin}}$ . In the last step the atomic force can capture the electron in a recombination event with the excess energy released in form of high-harmonic radiation. Within this three-step model the cut-off energy (Eq. 7.4) is the maximum excess energy the electron can release [76, 77]. Under certain (phase-matching) conditions [222] the high-harmonic radiation from individual atoms can add up coherently in the macroscopic medium giving rise to coherent high-energetic radiation.

By nature the high-harmonic radiation has an attosecond character because the electrons contributing to the energy cut-off recombine during a very short time interval. By applying a band-pass filter to the high-harmonic spectrum transmitting only the high-energy cut-off without distorting the phase relation attosecond bursts of radiation are created. If the pulse consists of many cycles of similar intensity the recombination process repeats with each half-cycle giving rise to an attosecond pulse train [223]. For few-cycle laser pulses isolated attosecond pulses can be created [224].

The Lewenstein model [225] is the quantum mechanical analog to the three-step model. It is based on the strong-field approximation (SFA), i.e. it neglects excited states and the influence of the Coulomb potential created by the atomic nucleus on the propagation of the electron during its excursion far from the atomic center. In this approximation the cut-off law is slightly modified accounting for the finite tunnel ionization radius [225]

$$E_{\max} \approx 1.3I_p + E_{\max}^{\text{kin}}. \quad (7.7)$$

The more important modification, however, is the presence of interference between trajectories that contribute to harmonics of the same energy. We will find this interference in the high-harmonic spectrum for beryllium and neon subject to few-cycle high-intense laser pulses. Beyond the SFA extensions of the Lewenstein model have been proposed that account for the influence of the atomic Coulomb potential [226, 227].

### 7.1.2. Quantum description

More accurate (and computationally more demanding) calculations of the high-harmonic spectrum can be performed by (approximately) solving the time-dependent Schrödinger equation. The high-harmonic spectrum is determined from the dipole acceleration  $a(t)$  by using the classical Lamor formula

$$I^{\text{HHG}}(\omega) = \frac{2}{3c} \left| \int a(t) e^{i\omega t} dt \right|^2. \quad (7.8)$$

In principle, there are two ways of calculating the dipole acceleration, either by evaluating the double time derivative

$$a(t) = \frac{d^2}{dt^2}d(t) \quad (7.9)$$

of the dipole moment

$$d(t) = \langle \Psi(t) | \sum_{n=1}^N \mathbf{r}_n | \Psi(t) \rangle \quad (7.10)$$

or by evaluating explicitly the expectation value of the acceleration operator via

$$\begin{aligned} a(t) &= -\langle \Psi(t) | \sum_{n=1}^N \frac{\partial V(\mathbf{r}_n)}{\partial \mathbf{r}_n} | \Psi(t) \rangle + NF(t) \\ &= -\int \frac{\partial V(\mathbf{r})}{\partial \mathbf{r}} \rho(\mathbf{r}, t) d\mathbf{r} + NF(t). \end{aligned} \quad (7.11)$$

Both approaches should eventually lead to the same result (which is related to the gauge-invariance of the numerical implementation). This is in fact a stringent test for the convergence of the calculation with respect to space and time discretization as well as box size. Possible differences in a numerical implementation result from the fact that convergent results for the dipole moment require to properly take into account electrons far from the central region which necessitates a large box size and high angular momenta. Convergence of the dipole acceleration calculated via Eq. 7.11, on the other hand, is strongly determined by the core region and necessitates a high resolution at the core as well as a high temporal resolution. The convergence behaviour of the dipole moment and the dipole acceleration is similar to convergence within length and velocity gauge. While convergence within length gauge in general requires a large box and high angular momenta velocity gauge requires good spatial and temporal resolution. From a computational point of view convergence with grid-spacing and time-discretization is easier to achieve. Therefore, using velocity gauge and calculating the acceleration directly via Eq. 7.11 is superior for calculating the high-harmonic spectrum [228].

As discussed in Chapter 2 the direct solution of the time-dependent Schrödinger equation is not possible, especially because HHG targets are usually multi-electron atoms due to their improved conversion efficiency [229]. A variety of approximations have been employed to calculate the time-dependent density and therefrom the dipole acceleration and the high-harmonic spectrum via Eq. 7.8 and Eq. 7.11.

Most prominently, the SAE approximation provided an important contribution to the theoretical understanding of HHG [76]. Meanwhile it has become one of the essential tools in the numerical simulation of HHG. Its simplicity is striking. The central assumption is that only the weakest bound electron interacts with the laser field. To account for the influence of the remaining electron the bare Coulomb potential  $V(\mathbf{r})$  created by the atomic nucleus is replaced by a static model potential  $V^{\text{model}}(\mathbf{r})$  that is tuned to give, e.g., the correct ionization potential [98]. The comparison between all-active-electron and frozen-electron calculations have

shown that the model potential  $V^{\text{model}}(\mathbf{r})$  has to be employed in Eq. 7.11 when calculating high-harmonic spectra via Eq. 7.8 [53]. Even though the SAE neglects doubly excited states and polarization of bound electrons the results obtained are often in good agreement with experiments [230].

The obvious drawback of the SAE approximation is that the dynamical interaction of the active electron with the remaining electrons (absorbed into the static model potential) is completely neglected. For high-intensities the simultaneous excitation of more than one electron, the time-dependent polarization of the bound electrons, and the electron-electron scattering during recollision are the most important contributions that go beyond the SAE approximation. Multi-electron effects have been investigated by exactly solving the two-electron Schrödinger equation [231–233] as well as TDDFT calculations for multi-electron atoms [20]. Comparison with SAE results identified collective effects arising from electronic correlations in the form of discrepancies for specific high-harmonics [17] as well as a lower cut-off predicted by the SAE approximation [19] caused by the missing dynamical screening from emitted electrons. The most advanced calculations of high-harmonic spectra today employ the time-dependent R-matrix method [234], the multiconfigurational Hartree-Fock method [53] as well as TDCI methods [235] (see Chapter 2.2). Within these approaches the response of the bound electrons to the laser field and the rescattered electron is fully taken into account.

The full quantum mechanical treatment of HHG via the solution of the Schrödinger equation allows to verify the ingredients of the semiclassical three-step model. On a qualitative level the three-step model predicts the intensity of the high-harmonic radiation emitted at recombination time  $t_r$  to be approximately

$$I^{\text{HHG}}(t_{\text{rec}}) \propto \dot{N}_{\text{ion}}(t_{\text{ion}})P_{\text{rec}}(t_{\text{rec}}), \quad (7.12)$$

where  $\dot{N}_{\text{ion}}(t_{\text{ion}})$  is the transient ionization rate at ionization time  $t_{\text{ion}}$  and  $P_{\text{rec}}(t_{\text{rec}})$  is the recombination probability at the recombination time  $t_{\text{rec}}$  (see Fig. 7.1). The transient ionization rate can be expressed in terms of the electronic density  $\rho(\mathbf{r}, t)$  at time  $t$  as

$$\dot{N}_{\text{ion}} = \frac{d}{dt} \int_{|\mathbf{r}|>R} \rho(\mathbf{r}, t) d\mathbf{r}, \quad (7.13)$$

with an appropriately chosen cut-off radius  $R$  that should be larger than the tunnelling-ionization radius  $R_t$  and smaller than the quiver radius  $R_q$  to include all electrons involved in the HHG process. The recombination probability  $P_{\text{rec}}$  can be approximated as the probability to find no electron to be ionized

$$P_{\text{rec}} = \int_{|\mathbf{r}_1|<R} \dots \int_{|\mathbf{r}_N|<R} |\Psi(\mathbf{x}_1 \dots \mathbf{x}_N, t)|^2 d\mathbf{x}_1 \dots d\mathbf{x}_N. \quad (7.14)$$

While calculating this quantity in MCTDHF and TDHF is straightforward, it requires more careful consideration within TDDFT and TD-2RDM since the full wavefunction  $\Psi(\mathbf{x}_1 \dots \mathbf{x}_N, t)$  is not available. In TDDFT the ionization probabilities are an unknown (implicit) functional of the density. Approximation usually involve the Kohn-Sham orbitals by approximating the

exact wavefunction with the Slater determinant constructed from the Kohn-Sham orbitals (Eq. 4.8)

$$\Psi^{\text{KS}}(\mathbf{x}_1 \dots \mathbf{x}_N, t) = |\psi_1(\mathbf{x}_1) \dots \psi_N(\mathbf{x}_N)|. \quad (7.15)$$

The validity of this approximation has remained an open question [45, 46]. The TD-2RDM method has the advantage that if triple ionization can be neglected it allows to accurately extract this information from the two-particle density as

$$P_{\text{rec}} = 1 - \int_{|\mathbf{r}|>R} \rho(\mathbf{r}) d\mathbf{r} + \int_{|\mathbf{r}_1|>R} \int_{|\mathbf{r}_2|>R} \rho(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2, \quad (7.16)$$

without invoking any read-out functional.

Further signatures of the three-step model are contained in the time-frequency analysis of the in the high-harmonic spectrum obtained by applying the short-time Fourier transformation

$$I^{\text{HHG}}(\omega, t_r) = \frac{2}{3c} \left| \int w\left(\frac{t-t_r}{\Delta T}\right) a(t) e^{i\omega t} dt \right|^2. \quad (7.17)$$

with the Blackman window function [236]

$$w(t) = \begin{cases} \frac{1-\alpha}{2} + \frac{1}{2} \cos(2\pi t) + \frac{\alpha}{2} \cos(4\pi t) & \text{for } t \in [-1/2, 1/2] \\ 0 & \text{else} \end{cases} \quad (7.18)$$

and  $\alpha = 0.16$  as proposed by Blackman. The time-frequency analysis gives insight at which time high-harmonic radiation of a given frequency is created. The resolution in time and frequency is controlled by the parameter  $\Delta T$ . In the limit  $\Delta T \rightarrow \infty$  all time information is lost and the full high-harmonic spectrum is recovered whereas in the limit  $\Delta T \rightarrow 0$  Eq. 7.17 reduces to the total energy release at time  $t_r$ . Intermediate values for  $\Delta T$  give a compromise between temporal and spectral resolution that is further improved by the continuous first derivative of the Blackman window. The time-frequency analysis allows to identify signatures of classical trajectories in HHG [237] as well as ATI spectra [238].

## 7.2. Strong-field ionization

Although not investigated in detail in this thesis we mention for completeness two other important strong field effects that can be observed for atoms interacting with near-infrared high-intense laser pulses: Above-threshold ionization and non-sequential double ionization. Above-threshold ionization is an effect contained in the kinetic energy spectrum of photoelectrons emitted from atoms subject to strong laser pulses. These spectra are characterized by the presence of two energy cut-offs. The first cut-off at  $2U_p$  is independent of the atomic species and originates from the maximum drift energy the electron can gain from the laser field when ionization happens near to the laser field minimum. The second cut-off can be understood in analogy to the HHG. Like in HHG the electron is first ionized and subsequently accelerated in the laser field. In the third step, however, instead of recombining with the

parent atoms the electron is backscattered and further accelerated in the laser field to kinetic energies of up to  $10U_p$ . Therefore, both processes HHG and ATI are complementary in that they are two different outcomes of the same recollision process.

Beyond recombination with the parent atom and backscattering at the nucleus the electron can scatter off another electron as well. This process enabled by the electron-electron interaction leads to excitation or ionization of the secondary electron [239]. If ionization happens a single emitted electron with high energy is converted into two emitted electrons with lower energy which is the fundamental process of NSDI. This contribution to double ionization competes with multiple ionization caused solely by the strong field without assistance of the recolliding electron. For intensities lower than the tunnel ionization threshold for the singly charged ion NSDI is the dominant double ionization process. For very high intensities capable of ionizing the single charged ion double ionization process is essentially a sequential process. The transition of sequential to NSDI is characterized by the famous knee in the doubly charged ion yield [99–102]. Simulations that investigated the "knee" structure in NSDI have been performed based on the exact solution of the Schrödinger equation for 1D systems [44, 45, 192, 240] and in 3D by employing TDDFT [241–243] and exact solution of two-electron systems [244, 245]. To reproduce the "knee" structure in NSDI within TDDFT both very accurate exchange-correlation functionals [188] as well as accurate read-out functionals are required [189]. With the experimental development of cold-target recoil-ion spectroscopy (COLTRIMS) and electron-ion coincidence NSDI can be studied in much more detail. The observed momentum distribution of the charged ions confirms the classical recollision model of NSDI [246, 247].

### 7.3. HHG in Molecules

While HHG from atomic targets is still the workhorse in technological and scientific applications HHG from molecular targets gives rise to many interesting effects specific to molecules. Initially HHG from molecular targets was mainly devoted towards the optimization of high-harmonic emission. Nowadays the capabilities to read out spatial and temporal information on the molecular structures from the high-harmonic spectra are in the forefront. One essential experimental development was the technique to align molecules by excitation of a rotational wave packet via ultra-fast laser pulses [248].

Conceptually, the three-step model holds for molecular HHG as well. However, recombination of the electron with the molecule gives rise to high-harmonic emission from different atomic centers of the molecule. High-harmonic radiation emitted from different centers interfere and give rise to geometry specific interference patterns superimposed over the high-harmonic spectrum [78, 79]. In the simplest case of diatomic molecules the interference patterns resemble a two-center interference [80, 249]. Beyond geometrical information the so-called tomographic reconstruction of molecular orbitals uses the high-harmonic spectra for different orientations between laser and molecular axis to image the highest-occupied molecular orbital (HOMO) [75]. Beyond the structural information encoded in the alignment dependent high-harmonic spectrum further information can be extracted from the ATI

spectrum at high energies created by the diffractive scattering of the recolliding electronic wave packet. Such experimental techniques are still in their infancy but they promise a sub-Ångström and sub-femtosecond resolution of the (time-dependent) molecular geometry [250].

Computationally the treatment of molecules in strong fields is significantly more demanding compared to atoms. Full ab-initio calculations of molecules in strong fields that take into account the nuclear as well as the electronic degrees of freedom are limited to the  $\text{H}_2^+$ -molecule [251, 252]. The influence of the nuclear dynamics as frequency modulation of the high-harmonic spectrum has been reported [253]. Going to longer wavelengths, the excursion time of the electron comes closer to the time scale of the nuclear motion coupling electronic and nuclear dynamics and giving rise to new interesting effects that can be used to gain temporal information on nuclear dynamics of molecules.

Even within the Born-Oppenheimer approximation the requirement for high spatial resolution within large box sizes in combination with non-central symmetric potentials makes simulations of strong-field processes in multi-electron molecules highly non-trivial. Prolate spheroidal coordinate systems have been employed to treat single photon ionization of diatomic molecules within MCTDHF [129]. Treatments of molecules in NIR fields beyond the  $\text{H}_2$  molecule [124, 254] are largely missing. The development of improved grids with efficient Poisson solvers will be essential to study strong-field effects in molecular systems [131].

The necessity to develop accurate ab initio approaches that account for multi-electron effects is underscored by the observation that in molecular HHG the SAE approximation often breaks down [239, 255]. In molecules not only the highest valence orbitals (HOMO) but also lower lying orbitals contribute to HHG [256–258]. The multi-channel interference from different ionization-recombination pathways leaves a fingerprint in the alignment dependent high-harmonic spectrum whose characteristics allow the identification of multi-electron dynamics [239].

While atoms in strong fields can only be either excited or ionized molecules may break into fragments that can be analyzed and provide a another reaction pathway revealing information on the underlying strong field process. Especially the dissociation of  $\text{N}_2$  following single and double ionization by strong laser pulses has been extensively studied. Most likely the dissociation of  $\text{N}_2$  happens in the channel  $\text{N}_2 \rightarrow \text{N}^+ + \text{N}^+$  [259]. By measuring the kinetic energy of the released fragments two regimes can be identified. High energies originating from the Coulomb explosion following NSDI and lower energies originating from sequential ionization [260].

To circumvent the numerical difficulties arising from the 3D treatment of molecules 1D model potentials are a convenient simplification that capture the essential properties of multi-electron molecules. In Chapter 9 we will apply the TD-2RDM method to the simulation of a 1D model of LiH and study the molecular HHG.



## 8. Simulation of HHG from single atoms

In this Chapter we present the results of the TD-2RDM method as applied to full 3D multi-electron atoms. To benchmark the TD-2RDM theory we use a state of the art MCTDHF implementation published recently [53] as well as TDDFT within LDA employing the Dirac exchange [108] and the VWN80 correlation functional [182] computed via the LIBXC library [261].

The many-body Hamiltonian (Eq. 2.2) of the laser-atom interaction contains the Coulomb potential of the nucleus

$$V(\mathbf{r}) = \frac{Z}{|\mathbf{r}|} \quad (8.1)$$

and (within dipole approximation) the external (laser) potential

$$V^{\text{ext}}(\mathbf{r}, t) = \begin{cases} F(t)z & \text{length gauge} \\ -iA(t)\frac{\partial}{\partial z} & \text{velocity gauge,} \end{cases} \quad (8.2)$$

where  $A(t)$  is the vector potential of the electric field,  $F(t) = -\frac{1}{c}\partial_t A(t)$  and we assume the laser field to be polarized in  $z$ -direction. The gauge invariance of the exact 2RDM equation of motion (Eq. 3.41) is guaranteed by that of the underlying time-dependent Schrödinger equation. The approximate equation of motion (Eq. 5.2) retains it if the employed reconstruction is invariant under unitary transformations of orbitals, which is the case for all the reconstructions discussed here (see Appendix B for more details) Due to the improved numerical efficiency of the velocity gauge for strong-field processes we employ the velocity gauge in all calculations presented in this chapter.

We simulate the atomic response for laser pulses created from a typical Ti:sapphire oscillator after chirped-pulse amplification and compression. Such pulses have a central wavelength of  $\lambda = 800$  nm and are commonly approximated by a  $\sin^2$ -envelop that rise and fall within a few cycles  $N_c$ . The functional form of the pulses employed in this and the following chapter is given by

$$F(t) = F_0 \cos(\omega t) \sin^2\left(\frac{\omega}{2N_c}t\right) \quad 0 \leq t \leq N_c \frac{2\pi}{\omega}, \quad (8.3)$$

where  $F_0$  is the amplitude of the electric field,  $\omega = 2\pi c/\lambda$  is the (mean) angular frequency and one optical cycle at this frequency is about  $T_c = 2,76$  fs. We use the scaled time  $\tau = t/T_c$  with  $0 \leq \tau \leq N_c$ , counting the fractional number of cycles that have passed.

The numerical implementation of the TD-2RDM method requires the simultaneous solution

of the orbital equations of motion (Eq. 6.26) together with the equation of motion for the 2RDM matrix elements (Eq. 6.27). The time propagation of the orbitals is performed using a second-order split-step method treating the one-body part  $h_1$  and the part containing the electron-electron interaction in orbital equations of motion (Eq. 6.26) separately. The angular part of the orbital equations of motion is solved by expanding the orbitals in spherical harmonics with a maximum angular momentum of  $L_{\max}$ . The radial part of the orbital equations of motion is numerically solved by employing a finite-element discrete variable representation. Further details on the numerical implementation can be found in Section 6.2.

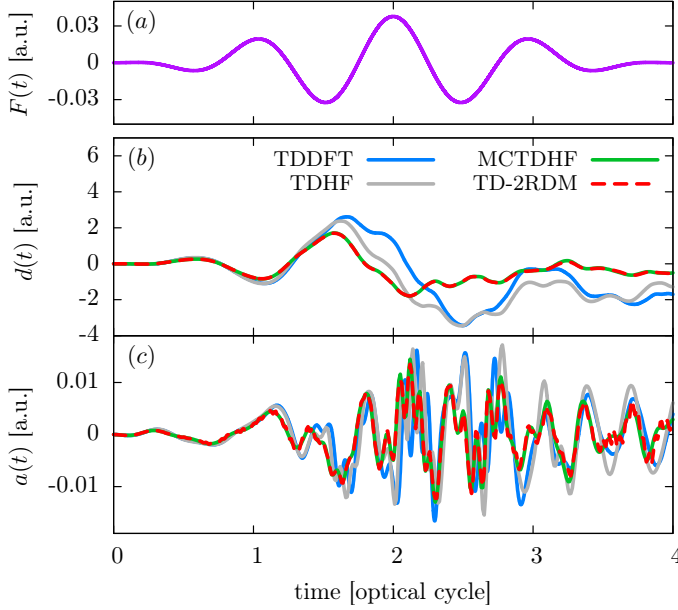
As mentioned in Subsection 7.1.2 convergence for the dipole moment and the dipole acceleration is controlled by different parameters. The dipole moment requires a large box size and a large maximum angular momentum of  $L_{\max}$  whereas the dipole acceleration requires good temporal and spatial resolution. To achieve the convergent results for the dipole acceleration presented in this chapter we employ a maximal angular momentum of  $L_{\max} = 47$ , a box size of 200 a.u., a time step of 0.0055 a.u. and a radial discretization of 50 finite elements with 20 basis points each. Absorbing boundary conditions are implemented by a  $\cos^{\frac{1}{4}}$  mask function starting at a radius of 160 a.u. with a transition length of 40 a.u. .

For a box size of 200 a.u. as chosen in our simulation the dipole moment  $d(t)$  calculated directly via Eq. 7.10 is not converged due to the missing contribution of the electrons that are absorbed in the absorbing boundary conditions. Since those absorbed electrons contribute with a large dipole moment (due to their large distance from the core) their missing contribution has a strong influence on Eq. 7.10. A convenient alternative is to calculate the dipole moment via the double time integral of the dipole acceleration

$$d(t) = \int_0^t \int_0^{t'} a(t'') dt'' dt'. \quad (8.4)$$

In this way the dipole contribution of absorbed electrons is fully taken into account while their acceleration is neglected. To be precise, only the acceleration in the Coulomb potential of the atomic nucleus is neglected (the acceleration in the laser field is given exactly by  $NF(t)$ , see Eq. 7.11). This approximation is well justified for the box size of 200 a.u. .

The propagation in imaginary time is employed to determine the MCTDHF ground state which also serves as the initial state for the TD-2RDM propagation. It should be noted that the "exact" MCTDHF ground state is, in general, not a stationary solution of the closed 2RDM equation of motion (Eq. 5.2) due to the finite error in the reconstruction. However, provided that the reconstruction is sufficiently accurate, the 2RDM of the MCTDHF ground state is close to the stationary solution of Eq. (5.2) and can be further improved upon by projecting out the residual excitations by time averaging over a field-free propagation (see Section 6.3).



**Figure 8.1.: Beryllium subject to a laser pulse of moderate intensity.** (a) The electric field  $F(t)$  (Eq. 8.3) of the four-cycle laser pulse with intensity  $I = 0.5 \times 10^{14} \text{W/cm}^2$  employed for the simulation of (b) the dipole moment  $d(t)$  (Eq. 8.4) and (c) the dipole acceleration  $a(t)$  (Eq. 7.11). The TD-2RDM method employing the contraction-consistent Nakatsuji-Yasuda reconstruction is compared to MCTDHF, TDHF, and TDDFT within LDA. The TD-2RDM propagation is performed without purification.

## 8.1. Beryllium

As the first application we study the nonlinear dipole response of beryllium subject in two different intensity regimes. As representative for moderate intensities we simulate beryllium in a four-cycle laser pulse with  $I = 0.5 \times 10^{14} \text{W/cm}^2$ . To simulate strong ionization accompanied by intense HHG we employ a two-cycle laser pulse with  $I = 4.0 \times 10^{14} \text{W/cm}^2$ . We find that the propagation of the TD-2RDM is stable in the moderate intensity regime even without purification while for the strong intensity regime purification is required to obtain stable results.

### 8.1.1. Moderate intensities

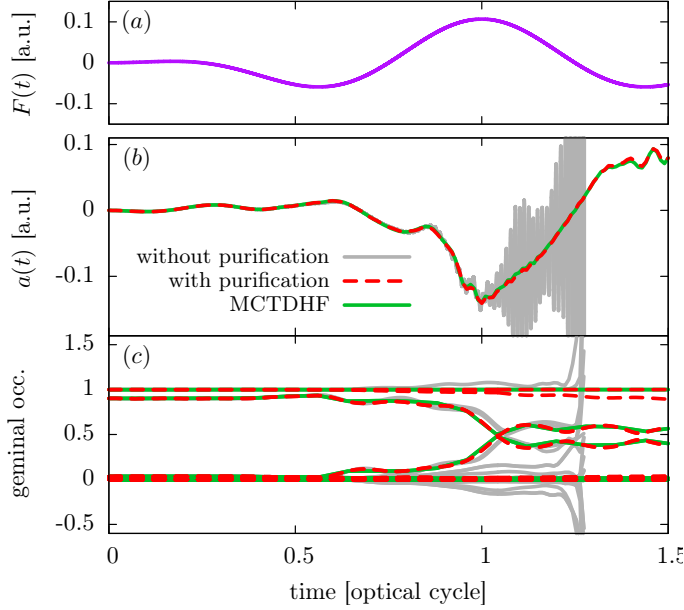
Due to the low ionization potential of beryllium  $I_p = 0.34$  a.u. the strong field regime is reached with comparable small pulse intensities. For a pulse with intensity  $I = 0.5 \times 10^{14} \text{W/cm}^2$  the Keldysh parameter (Eq. 7.3) is  $\gamma = 1.25$  and ionization after the four-cycle pulse [Fig. 8.1 (a)] measured by the probability to find exactly one particle outside a radius of  $R = 20$  a.u. is  $I^{(1)} = 11.2\%$ . The double ionization probability is significantly smaller with  $I^{(2)} = 0.35\%$ . The values extracted from the TD-2RDM calculation (neglecting triplet ionization) via the functionals

$$I^{(1)} = \int_{|\mathbf{r}|>R} \rho(\mathbf{r}) d\mathbf{r} - 2 \int_{|\mathbf{r}_1|>R} \int_{|\mathbf{r}_2|>R} \rho(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2, \quad (8.5)$$

$$I^{(2)} = \int_{|\mathbf{r}_1|>R} \int_{|\mathbf{r}_2|>R} \rho(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2, \quad (8.6)$$

are very similar with  $I^{(1)} = 11.0\%$  and  $I^{(2)} = 0.38\%$ .

More details on the time-dependent dynamics are contained in the dipole oscillation. Due



**Figure 8.2.: Influence of purification on the TD-2RDM method.**

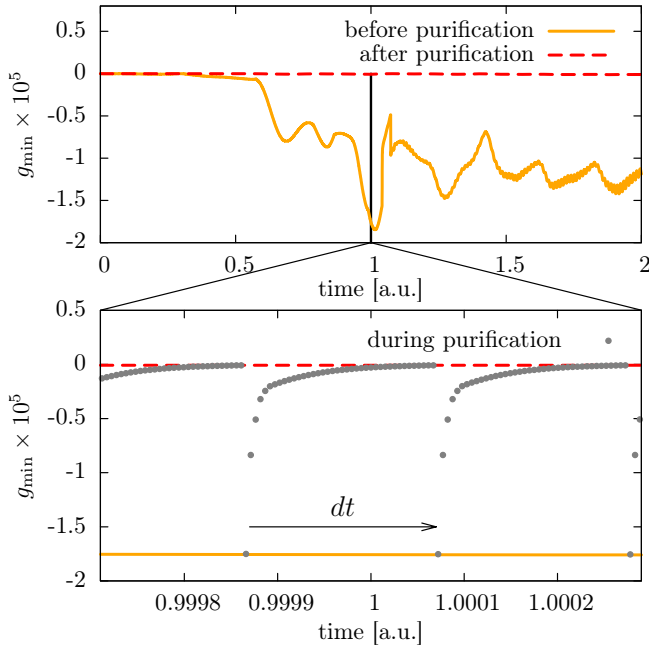
(a) The electric field  $F(t)$  of the two-cycle laser pulse with intensity  $I = 4.0 \times 10^{14} \text{W/cm}^2$ . (b) The dipole acceleration within the TD-2RDM method with and without purification compared to the MCTDHF reference calculation. (c) The time dependence of the geminal occupation numbers  $g_i$  (Eq. 3.19). The divergence in the dipole acceleration [shown in (b)] coincides with the divergence of the geminal occupation numbers [shown in (c)]. The purification fully restores stability.

to the spherical symmetry of the ground state the initial dipole moment is zero. In the presence of the laser pulse the atom gets polarized and the dipole moment starts to oscillate [Fig. 8.1 (b)]. Initially the dipole moment nearly adiabatically follows the electric field of the external laser pulse but soon after the first cycle nonlinear effects manifest themselves through the appearance of multiple frequencies. The very good agreement between the TD-2RDM method and MCTDHF shows that the TD-2RDM method is capable to accurately describe this kind of driven electron dynamics. In contrast, TDDFT and the TDHF methods show marked deviations especially after the peak at  $\tau \approx 1.5$  which marks the onset of (moderate) ionization.

While the dipole moment is very sensitive to the contribution of emitted electrons the dipole acceleration probes the local dynamics near the atomic center. The initiated oscillations in the dipole acceleration [Fig. 8.1 (c)] arise from the density fluctuations created by the superposition of several excited states. The good agreement between the TD-2RDM method and MCTDHF shows that this excitation process is accurately described. Also the mean-field methods TDDFT and TDHF are capable to reproduce the overall oscillatory pattern while the magnitude of the individual oscillation is slightly off.

### 8.1.2. High intensities without purification

We now increase the laser intensity to  $I = 4.0 \times 10^{14} \text{W/cm}^2$  and reduce the number of cycles from four to two. This pulse shape [Fig. 8.2 (a)] features one prominent central peak that leads to strong ionization. After the pulse the exclusive ionization probabilities are  $I^{(1)} = 51.7\%$  and  $I^{(2)} = 47.3\%$ . The Keldysh parameter for this pulse is given by  $\gamma = 0.44$  indicating that the ionization mechanism is dominated by tunnel ionization. Under such conditions the propagation of the 2RDM without purification fails. Shortly after the

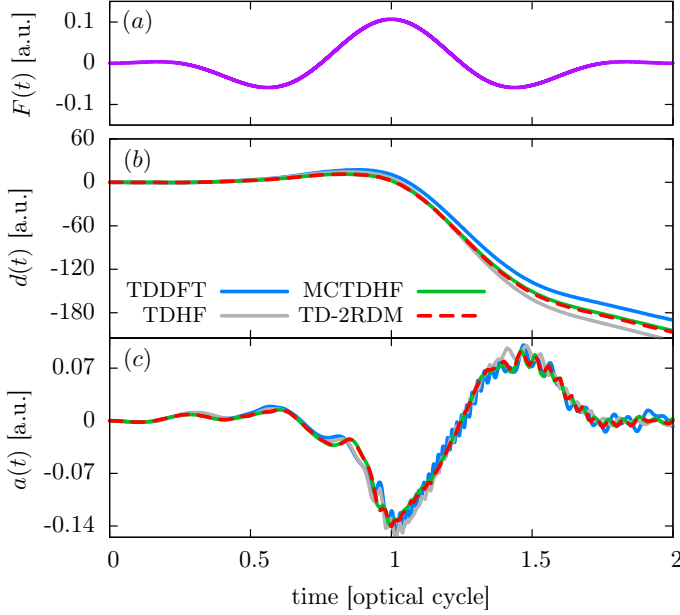


**Figure 8.3.: Details of the purification applied in Fig. 8.2.** The smallest geminal eigenvalue  $g_{\min}$  before and after the purification procedure for each time step of the simulated time-interval. The lower panel shows a close-up of the region with largest N-representability violation at  $\tau \approx 1$ . The grey dots depict the smallest geminal eigenvalue  $g_{\min}$  at each iteration of the purification. Convergence is achieved within 40 iterations. The time-interval between the propagation steps is indicated by an arrow with label  $dt$ . The process is repeated after every time step  $dt$ .

maximum of the central peak the dipole moment starts to oscillate and diverges [Fig. 8.2 (b)]. The origin of this instability can be unravelled as follows: With the onset of strong ionization the correlation (measured by the norm of the two-particle cumulant) increases. This increase in correlation reduces the accuracy of the 3RDM reconstruction functional which leads to error accumulation and violation of N-representability in the 2RDM. We find that at the time of divergence the geminal occupation numbers decrease and become strongly negative [Fig. 8.2 (c)]. Without a procedure to restore N-representability the TD-2RDM method would fail. As described in Section 5.3 the purification scheme allows to enforce a set of known necessary N-representability conditions and thereby stabilize the results obtained within the TD-2RDM method.

### 8.1.3. High intensities with purification

The purification is an *a posteriori* applied procedure that counteracts the N-representability violation during the self-contained propagation of the 2RDM (Eq. 5.2). It is an iterative process that successively leads to a reduction of negative geminal occupation numbers until they eventually approach zero (from below) (see Section 5.3). The iterative improvement is demonstrated in Fig. 8.3. We find that the violation of N-representability measured by the smallest geminal occupation number is not uniform during the simulation. As expected (qualitatively) the larger the error in the reconstruction the larger the violation of N-representability. To ensure convergence of the purification the total number of iterations has to be adapted to the largest violation of N-representability. For beryllium within the two-cycle laser pulse choosing 40 iterations is sufficient to purify the largest violation occur-



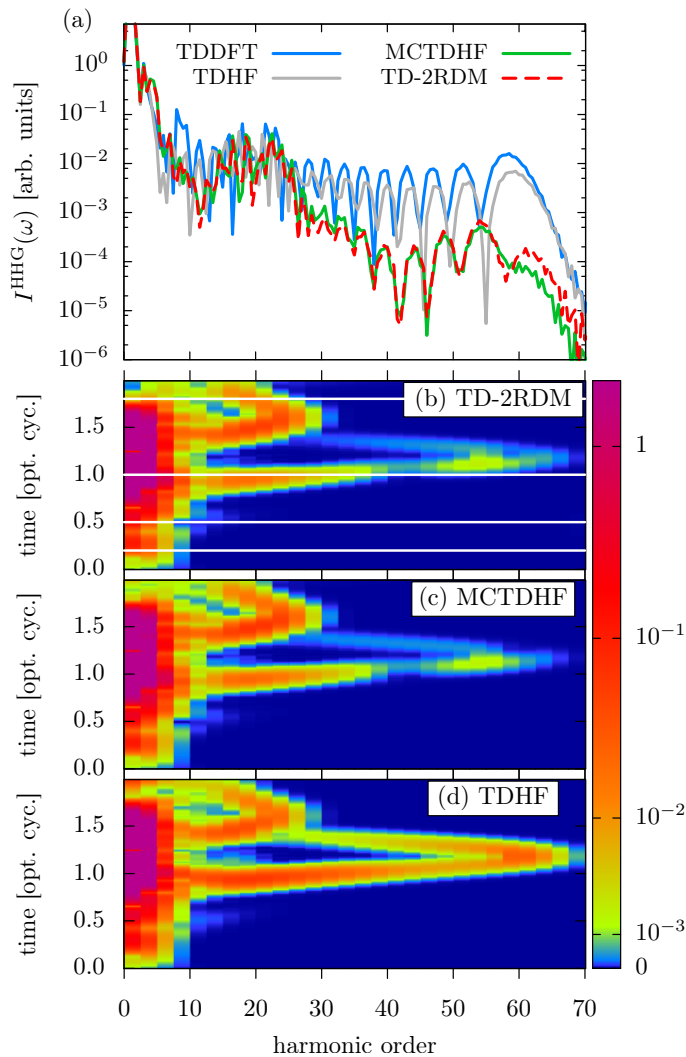
**Figure 8.4: Beryllium subject to a laser pulse of strong intensity.** (a) The electric field of the two-cycle laser pulse with intensity  $I = 4.0 \times 10^{14} \text{W/cm}^2$  employed to simulate (b) the dipole moment and (c) the dipole acceleration. Except for the shape and strength of the laser pulse the simulation parameters are the same as in Fig. 8.1. The TD-2RDM purification is performed with 40 iterations after each propagation steps.

ring at time  $\tau \approx 1$  (Fig. 8.3).

By employing the purification the quality of the TD-2RDM result can be drastically improved. Not only is the instability avoided also the agreement with the MCTDHF reference calculation is very good (Fig. 8.4). The slope in the dipole moment originates from emitted electrons that ultimately acquire a large excursion radius and, therefore, contribute strongly to the dipole moment [Fig. 8.4 (b)]. For the calculation of the high-harmonic spectrum the dipole acceleration is more relevant. The Fourier transformation (Eq. 7.8) of the dipole acceleration [Fig. 8.4 (c)] leads to the high-harmonic spectrum shown in [Fig. 8.5 (a)]. While the dipole acceleration is in overall good agreement among all investigated methods [Fig. 8.4 (c)] the high-harmonic spectrum shows a clear overestimation of TDDFT and TDHF while the TD-2RDM method is in very good agreement with the MCTDHF simulation [Fig. 8.5 (a)].

### Traces of the three-step model

To further investigate the structure of the high-harmonic radiation we perform a time-frequency analysis by applying the short-time Fourier transformation (Eq. 7.17) with  $\Delta T = 0.2$  a.u. [Fig. 8.5 (b, c, d)]. The structure of the time-frequency behaviour of the high-harmonic radiation shows clear signatures of the three-step model. High-harmonic radiation above the first ionization threshold (6th harmonic) is created during two bursts representing two recollision events. The first event is generated by recombination of electrons that have been accelerated in the strong central peak ( $\tau \approx 1$ ) of the two-cycle laser pulse [Fig. 8.4 (a)], and the second event by recombination of electrons accelerated in the subsequent smaller peak ( $\tau \approx 1.5$ ). While the first recollision is high in energy its intensity is modest due to the small ionization rate during the first oscillation of the laser pulse ( $\tau \approx 0.5$ ) when the trajectories that contribute to the energy cut-off are born [Fig. 8.6 (c)]. The second recoli-

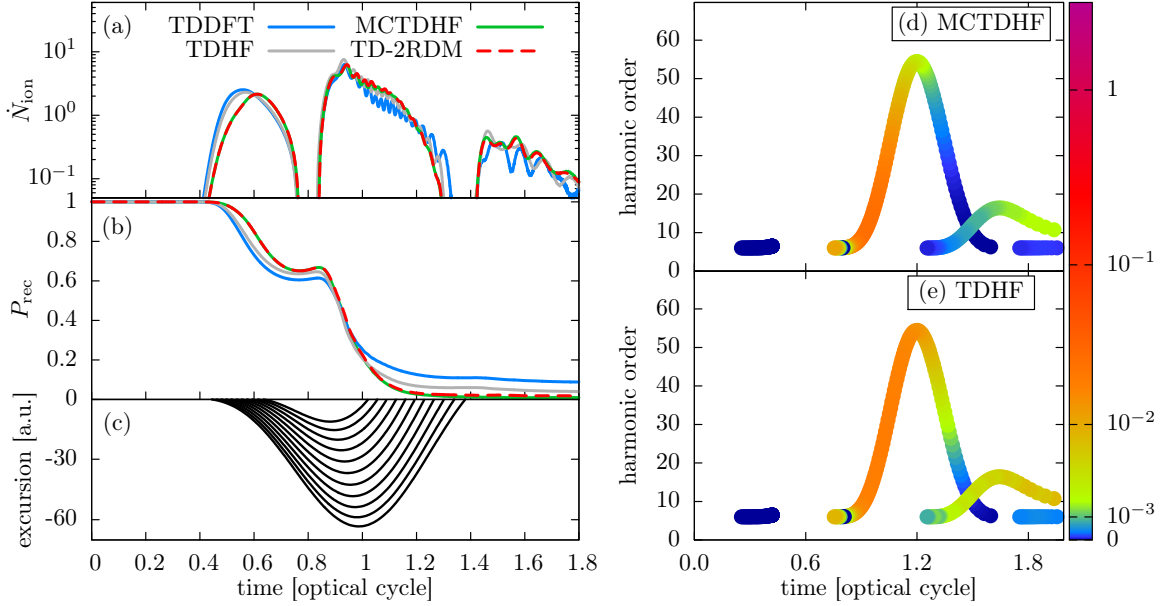


**Figure 8.5.: High-harmonic generation from beryllium.** (a) High-harmonic spectrum  $I^{\text{HHG}}(\omega)$  (Eq. 7.8) of beryllium calculated from the dipole acceleration depicted in Fig. 8.4 (c) compared among various methods. The time-frequency analysis of the high-harmonic spectrum calculated via Eq. 7.17 from (b) the TD-2RDM, (c) the MCTDHF, and (d) the TDHF simulation. The four white lines mark times  $\tau = 0.2$ ,  $\tau = 0.5$ ,  $\tau = 1.0$  and  $\tau = 1.8$  at which snapshots of the particle-hole distribution are taken in Fig. 8.8.

sion while lower in energy features a higher intensity due to the high ionization rate during the strong central peak ( $\tau \approx 1$ ) that gives birth to the trajectories of the second recollision event. Obviously, high-harmonic radiation with energy near the cut-off is generated during the first recollision.

In agreement with the results for the high-harmonic spectrum itself we find that the TD-2RDM method is capable of reproducing almost perfectly the MCTDHF time-frequency distribution [Fig. 8.5 (b, c)]. Comparing the time-frequency spectrum of the TDHF result with the MCTDHF result shows a pronounced overestimation during the first recollision [Fig. 8.5 (c, d)]. To unravel this discrepancy we approximate the intensity of the high-harmonic radiation according to Eq. 7.12. Focusing on trajectories that contribute to the high-energy cut-off [Fig. 8.6 (c)], the ionization rate at the birth times of these high-energy trajectories [Fig. 8.6 (a)] gives a qualitative prediction for the HHG yield at the energy cut-off. For TDDFT and TDHF these ionization rates are slightly enhanced compared to



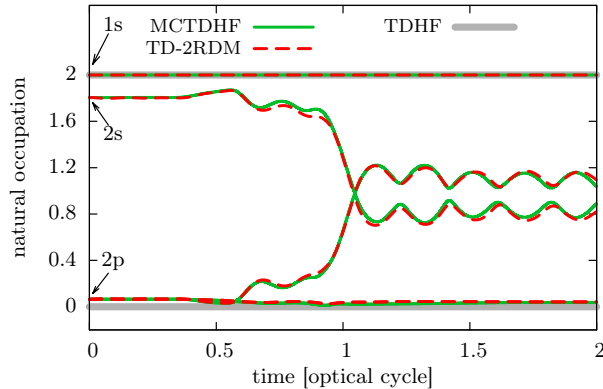


**Figure 8.6.:** Estimate for the high-harmonic yield based on the three-step model. According to Eq. 7.12 the intensity of the high-harmonics can be estimated from (a) the number of electrons ionized per time interval  $\dot{N}_{\text{ion}}(t_{\text{ion}})$  (Eq. 7.13) and (b) the recombination probability  $P_{\text{rec}}$  (Eq. 7.14). The trajectories that contribute to the high-energy cut-off are shown in (c). (d) and (e) show the recombination energy  $E_{\text{rec}} = I_p + E_{\text{kin}}$  of classical trajectories as a function of the recombination time  $t_r$  color-coded with the corresponding estimate for the high-harmonic yield.

MCTDHF resulting in an overestimated high-harmonic yield. In addition, the recombination probability (measured by the survival probability of the neutral) at times when the high-energy trajectories return is larger in TDDFT and TDHF compared to MCTDHF [Fig. 8.6 (b)]. While initially the overestimated ionization rate is visible as the increased decay of the survival probability further ionization is suppressed for  $\tau > 1$  [Fig. 8.6 (b)]. This suppression of ionization is caused by the missing screening contribution from emitted electrons. When the electron density near the core is reduced the unscreened bare Coulomb potential of the nucleus effectively stops further ionization. Both effects, the increased ionization rate and the increased recombination probability lead to the overestimated high-harmonic yield. Both quantities  $\dot{N}_{\text{ion}}(t_i)$  and  $P_{\text{rec}}(t_r)$  from the TD-2RDM method are in excellent agreement with the MCTDHF calculation [Fig. 8.6 (a, b)].

Plotting the recombination energy  $E_{\text{rec}} = I_p + E_{\text{kin}}$  (ionization plus kinetic energy) as a function of time in combination with the high-harmonic yield estimated via Eq. 7.12 reproduces, qualitatively, the time-frequency spectrum of the MCTDHF and TDHF calculation [compare Fig. 8.6 (d, e) and Fig. 8.5 (c, d)]. Further a close comparison of the recombination energies predicted by the three-step model [Fig. 8.6 (d)] and the quantum calculation [Fig. 8.5 (c)] reveals a small shift to slightly higher cut-off energies in the quantum mechanical calculation. This shift is most likely caused by two different effects. First, the semiclassical result for the recombination energy of the three-step model is modified if quantum mechanical corrections



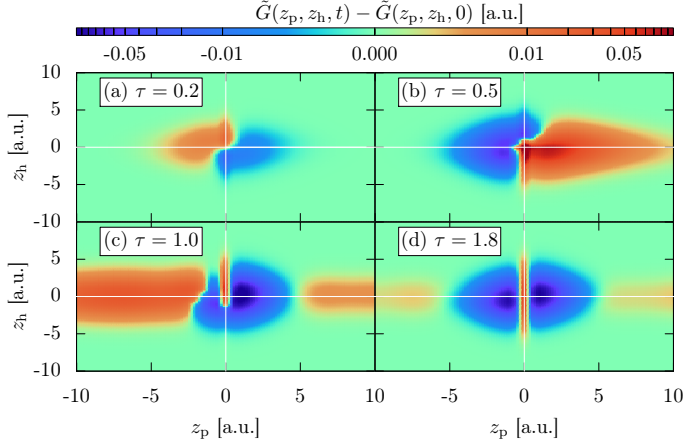


**Figure 8.7.:** Time-dependent natural occupation numbers during process depicted in Fig. 8.4. The initial orbital character ( $1s, 2s, 2p$ ) of the natural orbitals is indicated. In TDHF and TDDFT the wavefunction is represented by a single Slater determinant with fixed natural occupation numbers of either 2 or 0.

are properly taken into account. On the simplest level this modification is described by the Lewenstein model and predicts a slightly larger recombination energy (Eq. 7.7) compared to the standard three-step model. Second, since double ionization of beryllium is significant at these intensities the returning electron might encounter a less screened atomic Coulomb potential and is thus more strongly accelerated towards the atomic center. This increased acceleration expresses itself in an increased energy release.

### Time-dependent natural orbital occupation

From the discussion above we can conclude that accurate ionization probabilities are pivotal for accurate simulation of HHG. The good performance of the TD-2RDM method is based on the ability to represent dynamically varying orbital occupation numbers. This feature becomes particularly important for atoms with small ionization potentials such as beryllium. The time dependence initiated in the natural occupation numbers is a signature of the strong ionization taking place (Fig. 8.7). Separating one electron from the atom completely while all other electrons remain bound requires the occupation of the initial  $2s$  orbital to drop from two to about one [123] (Fig. 8.7). On the level of the TD-2RDM method this time-dependent population transfer is correctly described, whereas in TDDFT and TDHF the occupation numbers remain fixed (in the present case to two) which leads to artificially enhanced double ionization whenever single ionization occurs [262]. The, at first glance, somewhat counterintuitive consequence of the coupling between single and double ionization is that the overall probability for ionization is reduced. This follows from the "contamination" of pure single ionization by ionization of the second more deeply bound electron with binding energy of the second ionization potential. The variation of the natural occupation numbers is one of the essential features that cannot be easily reproduced by mean-field theories. Although the ionization process may seem, at first glance, to be a rather uncorrelated process it is in fact characterized by the correlated dynamics encoded in the natural orbital occupation numbers. The ability to account for such correlations is key to the success of the TD-2RDM method.



**Figure 8.8.: Correlated particle-hole dynamics during process depicted in Fig. 8.4.** Laser field induced deviation from the equilibrium particle-hole distribution function  $\tilde{G}^{\text{ph}}(z_p, z_h, t) - \tilde{G}^{\text{ph}}(z_p, z_h, 0)$  (Eq. 8.7) (note the logarithmic color scale). The times of the snapshots shown are marked in Fig. 8.5 (b).

### Particle-hole dynamics in HHG

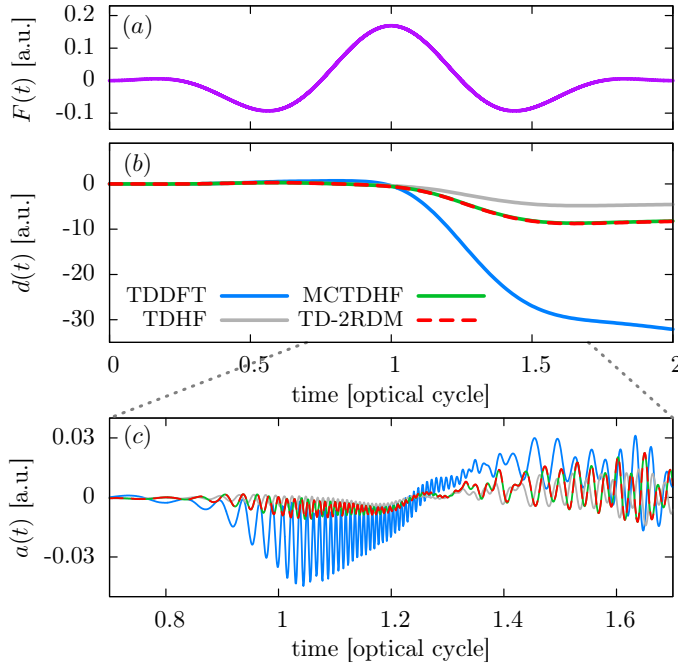
The present TD-2RDM method allows to explore also subtle many-body effects in the HHG process not easily extractable from single-particle or mean-field descriptions. To this end, we analyse the time evolution of the joint particle-hole distribution function

$$\tilde{G}(z_p, z_h) = \langle z_p \uparrow, z_h \downarrow | \mathcal{K}_2 G_{12} \mathcal{K}_2 | z_p \uparrow, z_h \downarrow \rangle, \quad (8.7)$$

where  $G_{12}$  is the particle-hole reduced density matrix (Eq. 3.97) and

$$\mathcal{K} = \sum_i |\phi_i^g\rangle \langle \phi_i^g| \quad (8.8)$$

is the projection operator onto the initial ground state orbitals  $\phi_i^g$ . The distribution function  $\tilde{G}(z_p, z_h)$  measures the probability to find a particle at  $z$ -coordinate  $z_p$  while leaving a hole of opposite spin in the ground state with  $z$ -coordinate  $z_h$ . We show the laser induced particle-hole dynamics by snapshots of the deviation from the equilibrium particle-hole distribution (Fig. 8.8). The snapshot at  $\tau = 0.2$  shows the polarization of the atom under the influence of the first weak maximum of the two-cycle laser pulse [Fig. 8.8 (a)]. Since the negatively charged particles and the positive holes move under the influence of the electric field in opposite directions, the joint particle-hole distribution is displaced to negative  $z_p$  and positive  $z_h$ , i.e. is polarized. The subsequent minimum of the laser pulse at  $\tau = 0.5$  coincides with the onset of ionization eventually leading to the creation of high-harmonic radiation upon recollision with the parent ion around the time  $\tau = 1.0$ . While the dependence of the joint particle-hole distribution on the particle coordinate closely mirrors the excursion from and return to the core as predicted by the (one-particle) three-step model, the residual hole does not remain frozen but dynamically responds to the motion of the ionized particle and the external field. The hole coordinate performs oscillations phase-shifted by  $\pi$  respective to the particle coordinate thereby enhancing the nonlinear dipole response of the atom [Fig. 8.8 (b, c)]. Near the end of the laser pulse at  $\tau = 1.8$  the particle-hole distribution deviates from its initial state predominantly due to emitted electrons missing in the the outer shell with  $|z_p| > 1$  [Fig. 8.8 (d)]. Conversely these emitted electrons have created holes which enhance the particle-hole distribution near the core ( $|z_p| < 1$ ).

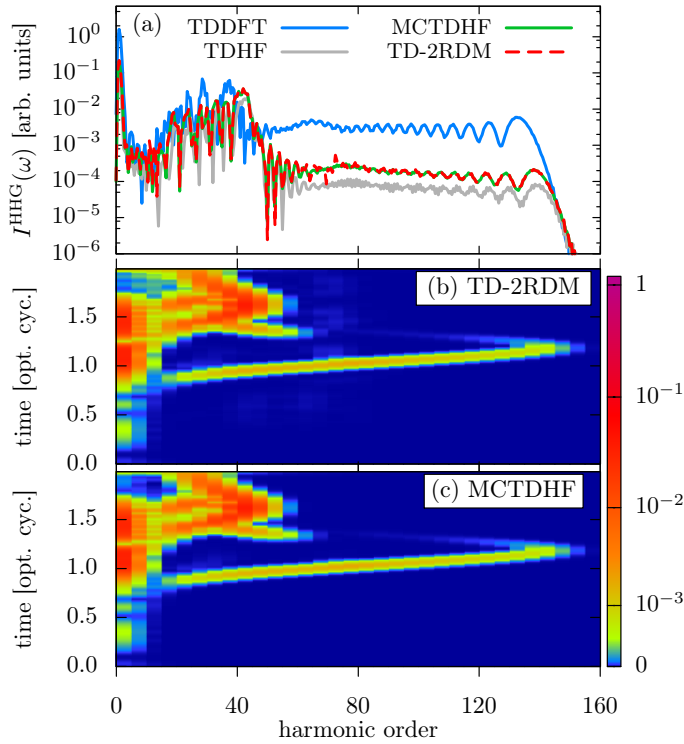


**Figure 8.9.: Electronic response of neon subject to a strong laser pulse.** (a) The electric field  $F(t)$  of the four-cycle laser pulse with intensity  $I = 10^{15}\text{W}/\text{cm}^2$  employed for the simulation of (b) the dipole moment  $d(t)$  and (c) the dipole acceleration  $a(t)$ . In analogy to the simulation of beryllium in the weak regime (Fig. 8.1) the TD-2RDM simulation employs the contraction-consistent Nakatsuji-Yasuda reconstruction, the TDDFT simulation uses LDA and the TD-2RDM propagation is performed without purification.

## 8.2. Neon

As the next application we investigate HHG from a single atom of a neon gas target. HHG in neon is of great importance as it is used as the workhorse for the generation of attosecond pulses [72]. Due to the larger ionization potential of neon  $I_p = 0.79$  the harmonic cut-off is shifted to high frequencies allowing for generation of XUV pulses with energies of up to 100 eV [72]. Ab-initio descriptions of this process are challenging as up to 10 active electrons need to be treated. To simulate HHG in neon we employ the same shape of the laser pulse as depicted in [Fig. 8.4 (a)] but with increased intensity  $I = 10^{15}\text{W}/\text{cm}^2$  [Fig. 8.9 (a)]. The large ionization potential of neon requires a higher intensity to enter the strong field regime. The Keldysh parameter for  $I = 10^{15}\text{W}/\text{cm}^2$  at  $\lambda = 800\text{nm}$  is  $\gamma = 0.42$ . Within this laser pulse the single and double ionization probabilities from MCTDHF are  $I^{(1)} = 7.25\%$  and  $I^{(2)} = 0.11\%$  to which the ionization probabilities from the TD-2RDM method are in very good agreement  $I^{(1)} = 7.35\%$  and  $I^{(2)} = 0.11\%$ . The moderate ionization yield is reflected in the occupation numbers of the natural orbitals which do not change strongly over time. This allows the present TD-2RDM simulation to be performed even without purification (similar to beryllium at low intensities, see Section 8.1.1).

The dipole moment within the TD-2RDM method is in excellent agreement with the MCTDHF calculation [Fig. 8.9 (b)]. Qualitatively, the response of the dipole moment of neon shows the same slope starting at  $\tau \approx 1$  as for the beryllium atom [Fig. 8.4 (b)]. This slope signifies the large excursion of the emitted electron driven by the peak electric field near  $\tau \approx 1$ . Based on the different steepness of the slope among MCTDHF, TDDFT and TDHF we can conclude that the ionization rate of TDDFT is much higher compared to MCTDHF while ionization rate of TDHF is much smaller [Fig. 8.9 (b)]. Within TDDFT using LDA the

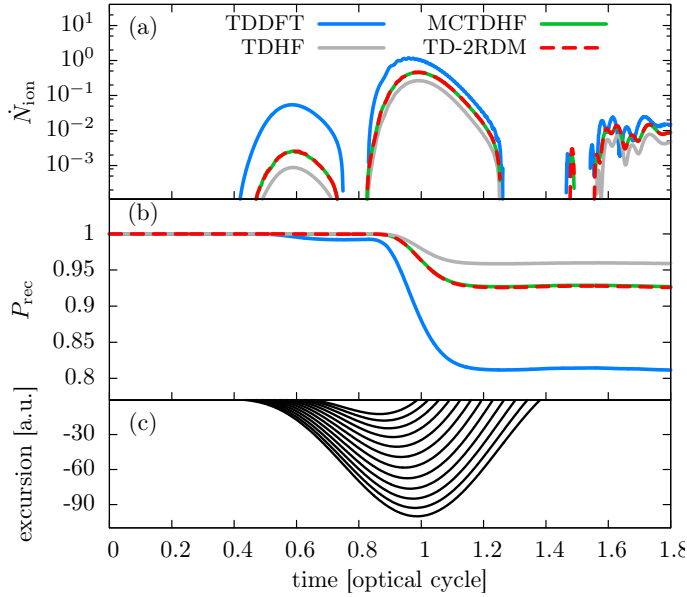


**Figure 8.10.: High-harmonic generation from neon.** (a) High-harmonic spectrum  $I^{\text{HHG}}(\omega)$  (Eq. 7.8) of neon calculated from the dipole acceleration depicted in Fig. 8.9 (c) compared among various methods. The time-frequency analysis of the high-harmonic spectrum calculated via Eq. 7.17 from (b) the TD-2RDM, and (c) the MCTDHF simulation.

overestimation of the ionization rate is a known deficiency that originates from the wrong asymptotic behaviour of the exchange-correlation functional. Corrections of these so called self-interaction effects inherent to LDA are necessary to ensure the proper Rydberg-series and more accurate ionization probabilities.

The large central peak of the laser pulse near  $\tau \approx 1$  not only leads to further ionization but also accelerates electrons ionized during the previously laser cycle to high energies. The recollision of these high-energy electrons is clearly visible in the dipole acceleration as a chirped oscillation [Fig. 8.9 (c)]. Via Eq. 7.8 the dipole acceleration determines the high-harmonic spectrum. We find very good agreement between the TD-2RDM method and MCTDHF for the total high-harmonic spectrum [Fig. 8.10 (a)]. As expected from the results for the dipole moment [Fig. 8.9 (b)] the higher (lower) ionization rate predicted by TDDFT (TDHF) leads to an overestimation (underestimation) of the HHG yield. Explicit evaluation of the ionization rate via Eq. 7.13 confirms that at the birth times of high-energy trajectories the ionization rate within TDDFT (TDHF) is overestimated (underestimated). In principle, the HHG yield (Eq. 7.12) depends also in the recombination probability (Eq. 7.14), however, since in the present case ionization is small ( $P_{\text{rec}} \approx 1$ ) the dynamical variation of the recombination probability is less important.

Additionally to the HHG spectrum we investigate the time-frequency spectrum of the high-harmonic radiation. We find very good agreement between the TD-2RDM and the MCTDHF result [Fig. 8.10 (b, c)]. In analogy to the time-frequency spectrum of beryllium (Fig. 8.5) the peak structure of the laser pulse is reflected in two recollision events clearly visible in the



**Figure 8.11.: Ingredients for the estimate of the high-harmonic yield based on the three-step model.** According to Eq. 7.12 the intensity of the high-harmonics can be estimated from (a) the number of electrons ionized per time interval  $\dot{N}_{\text{ion}}$  (Eq. 7.13) and (b) the recombination probability  $P_{\text{rec}}$  (Eq. 7.14). The trajectories that contribute to the high-energy cut-off are shown in (c).

time-frequency spectrum. The rising edge of the first recollision peak near  $\tau \approx 1$  represents the chirp in the acceleration [Fig. 8.9 (c)].

According to the three-step model for each energy below the high-harmonic cut-off there are two trajectories that contribute with equal energy, a long and a short trajectory. Since the excursion time is different for both trajectories they contribute with different phases causing the appearance of an interference pattern in the high-harmonic spectrum. While the high-harmonic spectrum of beryllium features pronounced oscillations in the plateau region due to this interference between short and long trajectories [Fig. 8.5 (a)] the plateau region of the high-harmonic spectrum of neon is almost flat [Fig. 8.10 (a)]. The time-frequency spectrum reveals that only short trajectories contribute. The missing contribution from long trajectories arise from two factors. First the ionization rate at the birth times of long trajectories is smaller due to the  $\sin^2$  envelope that favours ionization at later times when the short trajectories are born [Fig. 8.11 (a)]. Second, the spreading of the emitted electron wave-packet during the excursion in the long trajectories is more pronounced and leads to a reduction of the recombination probability.



## 9. Simulation of HHG from diatomic molecules

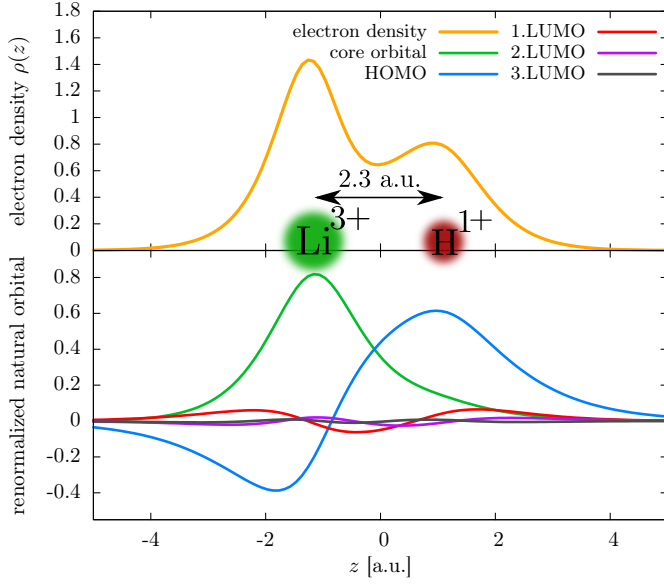
In this chapter we present the application of the TD-2RDM method to the simulation of HHG from a 1D LiH molecule in strong few-cycle laser pulses. While for atoms the rotational symmetry of the nuclear potential can be exploited to reduce the numerical effort by expansion in spherical harmonics such specified coordinate systems are in general not available for the 3D treatment of molecules in strong laser pulses. To circumvent the numerical difficulties arising from the 3D treatment of molecules we employ the aligned electron model. Within the aligned electron model the 3D electrostatic interaction is replaced by a 1D soft-Coulomb interaction corresponding to electrons whose movement is restricted to a line that is aligned with the polarization of the driving laser field ( $z$ -axis). This 1D model for molecules serves as a numerically efficient testing ground for full 3D calculations and has been used in the past to study various effects such as the double ionization of He [263] and H<sub>2</sub> [264] and the response of LiH in strong laser fields [52, 265]. Further we treat the molecule in Born-Oppenheimer approximation. Nuclear dynamics beyond the Born-Oppenheimer approximation takes place on the time scale of a few tens of femtoseconds which is longer than the laser pulses employed in this chapter. These effects are not within the scope of the present thesis.

We have chosen LiH since it displays a complex and rich multi-electron dynamics including ionization and, in particular, two-Coulomb-center effects, while still being numerically exactly solvable employing the MCTDHF method which allows to accurately benchmark the TD-2RDM method. To identify the role of multi-electron effects we compare also to TDHF and TDDFT calculations. We find enhancement and suppression of specific frequencies in the high-harmonic spectrum due to interference of high-harmonic radiation emitted from different atomic centres.

### 9.1. LiH within the aligned electron model

The numerical effort to solve the many-body problem can be significantly reduced by restricting the dimensionality of the electronic wavefunction. Within the aligned electron model the electrons move on a line ( $z$ -axis) with offset  $c$  from the nuclear center. Thereby the 3D electrostatic interaction is replaced by a 1D soft-Coulomb interaction [266]

$$V(z) = V^{\text{Li}}(z) + V^{\text{H}}(z) \tag{9.1}$$



**Figure 9.1.: Electron density of the LiH ground state.** The equilibrium bond length  $z_{\text{Li-H}} = 2.3$  between the Li nucleus and the proton is depicted. Additionally the renormalized natural orbitals (Eq. 4.13) of the ground state are shown in the lower panel. While the core orbital of the lithium atom is responsible for the peak of the electron density near the lithium nucleus the valence orbital (HOMO) is spread over the whole molecule and polarized toward the hydrogen core. Three of the lowest unoccupied molecular orbitals (LUMO) are shown.

with

$$V^{\text{Li}}(z) = -\frac{Z_{\text{Li}}}{\sqrt{(z - z_{\text{Li}})^2 + c}} \quad \text{and} \quad V^{\text{H}}(z) = -\frac{Z_{\text{H}}}{\sqrt{(z - z_{\text{H}})^2 + c}} \quad (9.2)$$

where the Li nucleus (charge  $Z_{\text{Li}} = 3$ ) and the proton (charge  $Z_{\text{H}} = 1$ ) are at fixed positions  $z_{\text{Li}} = -1.15$  and  $z_{\text{H}} = 1.15$  according to the equilibrium distance

$$z_{\text{Li-H}} = |z_{\text{Li}} - z_{\text{H}}| = 2.3. \quad (9.3)$$

The idea of the aligned electron model model has been extended to include electron-electron interaction [267]. To obtain finite results the electron-electron interaction is replaced with a soft-Coulomb potential

$$W(z_1, z_2) = \frac{1}{\sqrt{(z_1 - z_2)^2 + d}}. \quad (9.4)$$

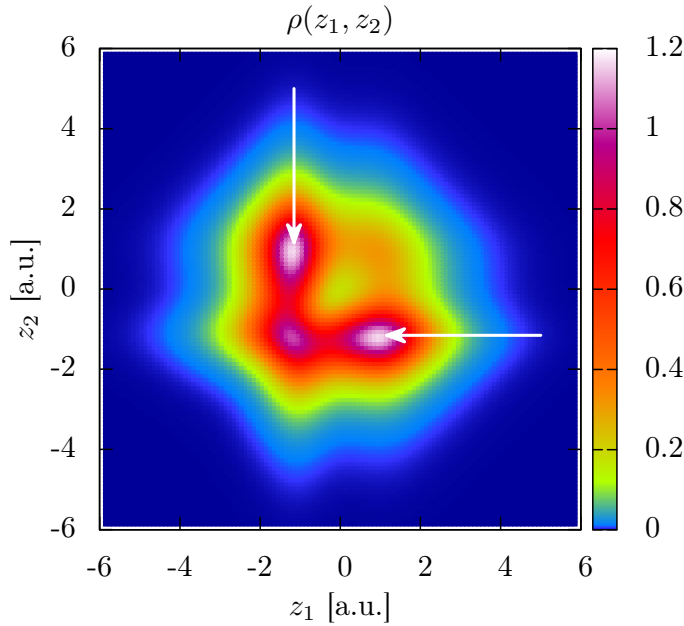
The total Hamiltonian within this model is given by

$$H_{1\dots N}(t) = \sum_{n=1}^N \left( -\frac{1}{2} \frac{\partial^2}{\partial z_n^2} + V(z_n) + z_n F(t) \right) + \sum_{n < m} W(z_n, z_m), \quad (9.5)$$

with the softening parameters  $c = 0.5$  and  $d = 1$  chosen according to literature [52].

For the numerical implementation we solve Eq. 6.32 on an equidistant grid with 6000 points and grid spacing  $\Delta z = 0.2$ . The ground state which serves as the initial state for the TD-2RDM method is calculated using imaginary time propagation within MCTDHF. The TD-2RDM method requires purification for all calculations presented in this chapter. We employ the purification iteratively with a total number of 10 purification steps after each propagation step.





**Figure 9.2.: Two-electron distribution of the LiH ground state.** The pair-density distribution  $\rho(z_1, z_2)$  shows two distinct peaks for inter-atomic pairs with one electron close to the lithium core while the other one is close to the proton (marked by arrows). Occupation along the diagonal  $z_1 = z_2$  is suppressed due to the electron-electron interaction.

The ground state electron density  $\rho_0(z)$  displays a distinct maximum near the Li atom (Fig. 9.1) which originates from the deeply bound doubly occupied core orbital of Li. The outer two electrons occupy the valence molecular orbital (HOMO) which is responsible for the chemical bond (Fig. 9.1). By Koopmans theorem [268] the first ionization energy  $I_p = 0.675$  is equal to the negative of the orbital energy of the HOMO. Due to the stronger electronegativity of the hydrogen atom compared to Li the HOMO is polarized towards the hydrogen atom (Fig. 9.1) leading to a static dipole moment of

$$d_0 = d^{\text{nuc}} - \int z \rho_0(z) dz = -0.88, \quad (9.6)$$

which consists of the nuclear dipole moment  $d^{\text{nuc}} = -2.3$  and the electronic contribution. Further, the stronger electronegativity of the hydrogen atom suppresses ionization along positive direction (pointing from the lithium to hydrogen) as compared to ionization along the opposite direction. Note that this single configuration picture of core and valence molecular orbitals is only a qualitative illustration. The numerical simulation within the MCTDHF and the TD-2RDM method includes further time-dependent spin orbitals to account for configuration interaction. For all numerical results presented in this chapter the TD-2RDM as well as the MCTDHF method, with which we compare, include 10 time-dependent spin orbitals to account for configuration interaction (Fig. 9.1). The latter has been shown to be sufficient to reach convergence for the investigated observables [52].

Further information on the distribution of electrons can be extracted from the pair density  $\rho(z_1, z_2)$ . In the ground state of the LiH molecule the electron pairs are predominantly distributed such that one electron is located near the Li core and the other near the H core (Fig. 9.2). This kind of distribution arises from the polarization of the HOMO and minimizes the interaction energy (Eq. 3.33).

## 9.2. Electron dynamics of LiH

We study the electron dynamics of LiH initiated by short few-cycles laser pulses (Eq. 8.3) in the NIR regime with 800 nm. In analogy to beryllium in Section 8.1 we investigate two different intensities regimes. A moderate four-cycle pulse with  $I = 10^{14}\text{W}/\text{cm}^2$  ( $F_0 = 0.053, \gamma = 1.32$ ), for which the response of the dipole moment is close to linear, and a strong pulse regime with  $I = 4 \times 10^{14}\text{W}/\text{cm}^2$  ( $F_0 = 0.107, \gamma = 0.47$ ) where a strongly nonlinear response is expected including substantial ionization. As a figure of merit for the comparison of the TD-2RDM method with the exact calculation as well as other approximate methods we use the induced time-dependent dipole moment

$$\Delta d(t) = d(t) - d(0) = \int z\rho(z,t)dz - \int z\rho_0(z)dz, \quad (9.7)$$

a one-particle observable for which an explicit functional in terms of the time-dependent density  $\rho(z,t)$  exists and which can thus be determined from TDDFT without invoking any read-out functional. As a generic two-particle observable we study the induced time-dependent interaction energy (Eq. 3.33)

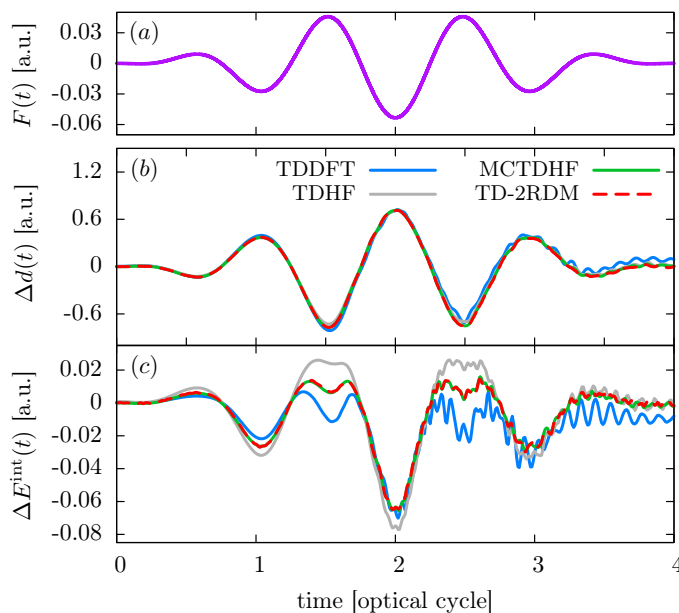
$$\Delta E^{\text{int}}(t) = E^{\text{int}}(t) - E^{\text{int}}(0). \quad (9.8)$$

Within the TD-2RDM method this observable is directly accessible. To express the interaction energy within TDDFT we use the Hartree energy plus the energy from the exchange-correlation functional.

### 9.2.1. Moderate intensities

As a representative for the regime of moderate intensities we employ a four-cycle laser pulse with intensity  $I = 10^{14}\text{W}/\text{cm}^2$  [Fig. 9.3 (a)]. Within this pulse the response of the LiH molecule is close to linear. The induced dipole moment (Eq. 9.7) closely resembles the form of the laser pulse with small oscillations present at the end of the simulation [Fig. 9.3 (b)]. These oscillations originate from excitation of the molecular system during the interaction with the laser pulse. The comparison between MCTDHF, TD-2RDM, TDHF and TDDFT calculations shows that the overall agreement between all of the investigated methods is good.

As an example for a two-particle observable we consider the induced time-dependent interaction energy (Eq. 9.8). The present calculation for LiH [Fig. 9.3 (c)] shows that the TD-2RDM method yields excellent agreement with the exact result and thus accounts for almost 100% of the interaction energy. The oscillation of the interaction energy can be understood by considering the structure of the LiH molecule. In our coordinate system the hydrogen atom is located right to the lithium atom (Fig. 9.1). If the induced dipole moment is directed towards positive values the HOMO is polarized towards the hydrogen core reducing the interaction energy between the valence electrons and the core electrons near the lithium atom. At times when the polarization of the HOMO is directed toward the lithium core the interaction between core and valence electrons is enhanced. This general feature is



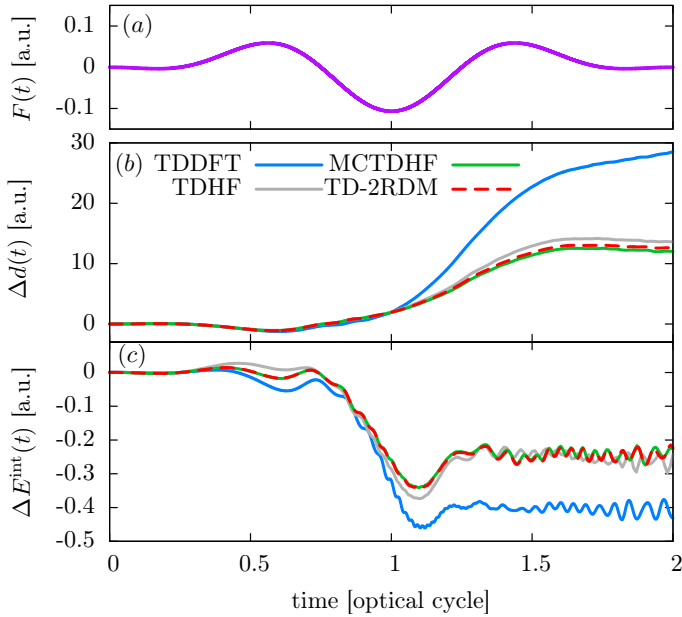
**Figure 9.3.: LiH subject to a laser pulse of moderate intensity.** (a) The electric field  $F(t)$  (Eq. 8.3) of the four-cycle laser pulse with intensity  $I = 10^{14}\text{W}/\text{cm}^2$  employed for the simulation of (c) the induced dipole moment  $\Delta d(t)$  (Eq. 9.7) and (b) the induced interaction energy  $\Delta E^{\text{int}}(t)$  (Eq. 9.8). The TD-2RDM method employing the contraction-consistent Nakatsuji-Yasuda reconstruction is compared to MCTDHF, TDHF, and TDDFT using LDA (see Appendix D for more details on the TDDFT calculation). The TD-2RDM purification is performed with 10 iterations after each propagation step.

reproduced by all of the employed methods qualitatively but only the TD-2RDM method is capable of reproducing the oscillation on a quantitative level [Fig. 9.3 (c)].

### 9.2.2. High intensities

As a representative example for a regime with significant ionization we study the electron dynamics of the LiH molecule in a two-cycle laser pulse with  $I = 4 \times 10^{14}\text{W}/\text{cm}^2$  [Fig. 9.4 (a)]. While for the moderate intensity the dipole moment and the interaction energy of the molecular system remain practically unchanged after the pulse compared to the initial state [Fig. 9.3 (b)] this is not the case for stronger pulses [Fig. 9.4 (b)]. For stronger pulses the emitted electrons acquire a large distance from the nucleus and consequently contribute significantly to the induced dipole moment. Due to the asymmetry of the laser pulse with a strong central peak (at  $\tau \approx 1$ ) the dominant contribution to ionization happens along the positive  $z$ -direction. This can be observed in the induced dipole moment as a slope in analogy to the behaviour found in atomic systems [Fig. 8.4 (b) and Fig. 8.9 (b)]. The fact that the slope for the TDDFT calculation is significantly steeper compared to MCTDHF shows that the ionization rate within TDDFT is overestimated [Fig. 9.4 (b)]. The overestimation of ionization by TDDFT is a signature of the missing self-interaction correction within LDA. Also TDHF overestimates ionization, while the agreement between TD-2RDM and MCTDHF is very good [Fig. 9.4 (b)].

The overall behavior of the interaction energy as a function of time can be traced back to the ionization of electrons. Ionization effectively dilutes the electron cloud around the molecule leading to a reduction of interaction energy [Fig. 9.4 (c)]. The steepest drop in interaction energy occurs during the central peak of the applied laser pulses ( $\tau \approx 1$ ). At this point in time the ionization rate is maximal. The minimum in the interaction energy at times  $\tau \approx 1.1$



**Figure 9.4.: LiH subject to a laser pulse of strong intensity.** (a) The electric field of the two-cycle laser pulse with intensity  $I = 4.0 \times 10^{14} \text{W/cm}^2$  employed to simulate (b) the induced dipole moment and (c) the induced interaction energy. Except for the shape and strength of the laser pulse the simulation parameters are the same as in Fig. 9.3.

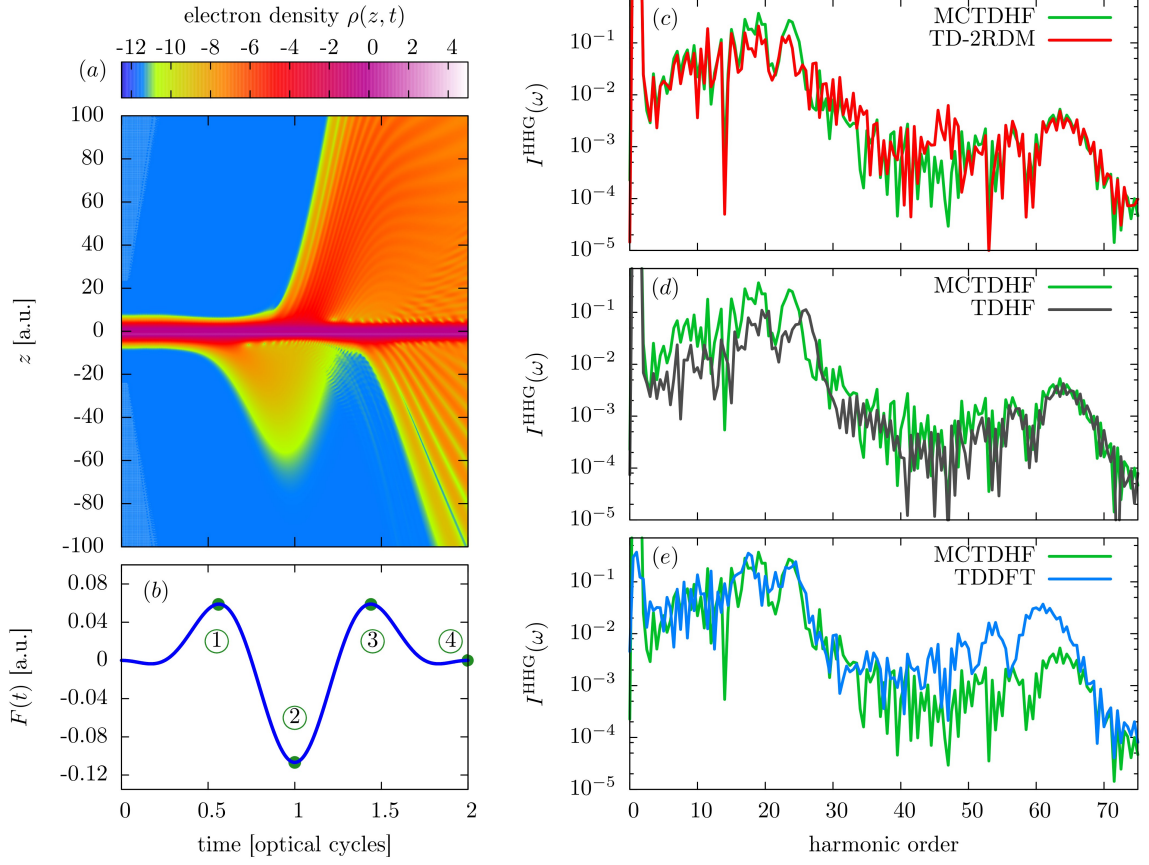
is created by the polarization of the HOMO away from the lithium core which temporarily reduces the interaction energy further. When the field flips sign after the central peak the polarized valence electrons return to the lithium core and the interaction energy is increased again [Fig. 9.4 (c)].

### High-harmonic spectrum from different methods

High-harmonic radiation created during the recollision of emitted electrons with the remnant molecule is sensitive to the detailed electron dynamics in LiH. We study the high-harmonic spectrum for LiH under the strong two-cycle laser pulse with  $I = 4 \times 10^{14} \text{W/cm}^2$  [Fig. 9.4 (a)] which gives a (classical) cut-off at the 63th harmonic according to the three-step model (Eq. 7.4). As expected from the overestimated ionization rate, the high-harmonic spectrum predicted by TDDFT overestimates the HHG yield especially in the cut-off region [Fig. 9.5 (e)]. The TD-2RDM as well as the TDHF method reproduce the cut-off accurately. The TD-2RDM method gives overall good agreement with the reference calculation [Fig. 9.5 (c)] also for the lower harmonics where the TDHF method shows deviations [Fig. 9.5 (d)]. One feature of the TD-2RDM method that is not present in the MCTDHF simulation is a small peak around the 50th harmonic. In the following we discuss a general feature of high-harmonic spectrum from diatomic molecules.

### Two-center interference in HHG from LiH

One of the special properties of HHG created in molecular systems not present in HHG from atoms is the possibility of the emitted electron to recombine at different nuclear centers. This gives rise to high-harmonic radiation that is emitted from different sources and interference effects can enhance or suppress certain parts of the high-harmonic spectrum. To test the



**Figure 9.5.: High-harmonic generation from single LiH molecules aligned with the laser axis.** (a) The time-dependent density  $\rho(z,t)$  of LiH subject the laser pulse depicted in [Fig. 9.4 (a)] reproduced in (b) for convenience. The high-harmonic spectrum  $I^{\text{HHG}}(\omega)$  calculated from the acceleration depicted in [Fig. 9.4 (c)] is compared among (c) the TD-2RDM, (d) the TDHF, (e) the TDDFT and the MCTDHF simulation.

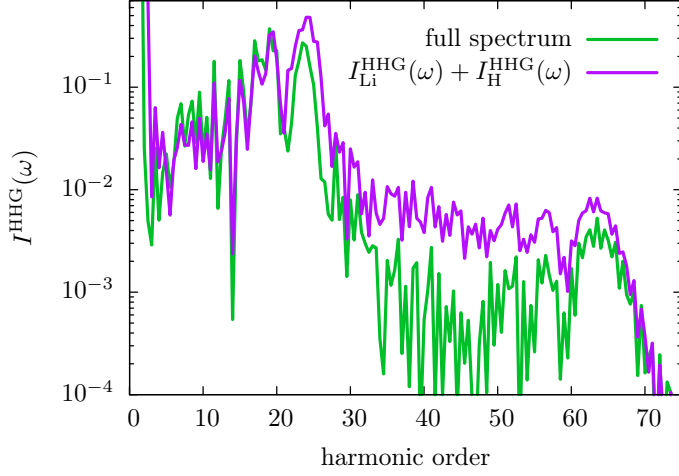
high-harmonic spectrum for such interference effects we separate the total dipole acceleration  $a(t)$  into acceleration in the force field of the hydrogen and lithium core, respectively, via

$$a(t) = a_{\text{H}}(t) + a_{\text{Li}}(t) + NF(t) \quad (9.9)$$

$$= - \int \frac{\partial V^{\text{H}}(z)}{\partial z} \rho(z,t) dz - \int \frac{\partial V^{\text{Li}}(z)}{\partial z} \rho(z,t) dz + NF(t), \quad (9.10)$$

where  $V^{\text{Li}}(z)$  and  $V^{\text{H}}(z)$  are given in Eq. 9.2. With this decomposition the full high-harmonic spectrum can be expanded into the high-harmonic radiation emitted from the lithium center

$$I_{\text{Li}}^{\text{HHG}}(\omega) = \frac{2}{3c} |a_{\text{Li}}(\omega)|^2 \quad (9.11)$$



**Figure 9.6.: Two-center interference in the high-harmonic spectra of LiH.** The high-harmonic spectrum  $I^{\text{HHG}}(\omega)$  calculated from the acceleration depicted in [Fig. 9.4 (c)] compared to the incoherent sum  $I_{\text{Li}}^{\text{HHG}}(\omega) + I_{\text{H}}^{\text{HHG}}(\omega)$  (Eq. 9.11 and Eq. 9.12) of the high-harmonic emission from the lithium and the hydrogen centers. The deviation corresponds to interference effects encoding structural information on the HOMO of the LiH molecule.

plus high-harmonic radiation emitted from the hydrogen center

$$I_{\text{H}}^{\text{HHG}}(\omega) = \frac{2}{3c} |a_{\text{H}}(\omega)|^2 \quad (9.12)$$

plus an interference term

$$I^{\text{HHG}}(\omega) = I_{\text{Li}}^{\text{HHG}}(\omega) + I_{\text{H}}^{\text{HHG}}(\omega) + \frac{4}{3c} \text{Re}(a_{\text{Li}}(\omega)a_{\text{H}}(\omega)). \quad (9.13)$$

By comparing the incoherent sum  $I_{\text{Li}}^{\text{HHG}}(\omega) + I_{\text{H}}^{\text{HHG}}(\omega)$  to the full high-harmonic spectrum generated from LiH molecules subject to the strong two-cycle laser pulse [Fig. 9.4 (a)] we can identify one region of constructive interference around the 12th harmonic and one region of destructive interference around the 45th harmonic (Fig. 9.6). Qualitatively, these interference effects can be understood by considering a returning electron with energy  $E$  and de-Broglie wavelength

$$\lambda_{\text{D}} = \frac{2\pi}{\sqrt{2E}}. \quad (9.14)$$

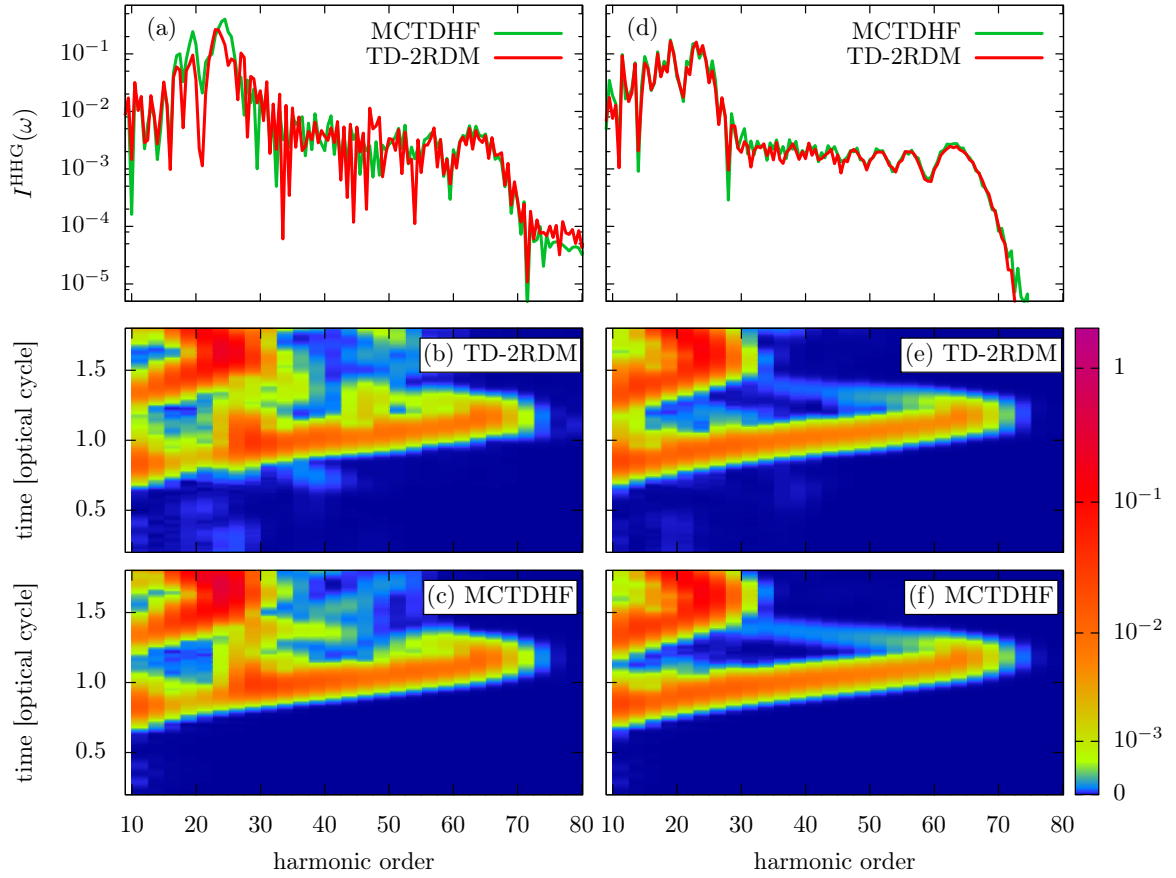
If the de-Broglie wavelength of the returning electron is a multiple of the bond length the molecular HHG shows either constructive or destructive interference. For systems whose HOMO is antisymmetric with respect to point reflection such as LiH (Fig. 9.1) constructive interference is achieved under the condition

$$z_{\text{Li-H}} = \frac{(2n+1)\lambda_{\text{D}}}{2} \quad (9.15)$$

and destructive interference under

$$z_{\text{Li-H}} = n\lambda_{\text{D}}, \quad (9.16)$$

for some  $n \in \mathbb{N}$ . For the bond length of LiH  $z_{\text{Li-H}} = 2.3$  a.u. constructive interference should occur at the 16th harmonic whereas the destructive interference should occur at the

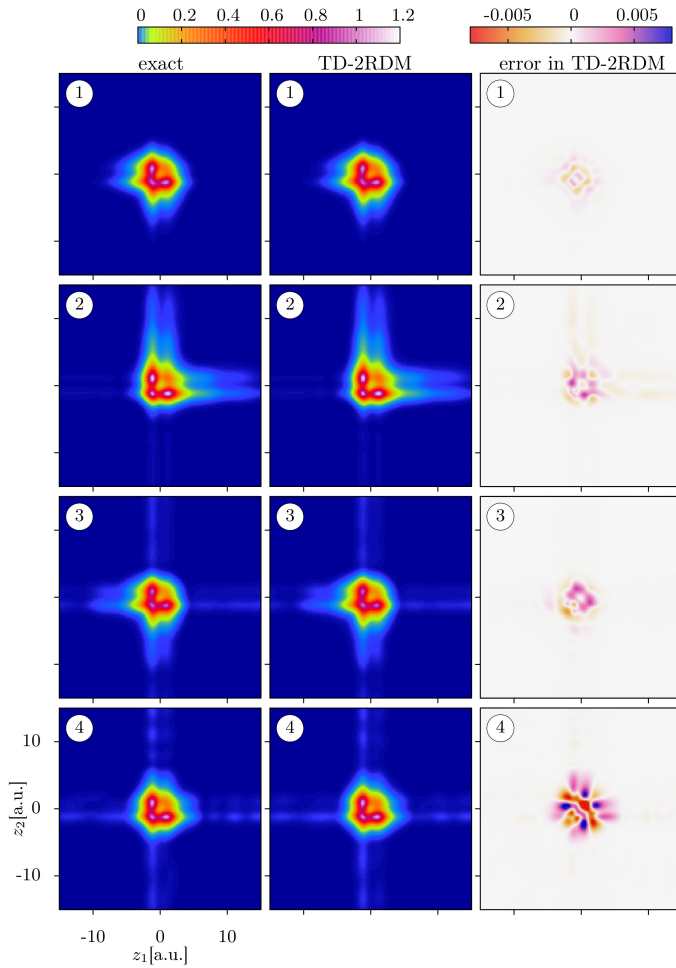


**Figure 9.7.: Separated contribution of the lithium and hydrogen center to the high-harmonic emission of LiH.** The spectrum of high-harmonics generated at (a) the lithium core  $I_{\text{Li}}^{\text{HHG}}(\omega)$  (Eq. 9.11) and (d) the hydrogen core  $I_{\text{H}}^{\text{HHG}}(\omega)$  (Eq. 9.12) compared among the MCTDHF and the TD-2RDM method. Further the time-frequency spectra (Eq. 7.17) of high-harmonics generated at (b, c) the lithium core and (e, f) the hydrogen core are compared.

65th harmonic. The deviation to the observed values originates from the asymmetry of the HOMO. Using different wavelengths and different intensities confirms that these regions of constructive and destructive interference are independent of the laser parameters and originate from properties of the molecule itself.

To identify the origin of the discrepancy in the high-harmonic spectrum obtained with the TD-2RDM method near the 50th harmonic we separately compare the high-harmonic spectrum from the lithium (Eq. 9.11) and hydrogen (Eq. 9.12) center obtained within the TD-2RDM method to the result obtained within MCTDHF. We find that the high-harmonic spectrum generated at the hydrogen core is in perfect agreement with the TD-2RDM method [Fig. 9.7 (d)]. The discrepancy in the TD-2RDM high-harmonic spectrum arises from the harmonics created near the lithium core [Fig. 9.7 (a)]. The time-frequency transformation of the individual HHG contributions demonstrates that the spectrum of the high-harmonics generated at the hydrogen center is much cleaner and the traces of the three-step model are





**Figure 9.8.: Time-dependent pair density of LiH.** The MCTDHF result (left column) for the time-dependent pair density  $\rho(z_1, z_2, t)$  is compared to the TD-2RDM simulation (middle column). The calculations is performed for the same simulation parameters as presented in (Fig. 9.4). The right column shows the difference between the MCTDHF and TD-2RDM result. The pair density is shown at four times [rows (1) to (4)] depicted in Fig. 9.5 (b).

clearly visible [Fig. 9.7 (e, f)]. The time-frequency transformation of high-harmonics generated at the lithium center contains contributions after the first recollision event ( $\tau \approx 1.2$ ) [Fig. 9.7 (b, c)]. These contributions between the 30th and 60th harmonic are not present in the high-harmonic spectrum from hydrogen center. Therefore we conclude that the influence of the lower lying core-electrons plays an important role in the generation of these features. The fact that the small deviation in the TD-2RDM result around the 50th harmonic occurs exactly in this region suggests that it originates from artificial coupling between energetically separated orbitals. Further we observe that this feature around the 50th harmonic of the TD-2RDM result is sensitive to the number of purification steps which leads us to the conclusion that the purification procedure might be the cause for these small discrepancy. Indeed the correction matrix  $D_{12}^{\text{cor}}$  (Eq. 5.75) employed to remove negative occupation numbers establishes such a coupling between core and valence orbitals. Improving the purification scheme by removing the coupling between energetically separated orbitals is planned as an upcoming project.

The spatio-temporal variation of the ionization process becomes directly visible in the pair density  $\rho(z_1, z_2, t)$ . The snapshots (Fig. 9.8) for LiH at different times [marked in



Fig. 9.5 (b)) display the pair density near the first peak (1), near the field maximum (2), near the second peak (3), and near the conclusion of the pulse (4). Overall, the agreement between the exact pair density and the one calculated by the TD-2RDM is excellent and differences are hardly visible. Minor deviations accumulate during the propagation. The fact that ionization happens almost exclusively along the coordinate axes with  $z_1 \approx 0$  or  $z_2 \approx 0$  shows that single ionization is the dominant contribution and double ionization which would show up along the diagonals  $|z_1| = |z_2|$  is comparatively weak for this laser pulse.



## 10. Summary and conclusions

The closure of the BBGKY hierarchy on the second level and by that the self-contained propagation of the 2RDM is a longstanding problem in the quantum many-body theory. The promise for a many-body method that scales polynomially with particle number and is at the same time accurate and versatile has motivated the development of the (TD-2RDM) method. We have presented in this thesis three advancements of the theory that are crucial in the application to realistic systems.

First, the closure of the equation of motion for the 2RDM requires the reconstruction of the 3RDM in terms of the 2RDM. Previously the implementations of the TD-2RDM method were limited to the cluster-expansion approach in which three-particle correlations were neglected as a whole. In this thesis we proceeded further by accounting for three-particle correlations via the reconstruction functional proposed by Nakatsuji-Yasuda [197]. This reconstruction functional is used for the first time within the context of the TD-2RDM method. Additionally, we developed a general procedure that guarantees conservation of norm, energy, and spin during time propagation by making the reconstruction contraction consistent. Contraction consistency was identified as one of the essential prerequisites for an accurate and proper closure of the BBGKY hierarchy. We found that the Nakatsuji-Yasuda reconstruction in combination with the enforcement of contraction consistency is able to significantly improve upon results obtained by using existing reconstruction functionals. In general, we found that contraction consistency of the reconstructed 3RDM is not only necessary for the conservation of symmetries in the propagation of the 2RDM but also improves the accuracy of the reconstruction significantly. To put the reconstruction on a solid basis we developed a diagrammatic approach and gave the rules for the evaluation of the RDM diagrams. The diagrammatic technique opens the road to a further improvement of the reconstruction functionals.

Second, for achieving stable propagation another key ingredient is crucial: due to the nonlinearity of the equation of motion, small errors rapidly (up to exponentially) magnify causing the propagated 2RDM to lose  $N$ -representability. We have therefore devised a dynamical purification protocol that iteratively restores  $N$ -representability after each time step by enforcing the positivity of the 2-RDM and the two-hole reduced density matrix (2-HRDM). This purification is necessary to avoid instabilities previously observed in several applications of the TD-2RDM method.

Third, we have implemented the TD-2RDM method for non-perturbative strong field processes of multi-electron atoms and molecules in ultra-short intense laser pulses. The simulation of the electronic response from atomic targets (beryllium and neon) has been performed in fully three-dimensional space whereas the molecular response of lithium hydride (LiH)

has been treated within the aligned electron model which reduces the dimensionality to a one-dimensional problem. We have focused on the high-harmonic spectrum as an observable to stringently benchmark the accuracy of the TD-2RDM method using state-of-the-art multiconfigurational time-dependent Hartree-Fock (MCTDHF) calculations as reference. The latter have been carefully checked for convergence and can serve as representative of the numerically exact solution.

The TD-2RDM results for the atomic polarization as well as high-harmonic spectra of beryllium and neon obtained are in excellent agreement with MCTDHF reference calculations for a variety of different laser durations and intensities. We have used the present TD-2RDM description to identify the influence of electronic correlations on the HHG process. We investigated the two-particle correlation functions describing the particle-hole dynamics controlling the harmonic emission. These two-body observables are, unlike in time-dependent density functional theory (TDDFT), directly accessible. The influence of correlation also manifests itself by the significant differences between the high-harmonic spectra calculated within the time-dependent Hartree-Fock (TDHF) method and the MCTDHF reference calculation. In particular, the high-harmonic spectrum of beryllium in a strongly ionizing laser pulse shows a pronounced overestimation of the HHG yield in the cutoff region if correlation is neglected. This effect can be accurately accounted for within the TD-2RDM method. Furthermore we have calculated the time-frequency spectrum of the emitted high-harmonic radiation. By comparing it to predictions of the three-step model the origin of the correlation induced suppression of the high-harmonic intensity can be delineated. The simulation of the electronic response of LiH has been equally successful. The high-harmonic spectra from LiH reveals suppression and enhancement effects that arise from the two-center interference between high-harmonic radiation emitted from the two nuclear centers of the diatomic molecule. These features as well as the overall shape of the high-harmonic spectra are well reproduced by the TD-2RDM method.

We anticipate that the present TD-2RDM theory should provide a tool to accurately describe a wide variety of many-body systems as long as the dynamics is given by a sequence of two-particle interactions. Further applications of the TD-2RDM method as presented in this thesis will be directed towards the description of strong field effects that are primarily driven by electron-electron interaction such as non-sequential double ionization of multi-electron atoms and molecules as well as the simulation of Auger decay initiated by core ionization via high-energy photons. These processes involve the interaction of several electrons in different orbitals in which case the beneficial scaling of the TD-2RDM method is crucial.

Other fields of application that allow to directly exploit the polynomial scaling of the TD-2RDM method include the simulation of dynamical processes of ultra-cold atoms in optical lattices. The generic model to simulate the such processes is the Hubbard-Fermi model. Due to the exponential scaling of the exact time-dependent simulation of the 2D Hubbard system is restricted to only a very few sites. Ground state calculations have been achieved to a maximum of 20 sites [269]. The TD-2RDM method holds the promise to go beyond this limitation and simulate e.g. the expansion dynamics of ultra-cold fermionic atoms recently measured in experiment [270].

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Further developments are planned along the lines of improving the reconstruction by including higher-order corrections. The presented diagrammatic technique allows to capture the missing contributions in recent reconstruction functionals. Including additional classes of diagrams into the reconstruction via infinite partial summations allows to further increase the accuracy of the TD-2RDM method. These reconstruction functionals yet to be developed would include the two-particle cumulant to higher and, eventually, to infinite order.



# A. Coordinate independent notation of RDMs and many-body operators

In this thesis we adopt a convenient coordinate independent notation for RDMs and many-body operators introduced by Bonitz [166]. Originating from the coordinate dependent representation of the wavefunction

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N, t) = \langle \mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N | \Psi(t) \rangle \quad (\text{A.1})$$

the  $p$ RDM in coordinate space can be defined by integrating out all but  $p$  particles from the dyadic product  $\Psi\Psi^*$  according to

$$D(\mathbf{x}_1 \dots \mathbf{x}_p; \mathbf{x}'_1 \dots \mathbf{x}'_p; t) = \frac{N!}{(N-p)!} \int \Psi(\mathbf{x}_1 \dots \mathbf{x}_p, \mathbf{x}_{p+1} \dots \mathbf{x}_N, t) \Psi^*(\mathbf{x}'_1 \dots \mathbf{x}'_p, \mathbf{x}_{p+1} \dots \mathbf{x}_N, t) d\mathbf{x}_{p+1} \dots d\mathbf{x}_N, \quad (\text{A.2})$$

The coordinate dependent  $p$ RDM can be understood as the spatial representation of a coordinate independent operator  $D_{12\dots p}$

$$\langle \mathbf{x}_1 \dots \mathbf{x}_p | D_{12\dots p}(t) | \mathbf{x}'_1 \dots \mathbf{x}'_p \rangle = D(\mathbf{x}_1 \dots \mathbf{x}_p; \mathbf{x}'_1 \dots \mathbf{x}'_p; t). \quad (\text{A.3})$$

Formally one can differ between RDMs operating on different subspaces of the particles. For example, the 2RDM  $D_{12}(t)$  acts upon the subspace of particle 1 and 2 while  $D_{23}(t)$  acts upon particle 2 and 3. This distinction between  $D_{12}$  and  $D_{23}$  is redundant for indistinguishable particles. Nonetheless it can be convenient for the coordinate independent representation of operations between RDMs and many-body operators. In the following we give a few examples for the translation between coordinate dependent and coordinate independent representations of operations that appear regularly within RDM theory

$$\begin{aligned} \langle \mathbf{x}_1 | D_1 D_1 D_1 | \mathbf{x}'_1 \rangle &= \int D(\mathbf{x}_1; \bar{\mathbf{x}}_1) D(\bar{\mathbf{x}}_1; \tilde{\mathbf{x}}_1) D(\tilde{\mathbf{x}}_1; \mathbf{x}'_1) d\bar{\mathbf{x}}_1 d\tilde{\mathbf{x}}_1 \\ \langle \mathbf{x}_1 \mathbf{x}_2 | D_{12} D_2 | \mathbf{x}'_1 \mathbf{x}'_2 \rangle &= \int D(\mathbf{x}_1 \mathbf{x}_2; \mathbf{x}'_1 \bar{\mathbf{x}}_2) D(\bar{\mathbf{x}}_2; \mathbf{x}'_2) d\bar{\mathbf{x}}_2 \\ \langle \mathbf{x}_1 | \text{Tr}_2 W_{12} D_2 | \mathbf{x}'_1 \rangle &= \int W(\mathbf{x}_1 \bar{\mathbf{x}}_2; \mathbf{x}'_1 \bar{\mathbf{x}}_2) D(\bar{\mathbf{x}}_2; \bar{\mathbf{x}}_2) d\bar{\mathbf{x}}_2 \\ &= \delta(\mathbf{x}_1 - \mathbf{x}'_1) \int W(|\mathbf{x}_1 - \bar{\mathbf{x}}_2|) D(\bar{\mathbf{x}}_2; \bar{\mathbf{x}}_2) d\bar{\mathbf{x}}_2 \end{aligned} \quad (\text{A.4})$$

In the last expression we used the representation of the interaction in coordinate space as

$$W(\mathbf{x}_1 \mathbf{x}_2; \mathbf{x}'_1 \mathbf{x}'_2) = W(|\mathbf{x}_1 - \mathbf{x}_2|) \delta(\mathbf{x}_1 - \mathbf{x}'_1) \delta(\mathbf{x}_2 - \mathbf{x}'_2) \quad (\text{A.5})$$

which is valid for spatially homogenous and isotropically interacting particles.

More general expressions can be formed by introducing the permutation operator  $\Lambda_{ij}$  which exchanges particles  $i$  and  $j$  according to

$$\Lambda_{12}|\mathbf{x}'_1\mathbf{x}'_2\rangle = |\mathbf{x}'_2\mathbf{x}'_1\rangle \quad (\text{A.6})$$

$$\langle\mathbf{x}_1\mathbf{x}_2|\Lambda_{12} = \langle\mathbf{x}_2\mathbf{x}_1|, \quad (\text{A.7})$$

which can be used to form, e.g., the following expressions

$$\langle\mathbf{x}_1\mathbf{x}_2|D_{12}\Lambda_{12}|\mathbf{x}'_1\mathbf{x}'_2\rangle = D(\mathbf{x}_1\mathbf{x}_2;\mathbf{x}'_2\mathbf{x}'_1) \quad (\text{A.8})$$

$$\langle\mathbf{x}_1\mathbf{x}_2|\Lambda_{12}D_{12}|\mathbf{x}'_1\mathbf{x}'_2\rangle = D(\mathbf{x}_2\mathbf{x}_1;\mathbf{x}'_1\mathbf{x}'_2). \quad (\text{A.9})$$

The antisymmetrization operator  $\hat{\mathcal{A}}$  is defined by fully anti-symmetrizing the expression. If two terms are equivalent due to the symmetry of the expression this term is not included in the antisymmetrization, e.g. anti-symmetrizing the product  $D_1D_2$  gives only 2 terms

$$\langle\mathbf{x}_1\mathbf{x}_2|\hat{\mathcal{A}}D_1D_2|\mathbf{x}'_1\mathbf{x}'_2\rangle = D(\mathbf{x}_1,\mathbf{x}'_1)D(\mathbf{x}_2,\mathbf{x}'_2) - D(\mathbf{x}_2,\mathbf{x}'_1)D(\mathbf{x}_1,\mathbf{x}'_2) \quad (\text{A.10})$$

since the remaining two terms  $D(\mathbf{x}_2,\mathbf{x}'_1)D(\mathbf{x}_1,\mathbf{x}'_2)$  and  $D(\mathbf{x}_2,\mathbf{x}'_2)D(\mathbf{x}_1,\mathbf{x}'_1)$  are equivalent to the two terms already included.

We stress here that there is a subtle difference between the coordinate independent notation of operators on the two-particle subspace, e.g.  $O_{12}$ , and the notation in second quantization

$$O = \sum_{i_1i_2j_1j_2} O_{j_1j_2}^{i_1i_2} a_{j_1}^\dagger a_{j_2}^\dagger a_{i_2} a_{i_1} \quad (\text{A.11})$$

Although both operators have the same matrix elements within the two-particle subspace

$$O_{j_1j_2}^{i_1i_2} = \langle i_1i_2|O_{12}|j_1j_2\rangle = \langle i_1i_2|O|j_1j_2\rangle \quad (\text{A.12})$$

the operator in second quantization  $O$  can act on Fock-Space elements with arbitrary number of particles while  $O_{12}$  can act only within the two-particle subspace. This becomes relevant when evaluating products of operators. The operator composition of operator  $O$  and  $K$  gives

$$\begin{aligned} O \cdot K &= \sum_{i_1i_2j_1j_2} O_{j_1j_2}^{i_1i_2} a_{j_1}^\dagger a_{j_2}^\dagger a_{i_2} a_{i_1} \sum_{i_1i_2j_1j_2} K_{j_1j_2}^{i_1i_2} a_{j_1}^\dagger a_{j_2}^\dagger a_{i_2} a_{i_1} \\ &= O_{12}K_{34} + O_{12}K_{23} - O_{12}\Lambda_{23}K_{23} - O_{12}\Lambda_{12}K_{23} + O_{12}\Lambda_{12}\Lambda_{23}K_{23} \\ &\quad + O_{12}K_{12} - O_{12}\Lambda_{12}K_{12}, \end{aligned} \quad (\text{A.13})$$

which can be checked by applying Wick's theorem [171]. In a simple picture Eq. A.13 can be interpreted as follows: (1)  $O_{12}K_{34}$  describes the individual excitation of particle 1 and 2, and the individual excitation of particle 3 and 4. (2)  $O_{12}K_{23}$  describes the excitation of particle 1 and 2 and consequently particle 2 and 3. The term  $O_{12}\Lambda_{12}K_{23}$  describes excitation and exchange of particle 1 and 2 and consequently excitation of particle 2 and 3. (3)  $O_{12}K_{12}$



describes the double excitation of particle 1 and 2 and  $O_{12}\Lambda_{12}K_{12}$  has an additional exchange of particle 1 and 2. One important application of the operator composition is the evaluation of the eigenstate condition for many-body states. Since the state is in an energy eigenstate if and only if the uncertainty vanishes. The eigenstate fulfills

$$\langle \tilde{H} \rangle^2 = \langle \tilde{H}^2 \rangle, \quad (\text{A.14})$$

which can be evaluated as

$$\langle \tilde{H} \rangle^2 = \text{Tr}_{12} \tilde{H}_{12} [ED_{12}] \quad (\text{A.15})$$

and

$$\begin{aligned} \langle \tilde{H}^2 \rangle &= \langle \tilde{H}_{12} \tilde{H}_{34} \rangle + \langle \tilde{H}_{12} \tilde{H}_{23} \rangle - \langle \tilde{H}_{12} \Lambda_{23} \tilde{H}_{23} \rangle - \langle \tilde{H}_{12} \Lambda_{12} \tilde{H}_{23} \rangle + \langle \tilde{H}_{12} \Lambda_{12} \Lambda_{23} \tilde{H}_{23} \rangle \\ &\quad + \langle \tilde{H}_{12} \tilde{H}_{12} \rangle - \langle \tilde{H}_{12} \Lambda_{12} \tilde{H}_{12} \rangle \\ &= \text{Tr}_{1234} \tilde{H}_{12} \tilde{H}_{34} D_{1234} + 4 \text{Tr}_{123} \tilde{H}_{12} \tilde{H}_{23} D_{123} + 2 \text{Tr}_{12} \tilde{H}_{12} \tilde{H}_{12} D_{12} \\ &= \text{Tr}_{12} \tilde{H}_{12} [\text{Tr}_{34} \tilde{H}_{34} D_{1234} + 4 \text{Tr}_3 \tilde{H}_{23} D_{123} + 2 \tilde{H}_{12} D_{12}]. \end{aligned} \quad (\text{A.16})$$

With this evaluation the eigenstate condition (Eq. A.14) is equivalent to

$$ED_{12} = \text{Tr}_{34} \tilde{H}_{34} D_{1234} + 4 \text{Tr}_3 \tilde{H}_{23} D_{123} + 2 \tilde{H}_{12} D_{12}, \quad (\text{A.17})$$

which is the so called contracted Schrödinger condition [11].



## B. Gauge invariance of the TD-2RDM method

The gauge invariance of the TD-2RDM method is a direct consequence of the gauge invariance of the Schrödinger equation. In more detail the gauge transformation of the (spin summed) 2RDM from length gauge to velocity gauge can be written as

$$D^V(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}'_2; t) = e^{i\mathbf{A}(t)(\mathbf{r}_1 - \mathbf{r}'_1)} e^{i\mathbf{A}(t)(\mathbf{r}_2 - \mathbf{r}'_2)} D^L(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}'_2; t). \quad (\text{B.1})$$

Inserting this transformation into the equation of motion for the 2RDM in length gauge which can be written as

$$\begin{aligned} i\partial_t D^L(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}'_2; t) = & \left[ -\frac{\nabla_1^2}{2} + \mathbf{E} \cdot \mathbf{r}_1 - \frac{\nabla_2^2}{2} + \mathbf{E} \cdot \mathbf{r}_2, D^L(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}'_2; t) \right] \\ & + \langle \mathbf{r}_1, \mathbf{r}_2 | [W_{12}, D_{12}^L] | \mathbf{r}'_1, \mathbf{r}'_2 \rangle + \langle \mathbf{r}_1, \mathbf{r}_2 | C_{12}^R [D_{12}^L] | \mathbf{r}'_1, \mathbf{r}'_2 \rangle \end{aligned} \quad (\text{B.2})$$

and using the general relation

$$-\frac{\nabla_1^2}{2} (e^{i\mathbf{A}\mathbf{r}_1} D(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}'_2)) = e^{i\mathbf{A}\mathbf{r}_1} \left( -\frac{(\nabla_1 - \mathbf{A})^2}{2} \right) D(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}'_2) \quad (\text{B.3})$$

gives the equation of motion for the (spin summed) 2RDM in velocity gauge

$$\begin{aligned} i\partial_t D^V(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}'_2; t) = & \left[ -\frac{(\nabla_1 + \mathbf{A})^2}{2} - \frac{(\nabla_2 + \mathbf{A})^2}{2}, D^V(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}'_2; t) \right] \\ & + \langle \mathbf{r}_1, \mathbf{r}_2 | [W_{12}, D_{12}^V] | \mathbf{r}'_1, \mathbf{r}'_2 \rangle + \langle \mathbf{r}_1, \mathbf{r}_2 | C_{12}^R [D_{12}^V] | \mathbf{r}'_1, \mathbf{r}'_2 \rangle \end{aligned} \quad (\text{B.4})$$

where we have used the unitary invariance of the 3RDM reconstruction, i.e. that the reconstructed 3RDM transforms as

$$\tilde{D}_{123} = U_1^\dagger U_2^\dagger U_3^\dagger D_{123} U_1 U_2 U_3 \quad (\text{B.5})$$

if the 1RDM and the 2RDM are transformed according to

$$\tilde{D}_1 = U_1^\dagger D_1 U_1 \quad (\text{B.6})$$

$$\tilde{D}_{12} = U_1^\dagger U_2^\dagger D_{12} U_1 U_2. \quad (\text{B.7})$$

This is the case for all reconstruction functionals tested in this theses.



## C. Unitray decomposition of three-particle matrices with arbitrary symmetry

While the existence of the unitray decomposition for  $p$ RDMs with arbitrary symmetry has been proven theoretically [210] the explicit form of the functionals has, to the best of our knowledge, not been determined for  $p > 2$ . The case  $p = 2$  was derived by Coleman for antisymmetric matrices and Alcoba [271] for RDMs of general symmetry <sup>2</sup> (for a review see, e.g., [12]). Briefly, any hermitian antisymmetric two-particle matrix  $M_{12}$  can be decomposed into

$$M_{12} = M_{12;\perp} + M_{12;K}, \quad (\text{C.1})$$

where  $M_{12;K}$  is the contraction-free component lying in the kernel of the contraction operator

$$\text{Tr}_2(M_{12;K}) = 0, \quad (\text{C.2})$$

and

$$M_{12;\perp} = \frac{\hat{\mathcal{A}}M_1\mathbf{1}_2}{2I - 2} - \frac{M\hat{\mathcal{A}}\mathbf{1}_1\mathbf{1}_2}{(2I - 1)(2I - 2)}, \quad (\text{C.3})$$

is an element of the orthogonal complement with  $M_1 = \text{Tr}_2 M_{12}$  and  $M = \text{Tr}_1 M_{12}$ ,  $\mathbf{1}_1$  is the identity and  $2I$  the number of spin orbitals. The component  $M_{12;\perp}$  is orthogonal to the contraction-free component  $M_{12;K}$  with respect to the Frobenius inner product for matrices [273]

$$\text{Tr}_{12}(M_{12;\perp}M_{12;K}) = 0. \quad (\text{C.4})$$

Similar to Eq. C.3, the unitary decomposition for hermitian symmetric two-particle matrices reads [274]

$$M_{12;\perp} = \frac{\hat{\mathcal{S}}M_1\mathbf{1}_2}{2I + 2} - \frac{M\hat{\mathcal{S}}\mathbf{1}_1\mathbf{1}_2}{(2I + 1)(2I + 2)}, \quad (\text{C.5})$$

where  $\hat{\mathcal{S}}$  is the symmetrization operator defined in analogy to the antisymmetrization operator  $\hat{\mathcal{A}}$ . Note that the orthogonal component  $M_{12;\perp}$  defined in Eq. C.3 and Eq. C.5 depends only on the contraction of the two-particle matrix  $M_1$ . For the unitary decomposition of

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<sup>2</sup> As a side remark we note that the unitary decomposition of two-particle matrices is equivalent to the Ricci decomposition of general relativity which is used to define the trace free part of the Riemann curvature tensor known as the Weyl tensor [272].

hermitian two-particle matrices with arbitrary symmetry [271] the orthogonal component  $M_{12;\perp}$  is uniquely determined from all diagonal and off-diagonal contractions of the two-particle matrix  $M_{12}$ .

The unitary decomposition of the antisymmetric matrices (in analogy to Eq. C.3) has been derived in Eq. 5.67. We extend now this unitary decomposition to hermitian three-particle matrices  $M_{123}$  with arbitrary symmetry. As we show below the orthogonal component  $M_{123;\perp}$  can be written as a functional of the 9 one-fold contractions

$$\begin{aligned}
^1M_{j_1j_2}^{i_1i_2} &= \sum_k M_{j_1j_2k}^{i_1i_2k} & ^2M_{j_1j_2}^{i_1i_2} &= \sum_k M_{j_1kj_2}^{i_1i_2k} & ^3M_{j_1j_2}^{i_1i_2} &= \sum_k M_{kj_1j_2}^{i_1i_2k} & ^4M_{j_1j_2}^{i_1i_2} &= \sum_k M_{j_1j_2k}^{i_1ki_2} \\
^5M_{j_1j_2}^{i_1i_2} &= \sum_k M_{j_1kj_2}^{i_1ki_2} & ^6M_{j_1j_2}^{i_1i_2} &= \sum_k M_{kj_1j_2}^{i_1ki_2} & ^7M_{j_1j_2}^{i_1i_2} &= \sum_k M_{j_1j_2k}^{ki_1i_2} & ^8M_{j_1j_2}^{i_1i_2} &= \sum_k M_{j_1kj_2}^{ki_1i_2} \\
^9M_{j_1j_2}^{i_1i_2} &= \sum_k M_{kj_1j_2}^{ki_1i_2}, & & & & & & 
\end{aligned} \tag{C.6}$$

the 18 two-fold contractions

$$\begin{aligned}
^1M_j^i &= \sum_{k_1k_2} M_{jk_1k_2}^{ik_1k_2} & ^2M_j^i &= \sum_{k_1k_2} M_{k_1jk_2}^{ik_1k_2} M_j^i & &= \sum_{k_1k_2} M_{k_1k_2j}^{ik_1k_2} & ^4M_j^i &= \sum_{k_1k_2} M_{jk_2k_1}^{ik_1k_2} \\
^5M_j^i &= \sum_{k_1k_2} M_{k_2jk_1}^{ik_1k_2} & ^6M_j^i &= \sum_{k_1k_2} M_{k_2k_1j}^{ik_1k_2} M_j^i & &= \sum_{k_1k_2} M_{jk_1k_2}^{k_1ik_2} & ^8M_j^i &= \sum_{k_1k_2} M_{k_1jk_2}^{k_1ik_2} \\
^9M_j^i &= \sum_{k_1k_2} M_{k_1k_2j}^{k_1ik_2} & ^{10}M_j^i &= \sum_{k_1k_2} M_{jk_2k_1}^{k_1ik_2} M_j^i & &= \sum_{k_1k_2} M_{k_2jk_1}^{k_1ik_2} & ^{12}M_j^i &= \sum_{k_1k_2} M_{k_2k_1j}^{k_1ik_2} \\
^{13}M_j^i &= \sum_{k_1k_2} M_{jk_1k_2}^{k_1k_2i} & ^{14}M_j^i &= \sum_{k_1k_2} M_{k_1jk_2}^{k_1k_2i} M_j^i & &= \sum_{k_1k_2} M_{k_1k_2j}^{k_1k_2i} & ^{16}M_j^i &= \sum_{k_1k_2} M_{jk_2k_1}^{k_1k_2i} \\
^{17}M_j^i &= \sum_{k_1k_2} M_{k_2jk_1}^{k_1k_2i} & ^{18}M_j^i &= \sum_{k_1k_2} M_{k_2k_1j}^{k_1k_2i}, & & & & 
\end{aligned} \tag{C.7}$$

and the 6 three-fold contractions

$$\begin{aligned}
^1M &= \sum_{k_1k_2k_3} M_{k_1k_2k_3}^{k_1k_2k_3} & ^2M &= \sum_{k_1k_2k_3} M_{k_1k_3k_2}^{k_1k_2k_3} \\
^3M &= \sum_{k_1k_2k_3} M_{k_2k_1k_3}^{k_1k_2k_3} & ^4M &= \sum_{k_1k_2k_3} M_{k_2k_3k_1}^{k_1k_2k_3} \\
^5M &= \sum_{k_1k_2k_3} M_{k_3k_1k_2}^{k_1k_2k_3} & ^6M &= \sum_{k_1k_2k_3} M_{k_3k_2k_1}^{k_1k_2k_3}.
\end{aligned} \tag{C.8}$$

Generalizing the ansatz for the orthogonal component of antisymmetric matrices (Eq. 5.67) we expand the orthogonal component of the three-particle matrices with arbitrary symmetry

as

$$\begin{aligned}
[M_{\perp}]_{j_1 j_2 j_3}^{i_1 i_2 i_3} &= \sum_{k=1}^6 \sum_{\tau \in S_3} a_{\tau}^k \delta_{j_{\tau(1)}}^{i_1} \delta_{j_{\tau(2)}}^{i_2} \delta_{j_{\tau(3)}}^{i_3} {}^k M \\
&+ \sum_{k=1}^{18} \sum_{\substack{\sigma, \tau \in S_3 \\ \sigma(1) < \sigma(2)}} b_{\tau, \sigma}^k \delta_{j_{\tau(1)}}^{i_{\sigma(1)}} \delta_{j_{\tau(2)}}^{i_{\sigma(2)}} {}^k M_{j_{\tau(3)}}^{i_{\sigma(3)}} \\
&+ \sum_{k=1}^9 \sum_{\sigma, \tau \in S_3} c_{\tau, \sigma}^k \delta_{j_{\tau(1)}}^{i_{\sigma(1)}} {}^k M_{j_{\tau(2)} j_{\tau(3)}}^{i_{\sigma(2)} i_{\sigma(3)}}, \tag{C.9}
\end{aligned}$$

where  $S_3$  denotes the permutation group of three elements and  $\delta_j^i$  is the Kronecker delta. For the rest of this chapter we will use the expansion in  $I$  orbitals, i.e. the trace of the Kronecker delta is given by  $\sum_i \delta_i^i = I$ . The restriction  $\sigma(1) < \sigma(2)$  in the second term is necessary since the Kronecker deltas ( $\delta$ ) can be commuted without creating a new coefficient. In this expansion there are  $6 \times 3!$  coefficients  $a_{\tau}^k$ ,  $18 \times 3! \times 3!/2$  coefficients  $b_{\tau, \sigma}^k$  and  $9 \times 3! \times 3!$  coefficients  $c_{\tau, \sigma}^k$  for which we will use the short hand notation  $\vec{a}$ ,  $\vec{b}$  and  $\vec{c}$ . To determine the coefficients we insert the expansion (Eq. C.9) into Eqs. C.6. Note that Eqs. C.7 and Eqs. C.8 do not give an additional set of conditions since they are implied by Eqs. C.6. In general the result of a one-fold contraction of the expansion Eq. C.9 has the following form ( $n \in \{1 \dots 9\}$ )

$$\begin{aligned}
{}^n M_{j_1 j_2}^{i_1 i_2} &= \sum_{k=1}^6 \sum_{\substack{\mu, \nu \in S_2 \\ \mu(1) < \mu(2)}} f_{\mu, \nu}^{n, k}(\vec{a}, \vec{b}) \delta_{j_{\nu(1)}}^{i_{\mu(1)}} \delta_{j_{\nu(2)}}^{i_{\mu(2)}} {}^k M \\
&+ \sum_{k=1}^{18} \sum_{\mu, \nu \in S_2} h_{\mu, \nu}^{n, k}(\vec{b}, \vec{c}) \delta_{j_{\nu(1)}}^{i_{\mu(1)}} {}^k M_{j_{\nu(2)}}^{i_{\mu(2)}} \\
&+ \sum_{k=1}^9 \sum_{\mu, \nu \in S_2} w_{\mu, \nu}^{n, k}(\vec{c}) {}^k M_{j_{\nu(1)} j_{\nu(2)}}^{i_{\mu(1)} i_{\mu(2)}}, \tag{C.10}
\end{aligned}$$

where  $f_{\mu, \nu}^{n, k}(\vec{a}, \vec{b})$ ,  $h_{\mu, \nu}^{n, k}(\vec{b}, \vec{c})$  and  $w_{\mu, \nu}^{n, k}(\vec{c})$  are linear functions of the coefficients, and  $\mu, \nu$  are permutations in the permutation group  $S_2$ . In order for Eq. C.10 to be an identity the terms on the right hand side containing either  ${}^k M$  or  ${}^k M_j^i$  must vanish and only the term containing  ${}^n M_{j_1 j_2}^{i_1 i_2}$  appearing on the left hand side must remain. Consequently,

$$f_{\mu, \nu}^{n, k}(\vec{a}, \vec{b}) = 0 \tag{C.11}$$

$$h_{\mu, \nu}^{n, k}(\vec{b}, \vec{c}) = 0 \tag{C.12}$$

and

$$\begin{aligned}
w_{\mu, \nu}^{n, k}(\vec{c}) &= 0 \quad \text{for } \mu, \nu \neq \text{id} \\
w_{\text{id}, \text{id}}^{n, k}(\vec{c}) &= \delta_n^k, \tag{C.13}
\end{aligned}$$

	$\gamma_1$	$\gamma_2$	$\gamma_3$	$\gamma_4$	$\gamma_5$	$\gamma_6$	$\gamma_7$	$\gamma_8$	$\gamma_9$	$\gamma_{10}$	$\beta_1$	$\beta_2$	$\beta_3$	$\beta_4$	$\beta_5$	$\beta_6$	$\beta_7$	$\alpha_1$	$\alpha_2$	$\alpha_3$
$A_1$	-3	3	3	-2	-2	-2	-2	2	2	2	-1	-1	-1	-1	1	1	1	1	1	1
$A_2$	3	3	3	2	2	2	2	2	2	2	1	1	1	1	1	1	1	1	1	1
$B_1$	6	-6	-6	-2	4	1	4	-4	-1	2	0	3	-3	0	-1	1	-2	2	-4	4
$B_2$	-6	-6	-6	2	-4	-1	-4	-4	-1	2	0	-3	3	0	-1	1	-2	2	-4	4
$C_1$	-3	$\frac{3}{2}$	6	$-\frac{5}{2}$	$\frac{1}{2}$	$\frac{5}{4}$	$-\frac{7}{4}$	$\frac{1}{2}$	-1	2	1	-2	-2	4	-2	-2	1	1	4	4
$C_2$	3	$\frac{3}{2}$	6	$\frac{5}{2}$	$-\frac{1}{2}$	$-\frac{5}{4}$	$\frac{7}{4}$	$\frac{1}{2}$	-1	2	-1	2	2	-4	-2	-2	1	1	4	4
$D_1$	0	0	0	4	-2	1	-2	2	-1	-4	2	-1	-1	-4	1	1	-2	-2	4	4
$D_2$	0	0	0	-4	2	-1	2	2	-1	-4	-2	1	1	4	1	1	-2	-2	4	4
$E_1$	0	3	-6	0	0	0	0	-1	2	-4	0	0	0	0	2	-2	4	-4	-10	10
$E_2$	0	0	0	-6	-6	3	3	0	0	0	0	0	0	0	0	0	0	0	0	0

**Table C.1.:** This table defines the auxillary variables used to define the coefficients in the unitary decomposition of the 3-RDM given in Table 2-4.

where id is the identity permutation. The  $9 \times 3! \times 3!$  coefficients  $\vec{c}$  are uniquely determined by the  $9 \times 9 \times 2! \times 2!$  conditions given by Eq. C.13. Once the coefficients  $\vec{c}$  are determined the  $18 \times 3! \times 3!/2$  coefficients  $\vec{b}$  can be calculated from the  $9 \times 18 \times 2! \times 2!$  conditions of Eq. C.12 and similarly the  $6 \times 3!$  coefficients  $\vec{a}$  can be calculated from the  $9 \times 6 \times 2! \times 2!/2$  conditions contained in Eq. C.11. Note that for the coefficients  $\vec{a}, \vec{b}$  there are more equations than variables so it is not a priori guaranteed that a solution exists. However, it turns out that the set of coupled equations Eq. C.11, Eq. C.12, and Eq. C.13 has a unique solution for all orbital dimensions  $I > 4$ . This shows that  $M_{123;\perp}$  is a unique functional of the one-fold contractions. The solution for the coefficients depends solely on the number of orbitals  $I$ . We solve the equations for the coefficients using symbolic computation performed with Mathematica. We find that all coefficients can be written in the following form

$$\begin{aligned}
X = & \frac{A_1}{I-4} + \frac{A_2}{I+4} + \frac{B_1}{I-3} + \frac{B_2}{I+3} \\
& + \frac{C_1}{I-2} + \frac{C_2}{I+2} + \frac{D_1}{I-1} + \frac{D_2}{I+1} + \frac{E_1}{I} + \frac{E_2}{I^2}
\end{aligned} \tag{C.14}$$

with rational coefficients  $A_1, \dots, E_2$ . Obviously the coefficients are well defined only for  $I > 4$ . A similar result holds also for the unitary decomposition of the 2-RDM for which  $I > 2$  has to be fulfilled.

We find that the number of distinct coefficients is quite limited. It is, therefore, convenient to introduce a new set of auxiliary variables build by the set of distinct coefficients. These auxiliary variables  $\alpha_i, \beta_i$  and  $\gamma_i$  are given in Table 1. To display the ansatz coefficients in a compact way we introduce the following numbering of the permutations  $\sigma, \tau$ :

$$1 = (1, 2, 3) \quad 2 = (1, 3, 2) \quad 3 = (2, 1, 3) \quad 4 = (2, 3, 1) \quad 5 = (3, 1, 2) \quad 6 = (3, 2, 1) \tag{C.15}$$

E.g., instead of the form  $c_{(1,3,2),(2,3,1)}^k$  we will use the abreviated notation  $c_{2,4}^k$ . With this notation and the auxillary variables in Table 1 the coefficients have the solution shown in Table 2-4.



	k=1	k=2	k=3	k=4	k=5	k=6	k=7	k=8	k=9
$c_{1,1}^k$	710	73	76	73	78	71	76	71	77
$c_{1,2}^k$	74	76	73	75	71	78	72	77	71
$c_{1,3}^k$	73	710	73	78	73	78	71	76	71
$c_{1,4}^k$	76	74	76	71	75	71	77	72	77
$c_{1,5}^k$	76	73	710	71	78	73	77	71	76
$c_{1,6}^k$	73	76	74	78	71	75	71	77	72
$c_{2,1}^k$	74	75	72	76	71	77	73	78	71
$c_{2,2}^k$	79	72	75	72	77	71	75	71	78
$c_{2,3}^k$	75	74	75	71	76	71	78	73	78
$c_{2,4}^k$	72	79	72	77	72	77	71	75	71
$c_{2,5}^k$	72	75	74	77	71	76	71	78	73
$c_{2,6}^k$	75	72	79	71	77	72	78	71	75
$c_{3,1}^k$	73	78	71	710	73	76	73	78	71
$c_{3,2}^k$	75	71	78	74	76	73	75	71	78
$c_{3,3}^k$	78	73	78	73	710	73	78	73	78
$c_{3,4}^k$	71	75	71	76	74	76	71	75	71
$c_{3,5}^k$	71	78	73	76	73	710	71	78	73
$c_{3,6}^k$	78	71	75	73	76	74	78	71	75
$c_{4,1}^k$	76	71	77	74	75	72	76	71	77
$c_{4,2}^k$	72	77	71	79	72	75	72	77	71
$c_{4,3}^k$	71	76	71	75	74	75	71	76	71
$c_{4,4}^k$	77	72	77	72	79	72	77	72	77
$c_{4,5}^k$	77	71	76	72	75	74	77	71	76
$c_{4,6}^k$	71	77	72	75	72	79	71	77	72
$c_{5,1}^k$	76	71	77	73	78	71	710	73	76
$c_{5,2}^k$	72	77	71	75	71	78	74	76	73
$c_{5,3}^k$	71	76	71	78	73	78	73	710	73
$c_{5,4}^k$	77	72	77	71	75	71	76	74	76
$c_{5,5}^k$	77	71	76	71	78	73	76	73	710
$c_{5,6}^k$	71	77	72	78	71	75	73	76	74
$c_{6,1}^k$	73	78	71	76	71	77	74	75	72
$c_{6,2}^k$	75	71	78	72	77	71	79	72	75
$c_{6,3}^k$	78	73	78	71	76	71	75	74	75
$c_{6,4}^k$	71	75	71	77	72	77	72	79	72
$c_{6,5}^k$	71	78	73	77	71	76	72	75	74
$c_{6,6}^k$	78	71	75	71	77	72	75	72	79

(C.16)

**Table C.2.:** This table defines  $c$ -coefficients in the unitary decomposition of the 3-RDM defined in Equation C.9

	k=1	k=2	k=3	k=4	k=5	k=6	k=7	k=8	k=9	k=10	k=11	k=12	k=13	k=14	k=15	k=16	k=17	k=18
$b_{1,1}^k$	$\beta_4$	$\beta_5$	$\beta_5$	$\beta_2$	$\beta_3$	$\beta_6$	$\beta_5$	$\beta_2$	$\beta_4$	$\beta_5$	$\beta_6$	$\beta_3$	$\beta_3$	$\beta_6$	$\beta_6$	$\beta_3$	$\beta_1$	$\beta_7$
$b_{1,2}^k$	$\beta_5$	$\beta_4$	$\beta_3$	$\beta_6$	$\beta_5$	$\beta_2$	$\beta_2$	$\beta_5$	$\beta_6$	$\beta_3$	$\beta_4$	$\beta_5$	$\beta_6$	$\beta_3$	$\beta_1$	$\beta_7$	$\beta_6$	$\beta_3$
$b_{1,3}^k$	$\beta_5$	$\beta_2$	$\beta_4$	$\beta_5$	$\beta_6$	$\beta_3$	$\beta_4$	$\beta_5$	$\beta_5$	$\beta_2$	$\beta_3$	$\beta_6$	$\beta_6$	$\beta_3$	$\beta_3$	$\beta_6$	$\beta_7$	$\beta_1$
$b_{1,4}^k$	$\beta_3$	$\beta_6$	$\beta_5$	$\beta_4$	$\beta_2$	$\beta_5$	$\beta_6$	$\beta_3$	$\beta_2$	$\beta_5$	$\beta_5$	$\beta_4$	$\beta_1$	$\beta_7$	$\beta_6$	$\beta_3$	$\beta_3$	$\beta_6$
$b_{1,5}^k$	$\beta_2$	$\beta_5$	$\beta_6$	$\beta_3$	$\beta_4$	$\beta_5$	$\beta_5$	$\beta_4$	$\beta_3$	$\beta_6$	$\beta_5$	$\beta_2$	$\beta_3$	$\beta_6$	$\beta_7$	$\beta_1$	$\beta_3$	$\beta_6$
$b_{1,6}^k$	$\beta_6$	$\beta_3$	$\beta_2$	$\beta_5$	$\beta_5$	$\beta_4$	$\beta_3$	$\beta_6$	$\beta_5$	$\beta_4$	$\beta_2$	$\beta_5$	$\beta_7$	$\beta_1$	$\beta_3$	$\beta_6$	$\beta_6$	$\beta_3$
$b_{2,1}^k$	$\beta_5$	$\beta_4$	$\beta_2$	$\beta_5$	$\beta_6$	$\beta_3$	$\beta_3$	$\beta_6$	$\beta_6$	$\beta_3$	$\beta_1$	$\beta_7$	$\beta_5$	$\beta_2$	$\beta_4$	$\beta_5$	$\beta_6$	$\beta_3$
$b_{2,2}^k$	$\beta_4$	$\beta_5$	$\beta_6$	$\beta_3$	$\beta_2$	$\beta_5$	$\beta_6$	$\beta_3$	$\beta_1$	$\beta_7$	$\beta_6$	$\beta_3$	$\beta_2$	$\beta_5$	$\beta_6$	$\beta_3$	$\beta_4$	$\beta_5$
$b_{2,3}^k$	$\beta_2$	$\beta_5$	$\beta_5$	$\beta_4$	$\beta_3$	$\beta_6$	$\beta_6$	$\beta_3$	$\beta_3$	$\beta_6$	$\beta_7$	$\beta_1$	$\beta_4$	$\beta_5$	$\beta_5$	$\beta_2$	$\beta_3$	$\beta_6$
$b_{2,4}^k$	$\beta_6$	$\beta_3$	$\beta_4$	$\beta_5$	$\beta_5$	$\beta_2$	$\beta_1$	$\beta_7$	$\beta_6$	$\beta_3$	$\beta_3$	$\beta_6$	$\beta_6$	$\beta_3$	$\beta_2$	$\beta_5$	$\beta_5$	$\beta_4$
$b_{2,5}^k$	$\beta_5$	$\beta_2$	$\beta_3$	$\beta_6$	$\beta_5$	$\beta_4$	$\beta_3$	$\beta_6$	$\beta_7$	$\beta_1$	$\beta_3$	$\beta_6$	$\beta_5$	$\beta_4$	$\beta_3$	$\beta_6$	$\beta_5$	$\beta_2$
$b_{2,6}^k$	$\beta_3$	$\beta_6$	$\beta_5$	$\beta_2$	$\beta_4$	$\beta_5$	$\beta_7$	$\beta_1$	$\beta_3$	$\beta_6$	$\beta_6$	$\beta_3$	$\beta_3$	$\beta_6$	$\beta_5$	$\beta_4$	$\beta_2$	$\beta_5$
$b_{4,1}^k$	$\beta_3$	$\beta_6$	$\beta_6$	$\beta_3$	$\beta_1$	$\beta_7$	$\beta_5$	$\beta_4$	$\beta_2$	$\beta_5$	$\beta_6$	$\beta_3$	$\beta_2$	$\beta_5$	$\beta_5$	$\beta_4$	$\beta_3$	$\beta_6$
$b_{4,2}^k$	$\beta_6$	$\beta_3$	$\beta_1$	$\beta_7$	$\beta_6$	$\beta_3$	$\beta_4$	$\beta_5$	$\beta_6$	$\beta_3$	$\beta_2$	$\beta_5$	$\beta_5$	$\beta_2$	$\beta_3$	$\beta_6$	$\beta_5$	$\beta_4$
$b_{4,3}^k$	$\beta_6$	$\beta_3$	$\beta_3$	$\beta_6$	$\beta_7$	$\beta_1$	$\beta_2$	$\beta_5$	$\beta_5$	$\beta_4$	$\beta_3$	$\beta_6$	$\beta_5$	$\beta_4$	$\beta_2$	$\beta_5$	$\beta_6$	$\beta_3$
$b_{4,4}^k$	$\beta_1$	$\beta_7$	$\beta_6$	$\beta_3$	$\beta_3$	$\beta_6$	$\beta_6$	$\beta_3$	$\beta_4$	$\beta_5$	$\beta_5$	$\beta_2$	$\beta_3$	$\beta_6$	$\beta_5$	$\beta_2$	$\beta_4$	$\beta_5$
$b_{4,5}^k$	$\beta_3$	$\beta_6$	$\beta_7$	$\beta_1$	$\beta_3$	$\beta_6$	$\beta_5$	$\beta_2$	$\beta_3$	$\beta_6$	$\beta_5$	$\beta_4$	$\beta_4$	$\beta_5$	$\beta_6$	$\beta_3$	$\beta_2$	$\beta_5$
$b_{4,6}^k$	$\beta_7$	$\beta_1$	$\beta_3$	$\beta_6$	$\beta_6$	$\beta_3$	$\beta_3$	$\beta_6$	$\beta_5$	$\beta_2$	$\beta_4$	$\beta_5$	$\beta_6$	$\beta_3$	$\beta_4$	$\beta_5$	$\beta_5$	$\beta_2$

**Table C.3.:** This table defines  $b$ -coefficients in the unitary decomposition of the 3-RDM defined in Equation C.9

	k=1	k=2	k=3	k=4	k=5	k=6
$a_1^k$	$\alpha_3$	$\alpha_1$	$\alpha_1$	$\alpha_2$	$\alpha_2$	$\alpha_1$
$a_2^k$	$\alpha_1$	$\alpha_3$	$\alpha_2$	$\alpha_1$	$\alpha_1$	$\alpha_2$
$a_3^k$	$\alpha_1$	$\alpha_2$	$\alpha_3$	$\alpha_1$	$\alpha_1$	$\alpha_2$
$a_4^k$	$\alpha_2$	$\alpha_1$	$\alpha_1$	$\alpha_3$	$\alpha_2$	$\alpha_1$
$a_5^k$	$\alpha_2$	$\alpha_1$	$\alpha_1$	$\alpha_2$	$\alpha_3$	$\alpha_1$
$a_6^k$	$\alpha_1$	$\alpha_2$	$\alpha_2$	$\alpha_1$	$\alpha_1$	$\alpha_3$

**Table C.4.:** This table defines  $a$ -coefficients in the unitary decomposition of the 3-RDM defined in Equation C.9

## D. TDDFT calculations in 1D

While in three dimensions TDDFT is a well established theory to describe the dynamics of atomic, molecular, and solid state systems with a large number of electrons, one-dimensional TDDFT has been studied rather recently [36, 275]. The principal difference between one and three dimensions is that the Coulomb interaction  $\sim 1/|z - z'|$  leads to diverging interaction energies in 1D. This can be avoided by introducing the softened Coulomb interaction (Eq. 9.4). The equations of motion in 1D of the time-dependent Kohn-Sham orbitals are [16]

$$i\partial_t\phi_i^{\text{KS}}(z, t) = \left( -\frac{1}{2}\frac{\partial^2}{\partial z^2} + V_{\text{eff}}[\rho(z, t)] \right)\phi_i^{\text{KS}}(z, t), \quad (\text{D.1})$$

with

$$V_{\text{eff}}[\rho(z, t)] = V_{\text{H}}[\rho(z, t)] + V_{\text{x}}[\rho(z, t)] + V_{\text{c}}[\rho(z, t)], \quad (\text{D.2})$$

where  $V_{\text{H}}[\rho]$  denotes the Hartree potential

$$V_{\text{H}}[\rho(z, t)] = \int \frac{\rho(z', t)}{\sqrt{(z - z')^2 + d}} dz', \quad (\text{D.3})$$

$V_{\text{x}}[\rho(z, t)]$  and  $V_{\text{c}}[\rho(z, t)]$  denotes the exchange and correlation potential, respectively. Within the local density approximation (LDA) the exchange and correlation potential is calculated from the uniform electron gas with the 1-RDM denoted by  $D^{\text{unif}}(z; z')$ . The exchange potential  $V_{\text{x}}[\rho]$  for the 1D electron gas with softened Coulomb interaction can be evaluated analytically yielding a Meijer G-function [275]

$$\begin{aligned} V_{\text{x}}[\rho] &= -\frac{1}{4}\frac{\delta}{\delta\rho} \int \frac{|D^{\text{unif}}(z; z')|^2}{\sqrt{(z - z')^2 + d}} dzdz' \\ &= -\frac{\rho}{4} G_{1,3}^{2,1} \left( \frac{1}{2} \middle| dk_{\text{F}}^2 \right), \end{aligned} \quad (\text{D.4})$$

where  $d$  is the Coulomb softening parameter and  $k_{\text{F}} = \frac{\pi\rho}{2}$ . The correlation potential  $V_{\text{c}}[\rho]$  within LDA can be derived by quantum Monte Carlo calculations for the uniform 1D electron gas with soft Coulomb potential as discussed in [36].



## E. Matrix representation of the orbital propagation

In this appendix we evaluate the matrix elements of the operators in the equation of motion for the orbitals Eq. 6.26. The evaluation of

$$\mathbf{h} = \mathbf{T} + \mathbf{V}^{\text{ion}} + \mathbf{V}^{\text{laser}}(t) \quad (\text{E.1})$$

is straightforward with use of

$$\mathbf{T} = -\frac{1}{2}\nabla_{q,q'}^2\delta_{l,l'}\delta_{m,m'} + \frac{l(l+1)}{2r_q^2}\delta_{q,q'}\delta_{l,l'}\delta_{m,m'} \quad (\text{E.2})$$

$$\mathbf{V}^{\text{ion}} = \frac{Z}{r_q}\delta_{q,q'}\delta_{l,l'\pm 1}\delta_{m,m'} \quad (\text{E.3})$$

$$\mathbf{V}^{\text{laser}} = \begin{cases} E(t)\alpha_{lm}r_q\delta_{q,q'}\delta_{l,l\pm 1}\delta_{m,m'} & \text{in length gauge} \\ -iA(t)\alpha_{lm}(\nabla_{q,q'} - \delta_{q,q'}\frac{l\pm 1}{r_q})\delta_{l,l\pm 1}\delta_{m,m'} & \text{in velocity gauge} \end{cases} \quad (\text{E.4})$$

$$\alpha_{lm} = \sqrt{\frac{(l+1)^2 - m^2}{(2l+1)(2l+3)}}. \quad (\text{E.5})$$

The matrix elements of the gradient in the FEDVR-basis  $\nabla_{q,q'} = \langle f_q | \nabla_r | f_{q'} \rangle$  can be found, e.g. in [215]. While these operators can be evaluated directly in the spherical basis the contribution from the particle-particle interaction  $\mathbf{F}_i$  requires more careful treatment. The most efficient way is to first evaluate  $\hat{F}_i(r, \theta, t)$  in coordinate representation as

$$F_i(r, \theta, t) = \sum_{vwtu} [D^{-1}]_i^u D_{ut}^v \phi_v(r, \theta, t) \hat{W}_w^t(r, \theta, t) \quad (\text{E.6})$$

with the mean-field contribution  $\hat{W}_w^t(r_q, \theta_j, t)$  calculated by solving the poisson equation

$$\nabla^2 \hat{W}_w^t(r, \theta, t) = -4\pi\phi_t^*(r, \theta, t)\phi_w(r, \theta, t). \quad (\text{E.7})$$

Finally  $\mathbf{F}_i$  is obtained by transforming into the angular momentum basis

$$F_i^{ql} = \int Y_{m_i}^l(\theta, \phi = 0) F_i(r_q, \theta, t) d\theta \quad (\text{E.8})$$

where  $m_i$  is the magnetic quantum number of orbital  $\phi_i$ .



# Bibliography

- [1] A. Szabo and N. S. Ostlund. *Modern Quantum Chemistry*. Dover Publications (1996).
- [2] R. G. Parr and W. Yang. *Density-Functional Theory of Atoms and Molecules*. Oxford University Press (1989).
- [3] M. Nakata, H. Nakatsuji, M. Ehara, M. Fukuda, K. Nakata, and K. Fujisawa. *Variational calculations of fermion second-order reduced density matrices by semidefinite programming algorithm*. J. Chem. Phys. **114**, 8282 (2001).
- [4] M. Nakata, M. Ehara, and H. Nakatsuji. *Density matrix variational theory: Application to the potential energy surfaces and strongly correlated systems*. J. Chem. Phys. **116**, 5432 (2002).
- [5] Z. Zhao, B. J. Braams, M. Fukuda, M. L. Overton, and J. K. Percus. *The reduced density matrix method for electronic structure calculations and the role of three-index representability conditions*. J. Chem. Phys. **120**, 2095 (2004).
- [6] D. A. Mazziotti. *Realization of Quantum Chemistry without Wave Functions through First-Order Semidefinite Programming*. Phys. Rev. Lett. **93**, 213001 (2004).
- [7] D. A. Mazziotti. *Anti-Hermitian Contracted Schrödinger Equation: Direct Determination of the Two-Electron Reduced Density Matrices of Many-Electron Molecules*. Phys. Rev. Lett. **97**, 143002 (2006).
- [8] C. Garrod and J. K. Percus. *Reduction of the N-Particle Variational Problem*. J. Math. Phys. **5**, 1756 (1964).
- [9] D. A. Mazziotti. *Variational minimization of atomic and molecular ground-state energies via the two-particle reduced density matrix*. Phys. Rev. A **65**, 062511 (2002).
- [10] H. Nakatsuji and K. Yasuda. *Direct Determination of the Quantum-Mechanical Density Matrix Using the Density Equation*. Phys. Rev. Lett. **76**, 1039 (1996).
- [11] D. A. Mazziotti. *Contracted Schrödinger equation: Determining quantum energies and two-particle density matrices without wave functions*. Phys. Rev. A **57**, 4219 (1998).
- [12] D. A. Mazziotti (ed.). *Reduced-Density-Matrix Mechanics: With Application to Many-Electron Atoms and Molecules*. Advances in Chemical Physics. Wiley (2007).

- [13] A. J. Coleman. *Structure of Fermion Density Matrices*. Rev. Mod. Phys. **35**, 668 (1963).
- [14] R. M. Erdahl. *Representability*. Int. J. Quant. Chem. **13**, 697 (1978).
- [15] D. A. Mazziotti. *Structure of Fermionic Density Matrices: Complete  $N$ -Representability Conditions*. Phys. Rev. Lett. **108**, 263002 (2012).
- [16] C. Ullrich. *Time-Dependent Density-Functional Theory: Concepts and Applications*. Oxford Graduate Texts. Oxford University Press (2012).
- [17] C. A. Ullrich and E. K. U. Gross. *Many-electron atoms in strong femtosecond laser pulses: A density-functional study*. Comments At. Mol. Phys. **33**, 211 (1997).
- [18] C. A. Ullrich, U. J. Gossmann, and E. K. U. Gross. *Density-Functional Approach to Atoms in Strong Laser Pulses*. Ber. Bunsenges. Phys. Chem. **99**, 488 (1995).
- [19] X.-M. Tong and S.-I. Chu. *Time-dependent density-functional theory for strong-field multiphoton processes: Application to the study of the role of dynamical electron correlation in multiple high-order harmonic generation*. Phys. Rev. A **57**, 452 (1998).
- [20] X.-M. Tong and S.-I. Chu. *Multiphoton ionization and high-order harmonic generation of He, Ne, and Ar atoms in intense pulsed laser fields: Self-interaction-free time-dependent density-functional theoretical approach*. Phys. Rev. A **64**, 013417 (2001).
- [21] X. Chu and S.-I. Chu. *Time-dependent density-functional theory for molecular processes in strong fields: Study of multiphoton processes and dynamical response of individual valence electrons of  $N_2$  in intense laser fields*. Phys. Rev. A **64**, 063404 (2001).
- [22] T. Kreibich, N. I. Gidopoulos, R. v. Leeuwen, and E. K. U. Gross. *Towards Time-Dependent Density-Functional Theory for Molecules in Strong Laser Pulses*. In N. I. Gidopoulos and S. Wilson (eds.), *The Fundamentals of Electron Density, Density Matrix and Density Functional Theory in Atoms, Molecules and the Solid State*, number 14 in Progress in Theoretical Chemistry and Physics, pp. 69–77. Springer Netherlands (2003).
- [23] A. Pohl, P.-G. Reinhard, and E. Suraud. *Towards Single-Particle Spectroscopy of Small Metal Clusters*. Phys. Rev. Lett. **84**, 5090 (2000).
- [24] D. Bauer, F. Ceccherini, A. Macchi, and F. Cornolti.  *$C_{60}$  in intense femtosecond laser pulses: Nonlinear dipole response and ionization*. Phys. Rev. A **64**, 063203 (2001).
- [25] J. A. Driscoll, S. Bubin, and K. Varga. *Laser-induced electron emission from nanostructures: A first-principles study*. Phys. Rev. B **83**, 233405 (2011).
- [26] G. Wachter, C. Lemell, J. Burgdörfer, M. Schenk, M. Krüger, and P. Hommelhoff. *Electron rescattering at metal nanotips induced by ultrashort laser pulses*. Phys. Rev. B **86**, 035402 (2012).



- [27] T. Otobe, M. Yamagiwa, J.-I. Iwata, K. Yabana, T. Nakatsukasa, and G. F. Bertsch. *First-principles electron dynamics simulation for optical breakdown of dielectrics under an intense laser field*. Phys. Rev. B **77**, 165104 (2008).
- [28] T. Otobe, K. Yabana, and J.-I. Iwata. *First-principles calculation of the electron dynamics in crystalline SiO<sub>2</sub>*. Journal of Physics: Condensed Matter **21**, 064224 (2009).
- [29] K. Yabana, T. Sugiyama, Y. Shinohara, T. Otobe, and G. F. Bertsch. *Time-dependent density functional theory for strong electromagnetic fields in crystalline solids*. Phys. Rev. B **85**, 045134 (2012).
- [30] G. Wachter, C. Lemell, J. Burgdörfer, S. A. Sato, X.-M. Tong, and K. Yabana. *Ab Initio Simulation of Electrical Currents Induced by Ultrafast Laser Excitation of Dielectric Materials*. Phys. Rev. Lett. **113**, 087401 (2014).
- [31] N. T. Maitra, F. Zhang, R. J. Cave, and K. Burke. *Double excitations within time-dependent density functional theory linear response*. J. Chem. Phys. **120**, 5932 (2004).
- [32] J. I. Fuks, P. Elliott, A. Rubio, and N. T. Maitra. *Dynamics of Charge-Transfer Processes with Time-Dependent Density Functional Theory*. J. Phys. Chem. Lett. **4**, 735 (2013).
- [33] J. I. Fuks and N. T. Maitra. *Challenging adiabatic time-dependent density functional theory with a Hubbard dimer: the case of time-resolved long-range charge transfer*. Phys. Chem. Chem. Phys. **16**, 14504 (2014).
- [34] J. I. Fuks, N. Helbig, I. V. Tokatly, and A. Rubio. *Nonlinear phenomena in time-dependent density-functional theory: What Rabi oscillations can teach us*. Phys. Rev. B **84**, 075107 (2011).
- [35] N. Helbig, J. I. Fuks, I. V. Tokatly, H. Appel, E. K. U. Gross, and A. Rubio. *Time-dependent density-functional and reduced density-matrix methods for few electrons: Exact versus adiabatic approximations*. Chem. Phys. **391**, 1 (2011).
- [36] N. Helbig, J. I. Fuks, M. Casula, M. J. Verstraete, M. A. L. Marques, I. V. Tokatly, and A. Rubio. *Density functional theory beyond the linear regime: Validating an adiabatic local density approximation*. Phys. Rev. A **83**, 032503 (2011).
- [37] M. Ruggenthaler and D. Bauer. *Rabi Oscillations and Few-Level Approximations in Time-Dependent Density Functional Theory*. Phys. Rev. Lett. **102**, 233001 (2009).
- [38] G. Vignale and W. Kohn. *Current-Dependent Exchange-Correlation Potential for Dynamical Linear Response Theory*. Phys. Rev. Lett. **77**, 2037 (1996).
- [39] G. Vignale, C. A. Ullrich, and S. Conti. *Time-Dependent Density Functional Theory Beyond the Adiabatic Local Density Approximation*. Phys. Rev. Lett. **79**, 4878 (1997).

- 
- [40] H. O. Wijewardane and C. A. Ullrich. *Time-Dependent Kohn-Sham Theory with Memory*. Phys. Rev. Lett. **95**, 086401 (2005).
- [41] Y. Kurzweil and R. Baer. *Quantum memory effects in the dynamics of electrons in gold clusters*. Phys. Rev. B **73**, 075413 (2006).
- [42] H. O. Wijewardane and C. A. Ullrich. *Real-Time Electron Dynamics with Exact-Exchange Time-Dependent Density-Functional Theory*. Phys. Rev. Lett. **100**, 056404 (2008).
- [43] Y. Kurzweil and R. Baer. *Adapting approximate-memory potentials for time-dependent density functional theory*. Phys. Rev. B **77**, 085121 (2008).
- [44] D. Bauer. *Two-dimensional, two-electron model atom in a laser pulse: Exact treatment, single-active-electron analysis, time-dependent density-functional theory, classical calculations, and nonsequential ionization*. Phys. Rev. A **56**, 3028 (1997).
- [45] D. G. Lappas and R. van Leeuwen. *Electron correlation effects in the double ionization of He*. J. Phys. B **31**, L249 (1998).
- [46] N. Rohringer, S. Peter, and J. Burgdörfer. *Calculating state-to-state transition probabilities within time-dependent density-functional theory*. Phys. Rev. A **74**, 042512 (2006).
- [47] F. Wilken and D. Bauer. *Momentum distributions in time-dependent density-functional theory: Product-phase approximation for nonsequential double ionization in strong laser fields*. Phys. Rev. A **76**, 023409 (2007).
- [48] J. Caillat, J. Zanghellini, M. Kitzler, O. Koch, W. Kreuzer, and A. Scrinzi. *Correlated multielectron systems in strong laser fields: A multiconfiguration time-dependent Hartree-Fock approach*. Phys. Rev. A **71**, 012712 (2005).
- [49] O. E. Alon, A. I. Streltsov, and L. S. Cederbaum. *Unified view on multiconfigurational time propagation for systems consisting of identical particles*. J. Chem. Phys. **127**, (2007).
- [50] D. Hochstuhl, C. Hinz, and M. Bonitz. *Time-dependent multiconfiguration methods for the numerical simulation of photoionization processes of many-electron atoms*. Eur. Phys. J. Special Topics **223**, 177 (2014).
- [51] K. L. Ishikawa and T. Sato. *A Review on Ab Initio Approaches for Multielectron Dynamics*. IEEE J. Sel. Top. Quantum Electron. **21**, 1 (2015).
- [52] T. Sato and K. L. Ishikawa. *Time-dependent complete-active-space self-consistent-field method for multielectron dynamics in intense laser fields*. Phys. Rev. A **88**, 023402 (2013).

- 
- [53] T. Sato, K. L. Ishikawa, I. Březinová, F. Lackner, S. Nagele, and J. Burgdörfer. *Time-dependent complete-active-space self-consistent-field method for atoms: Application to high-order harmonic generation*. Phys. Rev. A **94**, 023405 (2016).
- [54] T. Sato and K. L. Ishikawa. *Time-dependent multiconfiguration self-consistent-field method based on the occupation-restricted multiple-active-space model for multielectron dynamics in intense laser fields*. Phys. Rev. A **91**, 023417 (2015).
- [55] S. Haessler, J. Caillat, W. Boutu, C. Giovanetti-Teixeira, T. Ruchon, T. Auguste, Z. Diveki, P. Breger, A. Maquet, B. Carre, R. Taieb, and P. Salieres. *Attosecond imaging of molecular electronic wavepackets*. Nat. Phys. **6**, 200 (2010).
- [56] N. N. Bogoliubov and K. P. Gurov. *Kinetic Equations in Quantum Mechanics*. JETP (in Russian) **17**, 614 (1947).
- [57] N. N. Bogoliubov. *Lectures on Quantum Statistics*. Number Bd. 1 in Lectures on Quantum Statistics. Gordon and Breach science publishers (1967).
- [58] P. C. Martin and J. Schwinger. *Theory of Many-Particle Systems. I*. Phys. Rev. **115**, 1342 (1959).
- [59] D. B. Boercker and J. W. Dufty. *Degenerate quantum gases in the binary collision approximation*. Ann. Phys. **119**, 43 (1979).
- [60] W. Shun-jin and W. Cassing. *Explicit treatment of N-body correlations within a density-matrix formalism*. Ann. Phys. **159**, 328 (1985).
- [61] J. W. Dufty and D. B. Boercker. *Classical and quantum kinetic equations with exact conservation laws*. J. Stat. Phys. **57**, 827 (1989).
- [62] K.-J. Schmitt, P.-G. Reinhard, and C. Toepffer. *Truncation of time-dependent many-body theories*. Z. Phys. A **336**, 123 (1990).
- [63] W. Cassing and A. Pfitzner. *Self-consistent truncation of the BBGKY hierarchy on the two-body level*. Z. Phys. A **342**, 161 (1992).
- [64] F. Colmenero, C. Pérez del Valle, and C. Valdemoro. *Approximating q-order reduced density matrices in terms of the lower-order ones. I. General relations*. Phys. Rev. A **47**, 971 (1993).
- [65] M. Tohyama and P. Schuck. *Density-matrix formalism with three-body ground-state correlations*. Eur. Phys. J. A **45**, 257 (2010).
- [66] M. Tohyama and P. Schuck. *Truncation scheme of time-dependent density-matrix approach*. Eur. Phys. J. A **50**, 1 (2014).
- [67] P. Schuck and M. Tohyama. *Self-consistent RPA and the time-dependent density matrix approach*. Eur. Phys. J. A **52**, 307 (2016).

- [68] P. Schuck and M. Tohyama. *Progress in many-body theory with the equation of motion method: Time-dependent density matrix meets self-consistent RPA and applications to solvable models*. Phys. Rev. B **93**, 165117 (2016).
- [69] T. Ghorega, R. Krieg, P. G. Reinhard, and C. Toepffer. *Dynamics of correlations in a solvable model*. Nucl. Phys. A **560**, 166 (1993).
- [70] A. Akbari, M. J. Hashemi, A. Rubio, R. M. Nieminen, and R. van Leeuwen. *Challenges in truncating the hierarchy of time-dependent reduced density matrices equations*. Phys. Rev. B **85**, 235121 (2012).
- [71] B. Schäfer-Bung and M. Nest. *Correlated dynamics of electrons with reduced two-electron density matrices*. Phys. Rev. A **78**, 012512 (2008).
- [72] F. Krausz and M. Ivanov. *Attosecond physics*. Rev. Mod. Phys. **81**, 163 (2009).
- [73] P. Zeitoun, G. Faivre, S. Sebban, T. Mocek, A. Hallou, M. Fajardo, D. Aubert, P. Balcou, F. Burgy, D. Douillet, S. Kazamias, G. de Lachèze-Murel, T. Lefrou, S. le Pape, P. Mercère, H. Merdji, A. S. Morlens, J. P. Rousseau, and C. Valentin. *A high-intensity highly coherent soft X-ray femtosecond laser seeded by a high harmonic beam*. Nature **431**, 426 (2004).
- [74] A. D. Shiner, B. E. Schmidt, C. Trallero-Herrero, H. J. Wörner, S. Patchkovskii, P. B. Corkum, J.-C. Kieffer, F. Légaré, and D. M. Villeneuve. *Probing collective multi-electron dynamics in xenon with high-harmonic spectroscopy*. Nature Phys. **7**, 464 (2011).
- [75] J. Itatani, J. Levesque, D. Zeidler, H. Niikura, H. Pépin, J. C. Kieffer, P. B. Corkum, and D. M. Villeneuve. *Tomographic imaging of molecular orbitals*. Nature **432**, 867 (2004).
- [76] J. L. Krause, K. J. Schafer, and K. C. Kulander. *High-order harmonic generation from atoms and ions in the high intensity regime*. Phys. Rev. Lett. **68**, 3535 (1992).
- [77] P. B. Corkum. *Plasma perspective on strong field multiphoton ionization*. Phys. Rev. Lett. **71**, 1994 (1993).
- [78] T. Kanai, S. Minemoto, and H. Sakai. *Quantum interference during high-order harmonic generation from aligned molecules*. Nature **435**, 470 (2005).
- [79] C. Vozzi, F. Calegari, E. Benedetti, J.-P. Caumes, G. Sansone, S. Stagira, M. Nisoli, R. Torres, E. Heesel, N. Kajumba, J. P. Marangos, C. Altucci, and R. Velotta. *Controlling Two-Center Interference in Molecular High Harmonic Generation*. Phys. Rev. Lett. **95**, 153902 (2005).
- [80] M. Lein, N. Hay, R. Velotta, J. P. Marangos, and P. L. Knight. *Interference effects in high-order harmonic generation with molecules*. Phys. Rev. A **66**, 023805 (2002).

- 
- [81] F. Lackner, I. Březinová, T. Sato, K. L. Ishikawa, and J. Burgdörfer. *The time-dependent two-particle reduced density matrix method: LiH in strong laser fields*. J. Phys. Conf. Ser. **635**, 112084 (2015).
- [82] F. Lackner, I. Březinová, T. Sato, K. L. Ishikawa, and J. Burgdörfer. *High-harmonic spectra from time-dependent two-particle reduced-density-matrix theory*. Phys. Rev. A **95**, 033414 (2017).
- [83] F. Lackner, I. Březinová, T. Sato, K. L. Ishikawa, and J. Burgdörfer. *Time-Dependent Two-Particle Reduced Density Matrix Theory: Application to High-Harmonic Generation*. Journal of Physics: Conference Series **875**, 022032 (2017).
- [84] E. Schrödinger. *Quantisierung als Eigenwertproblem*. Annalen der Physik **384**, 361 (1926).
- [85] T. Brabec (ed.). *Strong Field Laser Physics*. Springer Series in Optical Sciences. Springer (2008).
- [86] C. Joachain, N. Kylstra, and R. Potvliege. *Atoms in Intense Laser Fields*. Cambridge University Press (2012).
- [87] K. J. Schafer and K. C. Kulander. *Energy analysis of time-dependent wave functions: Application to above-threshold ionization*. Phys. Rev. A **42**, 5794 (1990).
- [88] P. Antoine, B. Piraux, and A. Maquet. *Time profile of harmonics generated by a single atom in a strong electromagnetic field*. Phys. Rev. A **51**, R1750 (1995).
- [89] M. Dörr, O. Latinne, and C. J. Joachain. *Time evolution of two-photon population transfer between the 1s and 2s states of a hydrogen atom*. Phys. Rev. A **55**, 3697 (1997).
- [90] D. Bauer and P. Mulser. *Exact field ionization rates in the barrier-suppression regime from numerical time-dependent Schrödinger-equation calculations*. Phys. Rev. A **59**, 569 (1999).
- [91] P. Lambropoulos, P. Maragakis, and J. Zhang. *Two-electron atoms in strong fields*. Phys. Rep. **305**, 203 (1998).
- [92] J. S. Parker, E. S. Smyth, and K. T. Taylor. *Intense-field multiphoton ionization of helium*. J. Phys. B **31**, L571 (1998).
- [93] J. Feist, S. Nagele, R. Pazourek, E. Persson, B. I. Schneider, L. A. Collins, and J. Burgdörfer. *Nonsequential two-photon double ionization of helium*. Phys. Rev. A **77**, 043420 (2008).
- [94] V. P. Majety, A. Zielinski, and A. Scrinzi. *Photoionization of few electron systems: a hybrid coupled channels approach*. New J. Phys. **17**, 063002 (2015).

- [95] K. C. Kulander. *Time-dependent theory of multiphoton ionization of xenon*. Phys. Rev. A **38**, 778 (1988).
- [96] J. L. Krause, K. J. Schafer, and K. C. Kulander. *Calculation of photoemission from atoms subject to intense laser fields*. Phys. Rev. A **45**, 4998 (1992).
- [97] H. G. Muller. *Numerical simulation of high-order above-threshold-ionization enhancement in argon*. Phys. Rev. A **60**, 1341 (1999).
- [98] X. M. Tong and C. D. Lin. *Empirical formula for static field ionization rates of atoms and molecules by lasers in the barrier-suppression regime*. J. Phys. B **38**, 2593 (2005).
- [99] D. N. Fittinghoff, P. R. Bolton, B. Chang, and K. C. Kulander. *Observation of nonsequential double ionization of helium with optical tunneling*. Phys. Rev. Lett. **69**, 2642 (1992).
- [100] K. Kondo, A. Sagisaka, T. Tamida, Y. Nabekawa, and S. Watanabe. *Wavelength dependence of nonsequential double ionization in He*. Phys. Rev. A **48**, R2531 (1993).
- [101] B. Walker, B. Sheehy, L. F. DiMauro, P. Agostini, K. J. Schafer, and K. C. Kulander. *Precision Measurement of Strong Field Double Ionization of Helium*. Phys. Rev. Lett. **73**, 1227 (1994).
- [102] S. Larochelle, A. Talebpour, and S. L. Chin. *Non-sequential multiple ionization of rare gas atoms in a Ti:Sapphire laser field*. J. Phys. B **31**, 1201 (1998).
- [103] H. W. van der Hart, M. A. Lysaght, and P. G. Burke. *Time-dependent multielectron dynamics of Ar in intense short laser pulses*. Phys. Rev. A **76**, 043405 (2007).
- [104] L. A. A. Nikolopoulos, J. S. Parker, and K. T. Taylor. *Combined R-matrix eigenstate basis set and finite-difference propagation method for the time-dependent Schrödinger equation: The one-electron case*. Phys. Rev. A **78**, 063420 (2008).
- [105] L. R. Moore, M. A. Lysaght, J. S. Parker, H. W. van der Hart, and K. T. Taylor. *Time delay between photoemission from the 2p and 2s subshells of neon*. Phys. Rev. A **84**, 061404 (2011).
- [106] M. A. Lysaght, L. R. Moore, L. A. A. Nikolopoulos, J. S. Parker, H. W. van der Hart, and K. T. Taylor. *The RMT method for describing many-electron atoms in intense short laser pulses*. J. Phys. Conf. Ser. **388**, 012027 (2012).
- [107] J. Wragg, J. S. Parker, and H. W. van der Hart. *Double ionization in R-matrix theory using a two-electron outer region*. Phys. Rev. A **92**, 022504 (2015).
- [108] P. A. M. Dirac. *Note on Exchange Phenomena in the Thomas Atom*. Mathematical Proceedings of the Cambridge Philosophical Society **26**, 376 (1930).

- [109] A. D. McLachlan and M. A. Ball. *Time-Dependent Hartree-Fock Theory for Molecules*. Rev. Mod. Phys. **36**, 844 (1964).
- [110] D. R. Hartree. *The Wave Mechanics of an Atom with a Non-Coulomb Central Field. Part I. Theory and Methods*. Mathematical Proceedings of the Cambridge Philosophical Society **24**, 89 (1928).
- [111] V. Fock. *Näherungsmethode zur Lösung des quantenmechanischen Mehrkörperproblems*. Z. Phys. **61**, 126 (1930).
- [112] K. C. Kulander. *Time-dependent Hartree-Fock theory of multiphoton ionization: Helium*. Phys. Rev. A **36**, 2726 (1987).
- [113] P. Krause, T. Klamroth, and P. Saalfrank. *Time-dependent configuration-interaction calculations of laser-pulse-driven many-electron dynamics: Controlled dipole switching in lithium cyanide*. J. Chem. Phys. **123**, 074105 (2005).
- [114] L. Greenman, P. J. Ho, S. Pabst, E. Kamarchik, D. A. Mazziotti, and R. Santra. *Implementation of the time-dependent configuration-interaction singles method for atomic strong-field processes*. Phys. Rev. A **82**, 023406 (2010).
- [115] D. Hochstuhl and M. Bonitz. *Time-dependent restricted-active-space configuration-interaction method for the photoionization of many-electron atoms*. Phys. Rev. A **86**, 053424 (2012).
- [116] S. Pabst and R. Santra. *Strong-Field Many-Body Physics and the Giant Enhancement in the High-Harmonic Spectrum of Xenon*. Phys. Rev. Lett. **111**, 233005 (2013).
- [117] A. Karamatskou, S. Pabst, Y.-J. Chen, and R. Santra. *Calculation of photoelectron spectra within the time-dependent configuration-interaction singles scheme*. Phys. Rev. A **89**, 033415 (2014).
- [118] S. Bauch, L. K. Sørensen, and L. B. Madsen. *Time-dependent generalized-active-space configuration-interaction approach to photoionization dynamics of atoms and molecules*. Phys. Rev. A **90**, 062508 (2014).
- [119] S. Chattopadhyay, S. Bauch, and L. B. Madsen. *Electron-correlation effects in enhanced ionization of molecules: A time-dependent generalized-active-space configuration-interaction study*. Phys. Rev. A **92**, 063423 (2015).
- [120] J. Zanghellini, M. Kitzler, T. Brabec, and A. Scrinzi. *Testing the multi-configuration time-dependent Hartree-Fock method*. J. Phys. B **37**, 763 (2004).
- [121] M. Kitzler, J. Zanghellini, C. Jungreuthmayer, M. Smits, A. Scrinzi, and T. Brabec. *Ionization dynamics of extended multielectron systems*. Phys. Rev. A **70**, 041401 (2004).

- [122] D. Hochstuhl, S. Bauch, and M. Bonitz. *Multiconfigurational time-dependent Hartree-Fock calculations for photoionization of one-dimensional Helium*. J. Phys. Conf. Ser. **220**, 012019 (2010).
- [123] T. Sato and K. L. Ishikawa. *The structure of approximate two electron wavefunctions in intense laser driven ionization dynamics*. J. Phys. B **47**, 204031 (2014).
- [124] T. Kato and H. Kono. *Time-dependent multiconfiguration theory for electronic dynamics of molecules in an intense laser field*. Chem. Phys. Lett. **392**, 533 (2004).
- [125] G. Jordan, J. Caillat, C. Ede, and A. Scrinzi. *Strong field ionization of linear molecules: a correlated three-dimensional calculation*. J. Phys. B **39**, S341 (2006).
- [126] T. Kato and H. Kono. *Time-dependent multiconfiguration theory for ultrafast electronic dynamics of molecules in an intense laser field: Electron correlation and energy redistribution among natural orbitals*. Chem. Phys. **366**, 46 (2009).
- [127] D. Hochstuhl and M. Bonitz. *Two-photon ionization of helium studied with the multiconfigurational time-dependent Hartree-Fock method*. J. Chem. Phys. **134**, 084106 (2011).
- [128] D. J. Haxton, K. V. Lawler, and C. W. McCurdy. *Multiconfiguration time-dependent Hartree-Fock treatment of electronic and nuclear dynamics in diatomic molecules*. Phys. Rev. A **83**, 063416 (2011).
- [129] D. J. Haxton, K. V. Lawler, and C. W. McCurdy. *Single photoionization of Be and HF using the multiconfiguration time-dependent Hartree-Fock method*. Phys. Rev. A **86**, 013406 (2012).
- [130] H. R. Larsson, S. Bauch, L. K. Sørensen, and M. Bonitz. *Correlation effects in strong-field ionization of heteronuclear diatomic molecules*. Phys. Rev. A **93**, 013426 (2016).
- [131] R. Sawada, T. Sato, and K. L. Ishikawa. *Implementation of the multiconfiguration time-dependent Hartree-Fock method for general molecules on a multiresolution Cartesian grid*. Phys. Rev. A **93**, 023434 (2016).
- [132] Y. Ide, T. Kato, and K. Yamanouchi. *Non-Born-Oppenheimer molecular wave functions of  $H_2$  by extended multi-configuration time-dependent Hartree-Fock method*. Chem. Phys. Lett. **595-596**, 180 (2014).
- [133] T. Helgaker, P. Jørgensen, and J. Olsen. *Molecular electronic-structure theory*. Wiley (2000).
- [134] N. Rohringer, A. Gordon, and R. Santra. *Configuration-interaction-based time-dependent orbital approach for ab initio treatment of electronic dynamics in a strong optical laser field*. Phys. Rev. A **74**, 043420 (2006).



- 
- [135] H. Miyagi and L. B. Madsen. *Time-dependent restricted-active-space self-consistent-field theory for laser-driven many-electron dynamics*. Phys. Rev. A **87**, 062511 (2013).
- [136] H. Miyagi and L. B. Madsen. *Time-dependent restricted-active-space self-consistent-field singles method for many-electron dynamics*. J. Chem. Phys. **140**, 164309 (2014).
- [137] H. Miyagi and L. B. Madsen. *Time-dependent restricted-active-space self-consistent-field theory for laser-driven many-electron dynamics. II. Extended formulation and numerical analysis*. Phys. Rev. A **89**, 063416 (2014).
- [138] D. J. Haxton and C. W. McCurdy. *Two methods for restricted configuration spaces within the multiconfiguration time-dependent Hartree-Fock method*. Phys. Rev. A **91**, 012509 (2015).
- [139] G. Vidal. *Efficient Simulation of One-Dimensional Quantum Many-Body Systems*. Phys. Rev. Lett. **93**, 040502 (2004).
- [140] E. Ronca, Z. Li, C. A. Jimenez-Hoyos, and G. K.-L. Chan. *Time-step targeting time-dependent and dynamical density matrix renormalization group algorithms with ab initio Hamiltonians*. J. Chem. Theory Comput. (2017).
- [141] G. H. Booth, A. J. W. Thom, and A. Alavi. *Fermion Monte Carlo without fixed nodes: A game of life, death, and annihilation in Slater determinant space*. J. Chem. Phys. **131**, 054106 (2009).
- [142] K. Guthrie, W. Dobrautz, O. Gunnarsson, and A. Alavi. *Time propagation and spectroscopy of Fermionic systems using a stochastic technique*. arXiv:1709.00218 [cond-mat] (2017).
- [143] L. Kong, F. A. Bischoff, and E. F. Valeev. *Explicitly Correlated R12/F12 Methods for Electronic Structure*. Chem. Rev.s **112**, 75 (2012).
- [144] J. Rychlewski. *Explicitly Correlated Wave Functions in Chemistry and Physics: Theory and Applications*. Progress in Theoretical Chemistry and Physics. Springer Netherlands (2003).
- [145] A. J. Coleman and R. M. Erdahl. *Report of the Density Matrix Seminar*. Defense Technical Information Center (1970).
- [146] F. D. Peat. *Density Matrices*. In H. Eyring, D. Henderson, and W. Jost (eds.), *Physical Chemistry vol. XI A*. Academic Press Inc., San Francisco (1975).
- [147] E. Davidson. *Reduced Density Matrices in Quantum Chemistry*. Theoretical Chemistry. Academic Press (1976).
- [148] R. M. Erdahl and V. H. Smith. *Density Matrices and Density Functionals*. Springer (1987).

- [149] J. Cioslowski. *Many-Electron Densities and Reduced Density Matrices*. Mathematical and Computational Chemistry. Springer (2000).
- [150] A. Coleman and V. Yukalov. *Reduced Density Matrices: Coulson's Challenge*. Lecture Notes in Chemistry. Springer (2000).
- [151] J. von Neumann. *Wahrscheinlichkeitstheoretischer Aufbau der Quantenmechanik*. Nachrichten von der Gesellschaft der Wissenschaften zu Göttingen, Mathematisch-Physikalische Klasse **1927**, 245 (1927).
- [152] D. H. Kobe. *Natural Orbitals, Divergences, and Variational Principles*. J. Chem. Phys. **50**, 5183 (1969).
- [153] K. Husimi. *Some Formal Properties of the Density Matrix*. Proceedings of the Physico-Mathematical Society of Japan. 3rd Series **22**, 264 (1940).
- [154] P. O. Löwdin. *Quantum Theory of Many-Particle Systems. I. Physical Interpretations by Means of Density Matrices, Natural Spin-Orbitals, and Convergence Problems in the Method of Configurational Interaction*. Phys. Rev. **97**, 1474 (1955).
- [155] M. Rosina and C. Garrod. *The variational calculation of reduced density matrices*. J. Comput. Phys. **18**, 300 (1975).
- [156] R. M. Erdahl. *Two algorithms for the lower bound method of reduced density matrix theory*. Reports on Mathematical Physics **15**, 147 (1979).
- [157] D. A. Mazziotti. *Two-Electron Reduced Density Matrix as the Basic Variable in Many-Electron Quantum Chemistry and Physics*. Chem. Rev.s **112**, 244 (2012).
- [158] J. E. Mayer. *Electron Correlation*. Phys. Rev. **100**, 1579 (1955).
- [159] R. H. Tredgold. *Density Matrix and the Many-Body Problem*. Phys. Rev. **105**, 1421 (1957).
- [160] F. Bopp. *Ableitung der Bindungsenergie von N-Teilchen-Systemen aus 2-Teilchen-Dichtematrizen*. Z. Phys. **156**, 348 (1959).
- [161] A. Muller. *Explicit approximate relation between reduced two- and one-particle density matrices*. Phys. Lett. A **105**, 446 (1984).
- [162] M. Piris. *A new approach for the two-electron cumulant in natural orbital functional theory*. Int. J. Quantum Chem. **106**, 1093 (2006).
- [163] D. A. Mazziotti. *Approximate solution for electron correlation through the use of Schwinger probes*. Chem. Phys. Lett. **289**, 419 (1998).
- [164] W. Kutzelnigg and D. Mukherjee. *Cumulant expansion of the reduced density matrices*. J. Chem. Phys. **110**, 2800 (1999).

- 
- [165] J. T. Skolnik and D. A. Mazziotti. *Cumulant reduced density matrices as measures of statistical dependence and entanglement between electronic quantum domains with application to photosynthetic light harvesting*. Phys. Rev. A **88**, 032517 (2013).
- [166] M. Bonitz. *Quantum Kinetic Theory*. Teubner-Texte zur Physik. Teubner (1998).
- [167] A. A. Abrikosov, I. Dzyaloshinskii, L. P. Gorkov, and R. A. Silverman. *Methods of quantum field theory in statistical physics*. Dover (1975).
- [168] R. P. Feynman. *Space-Time Approach to Quantum Electrodynamics*. Phys. Rev. **76**, 769 (1949).
- [169] M. Gell-Mann and F. Low. *Bound States in Quantum Field Theory*. Phys. Rev. **84**, 350 (1951).
- [170] R. Mattuck. *A Guide to Feynman Diagrams in the Many-body Problem*. Dover Books on Physics Series. Dover Publications (1976).
- [171] G. C. Wick. *The Evaluation of the Collision Matrix*. Phys. Rev. **80**, 268 (1950).
- [172] K. A. Brueckner. *Many-Body Problem for Strongly Interacting Particles. II. Linked Cluster Expansion*. Phys. Rev. **100**, 36 (1955).
- [173] J. Goldstone. *Derivation of the Brueckner Many-Body Theory*. Proc. Royal Soc. A **239**, 267 (1957).
- [174] C. Møller and M. S. Plesset. *Note on an Approximation Treatment for Many-Electron Systems*. Phys. Rev. **46**, 618 (1934).
- [175] R. J. Bartlett. *Many-Body Perturbation Theory and Coupled Cluster Theory for Electron Correlation in Molecules*. Annu. Rev. Phys. Chem. **32**, 359 (1981).
- [176] K. J. H. Giesbertz, O. V. Gritsenko, and E. J. Baerends. *Time-Dependent Reduced Density Matrix Functional Theory*. In M. A. Marques, N. T. Maitra, F. M. Nogueira, E. Gross, and A. Rubio (eds.), *Fundamentals of Time-Dependent Density Functional Theory*, pp. 485–498. Springer (2012).
- [177] M. Brics and D. Bauer. *Time-dependent renormalized natural orbital theory applied to the two-electron spin-singlet case: Ground state, linear response, and autoionization*. Phys. Rev. A **88**, 052514 (2013).
- [178] L. H. Thomas. *The calculation of atomic fields*. Mathematical Proceedings of the Cambridge Philosophical Society **23**, 542 (1927).
- [179] E. Fermi. *Eine statistische Methode zur Bestimmung einiger Eigenschaften des Atoms und ihre Anwendung auf die Theorie des periodischen Systems der Elemente*. Z. Phys. **48**, 73 (1928).

- [180] P. Hohenberg and W. Kohn. *Inhomogeneous Electron Gas*. Phys. Rev. **136**, B864 (1964).
- [181] R. M. Dreizler and E. K. U. Gross. *Density Functional Theory: An Approach to the Quantum Many-Body Problem*. Springer (2012).
- [182] S. H. Vosko, L. Wilk, and M. Nusair. *Accurate spin-dependent electron liquid correlation energies for local spin density calculations: a critical analysis*. Can. J. Phys. **58**, 1200 (1980).
- [183] J. P. Perdew and Y. Wang. *Accurate and simple analytic representation of the electron-gas correlation energy*. Phys. Rev. B **45**, 13244 (1992).
- [184] W. Kohn and L. J. Sham. *Self-Consistent Equations Including Exchange and Correlation Effects*. Phys. Rev. **140**, A1133 (1965).
- [185] R. van Leeuwen. *Mapping from Densities to Potentials in Time-Dependent Density-Functional Theory*. Phys. Rev. Lett. **82**, 3863 (1999).
- [186] E. Runge and E. K. U. Gross. *Density-Functional Theory for Time-Dependent Systems*. Phys. Rev. Lett. **52**, 997 (1984).
- [187] K. J. Schafer. *Numerical Methods in Strong Field Physics*. In T. Brabec (ed.), *Strong Field Laser Physics*, pp. 111–145. Springer (2009).
- [188] M. Lein and S. Kümmel. *Exact Time-Dependent Exchange-Correlation Potentials for Strong-Field Electron Dynamics*. Phys. Rev. Lett. **94**, 143003 (2005).
- [189] F. Wilken and D. Bauer. *Adiabatic Approximation of the Correlation Function in the Density-Functional Treatment of Ionization Processes*. Phys. Rev. Lett. **97**, 203001 (2006).
- [190] H. Appel and E. K. U. Gross. *Time-dependent natural orbitals and occupation numbers*. EPL (Europhysics Letters) **92**, 23001 (2010).
- [191] B. C. Carlson and J. M. Keller. *Eigenvalues of Density Matrices*. Phys. Rev. **121**, 659 (1961).
- [192] M. Brics, J. Rapp, and D. Bauer. *Nonsequential double ionization with time-dependent renormalized-natural-orbital theory*. Phys. Rev. A **90**, 053418 (2014).
- [193] M. Brics, J. Rapp, and D. Bauer. *Strong-field absorption and emission of radiation in two-electron systems calculated with time-dependent natural orbitals*. Phys. Rev. A **93**, 013404 (2016).
- [194] M. Brics, J. Rapp, and D. Bauer. *Single-photon double ionization: renormalized-natural-orbital theory versus multi-configurational Hartree-Fock*. J. Phys. B **50**, 144003 (2017).

- 
- [195] A. K. Rajam, I. Raczkowska, and N. T. Maitra. *Semiclassical Electron Correlation in Density-Matrix Time Propagation*. Phys. Rev. Lett. **105** (2010).
- [196] T. L. Gilbert. *Hohenberg-Kohn theorem for nonlocal external potentials*. Phys. Rev. B **12**, 2111 (1975).
- [197] K. Yasuda and H. Nakatsuji. *Direct determination of the quantum-mechanical density matrix using the density equation. II*. Phys. Rev. A **56**, 2648 (1997).
- [198] D. A. Mazziotti. *Purification of correlated reduced density matrices*. Phys. Rev. E **65**, 026704 (2002).
- [199] F. Lackner, I. Březinová, T. Sato, K. L. Ishikawa, and J. Burgdörfer. *Propagating two-particle reduced density matrices without wave functions*. Phys. Rev. A **91**, 023412 (2015).
- [200] N. N. Bogoliubov. *Kinetic Equations*. Journal of Physics USSR **10**, 265 (1946).
- [201] M. Born, F. R. S, and H. S. Green. *A general kinetic theory of liquids I. The molecular distribution functions*. Proc. R. Soc. Lond. A **188**, 10 (1946).
- [202] J. G. Kirkwood. *The Statistical Mechanical Theory of Transport Processes I. General Theory*. J. Chem. Phys. **14**, 180 (1946).
- [203] M. S. Green. *Boltzmann Equation from the Statistical Mechanical Point of View*. J. Chem. Phys. **25**, 836 (1956).
- [204] H. D. Ursell. *The evaluation of Gibbs' phase-integral for imperfect gases*. Mathematical Proceedings of the Cambridge Philosophical Society **23**, 685 (1927).
- [205] D. A. Mazziotti. *Complete reconstruction of reduced density matrices*. Chem. Phys. Lett. **326**, 212 (2000).
- [206] R. Mattuck and A. Theumann. *Expressing the decoupled equations of motion for the Green's function as a partial sum of Feynman diagrams*. Adv. Phys. **20**, 721 (1971).
- [207] G. Stefanucci and R. van Leeuwen. *Nonequilibrium Many-Body Theory of Quantum Systems: A Modern Introduction*. Cambridge University Press (2013).
- [208] R. McWeeny and Y. Mizuno. *Density matrix in many-electron quantum mechanics. 2. Separation of space and spin variables - spin coupling problems*. Proc. R. Soc. London A **259**, 554 (1961).
- [209] J. E. Harriman. *Geometry of density matrices. IV. The relationship between density matrices and densities*. Phys. Rev. A **27**, 632 (1983).
- [210] C.-C. Sun, X.-Q. Li, and A.-C. Tang. *Lie algebra and unitarily invariant decomposition of Hermitian operators*. Int. J. Quantum Chem. **25**, 653 (1984).

- [211] C. Garrod and M. Rosina. *Particle-Hole Matrix: Its Connection with the Symmetries and Collective Features of the Ground State*. *J. Math. Phys.* **10**, 1855 (1969).
- [212] Y.-K. Liu, M. Christandl, and F. Verstraete. *Quantum Computational Complexity of the  $N$ -Representability Problem: QMA Complete*. *Phys. Rev. Lett.* **98**, 110503 (2007).
- [213] M. Altunbulak and A. Klyachko. *The Pauli Principle Revisited*. *Commun. Math. Phys.* **282**, 287 (2008).
- [214] D. R. Alcoba, F. J. Casquero, L. M. Tel, E. Pérez-Romero, and C. Valdemoro. *Convergence enhancement in the iterative solution of the second-order contracted Schrödinger equation*. *Int. J. Quant. Chem.* **102**, 620 (2005).
- [215] B. I. Schneider, J. Feist, S. Nagele, R. Pazourek, S. Hu, L. A. Collins, and J. Burgdörfer. *Recent Advances in Computational Methods for the Solution of the Time-Dependent Schrödinger Equation for the Interaction of Short, Intense Radiation with One and Two Electron Systems*, pp. 149–208. Springer (2011).
- [216] J. Crank and P. Nicolson. *A practical method for numerical evaluation of solutions of partial differential equations of the heat-conduction type*. *Advances in Computational Mathematics* **6**, 207 (1996).
- [217] W. H. Press, S. A. Teukolsky, W. T. Vetterling, and B. P. Flannery. *Numerical Recipes 3rd Edition: The Art of Scientific Computing*. Cambridge University Press (2007).
- [218] A. McPherson, G. Gibson, H. Jara, U. Johann, T. S. Luk, I. A. McIntyre, K. Boyer, and C. K. Rhodes. *Studies of multiphoton production of vacuum-ultraviolet radiation in the rare gases*. *J. Opt. Soc. Am. B* **4**, 595 (1987).
- [219] M. Ferray, A. L’Huillier, X. F. Li, L. A. Lompre, G. Mainfray, and C. Manus. *Multiple-harmonic conversion of 1064 nm radiation in rare gases*. *J. Phys. B* **21**, L31 (1988).
- [220] X. F. Li, A. L’Huillier, M. Ferray, L. A. Lompré, and G. Mainfray. *Multiple-harmonic generation in rare gases at high laser intensity*. *Phys. Rev. A* **39**, 5751 (1989).
- [221] P. A. Franken, A. E. Hill, C. W. Peters, and G. Weinreich. *Generation of Optical Harmonics*. *Phys. Rev. Lett.* **7**, 118 (1961).
- [222] P. Salières, A. L’Huillier, P. Antoine, and M. Lewenstein. *Study of The Spatial and Temporal Coherence of High-Order Harmonics*. In B. Bederson and H. Walther (eds.), *Advances In Atomic, Molecular, and Optical Physics*, volume 41, pp. 83–142. Academic Press (1999).
- [223] P. M. Paul, E. S. Toma, P. Breger, G. Mullot, F. Augé, P. Balcou, H. G. Muller, and P. Agostini. *Observation of a Train of Attosecond Pulses from High Harmonic Generation*. *Science* **292**, 1689 (2001).

- 
- [224] M. Hentschel, R. Kienberger, C. Spielmann, G. A. Reider, N. Milosevic, T. Brabec, P. Corkum, U. Heinzmann, M. Drescher, and F. Krausz. *Attosecond metrology*. *Nature* **414**, 509 (2001).
- [225] M. Lewenstein, P. Balcou, M. Y. Ivanov, A. L'Huillier, and P. B. Corkum. *Theory of high-harmonic generation by low-frequency laser fields*. *Phys. Rev. A* **49**, 2117 (1994).
- [226] M. Y. Ivanov, T. Brabec, and N. Burnett. *Coulomb corrections and polarization effects in high-intensity high-harmonic emission*. *Phys. Rev. A* **54**, 742 (1996).
- [227] C. C. Chirilă, C. J. Joachain, N. J. Kylstra, and R. M. Potvliege. *Interaction of Superintense Laser Pulses with Relativistic Ions*. *Phys. Rev. Lett.* **93**, 243603 (2004).
- [228] Y.-C. Han and L. B. Madsen. *Comparison between length and velocity gauges in quantum simulations of high-order harmonic generation*. *Phys. Rev. A* **81**, 063430 (2010).
- [229] T. Brabec and F. Krausz. *Intense few-cycle laser fields: Frontiers of nonlinear optics*. *Rev. Mod. Phys.* **72**, 545 (2000).
- [230] A. L'Huillier, P. Balcou, S. Candel, K. J. Schafer, and K. C. Kulander. *Calculations of high-order harmonic-generation processes in xenon at 1064 nm*. *Phys. Rev. A* **46**, 2778 (1992).
- [231] D. G. Lappas, A. Sanpera, J. B. Watson, K. Burnett, P. L. Knight, R. Grobe, and J. H. Eberly. *Two-electron effects in harmonic generation and ionization from a model He atom*. *J. Phys. B* **29**, L619 (1996).
- [232] S. Sukiasyan, C. McDonald, C. Destefani, M. Y. Ivanov, and T. Brabec. *Multielectron Correlation in High-Harmonic Generation: A 2D Model Analysis*. *Phys. Rev. Lett.* **102** (2009).
- [233] H. Shi-Lin and S. Ting-Yun. *Effect of electron correlation on high-order harmonic generation in helium model atom*. *Chinese Physics B* **22**, 013101 (2013).
- [234] A. Brown and H. van der Hart. *Extreme-Ultraviolet-Initiated High-Order Harmonic Generation: Driving Inner-Valence Electrons Using Below-Threshold-Energy Extreme-Ultraviolet Light*. *Phys. Rev. Lett.* **117**, 093201 (2016).
- [235] A. N. Artemyev, L. S. Cederbaum, and P. V. Demekhin. *Impact of two-electron dynamics and correlations on high-order-harmonic generation in He*. *Phys. Rev. A* **95**, 033402 (2017).
- [236] R. Blackman and J. Tukey. *The measurement of power spectra, from the point of view of communications engineering*. Dover books on engineering and engineering physics. Dover Publications (1958).

- [237] V. S. Yakovlev and A. Scrinzi. *High Harmonic Imaging of Few-Cycle Laser Pulses*. Phys. Rev. Lett. **91**, 153901 (2003).
- [238] D. Bauer. *Emergence of Classical Orbits in Few-Cycle Above-Threshold Ionization of Atomic Hydrogen*. Phys. Rev. Lett. **94**, 113001 (2005).
- [239] C. F. d. M. Faria and X. Liu. *Electron-electron correlation in strong laser fields*. J. Mod. Opt. **58**, 1076 (2011).
- [240] W.-C. Liu, J. H. Eberly, S. L. Haan, and R. Grobe. *Correlation Effects in Two-Electron Model Atoms in Intense Laser Fields*. Phys. Rev. Lett. **83**, 520 (1999).
- [241] M. Petersilka and E. K. U. Gross. *Strong-field double ionization of helium: a density-functional perspective*. Laser Phys. **9**, 105 (1999).
- [242] D. Bauer and F. Ceccherini. *Time-dependent density functional theory applied to nonsequential multiple ionization of Ne at 800 nm*. Opt. Express **8**, 377 (2001).
- [243] M. G. Pullen, B. Wolter, X. Wang, X.-M. Tong, M. Sclafani, M. Baudisch, H. Pires, C. D. Schröter, J. Ullrich, T. Pfeifer, R. Moshhammer, J. H. Eberly, and J. Biegert. *Transition from nonsequential to sequential double ionization in many-electron systems*. Phys. Rev. A **96**, 033401 (2017).
- [244] J. S. Parker, L. R. Moore, D. Dundas, and K. T. Taylor. *Double ionization of helium at 390 nm*. J. Phys. B **33**, L691 (2000).
- [245] H. G. Muller. *Non-sequential double ionization of helium and related wave-function dynamics obtained from a five-dimensional grid calculation*. Opt. Express **8**, 417 (2001).
- [246] R. Moshhammer, B. Feuerstein, W. Schmitt, A. Dorn, C. D. Schröter, J. Ullrich, H. Rottker, C. Trump, M. Wittmann, G. Korn, K. Hoffmann, and W. Sandner. *Momentum Distributions of Ne<sup>+</sup> Ions Created by an Intense Ultrashort Laser Pulse*. Phys. Rev. Lett. **84**, 447 (2000).
- [247] B. Bergues, M. Kubel, N. Kling, C. Burger, and M. Kling. *Single-Cycle Non-Sequential Double Ionization*. IEEE J. Sel. Top. Quantum Electron. **21**, 1 (2015).
- [248] R. Torres, R. de Nalda, and J. P. Marangos. *Dynamics of laser-induced molecular alignment in the impulsive and adiabatic regimes: A direct comparison*. Phys. Rev. A **72**, 023420 (2005).
- [249] G. L. Kamta and A. D. Bandrauk. *High-order harmonic generation from two-center molecules: Time-profile analysis of nuclear contributions*. Phys. Rev. A **70**, 011404 (2004).
- [250] M. Lein. *Molecular imaging using recolliding electrons*. J. Phys. B **40**, R135 (2007).



- [251] M.-Z. Li, G.-R. Jia, and X.-B. Bian. *Alignment dependent ultrafast electron-nuclear dynamics in molecular high-order harmonic generation*. J. Chem. Phys. **146**, 084305 (2017).
- [252] H. Ahmadi, M. Vafaee, and A. Maghari. *Understanding molecular harmonic emission at relatively long intense laser pulses: Beyond the Born-Oppenheimer approximation*. Phys. Rev. A **94**, 033415 (2016).
- [253] X.-B. Bian and A. D. Bandrauk. *Probing Nuclear Motion by Frequency Modulation of Molecular High-Order Harmonic Generation*. Phys. Rev. Lett. **113**, 193901 (2014).
- [254] K. Harumiya, H. Kono, Y. Fujimura, I. Kawata, and A. D. Bandrauk. *Intense laser-field ionization of H<sub>2</sub> enhanced by two-electron dynamics*. Phys. Rev. A **66**, 043403 (2002).
- [255] S. Patchkovskii, Z. Zhao, T. Brabec, and D. M. Villeneuve. *High Harmonic Generation and Molecular Orbital Tomography in Multielectron Systems: Beyond the Single Active Electron Approximation*. Phys. Rev. Lett. **97**, 123003 (2006).
- [256] B. K. McFarland, J. P. Farrell, P. H. Bucksbaum, and M. Gühr. *High Harmonic Generation from Multiple Orbitals in N<sub>2</sub>*. Science **322**, 1232 (2008).
- [257] O. Smirnova, Y. Mairesse, S. Patchkovskii, N. Dudovich, D. Villeneuve, P. Corkum, and M. Y. Ivanov. *High harmonic interferometry of multi-electron dynamics in molecules*. Nature **460**, 972 (2009).
- [258] C. Figueira de Morisson Faria and B. B. Augstein. *Molecular high-order harmonic generation with more than one active orbital: Quantum interference effects*. Phys. Rev. A **81**, 043409 (2010).
- [259] C. Guo, M. Li, and G. N. Gibson. *Charge Asymmetric Dissociation Induced by Sequential and Nonsequential Strong Field Ionization*. Phys. Rev. Lett. **82**, 2492 (1999).
- [260] W. Lai, L. Pei, and C. Guo. *Dissociation of doubly and triply charged N<sub>2</sub> in strong laser fields*. Phys. Rev. A **84**, 043413 (2011).
- [261] M. A. Marques, M. J. Oliveira, and T. Burnus. *Libxc: A library of exchange and correlation functionals for density functional theory*. Comput. Phys. Commun. **183**, 2272 (2012).
- [262] D. Hochstuhl and M. Bonitz. *Two-photon ionization of helium studied with the multiconfigurational time-dependent Hartree-Fock method*. J. Chem. Phys. **134**, 084106 (2011).
- [263] N. E. Dahlen and R. van Leeuwen. *Double ionization of a two-electron system in the time-dependent extended Hartree-Fock approximation*. Phys. Rev. A **64**, 023405 (2001).

- [264] H. Yu, T. Zuo, and A. D. Bandrauk. *Molecules in intense laser fields: Enhanced ionization in a one-dimensional model of H<sub>2</sub>*. Phys. Rev. A **54**, 3290 (1996).
- [265] K. Balzer, S. Bauch, and M. Bonitz. *Time-dependent second-order Born calculations for model atoms and molecules in strong laser fields*. Phys. Rev. A **82**, 033427 (2010).
- [266] J. Javanainen, J. H. Eberly, and Q. Su. *Numerical simulations of multiphoton ionization and above-threshold electron spectra*. Phys. Rev. A **38**, 3430 (1988).
- [267] M. S. Pindzola, D. C. Griffin, and C. Bottcher. *Validity of time-dependent Hartree-Fock theory for the multiphoton ionization of atoms*. Phys. Rev. Lett. **66**, 2305 (1991).
- [268] T. Koopmans. *Über die Zuordnung von Wellenfunktionen und Eigenwerten zu den Einzelnen Elektronen Eines Atoms*. Physica **1**, 104 (1934).
- [269] T. Tohyama, Y. Inoue, K. Tsutsui, and S. Maekawa. *Exact diagonalization study of optical conductivity in the two-dimensional Hubbard model*. Phys. Rev. B **72**, 045113 (2005).
- [270] U. Schneider, L. Hackermüller, J. P. Ronzheimer, S. Will, S. Braun, T. Best, I. Bloch, E. Demler, S. Mandt, D. Rasch, and A. Rosch. *Fermionic transport and out-of-equilibrium dynamics in a homogeneous Hubbard model with ultracold atoms*. Nature Phys. **8**, 213 (2012).
- [271] D. R. Alcoba. *Unitarily invariant decomposition of arbitrary Hermitian matrices of physical interest*. Int. J. of Quant. Chem. **97**, 776 (2004).
- [272] R. Wald. *General Relativity*. University of Chicago Press (1984).
- [273] J. E. Harriman. *Grassmann products, cumulants, and two-electron reduced density matrices*. Phys. Rev. A **65**, 052507 (2002).
- [274] C.-C. Sun, X.-Q. Li, and A.-C. Tang. *On the unitarily invariant decomposition of Hermitian operators*. Int. J. Quantum Chem. **25**, 1045 (1984).
- [275] L. O. Wagner, E. M. Stoudenmire, K. Burke, and S. R. White. *Reference electronic structure calculations in one dimension*. Phys. Chem. Chem. Phys. **14**, 8581 (2012).

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