Christian-Albrechts Universität zu Kiel
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Diploma Thesis

Unrestricted Hartree-Fock Theory of Nonideal Bose Systems

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1 Introduction

1.1 Motivation

The interest and investigation of bosonic systems dates back to the beginning of quantum mechanics and is nowadays far from being restricted to the investigation of Bose-Einstein-condensation (BEC) and superfluidity. There are several aspects and phenomena in condensed matter and atomic physics that are closely connected to Bose statistics.

In 1924 Satyendra Nath Bose marked the starting point in the investigation of bosonic systems with a proposal for a quantum statistical treatment of photons [1]. This work inspired Einstein, who applied the idea to atoms and predicted the BEC. It is remarkable that the theoretical prediction of BEC in 1925 and its experimental realization differ 70 years in time. In 1995, the group of C. E. Wieman and E. A. Cornell observed the condensation of alkali atoms that where confined in a trap by magnetic fields and evaporatively cooled [2], a success that brought this group the Nobel Prize in 2001. Experimentalists owe a lot of this success to the preeminent physical and technical spadeworks such as laser cooling [3] or Paul trapping [4].

Superfluidity is a phase of matter which is strongly connected to BEC. The first experimental observation of this phenomenon traces back to the two groups of Pyotr Kapitza in Moscow and Don Misener in Cambridge in 1937. Kapitza was awarded the Nobel Prize for his discoveries. The theoretical explanation of superfluidity is due to Lev Davidovich Landau which earned him the Nobel Prize.

The so called fermionization of bosonic systems was predicted by Girardeau in 1960 [5] and had to wait more than 40 years for its experimental realization [6] by the group of Belén Paredes. In this so called Tonks-Girardeau regime, the repulsive interactions between bosonic particles confined to one dimension dominate the physics of the system and its physical properties resemble those of fermions with the same interaction. This can be understood intuitively, by regarding the strong repulsive interaction as a mimic of the Pauli exclusion principle for fermions.

The investigation of bosonic systems is not only highly interesting for fundamental physics, but is also important for several applications, for instance the realization of an atom laser [7] or quantum information [8]. Bosons that are trapped in an optical lattice evince other interesting phenomena. In 2002, the group of M. Greiner detected a Mott-insulator phase transition between a superfluid and a Mott-insulator phase of bosons trapped in an optical lattice [9].

There exist a variety of methods to analyze bosonic many particle systems theoretically, including extensive computer simulations. In contrast to fermions, bosonic particles are well approachable with Path-Integral Monte-Carlo (PIMC) [10]. It achieves

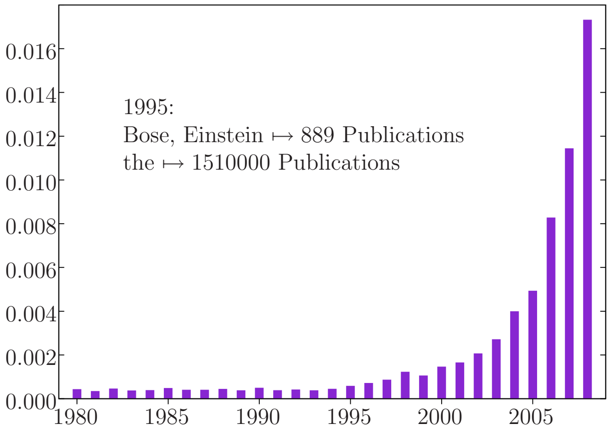

Figure 1.1: *Number of publications that contain the words "Bose" and "Einstein", divided by the number of publications containing the word "the" as normalization. The absolute numbers of publications of the year 1995 are given in the graphic.*

exact results for systems with particle numbers up to several 100 bosons and serves well for the numerical treatment of phenomena as mentioned above. Unfortunately, this method does not provide the possibility to consider time-dependent systems. Furthermore, for the interpretation and understanding of physical phenomena, approaches are needed that are not just a mathematical method, but rather a physical model.

The Gross-Pitaevskii approximation (GP) is a good approach to analyze the wave function of the condensate fraction. It even holds for time-dependent systems and serves to explain phenomena such as solitons [11]. However, its basic assumptions do not suit such systems as considered in this work. The main topic of this work will be the analysis and implementation of an approximation scheme that is very closely connected to GP but goes beyond and hence is able to explain more effects that appear in bosonic systems. It was first introduced by Igor Romanovsky in 2004 [12]. This approximations will be applied to systems of up to 8 charged bosons trapped in a one- and two-dimensional harmonic confinement. I will explain the relation of this method to others that are able to deal with the same kind of systems and compare their capability to explain the here mentioned phenomena.

1.2 Outline

The content of this thesis is subdivided as follows:

Chapter 2 gives an overview of the thermodynamics of bosonic systems. It starts with the introduction of the reduced one-body density matrix, which is needed for the calculation of the expectation values of observables and can be used to determine the condensate fraction. Furthermore, the physical interpretation for systems with lower dimensionality is given and the phenomenon of fermionization is discussed, which only arises in one-dimensional systems. The final section emphasizes that for bosonic systems with fixed particle number, the description in the canonical ensemble is required instead of the grand canonical ensemble.

A summary of all single permanent ansatz approximations that apply the Ritz principle is presented in chapter 3. The commonalities, differences, and features are emphasized. Special attention is given to the GP approximation. All these ansatzes can be extended to the time-dependent regime via the time-dependent variational principle, which is also explained within this chapter.

Chapter 4 goes more into detail with the most general case of the single Slater permanent ansatz – the so called unrestricted bosonic Hartree-Fock approximation (UBHF). The crucial equations are derived and a numerical scheme for solving these equations is presented. Some special properties are discussed, such as the occupation numbers of the natural orbitals in UBHF. The equations of motion of the time-dependent extension of this ansatz are derived.

Chapter 5 presents the results obtained with UBHF and compares some quantitative and qualitative results with the results obtained by the GP approximation and an exact method called configuration interaction. It is shown that with the UBHF approximation metastable solutions can be obtained. For two dimensional systems, the breaking of the rotational symmetry is discussed. Finally, a comparison of the time-dependent UBHF approximation with an exact method is shown.

Chapter 6 deals with the programs that were developed for the diploma thesis. It gives an overview of the structure of the programs. Also, it can be used as a manual for people who want to analyze bosonic systems with this implementation.

The last chapter summarizes the results of this work followed by some remarks on unsolved problems and possible extensions of the UBHF approximations.

The appendix presents either some detailed calculations that are needed for understanding the mathematical derivations in this work, or calculations that are related to the topic of this work, but do not fit into the main chapters. Some important recursion relations for the canonical treatment of ideal many particle systems that are not present in the literature are derived in appendix F. In E, a generalization of the Ryser algorithm to a special type of matrices is given. Appendix D presents an alternative approach to the usual derivation of the Hartree-Fock Hamiltonian in the grand canonical ensemble.

2 Bose systems

Bosons are particles with integer spin. Their many-body wave function is symmetric under an arbitrary permutation of the arguments, where each argument contains all required quantum numbers of the single particle state (coordinate, spin, isospin, etc.). Thus bosons do not obey the Pauli principle and can accumulate in the same state. In the introduction a short overview of the main properties and phenomena of bosonic systems was given. This chapter introduces the required mathematical techniques and presents further details of some bosonic effects.

2.1 The reduced one-body density matrix

An important entity that helps to indicate the appearance of a condensate is the reduced one-bode density matrix (ROBDM). [1] It can be defined for arbitrary mixtures or pure states.

BEC is associated with the condensation of atoms in the state of lowest energy. The question that arises directly from this definition, is in which state the system condenses if no single particle orbital can be related with an energy as is the case for interacting particles. Thus for nonideal systems a generalized definition of the orbital of the condensate is needed. Hence we need to find the orbital φ that maximizes the functional

$$n[\varphi] = \langle \hat{n}_\varphi \rangle \,, \tag{2.1}$$

where $\hat{n}_\varphi$ is the occupation number operator of the state φ and $\langle\rangle$ denotes the expectation value with respect to an arbitrary mixture of states. Such a mixture can always be represented by the statistical density operator $\hat{\rho}$. The expectation value $\langle \hat{A} \rangle$ of an arbitrary operator $\hat{A}$ with respect to a mixture given by $\hat{\rho}$ can be expressed by the trace

$$\langle \hat{A} \rangle = \mathrm{Tr}(\hat{A}\hat{\rho}) = \sum_\alpha \langle \alpha | \hat{A}\hat{\rho} | \alpha \rangle \,, \tag{2.2}$$

with the sum ranging over a complete orthonormal set of states. The operator $\hat{n}_\varphi$ in equation (2.1) can be expressed as a product of the creation operator $\hat{a}^\dagger_\varphi$ and the annihilation operator $\hat{a}_\varphi$ of second quantization formalism. The action of $\hat{a}^\dagger_\varphi$ ($\hat{a}_\varphi$) yields a state with the occupation number of the state $|\varphi\rangle$ being increased (decreased) by one. The operators $\hat{a}^\dagger_\varphi$ and $\hat{a}_\varphi$ themselves can be expressed via the field operators $\hat{\Psi}^\dagger(x)$ and

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[1] The ROBDM is fundamentally different to the thermodynamical density operator $\hat{\rho} = \frac{1}{Z} e^{-\beta \hat{H}}$, which is (also) called density matrix, if it is regarded in coordinate space representation [13].

$\hat{\Psi}(x)$ [2]:

$$\hat{n}_\varphi = \hat{a}^\dagger_\varphi \hat{a}_\varphi = \Big(\int \mathrm{d}x\, \varphi(x)\hat{\Psi}^\dagger(x)\Big)\Big(\int \mathrm{d}y\, \varphi^*(y)\hat{\Psi}(y)\Big) = \int \mathrm{d}x\, \mathrm{d}y\, \varphi(x)\varphi^*(y)\, \hat{\Psi}^\dagger(x)\hat{\Psi}(y)\ . \tag{2.3}$$

This expression can be used for $\hat{n}_\varphi$ in equation (2.1). As φ has to be normalized, a Lagrange multiplier ν that guarantees this side condition is introduced. Thus one obtains the following functional, which is of high importance for determining the condensate fraction

$$\int \mathrm{d}x\, \mathrm{d}y\, \varphi^*(x)\, \mathfrak{g}(x,y)\, \varphi(y) - \nu \int \mathrm{d}x \varphi^*(x)\varphi(x)\ , \tag{2.4}$$

where the one-body density matrix has been defined as:

$$\mathfrak{g}(x,y) := \langle \hat{\Psi}^\dagger(x)\hat{\Psi}(y)\rangle\ . \tag{2.5}$$

It can be considered as the kernel of an operator that will henceforth be called reduced one-body density operator (ROBDO).

In order to find the wave function φ that minimizes (2.4), the variational derivative with respect to φ^* of (2.4) must be performed. This yields the equation

$$\frac{\delta}{\delta\varphi^*(x)}\Big(\int \mathrm{d}z\, \mathrm{d}y\, \varphi^*(z)\, \mathfrak{g}(z,y)\, \varphi(y) - \nu \int \mathrm{d}z \varphi^*(z)\varphi(z)\Big) = \int \mathrm{d}y \mathfrak{g}(z,y)\varphi(y) - \nu\varphi(z) \overset{!}{=} 0$$

$$\Longleftrightarrow \qquad \int \mathrm{d}y\, \mathfrak{g}(x,y)\varphi(y) = \nu\varphi(x)\ . \tag{2.6}$$

The reduced one-body density matrix is the kernel of the before mentioned abstract operator ROBDO that acts on the one-particle Hilbert space (see Chap. 2.1.1). As this operator is hermitian, a CONS of solutions $\varphi(x)$ of equation (2.6) is obtained. By multiplying (2.6) with $\varphi(x)$ and integrate over $\mathrm{d}x$, one recognizes the Lagrange multiplier ν as the occupation number of the orbital φ. Thus the orbital with the highest eigenvalue (highest occupation number) is the orbital of the condensate – supposing the system is in a condensed phase.

Even if the system is not Bose-Einstein condensed, the reduced one-body density matrix is a very useful entity. E.g., it allows one to calculate the expectation value of all one-body operators.

2.1.1 Symmetries of the one-body density matrix

The natural orbitals of a quantum mechanical system are obtained by solving the eigenvalue problem (2.6). In this section, only thermodynamical averaging or averages over pure states, which are eigenstates of the Hamiltonian are considered for the definition of the reduced one-body density matrix (2.5).

The eigenvalues n_i are the occupation numbers of the orbitals with the wave function φ_i. With the definition of the field operators $\hat{\Psi}(x) = \sum_k \phi_k(x)\hat{a}_k$ – with k representing an arbitrary CONS – equation (2.6) converts to

$$\sum_{kl} \underbrace{\int \mathrm{d}y \phi^*_k(y)\varphi_i(y)}_{=:c_{ik}}\, \phi_l(x)\, \langle \hat{a}^\dagger_l \hat{a}_k\rangle = \sum_{kl} c_{ik}\phi_l(x)\, \langle \hat{a}^\dagger_l \hat{a}_k\rangle = n_i\varphi_i(x) \tag{2.7}$$

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[2] For a detailed introduction into the second quantization formalism see e.g. [14].

In order to obtain the lth expansion coefficient c_{li} of $\varphi_i(x)$ with respect to the considered basis $\{\phi_k\}$, the latter equation is multiplied with $\phi_l^*(x)$ and integrated over $\mathrm{d}x$ [3]:

$$\sum_k \langle \hat{a}_l^\dagger \hat{a}_k \rangle \, c_{ki} = n_i c_{li} \tag{2.8}$$

Thus the definition of the natural orbitals is independent of the basis in which the reduced one-body density matrix is represented and it is appropriate to write down equation (2.6) in an abstract way:

$$\hat{\mathfrak{g}} \, |i\rangle = n_i \, |i\rangle \tag{2.9}$$

$\hat{\mathfrak{g}}$ is the before mentioned ROBDO and is defined by

$$\hat{\mathfrak{g}} = \sum_{kl} \langle \hat{a}_k^\dagger \hat{a}_l \rangle \, |k\rangle \, \langle l| \tag{2.10}$$

where $|k\rangle$ and $|l\rangle$ represent an arbitrary CONS. With this definition, it can easily be seen that the operator $\hat{\mathfrak{g}}$ is hermitian and hence has a complete set of eigenvectors. Now it is of interest, wether the ROBDO commutes with any hermitian operator $\hat{O}$ that in turn commutes with the Hamiltonian $\hat{H}$:

$$[\hat{H}, \hat{O}] = 0 \qquad \Longrightarrow \qquad [\hat{O}, \hat{\mathfrak{g}}] = 0 \; , \tag{2.11}$$

what turns out to be the case for one-body operators, if the averaging is thermal. If necessary, the operators $\hat{H}, \hat{O}$ and $\hat{\mathfrak{g}}$ can be considered in second quantization. Implication (2.11) is valid if $\hat{O}$ is a pure one-body operator, what will be shown in now. Without loss of generality, $\hat{\mathfrak{g}}$ will be regarded in the representation respective to the CONS of eigenstates of $\hat{O}$ (Choose $|k\rangle$ and $|l\rangle \, l$ in Eq. (2.10) such that $\hat{O} \, |k\rangle = o_k \, |k\rangle$). Then the commutator of $\hat{\mathfrak{g}}$ and $\hat{O}$ is written as

$$[\hat{\mathfrak{g}}, \hat{O}] = \sum_{kl} \langle \hat{a}_k^\dagger \hat{a}_l \rangle \, [\, |k\rangle \, \langle l| \, , \hat{O}] = \sum_{kl} \langle \hat{a}_k^\dagger \hat{a}_l \rangle \, (o_l - o_k) \, |k\rangle \, \langle l| \; . \tag{2.12}$$

Now it needs to be shown that for an average with the density operator $\hat{\rho}$ given by $\hat{\rho} = \frac{1}{Z} e^{-\beta \hat{H}}$ (thermal average), the density matrix holds

$$\langle \hat{a}_k^\dagger \hat{a}_l \rangle \, (o_l - o_k) = 0 \tag{2.13}$$

If the averaging is to be performed in the grand canonical ensemble, the additional conditions $[\hat{N}, \hat{O}] = [\hat{H}, \hat{N}] = [\hat{H} - \mu \hat{N}, \hat{O}] = 0$ are required. The auxiliary term with the chemical potential μ that arises in the exponent for the grand canonical averaging can be pushed into the one-particle part of the Hamiltonian where it only leads to a shift of the zero point of the potential. Thus if $[\hat{H}, \hat{O}] = 0$ is valid, then

$$\left[\frac{1}{Z} e^{-\beta \hat{H}} \; , \, \hat{O} \right] = 0. \tag{2.14}$$

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[3] Perform the scalar product with ϕ_l from the left.

It will be shown that $\langle \hat{a}_k^\dagger \hat{a}_l \rangle$ differs from zero if and only if $o_k = o_l$.

Consider the action of the operators $\hat{\rho}$ and $\hat{a}_k^\dagger \hat{a}_l$ on the many-particle eigenstate $|n_1 n_2 \ldots\rangle$ of $\hat{O}$ – with n_k being the occupation number of the kth eigenstate of $\hat{O}$. The action of the density operator $\hat{\rho}$ does not change the eigenvalue with respect to $\hat{O}$ (because $[\hat{H}, \hat{O}] \Rightarrow [\frac{1}{Z} e^{-\beta \hat{H}}, \hat{O}]$). However, the operator $\hat{a}_k^\dagger \hat{a}_l$ does if $o_k \neq o_l$, since

$$\hat{O}\hat{a}_k^\dagger \hat{a}_l |n_1 n_2 \ldots\rangle = \sqrt{n_l(n_k+1)}\Big(\sum_i n_i o_i + o_k - o_l\Big) |n_1 \ldots n_k + 1 \ldots n_l - 1 \ldots\rangle \tag{2.15}$$

The product states $|n_1 n_2 \ldots\rangle$ serve as a CONS for the performance of the trace for the average (Eq. (2.2)). The summand appearing under the trace holds

$$\langle n_1 n_2 \ldots | \hat{\rho} \hat{a}_k^\dagger \hat{a}_l |n_1 n_2 \ldots\rangle = 0, \qquad \text{for } o_k \neq o_l \tag{2.16}$$

$$\Rightarrow \langle \hat{a}_k^\dagger \hat{a}_l \rangle = 0, \qquad \text{for } o_k \neq o_l \tag{2.17}$$

$$\Rightarrow \langle \hat{a}_k^\dagger \hat{a}_l \rangle (o_l - o_k) = 0, \qquad \text{for all } k, l \tag{2.18}$$

Inserting this in Eq. (2.12) yields

$$[\hat{H}, \hat{O}] = 0 \qquad \Longrightarrow \qquad [\hat{O}, \hat{\mathfrak{g}}] = 0 \tag{2.19}$$

for all hermitian one-body operators $\hat{O}$. This gives rise to the question, why this is not the case for two-body operators or higher. The main problem is that the eigenstates of operators that contain a two-particle operator cannot be represented in the simple fashion as symmetrized product states, as in equation (2.16). In Chap. 5 it will be seen that the approximations that are analyzed in this work break certain symmetries of the system, such as rotational symmetry.

2.2 Bose systems in lower dimensions

Although the physical coordinate space has three dimensions, there exist several experimental justifications for the theoretical treatment of systems with lower dimensionality. In the one-particle model such a simplification can be made, if the Hamilton operator is composed additively by commuting Hamiltonians for systems with lower dimensions, e.g. the three-dimensional harmonic oscillator or the free particle.

The Hamiltonian for interacting many particle systems can in general not be decomposed this way. But also for ideal systems where this decomposition is still possible, it is unsuitable for the necessary consideration of particle statistics. E.g. for fermions, the Pauli principle forbids two particles to reside in the same orbital respective to the full Hamiltonian. If the orbitals can be decomposed as products of orbitals with lower dimensionality, a one-dimensional part of an *orbital* can be multiply *occupied* in the sense that there can be several occupied 3D-orbitals that have the same 1D-part in the same direction as a factor. This is also intimated by the fact that the partition function (either canonical or grand canonical) for an ideal system with a decomposable Hamiltonian does not factorize into partition functions for each dimension.

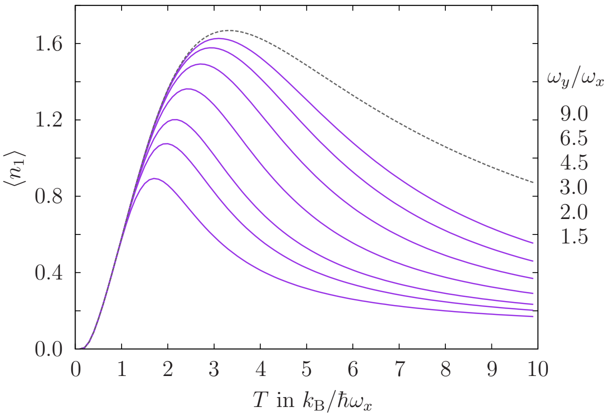

Figure 2.1: *Thermal mean occupation number of the orbital with the second lowest energy for systems with* $N = 8$ *particles in different cases of anisotropy in the 2D harmonic oscillator. The dashed black line is the occupation number for 1D systems. The order of the ratios of the trap frequencies (given on the left) are related to the maximum values of the corresponding graphs (from top to bottom). Note that for the isotropic case* ($\omega_y/\omega_x = 1.0$) *the considered orbital belongs to a two-fold degenerate energy level.*

The reduction to lower dimensions in these cases can be justified for extremely anisotropic systems, where the excitation of the system preferentially occurs in a certain direction. As illustrative example, consider an anisotropic harmonic oscillator with $\omega_y = 3\omega_x$. The energy of the orbital $|n_x n_y\rangle$ is given by $E_{n_x n_y} = \hbar\omega_x(2 + n_x + 3 \cdot n_y)$. Thus the four orbitals with the lowest energy are

$$|00\rangle \rightarrow 2\hbar\omega_x, \qquad |20\rangle \rightarrow 4\hbar\omega_x,$$
$$|10\rangle \rightarrow 3\hbar\omega_x, \qquad |30\rangle, |01\rangle \rightarrow 5\hbar\omega_x\ .$$

I.e., an excitation in y-direction is not given until the fourth energy level. For extremely anisotropic cases, one can neglect the effects that arise from the excitation of the system in the direction of steeply increasing values for the energy levels. Such a tendency is called “freezing out a dimension”. In figure 2.1 the occupation number of the orbital with the second lowest energy eigenvalue is shown for different cases of anisotropy. It can be seen that for low temperatures and high anisotropy ($\omega_y/\omega_x \gg 1$), the graphs resemble the 1D case. Hence, in this regime, the 1D model of the system is suitable.

2.3 Fermionization of 1D Bose systems

In 1960 M. Girardeau predicted that one-dimensional Bose systems have the same density and energy spectrum as spinless[4] fermions if the particle interaction contains an impenetrable hard core [5]. This means that if the particle interaction of a 1D system demands the wave function to vanish if the distance of two particles becomes less than a certain limit a

$$\Psi(x_1, \ldots, x_N) = 0 \ \text{ if exist } \ i, j : \ |x_i - x_j| \leq a\ , \tag{2.20}$$

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[4] Or spinpolarised

the bosonic (Ψ^B) and the fermionic (Ψ^F) wave functions that solve the Schrödinger equation of the system are related to each other as follows:

$$\Psi^B(x_1,\dots,x_N) = \Psi^F(x_1,\dots,x_N)\prod_{i<j}\mathrm{sign}(x_i - x_j)\ , \tag{2.21}$$

where the product on the left side rebuilds the correct symmetry of the bosonic wave function. This so called Tonks-Girardeau gas has first been observed by the group of B. Paredes with ultracold rubidium atoms held in an optical lattice [6]. The mapping – given by Eq. (2.20) – does not imply that the bosonic many particle state fulfills such a simple relation in other representations than coordinate space (e.g. momentum space). The momentum space distribution of the bosonic state differs crucially from the fermionic case, even phenomena such as condensation are still observed in the Tonks-Girardeau limit [15]. This implies that the density matrix is not a good entity by which to detect the fermionization limit of the system. For such analizations, the two-particle density is required, which is explained in the following.

2.3.1 The two-particle density

The two-particle density $\mathbf{n}(x,x')$ is the only function necessary to determine the interaction energy. Thus for a system with a hard core interaction, the two-particle density must also vanish if the distance $|x-x'|$ enters the forbidden sphere. Thus, the probability of finding two particles at the same place

$$p_{\text{together}} = \int \mathbf{n}(x,x)\,\mathrm{d}x\ , \tag{2.22}$$

is a good indicator for the fermionization of the system.

An example for an interaction with a hard core is the one dimensional Coulomb interaction [5]

$$w(x,x') = \frac{\lambda}{|x-x'|}\ , \tag{2.23}$$

which is of particular interest in this work. The coupling parameter λ will be explained later in Chap. 5. To show that this interaction indeed has a hard core, it has to be shown that the interaction energy diverges if $\mathbf{n}(x,x)\neq 0$ for at least one x. The total interaction energy is calculated by

$$\langle\hat{W}\rangle = \frac{1}{2}\lambda\iint \mathrm{d}x_1\,\mathrm{d}x_2\frac{\mathbf{n}(x_1,x_2)}{|x_1-x_2|}\ . \tag{2.24}$$

Transformation to relative and center of mass coordinates $\binom{y_1}{y_2} = \frac{1}{\sqrt{2}}\binom{x_1+x_2}{-x_1+x_2}$ leads to

$$\langle\hat{W}\rangle = \frac{\lambda}{2}\int \mathrm{d}y_2\frac{1}{|y_2|}\underbrace{\int \mathrm{d}y_1\tilde{\mathbf{n}}(y_1,y_2)}_{=:I(y_2)\geq 0} = \frac{\lambda}{2}\int \mathrm{d}y\frac{I(y)}{|y|}\ .$$

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[5] Here the 1D Coulomb interaction is just the restriction of the familiar 3D Coulomb interaction to particles that have only one spatial degree of freedom. Not to be confused with the Green's function of the one dimensional Laplace operator

The latter integral is only defined if $I(0) = 0$. As the density with the substituted parameters is always positive ($\tilde{\mathbf{n}}(y_1, y_2) \geq 0$ for all y_1, y_2), this is only given if $\tilde{\mathbf{n}}(y_1, y_2)|_{y_2=0} \equiv 0 \Leftrightarrow \mathbf{n}(x, x) \equiv 0$. In Chap. 5, systems with shielded Coulomb interaction (equation (5.1)) are considered. In this case, the transition to fermionic systems proceeds very slowly with respect to small shielding parameters [16].

2.4 Canonical versus grand canonical ensemble

The prevailing literature about quantum statistics performs its analysis in the grand canonical ensemble. This is motivated by the simplicity of the grand canonical probability distributions for ideal systems, which are given by the Bose-Einstein or the Fermi-Dirac distributions (see Eq. (F.1) in App. F) as well as by the equivalence of both ensembles in the oftend considered thermodynamic limit. However, for bosonic systems with finite particle numbers, the differences between both ensembles are crucial. In this section some aspects of this difference are presented. In particular, the problems that arise with the fixation of the particle number by a corresponding choice of the chemical potential μ are analyzed.

2.4.1 Particle number fluctuation

In the grand canonical ensemble, the particle number is a fluctuating observable due to the coupling to a bath that allows the exchange of particles. This has to be factored in when dealing with the grand canonical ensemble for systems that have fixed particle numbers, which will be considered in the subsequent chapters. Some probability distributions for a systems with mean value of the particle numbers fixed to $\langle N \rangle = 8$ are shown in Fig. 2.2. For high temperatures, the distribution has the shape of a Gaussian with the maximum near the average particle number. However, for low temperatures the skewness of the distribution increases and the local maximum moves toward $N = 0$.

In appendix D.2 a relationchip between the first and the second moment of the occupation numbers is derived (Eq. (D.18)). This equation directly yields the variance of the occupation numbers of a certain energy level

$$(\Delta n_k)^2 = \langle n_k \rangle^2 + \langle n_k \rangle \ . \tag{2.25}$$

Thus the fluctuation of the occupation number is very high, if the occupation number itself has a high value. In the thermodynamic limit, the relative variance $\frac{\Delta n_k}{\langle n_k \rangle}$ becomes 1. This is a good explanation for the increasing fluctuation of the particle numbers in the Bose condensed phase. Hence, the analysis of observables that are coupled to the correlation of the occupation numbers $\langle n_k n_l \rangle$, depend crucially on the regarded ensemble in this parameter region. This implies that for temperatures below a critical value (often connected with a phase transition such as BEC [17]), formalisms that apply for a grand canonical treatment of interacting systems are not suitable for small systems with a fixed particle number, as the interaction is a prime example for observables that depend on $\langle n_k n_l \rangle$. A comparison of the behavior of these entities for both ensembles is given in Fig. 2.3. It can be seen that the main difference between both ensembles lies in the

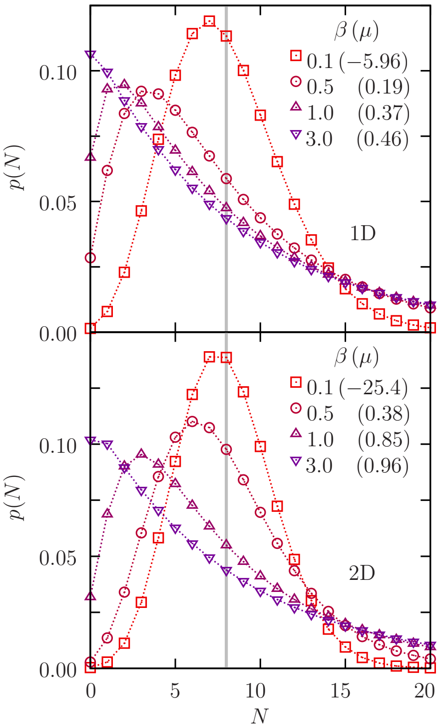

Figure 2.2: *Distribution of the particle number N in the grand canonical ensemble for different inverse temperatures β in the 1D (upper panel) and the isotropic 2D (lower panel) harmonic oscillator. β is given in $\hbar\omega$. The chemical potential μ – given in parenthesis behind the temperatures in natural units $\hbar\omega$ – is chosen such that $\langle N\rangle(\mu,\beta) = 8$ (vertical gray line) for all distributions. The probability distribution is only defined for integer numbers – the lines are drawn as a guide to the eye.*

ground state orbital, while for higher orbitals the behavior is very similar. I expect this difference between the ensembles to be responsible for the high difference of the energy values obtained with the Green's-function formalism and an exact method. In [18] a Green's-function formalism for the canonical ensemble is proposed and is extended to the nonequilibrium in [19]. However, these methods have an extremely more complicated structure than the grand canonical analog and lack computational implementations.

The mathematics needed for the calculation of the graphs shown in Fig. 2.2 and 2.3 is presented in appendix F.

In contrast to bosonic systems, for fermions the fluctuation of the particle number decreases for low temperatures. The variance of the occupation number for ideal fermions in the grand canonical ensemble reads

$$(\Delta n_k)^2 = \langle n_k\rangle (1 - \langle n_k\rangle) \,. \tag{2.26}$$

This equation can be derived in a way similar to that for the bosonic case given in equation (D.18). For low temperatures all orbitals are either fully occupied ($\langle n_k\rangle = 1$), or empty ($\langle n_k\rangle = 0$), except near the Fermi edge if some energy shell is not closed. And for $\langle n_k\rangle = 1, 0$ the variance of the occupation numbers (2.26) is zero.

Summary

A mathematical analysis of some features of bosonic systems that are relevant for this work was given in this chapter. Some properties of the ROBDM within the approximations to be presented will be analyzed later. The comparison of the thermodynamic

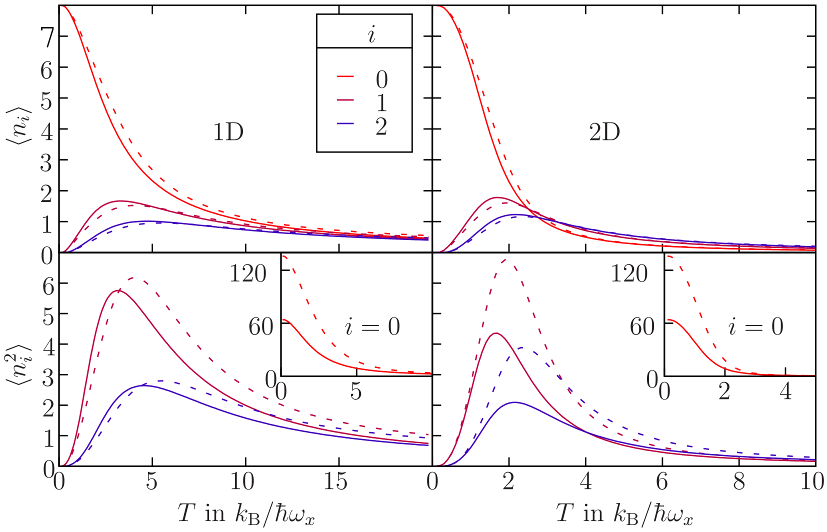

Figure 2.3: *First and second moment of the occupation numbers of the first three energy levels in canonical (solid line) and grand canonical (dashed line) ensemble for a system with the particle number fixed to* $N = 8$ *(in the grand canonical case via the correct choice of* μ*). The second moment of the occupation of the ground state is given as inset, because of the extremely different scales. In the 2D case, the second and third energy level is two- and three-fold degenerate.*

ensembles was needed to explain why approximations that are explicitly designed for grand canonical systems are not applicable to the systems of interest in this work. Furthermore, the approximations presented in Chap. 3 can be understood as a zero temperature limit of a canonical treatment.

3 Approximation methods

> As is well-known, a variational principle is a blind and dumb procedure that always provides an answer, but its accuracy depends crucially on the choice of the trial function.
>
> *(Peter Kramer and Marcos Saraceno, 1981)*

Usually the problem of finding stationary states of interacting many body systems cannot be solved analytically; neither in the classical nor in quantum mechanical case. Nevertheless, analytical approaches exist for nearly all physical problems – normally including approximations or restricting assumptions – which are able to explain at least the main qualitative behavior of the system. Consider e.g. the prediction of the BEC by Einstein. He was able to predict the appearance of a new phase of matter and the related point of transition. Although this kind of approach proposes and uses several idealizations, the obtained results can tell us something about the reality the idealized model attempts to describe.

Nowadays, as computational methods offer the possibility to avoid approximations by performing the calculations numerically with high accuracy, the focus of theoretical analysis of physical systems has changed. The efficiency of toady's computers makes precise quantitative predictions of physical systems easily possible. However, still though computers and programs have opened the doors to an enormous number of problems, even their use has constraints. Thus approximation methods are required just as ever. Each approximation has its typical regimes of validity with respect to the system parameters, and usually reflects only a limited range of phenomena that the system provides.

In this chapter, an overview of a special class of approximations for the analysis of Bose systems is presented. They can all be derived by using the Ritz method, and the main ansatz, to which the Ritz method is applied, can be considered the same for all presented approximations. After a short, outlining introduction to the Ritz principle, which serves as a basis for the following sections, this chapter starts with the Gross-Pitaevskii (GP) equation and ends with *unrestricted bosonic Hartree-Fock* (UBHF). GP is the most special case of the main ansatz and UBHF is the most general one. Another approximation scheme (called Multiconfigurational Hartree for Bosons) that goes beyond this ansatz is discussed within this chapter, as it is strongly connected to the others and can be regarded as their most obvious generalization.

3.1 Variational methods

3.1.1 The Ritz principle (stationary systems)

The approximations presented here can all be derived by applying variational methods to the Ritz principle (Actually the Rayleigh-Ritz-principle). It states that the expectation value of the energy of an arbitrary state is higher or equal than the ground state energy:

$$E_0 \leq \frac{\langle \Phi | \hat{H} | \Phi \rangle}{\langle \Phi | \Phi \rangle} \ . \tag{3.1}$$

Thus, if the ground state of a Hamiltonian needs to be found, one can make use of this principle by making an ansatz for the wave function Φ that depends on a set of real parameters $(q_1, q_2, \ldots) =: \mathbf{q}$. The function $\Phi(\mathbf{q})$ is called a trial function. With this ansatz, only a fixed subset of the full Hilbert space is reached, which, in general, does not have the properties of a subspace (except for CI [20], what will be explained in section 5.4.1). Theoretically, this set of parameters can be infinite, but of course for practical use one has to limit the set to a finite one. The best approximation of the ground state $|\Phi_{\mathrm{min}}\rangle$ within this ansatz, is the state that minimizes the expectation value of the total energy. Mathematically, this can be expressed by finding the state that makes the gradient of the total energy with respect to its parameters vanish:

$$\left. \frac{\partial}{\partial q_i} \frac{\langle \Phi | \hat{H} | \Phi \rangle}{\langle \Phi | \Phi \rangle} \right|_{\mathbf{q}_{\mathrm{min}}} \overset{!}{=} 0, \qquad \text{for all } i. \tag{3.2}$$

In order to avoid the differentiation of a fraction in (3.2), one can replace the functional for the energy by $E = \langle \Phi | \hat{H} | \Phi \rangle$ and demand the state Φ to be normalized by introducing a Lagrange parameter $\mathscr{E}$:

$$\left. \frac{\partial}{\partial q_i} \big(\langle \Phi | \hat{H} | \Phi \rangle - \mathscr{E}(\langle \Phi | \Phi \rangle - 1) \big) \right|_{\mathbf{q}_{\mathrm{min}}} \overset{!}{=} 0 \qquad \text{for all } i. \tag{3.3}$$

By transforming this equation, it can be shown that the Lagrange multiplicator is the expectation value of the energy

$$\mathscr{E} = \frac{\langle \Phi | \hat{H} | \Phi \rangle}{\langle \Phi | \Phi \rangle} \ . \tag{3.4}$$

Of course, it is possible to restrict the parameters in arbitrary ways, e.g. to avoid a symmetry breaking of the system due to the chosen ansatz. But as rule of thumb one can say that the results are better – or in this case: the energy lower – the less restrictions one imposes on the ansatz. In section 4.7 a paradigmatic example for a skillfull reduction of the parameter number by making reasonable assumptions is given.

Creating an ansatz for the sought after quantum mechanical state is the part of the application of the Ritz Principle that requires the most intuition in physics. The rest is just mathematics. However, solving the crucial equation (3.3) numerically can be very difficult and usually some further tricks may be needed. E.g. in the case considered here convert the equation into a self consistent generalized eigenvalueproblem and solve it iteratively.

A good ansatz for the sought after state should fulfill the two somehow mutually conflicting qualities: It should be easy to handle numerically and provide good, or at least acceptable, results. In the subsequent part of this chapter the Ritz principle is applied to bosonic N-particle states with the ansatz

$$\boxed{|\Phi\rangle = |\Phi(|q_1\rangle, |q_2\rangle, \ldots, |q_N\rangle)\rangle = \hat{S}_+\Big\{\, |q_1\rangle \otimes |q_2\rangle \otimes \cdots \otimes |q_N\rangle \,\Big\}.} \tag{3.5}$$

Here $\otimes$ denotes the tensor product which is explained in greater depth in [14]. The operator $\hat{S}_+$ brings the tensor product in the correct symmetry with respect to a permutation of the ordering in the product. $\hat{S}_+$ is called a symmetrizer and is deeper explained in Chap 4. In this case, each of the parameters $|q_i\rangle$ is a one-particle Hilbert space state. Thus, each of the parameters in itself consists of an, in principle, infinite tuple of parameters. So the differentiation with respect to each parameter is a gradient itself and one has to perform the differentiation with respect to all expansion coefficients respective to a chosen basis of all (parameter-) states $|q_i\rangle$. In appendix A a set of rules for the calculation of a basis independent (abstract) differentiation of this functional is given.

The symmetrized product state given in Eq. 3.5 is called a Slater permanent. An arbitrary state of the N-body Hilbert space can be given as a superposition of such Slater permanents. The ansatz for the many body state in Eq. 3.5 is called a single Slater permanent ansatz. This chapter will present different realizations of this ansatz differing only in the restrictions on the states $|q_i\rangle$.

3.1.2 The time-dependent variational principle

For time dependent systems, an approximation exists that implies the Ritz principle as a special case and is based on quite similar ideas. It takes advantage of the fact, that the solution of the time-dependent Schrödinger equation minimizes the action integral [21]

$$S'[\Phi] = \int \frac{\langle\Phi|\hat{H} - i\frac{\mathrm{d}}{\mathrm{d}t}|\Phi\rangle}{\langle\Phi|\Phi\rangle}\,\mathrm{d}t = \int \mathcal{L}'(\langle\Phi|\,,|\Phi\rangle)\,\mathrm{d}t \tag{3.6}$$

and is called time-dependent variational principle (TDVP). It is a well known and rigorously analyzed principle, see [22] or the review [23]. Dirac was the first to derive the time-dependent Hartree-Fock equations for fermions from it [24]. This principle can be deduced by performing the variational derivative with respect to the expansion coefficients regarding an arbitrary basis set of the Hilbert space. The Lagrangian $\mathcal{L}'$ can be transformed into a real one by adding the total time derivative $\frac{i}{2}\frac{\mathrm{d}}{\mathrm{d}t}\ln(\langle\Phi|\Phi\rangle)$. Just as in classical mechanics, this transformation does not change the equations of motion.

As before, approximate equations of motion are obtained by making a reasonable ansatz for $|\Phi\rangle$ including a tuple of time-dependent parameters $\mathbf{q}(t)$. This restricts the possible motions of $|\Phi\rangle$ to lie in a certain predetermined region of Hilbert space. The map $\Phi(\mathbf{q})$ of the trajectory $\mathbf{q}(t)$ in the parameter space that minimizes (3.6) is the best approximation of the exact trajectory within the considered region. The action (3.6) can – in analogy to the stationary case – be transformed into a term that does not contain a denominator by introducing a time-dependent Lagrange multiplier $\mathscr{E}$. By additionally factoring in, that the action in fact depends on the parameters $\mathbf{q}$, the action reads

$$\boxed{S[\mathbf{q},\mathscr{E}(t)] = \int \langle\Phi(\mathbf{q})|\hat{H} - i\frac{\mathrm{d}}{\mathrm{d}t} - \mathscr{E}(t)|\Phi(\mathbf{q})\rangle \;\mathrm{d}t\,.} \tag{3.7}$$

The total time derivative can be calculated via the chain rule

$$\frac{\mathrm{d}}{\mathrm{d}t}\,|\Phi\rangle = \sum_l \underbrace{\frac{\partial\,|\Phi\rangle}{\partial q_l}}_{=:|\Phi_l\rangle}\,\dot{q}_l\;. \tag{3.8}$$

This leads to an action that can be considered as a time integral over a Lagrangian that resembles that of classical mechanics[1]

$$S[\mathbf{q},\mathscr{E}(t)] = \int \underbrace{\langle\Phi|\hat{H} - \mathscr{E}(t)|\Phi\rangle - i\sum_l \langle\Phi|\Phi_l\rangle\,\dot{q}_l}_{\mathcal{L}(\mathbf{q},\dot{\mathbf{q}},t)}\;\mathrm{d}t \tag{3.9}$$

and the trajectory in parameter space, which minimizes (3.9) is obtained by the well known Euler-Lagrange equations, which in this case read

$$\begin{aligned}
\frac{\partial\mathcal{L}}{\partial\dot{q}_k} &= -i\,\langle\Phi|\Phi_k\rangle \\
\Rightarrow\;\frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial\mathcal{L}}{\partial\dot{q}_k} &= -i\sum_l\big(\,\langle\Phi_k|\Phi_l\rangle + \langle\Phi|\underbrace{\frac{\partial}{\partial q_l}\,|\Phi_k\rangle}_{=:|\Phi_{kl}\rangle}\,\big)\dot{q}_l \\
\frac{\partial\mathcal{L}}{\partial q_k} &= \langle\Phi_k|\hat{H} - \mathscr{E}(t)|\Phi\rangle + \langle\Phi|\hat{H} - \mathscr{E}(t)|\Phi_k\rangle - i\sum_l\big(\,\langle\Phi_k|\Phi_l\rangle + \langle\Phi|\Phi_{lk}\rangle\,\big)\dot{q}_l,
\end{aligned} \tag{3.10}$$

$$\begin{aligned}
&\text{thus}\quad \frac{\partial\mathcal{L}}{\partial q_k} - \frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial\mathcal{L}}{\partial\dot{q}_k} = 0 \\
&\Leftrightarrow\qquad \langle\Phi_k|\hat{H} - \mathscr{E}(t)|\Phi\rangle + \langle\Phi|\hat{H} - \mathscr{E}(t)|\Phi_k\rangle = i\sum_l\{\langle\Phi_k|\Phi_l\rangle - \langle\Phi_l|\Phi_k\rangle\}\dot{q}_l\;.
\end{aligned} \tag{3.11}$$

This equation of motion is not invertible in some cases, as will be seen in later sections.

Case $|\Phi(\mathbf{q})\rangle^\dagger = \langle\Phi(\mathbf{q}^*)|$

It can be favorable to consider the parameters to be complex, which will be the case in this chapter. For complex parameters, one has the choice either to treat the real and imaginary part of a parameter as independent, or one has to treat the parameter q_i and its conjugated q_i^* as independent variables and perform the derivative respective to both.

---

[1] Also referred to as dequantization of the system and its observables [25].

The differentiation with respect to a complex variable can be expressed in differentiations with respect to its real and imaginary part [26]:

$$
\begin{aligned}
z = x + iy : \qquad & \frac{\partial}{\partial z} = \frac{1}{2}\left(\frac{\partial}{\partial x} - i\frac{\partial}{\partial y}\right) \\
& \frac{\partial}{\partial z^*} = \frac{1}{2}\left(\frac{\partial}{\partial x} + i\frac{\partial}{\partial y}\right) && (3.12) \\
& \Longrightarrow \left(\frac{\partial}{\partial z}\right)^* = \frac{\partial}{\partial z^*} \; . && (3.13)
\end{aligned}
$$

Before going on to the GP-equation, an ansatz for the wave function with complex parameters, but with the ket-vector being independent of the complex conjugated of the parameters and vice versa for the bra-vector, is considered.

$$\text{I.e.} \quad \frac{\partial}{\partial q_k^*} |\Phi\rangle = 0 \quad \text{and} \quad \frac{\partial}{\partial q_k} \langle\Phi| = 0 \tag{3.14}$$

For later purpose it is shown, that for an ansatz that fulfills these properties, it is not necessary to regard the differentiation of the related functional with respect to both the parameter and its complex conjugated, because the differentiation with respect to the parameter yields the complex conjugated equation of the equation that is obtained by the differentiation with respect to the complex conjugated parameter.

The parameters are treated as independent to their complex conjugated, hence the summation index in equation (3.11) runs over all parameters and their complex conjugated. The notation $\frac{\partial}{\partial q_k}|\Phi\rangle = |\Phi_k\rangle$ is misleading in the case considered here, as it does not distinguish between the derivative respective to a parameter and the derivative respective to its complex conjugated. For that reason the term $\frac{\partial}{\partial q_k}|\Phi\rangle$ will be written as $\left|\frac{\partial\Phi}{\partial q_k}\right\rangle$ and analogous notation is used for the bra-vectors. For complex parameters, two sets of equations are present, one for the parameters and one for their complex conjugated. The related Euler-Lagrange equations for each set are calculated here:

$$
\begin{aligned}
&\underbrace{\Big\langle \frac{\partial\Phi}{\partial q_k}}_{=0}\Big|\hat{H} - \mathscr{E}(t)\Big|\Phi\Big\rangle + \Big\langle\Phi\Big|\hat{H} - \mathscr{E}(t)\Big|\frac{\partial\Phi}{\partial q_k}\Big\rangle \\
&\qquad = i\sum_l \left\{\Big\langle \underbrace{\frac{\partial\Phi}{\partial q_k}}_{=0}\Big|\frac{\partial\Phi}{\partial q_l}\Big\rangle - \Big\langle\underbrace{\frac{\partial\Phi}{\partial q_l}}_{=0}\Big|\frac{\partial\Phi}{\partial q_k}\Big\rangle\right\}\dot{q}_l + \left\{\Big\langle\underbrace{\frac{\partial\Phi}{\partial q_k}}_{=0}\Big|\underbrace{\frac{\partial\Phi}{\partial q_l^*}}_{=0}\Big\rangle - \Big\langle\frac{\partial\Phi}{\partial q_l^*}\Big|\frac{\partial\Phi}{\partial q_k}\Big\rangle\right\}\dot{q}_l^*
\end{aligned}
$$

$$\Leftrightarrow \Big\langle\Phi\Big|\hat{H} - \mathscr{E}(t)\Big|\frac{\partial\Phi}{\partial q_k}\Big\rangle = -i\sum_l \Big\langle\frac{\partial\Phi}{\partial q_l^*}\Big|\frac{\partial\Phi}{\partial q_k}\Big\rangle\dot{q}_l^* \; . \tag{3.15}$$

With an analogous calculation, the following equations for the complex conjugated of the parameters are obtained:

$$\Leftrightarrow \Big\langle\frac{\partial\Phi}{\partial q_k^*}\Big|\hat{H} - \mathscr{E}(t)\Big|\Phi\Big\rangle = i\sum_l \Big\langle\frac{\partial\Phi}{\partial q_k^*}\Big|\frac{\partial\Phi}{\partial q_l}\Big\rangle\dot{q}_l \; . \tag{3.16}$$

With (3.13) the latter equation can be identified as the complex conjugated of (3.15). This implies that one only has to solve the equation of motion for one set (parameters or their c.c.) since the equation of the complement set is automatically fulfilled. For the equation of stationary systems, the same result is obtained

$$\Big\langle \Phi \Big| \hat{H} \Big| \frac{\partial \Phi}{\partial q_k} \Big\rangle = \mathscr{E} \Big\langle \Phi \Big| \frac{\partial \Phi}{\partial q_k} \Big\rangle \quad \text{and} \quad \Big\langle \frac{\partial \Phi}{\partial q_k^*} \Big| \hat{H} \Big| \Phi \Big\rangle = \mathscr{E} \Big\langle \frac{\partial \Phi}{\partial q_k^*} \Big| \Phi \Big\rangle \,. \tag{3.17}$$

3.2 The Gross-Pitaevskii approximation (GP)

3.2.1 Stationary GP

The most restricted implementation of the ansatz (3.5) is presented first. In this ansatz, the many-particle state is assumed to be fully Bose condensed. This means, all N particles reside in exactly the same orbital

$$|\Phi\rangle = \underbrace{|\varphi\rangle \otimes |\varphi\rangle \otimes \ldots \otimes |\varphi\rangle}_{N\text{-fold tensor product}} \,. \tag{3.18}$$

A symmetrization is not required, as all orbitals are equal. Thus, a permutation does not have any effect on the product state. The GP approximation is designed for nonideal systems. Thus the full Hamiltonian $\hat{H}$ of the interesting systems can be decomposed additively into a single particle part and an interaction part:

$$\hat{H} = \hat{h} + \hat{W} = \sum_{ij} h_{ij} \hat{a}_i^\dagger \hat{a}_j + \frac{1}{2} \sum_{ijkl} w_{ij,kl} \hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_k \hat{a}_l, \tag{3.19}$$

where in the latter term, the Hamiltonian is expressed in second quantization formalism with respect to an arbitrary CONS of single particle states. The matrix elements of the single particle Hamiltonian are given by $h_{ij} = \langle i|\hat{h}|j\rangle$ and the two-particle integrals $w_{ij,kl}$ are defined appendix A Eq. (A.5).

In this case, the total energy for a normalized φ can be easily calculated with the second quantization formalism using creation and annihilation operators respect to the orbital φ

$$\langle\Phi| \langle\varphi|\hat{h}|\varphi\rangle \, \hat{a}_\varphi^\dagger \hat{a}_\varphi + \frac{1}{2} w_{\varphi\varphi,\varphi\varphi} \hat{a}_\varphi^\dagger \hat{a}_\varphi^\dagger \hat{a}_\varphi \hat{a}_\varphi |\Phi\rangle = N \langle\varphi|\hat{h}|\varphi\rangle + \frac{1}{2} N(N-1) w_{\varphi\varphi,\varphi\varphi} \,. \tag{3.20}$$

The norm of the GP-state with an unnormalized orbital φ is

$$\|\Phi\| = \left(\sqrt{\langle\varphi|\varphi\rangle}\right)^N \,. \tag{3.21}$$

Thus it is normalized if and only if $\langle\varphi|\varphi\rangle = 1$ and it is adequate to demand directly that the orbital φ is normalized.

The orbital φ can be considered as an abstract parameter, that in practice is represented by a finite set of parameters depending on the chosen basis. Suppositionally the one particle state φ is given by a tuple of expansion coefficients $(c_1, c_2, \ldots)$ respective to a given CONS. It is then sufficient to perform the differentiation only with respect to either the coefficients or their complex conjugated, as shown in the previous section. In appendix A it is shown, that the differentiation of matrix elements such as appear in (3.20) with respect to the kth expansion coefficient c_k^* of $\langle\varphi|$ can be expressed in the following way

$$\frac{\partial}{\partial c_k^*} = \langle k| \frac{\delta}{\delta \langle\varphi|}. \tag{3.22}$$

Here $\langle k|$ is the basis state that is related to the considered expansion coefficient and the differentiation with respect to an abstract Hilbert space vector $\frac{\delta}{\delta\langle\varphi|}$ is defined in appendix A. Hence it is not necessary to assume φ to be given as expansion with respect to a certain basis. The differentiation can be performed with respect to an abstract vector (using the rules given in appendix A) and, for numerical purposes, one can later simply project the equation onto each state of the given basis. Thus, the determining equation for the state φ that minimizes the total functional

$$E(\varphi, \mathscr{E}) = \langle\varphi|\hat{h}|\varphi\rangle + \frac{1}{2}(N-1)w_{\varphi\varphi,\varphi\varphi} - \mathscr{E}\langle\varphi|\varphi\rangle \tag{3.23}$$

can easily be obtained:

$$\begin{aligned}\frac{\delta}{\delta\langle\varphi|}\left\{\langle\varphi|\hat{h}|\varphi\rangle + \frac{1}{2}(N-1)w_{\varphi\varphi,\varphi\varphi} - \mathscr{E}\langle\varphi|\varphi\rangle\right\}& \\ = \hat{h}\,|\varphi\rangle + \frac{N-1}{2}(\hat{J}_{\varphi\varphi}\,|\varphi\rangle + \hat{J}_{\varphi\varphi}\,|\varphi\rangle\,) - \mathscr{E}\,|\varphi\rangle &\overset{!}{=} 0 \\ \Longleftrightarrow \boxed{\left(\hat{h} + (N-1)\hat{J}_{\varphi\varphi}\right)|\varphi\rangle = \mathscr{E}\,|\varphi\rangle}&\end{aligned} \tag{3.24}$$

Here the multiplier $\mathscr{E}$ is the energy per particle of the system. The appearing Hartree operator $\hat{J}_{\varphi\varphi}$ is defined in Eq. (A.8). The operator in parenthesis on the left side can be considered as an effective Hamilton operator. Hence, the GP equation is a Mean-Field-approximation. It is also called nonlinear Schrödinger equation. The two-particle density in this ansatz is $\mathbf{n}(x_1, x_2) = |\varphi(x_1)|^2 \cdot |\varphi(x_2)|^2$, which always has non-negative values on the diagonal $x_1 = x_2$. Thus the GP approximation cannot, by definition, explain phenomena such as fermionization or depletion (occupation of higher orbitals).

3.2.2 Time-dependent GP

To solve the GP equation numerically, it is necessary to derive the equation of motion for the orbital φ for time-dependent systems, so the state φ, that minimizes (3.24) can be found by starting with an arbitrary initial state and perform imaginary time stepping. Imaginary time stepping is a method that makes usage of the fact that the time evolution in negative imaginary time of an arbitrary state (that is nonorthonormal to the ground state) converges into the ground state for long times.

Furthermore, this derivation helps to better understand the equations of motion derived in section 3.4 for the most general case of the ansatz (3.5), as the main concepts are quite similar.

The time-dependent GP approximation consists of the assumption, that the many particle state is at all times fully condensed, with only the shape of the condensate orbital varying in time. Thus, the Lagrangian for this motion is

$$\langle\Phi|\hat{H} - i\frac{\mathrm{d}}{\mathrm{d}t} - \mathscr{E}(t)|\Phi\rangle = N(\,\langle\varphi|\hat{h} - \mathscr{E}(t)|\varphi\rangle + \frac{N(N-1)}{2}w_{\varphi\varphi,\varphi\varphi} - i\,\langle\varphi|\dot{\varphi}\rangle\,)\ . \tag{3.25}$$

Just as above, the differentiation is performed with respect to $\langle\varphi|$ – this corresponds to a derivative with respect to all complex conjugated expansion coefficients c_k^*. By taking advantage of the fact, that the upper equation is independent of $\langle\dot{\varphi}|$,

$$(\hat{h} + \hat{J}_{\varphi\varphi} - \mathscr{E}(t))\,|\varphi\rangle = i\frac{\mathrm{d}}{\mathrm{d}t}\,|\varphi\rangle \tag{3.26}$$

is readily obtained as the equation of motion (Euler-Lagrange). A closed expression for the time-dependent Lagrange multiplier $\mathscr{E}(t)$ can be obtained by scalarly multiplying Eq. (3.26) from the right with $\langle\varphi|$ and taking advantage of the fact, that the Lagrange multiplier guarantees a normalization of φ at all times

$$\mathscr{E}(t) = \langle\varphi|\,\hat{h} + \hat{J}_{\varphi\varphi} - i\frac{\mathrm{d}}{\mathrm{d}t}\,|\varphi\rangle\ . \tag{3.27}$$

Inserting this expression in equation (3.26) yields the new equation of motion:

$$\hat{\mathsf{P}}i\frac{\mathrm{d}}{\mathrm{d}t}\,|\varphi\rangle = \hat{\mathsf{P}}[\hat{h} + \hat{J}_{\varphi\varphi}]\,|\varphi\rangle\ . \tag{3.28}$$

The projector $\hat{\mathsf{P}} := 1 - |\varphi\rangle\,\langle\varphi|$ appearing on both sides prevents the equation from being invertible. Fortunately, this problem can be fixed by making a gauge transformation of φ such that

$$\langle\varphi|\dot{\varphi}\rangle \overset{!}{=} 0. \tag{3.29}$$

This condition is equivalent to making the assignment of the time-dependent phase $|\varphi\rangle \rightarrow \exp(\int\langle\varphi|\dot{\varphi}\rangle\,\mathrm{d}t)\,|\varphi\rangle$, which effaces the effect of the projector: $\hat{\mathsf{P}}\,|\dot{\varphi}\rangle = |\dot{\varphi}\rangle$. Hence, an equation of motion that is already resolved for the time derivative is obtained, and provides the possibility to solve the stationary GP equation by performing imaginary time-stepping.

$$i\frac{\mathrm{d}}{\mathrm{d}t}\,|\varphi\rangle = \hat{\mathsf{P}}(\hat{h} + \hat{J}_{\varphi\varphi})\,|\varphi\rangle\,. \tag{3.30}$$

It is shown in [27], that the projector $\hat{\mathsf{P}}$ still appearing on the right side of (3.30) can be totally omitted.

3.3 Multi orbital mean-field (MOMF)

For strong coupling, GP is a rough approximation, as it assumes that all particles reside in the same orbital. And, for one-dimensional Coulomb systems without shielding parameter, the energy would explode in this approximation. In [28] L. Cederbaum introduces another ansatz which also consists of a single Slater permanent, but with more than one orbital. In this ansatz, two particles reside either in the same orbital or in mutually orthogonal orbitals. Thus, it is convenient to represent the sought after product state by the occupation numbers of the orbitals that have to be minimized. The related functional, including all necessary Lagrange multipliers, reads

$$E(\varphi_i, n_i, \mu_{ij}) = \sum_k \hat{h}_{kk} n_k + \frac{1}{2} \sum_{kl} n_k n_l [w_{kl,kl} + w_{kl,lk}] - \sum_{k<l} \mu_{kl} (\langle \varphi_k | \varphi_l \rangle - 1) \ , \qquad (3.31)$$

with the sums running over all n_o sought after orbitals. This ansatz is able to include effects such as condensate depletion and may provide lower energies for the approximated ground state. However, this ansatz has some disadvantages.

As they are integer numbers, it does not make sense to additionally consider the derivative with respect to the occupation numbers. I.e., one has to choose the occupation numbers as input parameters. The introduction of $\frac{1}{2} n_o(n_o - 1)$ Lagrange multipliers due to the demanded orthonormality of the orbitals makes this ansatz unwieldy.

In [28–30] the occupation numbers are considered as floating point numbers with the justification that the described systems have particle numbers in the range of a few thousand. Thus, the relative occupation numbers are finely quantized. However, for small particle numbers this assumption cannot be applied and fractional occupation numbers of the system are, in principle, not obtained by this ansatz. In [31] this ansatz is extended to the time-dependent regime by O. Alon and A. Streltsov in the group of Cederbaum.

An extension of this ansatz to multi configurational states, where the state is supposed to be a superposition of more than one Slater permanent, has been suggested and implemented by this group in various pieces of work [32–34], including time-dependent systems. It is called Multi Configurational Hartree for Bosons (MCHB) or Multi Configurational Time-Dependent Hartree for Bosons (MCTDHB) respectively.

3.4 Unrestricted bosonic Hartree-Fock (UBHF)

The bosonic analog to the Slater determinant is the Slater permanent. Although the definitions and the properties of the permanent and the determinant are very similar, their differences are crucial for both the quantum statistical behavior of the related particle types and the complexity required to calculate them. The determinant of an $n \times n$-Matrix can be calculated via the Gauß algorithm within ca. n^3 steps [35]. In contrast to the determinant, a permanent cannot be calculated in polynomial time [2] by any method[3].

UBHF was first introduced and computationally implemented by Romanovsky in 2004 [12, 37]. It is the most general form of a single permanent ansatz, and hence

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[2] An algorithm, whose number of needed steps for its performance increases with n^α – where n marks the size of the problem to be solved (e.g. dimension of the matrix) – is said to be an algorithm solvable in polynomial time.

[3] Actually, the existence of an algorithm for the calculation of the permanent in polynomial time would imply the equality of the complexity classes $FP = \sharp P$, which is an even stronger statement than $P = NP$ in computational complexity theory. The last statement $P = NP$ is one of the seven famous Millennium Prize Problems [36].

provides better results than the above mentioned ones. It demands no further restriction to the orbitals contained in the symmetrized product state given in Eq. (3.5). The calculation of the total energy and the derivative of the related functional is much more complicated because of the difficulties with treating the permanent. It is for this reason, that it is only applicable to small systems with a handful of particles.

As this work concentrates especially on this ansatz, a separate chapter is dedicated to the derivation of the determining equations of the orbitals in the product state (3.5).

3.5 Multiconfigurational Hartree for Bosons (MCHB)

The approximation methods presented in this chapter are all linked in a special way. They all consist of the same principle ansatz (3.5) with different types of restrictions. The MCHB approximation mentioned at the end of section 3.3 goes beyond the ansatz of a single Slater permanent. UBHF can be understood as a very special case of this approximation, which is shown in this section.

3.5.1 Relationship between MCHB and UBHF

For this purpose, the construction of an orthonormal system of vectors (ONS) $|\tilde{1}\rangle, \ldots, |\tilde{N}\rangle$ which spans the same subspace of the one-particle Hilbert space as the spinor orbitals $|1\rangle, \ldots, |N\rangle$ is needed. Furthermore, this set shall have the property, that for the representation of the kth spinor orbital $|k\rangle$ only the first k vectors of the ONS are needed.

This can be arranged by performing the Gram-Schmidt process with the spinor orbitals. In that manner, an ONS where the kth vector $|\tilde{k}\rangle$ is a superposition of the first k spinor orbitals is obtained. The matrix of the coefficients that are needed to represent each vector $|\tilde{k}\rangle$ is a lower triangular matrix. Thus, its inverse is also in triangular form. By this procedure, the necessary ONS is constructed.

The symmetrized product state related to the spinor $|\Psi\rangle$ can then be transformed in the following way

$$\begin{aligned} |\Phi\rangle &= \hat{S}_+ \Big\{ |1\rangle \otimes |2\rangle \otimes \ldots \otimes |N\rangle \Big\} \\ &= \hat{S}_+ \Big\{ \Big(c_{11} |\tilde{1}\rangle \Big) \otimes \Big(c_{21} |\tilde{1}\rangle + c_{22} |\tilde{2}\rangle \Big) \otimes \ldots \otimes \Big(c_{N1} |\tilde{1}\rangle + \ldots + c_{NN} |\tilde{N}\rangle \Big) \Big\} \\ &= \hat{S}_+ \Big\{ \bigotimes_{s=1}^{N} c_{s1} |\tilde{1}\rangle \Big\} + \hat{S}_+ \Big\{ c_{11} |\tilde{1}\rangle \otimes \bigotimes_{s=2}^{N} c_{s2} |\tilde{2}\rangle \Big\} + \ldots + \hat{S}_+ \Big\{ \bigotimes_{s=1}^{N} c_{s1} |\tilde{s}\rangle \Big\} , \end{aligned} \tag{3.32}$$

where the distributivity of the tensor product was used. In the fermionic case – obtained by replacing the symmetrizer $\hat{S}_+$ with an antisymmetrizer $\hat{S}_-$ – the last term in the latter expression of the equality chain is the only term which would *survive* the antisymmetrization, because it is the only one with all orbitals being different. Hence, UBHF would lead to the well known fermionic Hartree-Fock approximation if fermions are considered.

The latter expression in equation (3.32) is a superposition of product states, with orbitals that form an ONS. Hence UBHF can be understood as a special case of MCHB.

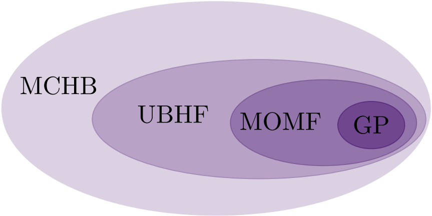

Figure 3.1: *Illustration of the implications of the discussed ansatzes.*

Note that the other direction is not applicable; a MCHB ansatz cannot, in general, be converted into UBHF.

Conclusion: Confusion

An overview over a set of related approximation methods for bosonic systems that are all denoted as Hartree, Hartree-Fock or Mean-Field type has been given in this chapter. It may appear confusing or even disappointing, that a simple and unique Hartree-Fock approximation, as in the fermionic case, does not exist for Bose systems. One could add to this list the Bogoliubov approximation and the Hartree-Fock approximation proposed in [38]. The UBHF ansatz is the most general one and provides the best results, but it is very difficult to handle; and due to its complexity, it is only applicable to systems with small particle numbers. GP is the most restricted version of the single Slater permanent ansatz, and hence, its validity regime is quite limited, but it has a very simple form and is easy to implement. It is also the best analyzed approximation in the literature. The implication of the mentioned approximations as special cases of others is visualized in Fig. 3.1. The inclusion of UBHF in MCHB does not imply at all, that MCHB provides in general more exact results than UBHF. In MCHB one has to choose the number of single particle orbitals to construct symmetrized product states with, and the number of symmetrized product states to take into account for the construction of many body states. Thus, for a certain choice of these parameters, it can provide better, worse, or exactly the same results as UBHF. Furthermore, UBHF is a single permanent ansatz and MCHB is not. CI – what is deeper discussed in section 5.4.1 – can be considered as a very special case of MCHB.

Mean-Field type approximations is a misnamed denomination for all discussed methods except GP. For all other approximations, it is not possible to express the encountered ground state (within this ansatz) as a ground state of an effective single particle Hamiltonian.

Special attention will be given to UBHF in the following chapter, as the results of its numerical implementation are presented in this work.

4 More on UBHF

A rigorous derivation and analysis of the equations for determining the optimal state in UBHF approximation is presented in this chapter. The derivation of the determining equations presented here differs slightly from the way chosen by Romanovsky in [39]. While in [39] each orbital of the product state is demanded to be normalized, in this work, the only restriction is the normalization of the entire many particle state. Due to this weaker restriction, the uniqueness of the solution is given up and a gauge freedom of the set of orbitals is obtained. Furthermore, a new scheme for solving the determining equations is presented for the first time. Also new in this work is the extension of this ansatz to the time-dependent regime via the TDVP.

4.1 Stationary UBHF

Dealing with symmetrized product states that consist of nonorthonormal orbitals is far more difficult than dealing with orthonormal ones, as the formalism of second quantization is not applicable in such a simple manner as in the usual case. Thus, for understanding the subsequent calculations, one has to recall the mathematical formalism of tensor products of Hilbert spaces and the action of operators on them. A good introduction to this topic is given in [14]. Before going on with UBHF, a short overview of the special mathematical formalism that is needed here is given.

4.1.1 Spinor calculus

Within the single Slater permanent ansatz, the many-body wave function is fully determined by the set of single particle states $|1\rangle, |2\rangle, \ldots, |N\rangle$ and can be represented by the tuple

$$\begin{pmatrix} |1\rangle \\ \vdots \\ |N\rangle \end{pmatrix} =: |\Psi\rangle \ , \tag{4.1}$$

In order to distinguish the resulting state $|\Phi\rangle$ that is obtained by building the symmetrized product state from this set of orbitals, the tuple will be denoted with Ψ henceforth ($|\Phi\rangle = |\Phi(\Psi)\rangle$). This notation is redolent of the representation of a particle with spin. That is why $|\Psi\rangle$ will be called spinor subsequently. Its components $|1\rangle, \ldots, |N\rangle$ will be called spinor orbitals. For later purpose, it is useful to mention, that any operator $\underline{\hat{O}}$ that acts on this spinor is a matrix of single particle operators and its action is similar to the action of a matrix on a column vector

$$\underline{\hat{O}}\,|\Psi\rangle = \begin{pmatrix} \hat{O}_{11} & \dots & \hat{O}_{1N} \\ \vdots & \ddots & \vdots \\ \hat{O}_{N1} & \dots & \hat{O}_{NN} \end{pmatrix} \begin{pmatrix} |1\rangle \\ \vdots \\ |N\rangle \end{pmatrix} = \begin{pmatrix} \hat{O}_{11}\,|1\rangle + & \dots & +\hat{O}_{1N}\,|N\rangle \\ \vdots & \ddots & \vdots \\ \hat{O}_{N1}\,|1\rangle + & \dots & +\hat{O}_{NN}\,|N\rangle \end{pmatrix}. \tag{4.2}$$

Such kind of operator will subsequently be called spinor operator.

What will be needed as well, is the definition of the spinor of the dual space

$$(|\Psi\rangle)^\dagger = \langle\Psi| := (\langle 1|, \dots, \langle N|) \tag{4.3}$$

and the hermitian adjoint operators acting on them

$$\underline{\hat{O}}^\dagger := \begin{pmatrix} \hat{O}^\dagger_{11} & \dots & \hat{O}^\dagger_{N1} \\ \vdots & \ddots & \vdots \\ \hat{O}^\dagger_{1N} & \dots & \hat{O}^\dagger_{NN} \end{pmatrix}. \tag{4.4}$$

With this definition, the action of an arbitrary operator on the dual space spinor is given by $\langle\Psi|\,\underline{\hat{O}} = (\underline{\hat{O}}^\dagger\,|\Psi\rangle)^\dagger$ and equation (4.2). Finally the dyadic product of a spinor $|\Psi\rangle$ with a dual spinor $\langle\Psi'|$ is defined

$$|\Psi\rangle\langle\Psi'| = \begin{pmatrix} |1\rangle\langle 1'| & \dots & |1\rangle\langle N'| \\ \vdots & \ddots & \vdots \\ |N\rangle\langle 1'| & \dots & |N\rangle\langle N'| \end{pmatrix}. \tag{4.5}$$

All these definitions seem to be intuitive or even obvious, but their formulation is necessary to avoid ambiguity.

4.1.2 Single Slater permanent calculus

The explicit way of building a fully symmetrized product state like in Eq. (3.5) is given by the Slater permanent

$$|\Phi\rangle = \hat{S}_+\Big\{\,|1\rangle \otimes |2\rangle \otimes \dots \otimes |N\rangle\,\Big\} = \frac{1}{N!}\sum_{\pi\in S_N}\bigotimes_{s=1}^{N}|\pi(s)\rangle\ , \tag{4.6}$$

where S_N denotes the group of all permutations of $1, \dots, N$ (the symmetric group). Thus each element π of S_N brings the *factors* of the product $|1\rangle \otimes |2\rangle \otimes \ldots \otimes |N\rangle$ into another ordering[1]. The symmetrization operator $\hat{S}_+$ is hermitian $\hat{S}^\dagger_+ = \hat{S}_+$ and with the factor $\frac{1}{N!}$ [2] , it has the properties of a projector $\hat{S}^2_+ = \hat{S}_+$. For the calculation of the total energy of this product state, the commutation of $\hat{S}_+$ with an arbitrary operator $\hat{O}$

---

[1] Note, that the tensor product does not commute.

[2] In the literature, this operator is used with the factor $\frac{1}{\sqrt{N!}}$ instead of $\frac{1}{N!}$. This is because with this factor and the set of orbitals $|1\rangle, \dots, |N\rangle$ being orthonormal, the whole symmetrized product state would be normalized. But this work is dealing with a nonorthonormal set of orbitals anyway and this replacement of the factor would not have any use.

that is related to an observable $[\hat{S}_+, \hat{O}] = 0$ and its projector properties and can be used. Thus it is only necessary to perform the symmetrization on one side of a scalarproduct

$$\underbrace{\hat{S}_+ \hat{H}}_{=\hat{H}\hat{S}_+} \hat{S}_+ = \hat{H} \underbrace{\hat{S}_+ \hat{S}_+}_{=\hat{S}_+} = \hat{H}\hat{S}_+ \tag{4.7}$$

$$\Rightarrow \left(\langle 1| \otimes \ldots \langle N| \right) \hat{S}_+ \hat{H} \hat{S}_+ \left(|1\rangle \otimes \ldots |N\rangle \right) = \left(\langle 1| \otimes \ldots \langle N| \right) \hat{H} \hat{S}_+ \left(|1\rangle \otimes \ldots |N\rangle \right). \tag{4.8}$$

This leads to the following term for the total energy of a single Slater permanent [14]

$$\frac{\langle \Phi | \hat{H} | \Phi \rangle}{\|\Phi\|^2} = \frac{1}{\|\Phi\|^2 N!} \sum_{\pi \in S_N} \sum_{l=1}^{N} \Big(\prod_{s \neq l} \langle s | \pi(s) \rangle \langle l | \hat{h} | \pi(l) \rangle + \frac{1}{2} \sum_{k \neq l} \prod_{s \neq k,l} \langle s | \pi(s) \rangle \, w_{kl,\pi(k)\,\pi(l)} \Big) \, . \tag{4.9}$$

The two-particle integrals $w_{ij,kl}$[3] are defined in the appendix (Eq. (A.5)) and the norm of the state Φ is given by

$$\|\Phi\|^2 = \frac{1}{N!} \sum_{\pi \in S_N} \prod_{s=1}^{N} \langle s | \pi(s) \rangle \ . \tag{4.10}$$

Thus the Ritz principle is applicable to the functional of the total energy. To avoid the appearance of the norm of the state Φ in the denominator, a Lagrange multiplier $\mathscr{E}$ for the restriction of a normalized state is introduced. The resulting functional that has to be minimized has the form

$$E(|1\rangle, \ldots, |N\rangle, \mathscr{E}) = \langle \Phi | \hat{H} | \Phi \rangle - \mathscr{E} \langle \Phi | \Phi \rangle \ . \tag{4.11}$$

For further calculations the rules for the differentiation with respect to abstract Hilbert space vectors presented in appendix A will be applied for the same reasons as in section 3.2. As the ket-vector $|\Phi\rangle$ only depends on the ket-vectors $|1\rangle, \ldots, |N\rangle$ and vice versa for the bra $\langle \Phi|$, the fact that the derivative with respect to $\langle k|$ of the functional (4.11) is just the hermitian adjoint of the derivative with respect to $|k\rangle$ of this functional can be used.

Before performing the calculation of the variational derivative with respect to $\langle k|$, the definition of the following entity with a variational number of subscripts is needed

$$P_{i_1 \ldots i_n} = P_{i_1 \ldots i_n}(\pi) = \prod_{s \neq i_1 \ldots i_n} \langle s | \pi(s) \rangle \, , \tag{4.12}$$

where π denotes an arbitrary element of the symmetric group S_N. Without any index (P), this definition still holds and the product in Eq. (4.12) runs over all $s = 1, \ldots, N$. The variational derivative of the functional in Eq. (4.11) reads

$$\frac{\delta}{\delta \langle n|} \Big(\langle \Phi | \hat{H} | \Phi \rangle - \mathscr{E} \langle \Phi | \Phi \rangle \Big) \overset{!}{=} 0 \qquad \text{for all } n = 1, 2, \ldots, N \tag{4.13}$$

---

[3] Note, that the conventions for the definition of the two-particle integrals differ in literature.

$$
\begin{aligned}
\Leftrightarrow \quad & \frac{\delta}{\delta \langle n|} \sum_{\pi \in S_N} \sum_{l=1}^{N} \left\{ P_l \langle l|\hat{h}|\pi(l)\rangle + \frac{1}{2} \sum_{k \neq l} P_{lk} w_{kl,\pi(k)\,\pi(l)} \right\} = \mathscr{E} \frac{\delta}{\delta \langle n|} \sum_{\pi \in S_N} P \\
\Leftrightarrow \quad & \sum_{\pi \in S_N} \sum_{l=1}^{N} \Bigg\{ \delta_{nl} P_l \hat{h} |\pi(l)\rangle + (1 - \delta_{ln}) P_{nl} \langle l|\hat{h}|\pi(l)\rangle |\pi(n)\rangle \\
& + \frac{1}{2} \sum_{k \neq l} P_{lk} \Big(\delta_{kn} \hat{J}_{l\pi(l)} |\pi(k)\rangle + \delta_{ln} \hat{J}_{k\pi(k)} |\pi(l)\rangle + (1 - \delta_{kn} - \delta_{ln}) P_{kln} w_{kl\pi(k)\pi(l)} \Big) \Bigg\} \\
& = \sum_{\pi \in S_N} P_n |\pi(n)\rangle \\
\Leftrightarrow \quad & \sum_{\pi \in S_N} \Bigg\{ P_n \hat{h} |\pi(n)\rangle + \sum_{l \neq n} P_{nl} \langle l|\hat{h}|\pi(l)\rangle |\pi(n)\rangle + \sum_{l \neq n} P_{nl} \hat{J}_{l\pi(l)} |\pi(n)\rangle \\
& + \frac{1}{2} \sum_{\substack{k,l \neq n \\ k \neq l}} P_{nlk} w_{kl,\pi(k)\pi(l)} |\pi(n)\rangle \Bigg\} = \mathscr{E} \sum_{\pi \in S_N} P_n |\pi(n)\rangle \quad (\text{ for all } n) \qquad (4.14)
\end{aligned}
$$

The Hartree operator $\hat{J}_{kl}$ is defined in Eq. (A.8). This set of equations will be called UBHF equations in the following. Unfortunately, these equations are very unwieldy but in order to reveal their main structure, the definitions of the following two-fold subscripted operators are needed

$$
\begin{aligned}
\hat{\mathcal{H}}_{nm} &:= \sum_{\substack{\pi \in S_N \\ \pi(n)=m}} \left[P_n \hat{h} + \sum_{k \neq n} P_{kn} \Big[\langle k|\hat{h}|\pi(k)\rangle + \hat{J}_{k\,\pi(k)} \Big] + \sum_{l \neq k,n} P_{kln} w_{kl,\pi(k)\pi(l)} \right] \\
\hat{\mathcal{O}}_{nm} &:= \sum_{\substack{\pi \in S_N \\ \pi(n)=m}} P_n \quad . \qquad (4.15)
\end{aligned}
$$

With these definitions, the UBHF equations (4.14) take on the appealing form

$$
\sum_m \hat{\mathcal{H}}_{nm} |m\rangle = \mathscr{E} \sum_m \hat{\mathcal{O}}_{nm} |m\rangle \quad \text{for all } n,
$$

$$
\Longleftrightarrow \quad \boxed{\underline{\hat{\mathcal{H}}} |\Psi\rangle = \mathscr{E} \underline{\hat{\mathcal{O}}} |\Psi\rangle \ ,} \qquad (4.16)
$$

which has the form of a selfconsistent general eigenvalue problem just as in the fermionic case. A detailed calculation that demonstrates the correctness of Eq. (4.16) with the definitions given in Eq. (4.15) is presented in appendix B. If one of the operators $\underline{\hat{\mathcal{H}}}$ or $\underline{\hat{\mathcal{O}}}$ would be positive definite, there would exist a complete set of eigenvectors that solve the considered generalized eigenvalue problem. Note that the operators $\underline{\hat{\mathcal{H}}}$ and $\underline{\hat{\mathcal{O}}}$ are both hermitian. Unfortunately, the positive definiteness is only given for the case of two particles, hence solving this equation iteratively only provides results for this case. If non of the operators is positive definite, it is possible that equation (4.16) has complex eigenvalues as solution. This makes it impossible to choose the solution with the lowest eigenvalue for the next iteration[4].

The solution to this problem consists in the fact that there are many ways to define operators $\underline{\hat{\mathcal{H}}}$ and $\underline{\hat{\mathcal{O}}}$ such that the UBHF equations (4.14) take on the form of equation (4.16). This can be explained with the following example. For the case of two particles the term $\langle 2|1\rangle \, \hat{h} \, |2\rangle$ arises in the determining equation for the orbital $|1\rangle$. This expression can be regarded as the result of the action of an operator on one of the two orbitals:

$$\langle 2|1\rangle \, \hat{h} \, |2\rangle = \underbrace{\left(\langle 2|1\rangle \, \hat{h} \right)}_{\hat{\mathcal{A}}_1} |2\rangle = \underbrace{\left(\hat{h} \, |2\rangle \, \langle 2| \right)}_{\hat{\mathcal{A}}_2} |1\rangle \, . \tag{4.17}$$

I.e., for 2 particles there exist 16 ways[5] to define operators $\underline{\hat{\mathcal{O}}}$ to bring equation (4.14) into the form of Eq. (4.16). For an arbitrary particle number it is very difficult to calculate this combinatorial factor, but as the number of summands in Eq. (4.14) is $N!$, this factor grows at least with this order of magnitude. With a convenient choice of the definition of the operators it is possible to transform equation (4.16) into an already blockwise diagonalized form:

$$\hat{\mathcal{H}}_{nm} = \delta_{nm} \hat{\mathcal{H}}_n \qquad \text{and} \qquad \hat{\mathcal{O}}_{nm} = \delta_{nm} \hat{\mathcal{O}}_n \, , \tag{4.18}$$

with the operator $\hat{\mathcal{O}}_n$ being positive-definite. So the general eigenvalue problem (4.16) becomes a set of N generalized eigenvalue problems with a complete set of solutions. For this purpose, one has to make sure, that the orbital $|n\rangle$ in the UBHF equations (4.14) is extracted to the right. The resulting operators read

$$\begin{aligned}
\hat{\mathcal{H}}_n = \sum_{\pi \in S_N} \Bigg\{ & \delta_{n\pi(n)} \Bigg[P_n \hat{h} + \sum_{l \neq n} P_{ln} \Big(\langle l|\hat{h}|\pi(l)\rangle + \hat{J}_{l\pi(l)} \Big) + \frac{1}{2} \sum_{\substack{k,l \neq n \\ k \neq l}} P_{kln} w_{kl,\pi(k)\pi(l)} \Bigg] \\
& + (1 - \delta_{\pi(n)n}) \Bigg[P_{n\pi^{-1}(n)} \Big(\hat{h} \, |\pi(n)\rangle \, \langle \pi^{-1}(n)| + |\pi(n)\rangle \, \langle \pi^{-1}(n)| \, \hat{h} + \hat{K}_{\pi^{-1}(n)\pi(n)} \Big) \\
& \quad + \sum_{\substack{l \neq \pi^{-1}(n) \\ l \neq n}} P_{ln\pi^{-1}(n)} \Big(\langle l|\hat{h}|\pi(l)\rangle \, |\pi(n)\rangle \, \langle \pi^{-1}(n)| + \hat{J}_{l\pi(l)} \, |\pi(n)\rangle \, \langle \pi^{-1}(n)| \\
& \qquad \qquad + |\pi(n)\rangle \, \langle \pi^{-1}(n)| \, \hat{J}_{l\pi(l)} \Big) \\
& \qquad \qquad + \frac{1}{2} \sum_{\substack{k,l \neq n\pi^{-1}(n) \\ k \neq l}} P_{kln\pi^{-1}(n)} w_{kl,\pi(k)\pi(l)} \, |\pi(n)\rangle \, \langle \pi^{-1}(n)| \Bigg] \Bigg\}
\end{aligned} \tag{4.19}$$

---

[4] It may appear odd for the reader that this nearly useless equation is mentioned at all, but the implementation of this equation is a time and nerve consuming procedure and it is also a goal of this work to prevent others from loosing their time by following ideas that do not work.

[5] This number is explained in this footnote: For two particles, the left hand side of equation (4.14) is a superposition of two orbitals. E.g. for $n = 1$: $\mathscr{E}(\langle 2|2\rangle \, |1\rangle + \langle 2|1\rangle \, |2\rangle)$. According to Eq. (4.17), there exist four possibilities of defining operators $\hat{c}_1$ and $\hat{c}_2$ such that $\mathscr{E}(\langle 2|2\rangle \, |1\rangle + \langle 2|1\rangle \, |2\rangle) = \mathscr{E}(\hat{c}_1 \, |1\rangle + \hat{c}_2 \, |2\rangle)$. Those possibilities are $(\hat{c}_1, \hat{c}_2) = (\langle 2|2\rangle \, , \langle 2|1\rangle)$, $(\langle 2|2\rangle + |2\rangle \, \langle 2| \, , 0)$, $(0, \langle 2|1\rangle + |1\rangle \, \langle 2|)$ or $(|2\rangle \, \langle 2| \, , |1\rangle \, \langle 2|)$. The same possibilities hold for the second equation ($n = 2$). A combination of all these possibilities yield $4 \cdot 4 = 16$ ways of defining such a spinor operator $\underline{\hat{\mathcal{O}}}$.

$$\hat{\mathcal{O}}_n = \sum_{\pi\in S_N} \Big\{ \delta_{n\pi(n)} P_n + (1-\delta_{\pi(n)n}) P_{n\pi^{-1}(n)} \left|\pi(n)\right\rangle \left\langle \pi^{-1}(n)\right| \Big\} \tag{4.20}$$

The definitions of these operators are even more unpleasant to handle than the ones given in Eq. (4.15) but as these definitions provide an efficient way to solve the UBHF equations, we have to grapple with them. The appearing operator $\hat{K}_{kl}$ is defined in the appendix A in Eq. (A.8). π^{-1} denotes the inverse permutation of π and is also a member of S_N. Appendix B presents a detailed derivation of these two sets of operators.

As already mentioned before, it is also a goal of this work to point out what ideas do not work. I allude, that it is not sufficient to take the operator $\underline{\hat{\mathcal{H}}}$ in (4.15) and the here defined operator $\underline{\hat{\mathcal{O}}}$ and merge them to a new generalized eigenvalue problem, although the entire operator $\underline{\hat{\mathcal{O}}}$ is positive definite – as it is a blockwise diagonalized operator with positive definite blocks.

The proof of the positive definiteness of the operators $\hat{\mathcal{O}}_n$ for all n will be given now. For this purpose consider the diagonal matrix element $\langle\eta|\hat{\mathcal{O}}_n|\eta\rangle$, with η being an arbitrary nonzero one-particle Hilbert space state. The statement $\langle\eta|\hat{\mathcal{O}}_n|\eta\rangle > 0$ for an arbitrary η, implies the positive definiteness of $\hat{\mathcal{O}}_n$. Note, that in the definition of $\hat{\mathcal{O}}_n$ the state n does not occur. Consider now the special diagonal matrix element

$$\begin{aligned}
\langle n|\hat{\mathcal{O}}_n|n\rangle &= \langle n| \sum_{\pi\in S_N} \Big\{ \delta_{n\pi(n)} P_n + (1-\delta_{\pi(n)n}) P_{n\pi^{-1}(n)} \left|\pi(n)\right\rangle \left\langle \pi^{-1}(n)\right| \Big\} |n\rangle \\
&= \sum_{\pi\in S_N} \Big\{ \delta_{n\pi(n)} \underbrace{P_n \langle n|n\rangle}_{=P} + (1-\delta_{\pi(n)n}) \underbrace{P_{n\pi^{-1}(n)} \langle n|\pi(n)\rangle \langle \pi^{-1}(n)|n\rangle}_{=P(\pi)} \Big\} \\
&= \sum_{\pi\in S_N} \big(\underbrace{\delta_{n\pi(n)} + (1-\delta_{\pi(n)n})}_{=1} \big) \prod_{s=1}^{N} \langle s|\pi(s)\rangle = \langle\Phi|\Phi\rangle
\end{aligned} \tag{4.21}$$

This implies, that $\langle\eta|\hat{\mathcal{O}}_n|\eta\rangle$ (for an arbitrary η) is just the squared norm of the state, that is obtained by exchanging the state n with the state η. And the squared norm is by definition nonzero for nonzero vectors. In the same manner it can be shown that

$$\langle n|\hat{\mathcal{H}}_n|n\rangle = \langle\Phi|\hat{H}|\Phi\rangle \,. \tag{4.22}$$

Just as above, this implies that the diagonal matrix element $\langle\eta|\hat{\mathcal{H}}_n|\eta\rangle$ is the total energy of the state, which is obtained by making the just mentioned replacement multiplied by the norm of the resulting product state.

4.2 Scheme for solving the UBHF equations

Of course it is possible to solve the UBHF equations (4.14) by applying a multidimensional minimization routine provided by a numerical programming library. This section presents a scheme for solving the UBHF equations iteratively by making use of the special structure of these equations.

The properties of the just defined and analyzed operators $\hat{\mathcal{O}}_n$ and $\hat{\mathcal{H}}_n$ enable us to develop an iteration scheme for solving Eq. (4.14) which guarantees, that the total energy of the state Φ decreases at each step. The principle idea is quite simple. In each step one has to find the vector $\eta_{n,0}$ for each n, that minimizes the functional

$$E_n(\eta) := \frac{\langle\eta|\hat{\mathcal{H}}_n|\eta\rangle}{\langle\eta|\hat{\mathcal{O}}_n|\eta\rangle}, \tag{4.23}$$

as it is the total energy of the state that is obtained by replacing the state n with η. Then one has to find the state n_0, for which the minimum of $E_n(\eta)$ has the minimal value and replace this η by n_0.

The functional derivative of the functional E_n reads

$$\frac{\delta}{\delta\langle\eta|}\frac{\langle\eta|\hat{\mathcal{H}}_n|\eta\rangle}{\langle\eta|\hat{\mathcal{O}}_n|\eta\rangle^2} = \frac{1}{\langle\eta|\hat{\mathcal{O}}_n|\eta\rangle}\cdot\left(\hat{\mathcal{H}}_n|\eta\rangle\langle\eta|\hat{\mathcal{O}}_n|\eta\rangle - \langle\eta|\hat{\mathcal{H}}_n|\eta\rangle\,\hat{\mathcal{O}}_n|\eta\rangle\,\right).$$

The quotient rule is applicable, because the functional derivative can always be mapped onto a derivative with respect to an expansion coefficient with respect to an arbitrary basis. With $\mathscr{E} = \frac{\langle\eta|\hat{\mathcal{H}}_n|\eta\rangle}{\langle\eta|\hat{\mathcal{O}}_n|\eta\rangle}$ this equation takes on the form of a generalized eigenvalue problem

$$\hat{\mathcal{H}}_n|\eta\rangle = \mathscr{E}_n\hat{\mathcal{O}}_n|\eta\rangle\,. \tag{4.24}$$

Thus for fixed operators $\hat{\mathcal{H}}_n$ and $\hat{\mathcal{O}}_n$, the state that minimizes E_n can easily be obtained by solving the generalized eigenvalue problem (4.24) and picking out the state η_0 that is related to the smallest eigenvalue.

For better comprehension, the total scheme for a numeric implementation is given in the following enumeration and is visualized in Fig. 4.1.

1. Choose a basis in which the calculation shall be performed. In this basis, the orbitals $|k\rangle$ are column vectors (tuples) and the operators $\hat{\mathcal{H}}_n$ and $\hat{\mathcal{O}}_n$ are matrices. The matrix elements of the one particle part of the Hamilton operator and the two-particle integrals have to be calculated before starting the iteration. For my calculations which are presented in Chap. 5, I chose the eigenstates of the ideal system as basis. In the following n_b denotes the number of chosen basis vectors.

2. Guess an initial value for the Spinor Ψ. In my implementation, this is done by a random number generator, that creates an initial state close to the ground state. In practice the iteration leads favorably to a metastable state instead of the absolute minimum if two of the initial spinor orbitals are orthogonal. However, the N initial spinor orbitals should be linearly independent.

3. Calculate for all n the operators $\hat{\mathcal{H}}_n$ and $\hat{\mathcal{O}}_n$ and solve the generalized eigenvalue problem (4.24). For each n, a set of n_b eigenvalues with associated eigenstates is obtained.

4. Find the component n_{min}, whose associated eigenvalue problem has the smallest minimal eigenvalue

   $$\mathscr{E}_{\text{min}} = \min\left\{\mathscr{E}_{ln}\middle|\;\hat{\mathcal{H}}_n|\eta_l\rangle = \mathscr{E}_{ln}\hat{\mathcal{O}}_n|\eta_l\rangle\; l=1,\dots,n_b,\, n=1,\dots,N\right\}.$$

   Thus the n with $\mathscr{E}_{0n} = \mathscr{E}_{\text{min}}$. This n will be called n_{min}.

5. Replace the spinor orbital $|n_{\mathrm{min}}\rangle$ in the spinor $|\Psi\rangle$ with the vector $|\eta\rangle$ related to the smallest minimal eigenvalue. The energy that is related with the new spinor $|\Psi\rangle$ has now the value $\mathscr{E}_{\mathrm{min}}$. The important feature of this iteration is that the total energy can not possibly increase by this replacement.

6. Bring the new spinor into the desired gauge (see section 4.4).

7. Start again with the new $|\Psi\rangle$ at 3 until the total change $\Delta = D(\Psi_{i+1}, \Psi_i)$ of the spinor after the execution of one iteration step drops below a given value that expresses the accuracy of the result. The total change Δ can either be the energy change of the iteration step, or another quantity resembling a distance. For the choice of D, one has to take into account, that it does not make any difference wether n_{min} is replaced by η or its negative. In my implementation of this algorithm the total change is calculated by

$$D(\Psi_{i+1}, \Psi_i) = \sum_{\alpha n} \left| |c^i_{\alpha n}| - |c^{i+1}_{\alpha n}| \right| , \tag{4.25}$$

where $c^i_{\alpha n}$ denotes the αth expansion coefficient of the nth spinor orbital of the spinor in the ith iteration step.

4.3 Time-dependent UBHF

The derivation of the equation of motion for the spinor is not only useful for the consideration of nonequilibrium systems but also provides the possibility to determine the minimum of the functional given in Eq. (4.11) by performing imaginary time stepping. The sought after trajectory of the spinor minimizes the functional in Eq. (3.7) with $|\Phi\rangle = |\Phi(\Psi)\rangle$. The diagonal matrix element of the time derivative reads

$$\langle\Phi|\frac{\mathrm{d}}{\mathrm{d}t}|\Phi\rangle = \frac{1}{N!} \sum_{\pi\in S_N} \sum_{l=1}^{N} P_l \, \langle l|\frac{\mathrm{d}}{\mathrm{d}t}|\pi(l)\rangle \tag{4.26}$$

which results directly from the product rule.

For the derivation of the Euler-Lagrange equations, the fact that a differentiation with respect to $|n\rangle$ results in the hermitian adjoint equations to those obtained by a differentiation with respect to $\langle n|$, is used by performing the derivative only with respect to the bra-vectors. Note that the Lagrangian does not depend on their time derivative. Fortunately the differentiation of the part $\langle\Phi|\hat{H} - \mathscr{E}(t)|\Phi\rangle$ has already been done in

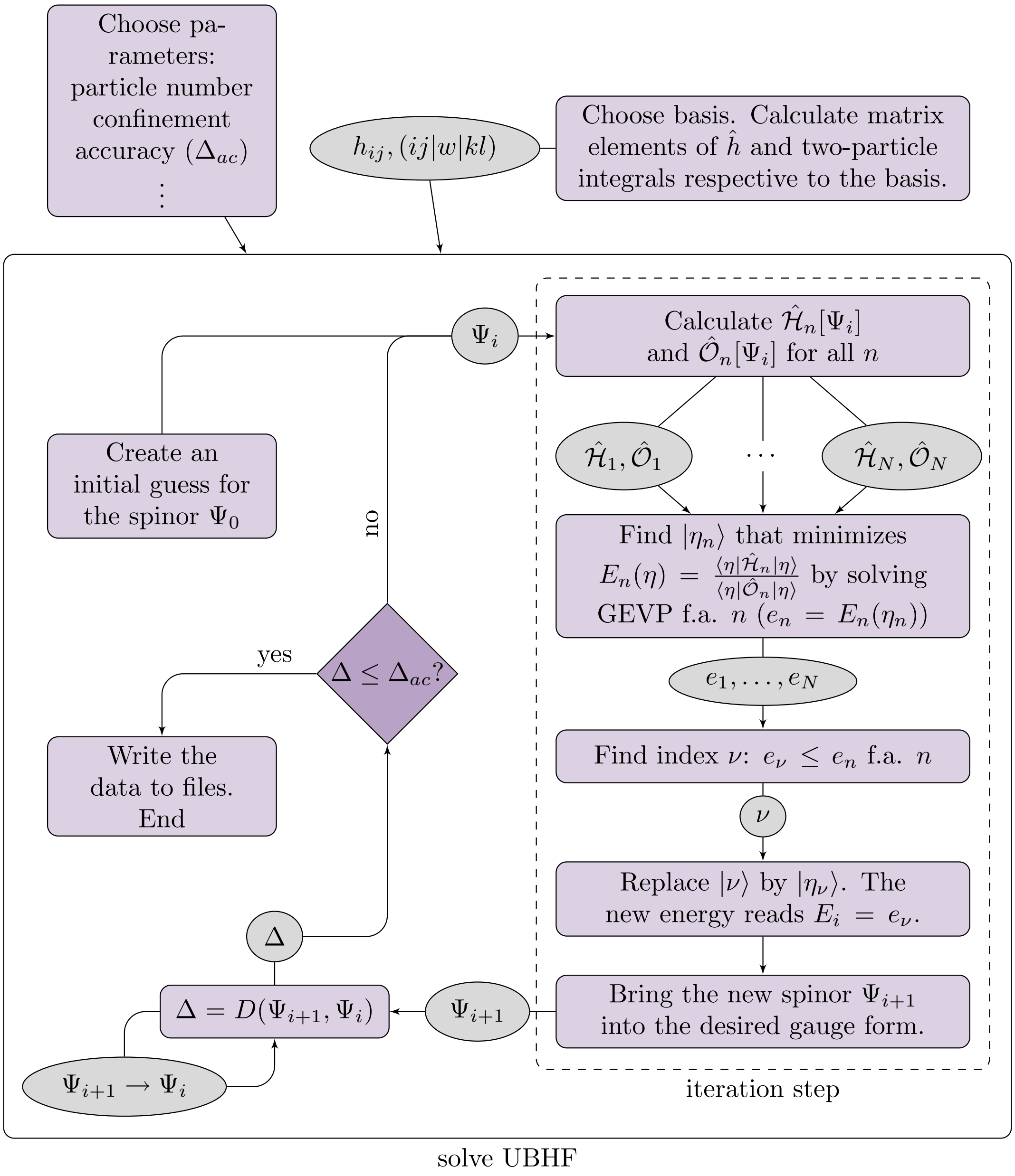

Figure 4.1: *Diagrammatic overview of the iteration scheme for solving the UBHF equations* (4.14) *proposed in this chapter. The oval gray nodes mark the important handover parameters of the procedures in the violet rectangle nodes. Disregarding the details of the iteration step (box with dashed line), the scheme shows the usual process of finding a fix point of an iteration as it is also known for the solving scheme of the fermionic Hartree-Fock approximation.*

section 4.1, so it is only necessary to differentiate the part with the time-derivative:

$$
\begin{aligned}
\frac{\delta}{\delta\langle n|}\langle\Phi|\frac{\mathrm{d}}{\mathrm{d}t}|\Phi\rangle &= \frac{1}{N!}\sum_{\pi\in S_N}\sum_{l=1}^{N}\Big(\frac{\delta}{\delta\langle n|}P_l\Big)\langle l|\frac{\mathrm{d}}{\mathrm{d}t}|\pi(l)\rangle + P_l\Big(\frac{\delta}{\delta\langle n|}\langle l|\frac{\mathrm{d}}{\mathrm{d}t}|\pi(l)\rangle\Big)\\
&= \frac{1}{N!}\sum_{\pi\in S_N}\sum_{l=1}^{N}(1-\delta_{nl})P_{nl}\,|\pi(n)\rangle\,\langle l|\frac{\mathrm{d}}{\mathrm{d}t}|\pi(l)\rangle + \delta_{nl}P_l\frac{\mathrm{d}}{\mathrm{d}t}\,|\pi(l)\rangle\\
&= \frac{1}{N!}\sum_{l=1}^{N}\sum_{\pi\in S_N}\Big((1-\delta_{nl})P_{nl}\,|\pi(n)\rangle\,\langle l| + \delta_{nl}P_l\Big)\frac{\mathrm{d}}{\mathrm{d}t}\,|\pi(l)\rangle\\
&= \frac{1}{N!}\sum_{m=1}^{N}\left(\sum_{\pi\in S_N}(1-\delta_{n\pi^{-1}(m)})P_{n\pi^{-1}(m)}\,|\pi(n)\rangle\,\langle\pi^{-1}(m)| + \delta_{n\pi^{-1}(m)}P_{\pi^{-1}(m)}\right)\frac{\mathrm{d}}{\mathrm{d}t}\,|m\rangle\\
&= \frac{1}{N!}\sum_{m=1}^{N}\hat{\mathcal{T}}_{nm}\frac{\mathrm{d}}{\mathrm{d}t}\,|m\rangle\ .
\end{aligned}
\tag{4.27}
$$

The penultimate term is easy to understand if one makes the transformation from this term to the first. In the last expression, a new operator

$$
\hat{\mathcal{T}}_{nm} := \sum_{\pi\in S_N}(1-\delta_{n\pi^{-1}(m)})P_{n\pi^{-1}(m)}\,|\pi(n)\rangle\,\langle\pi^{-1}(m)| + \delta_{n\pi^{-1}(m)}P_{\pi^{-1}(m)} \tag{4.28}
$$

is introduced. In contrast to equation (4.16), equation (4.27) does not leave any freedom to define $\hat{\mathcal{T}}_{nm}$ such that equation (4.27) holds, because the spinor component that is differentiated with respect to t shall not be involved in the definition of $\hat{\mathcal{T}}_{nm}$. Using this variational derivative together with the already performed derivative of the remaining part of the Lagrangian, the Euler-Lagrange Equation of this system reads

$$
\underline{\hat{\mathcal{H}}}\,|\Psi\rangle - \mathscr{E}(t)\underline{\hat{\mathcal{O}}}\,|\Psi\rangle = i\underline{\hat{\mathcal{T}}}\partial_t\,|\Psi\rangle\ . \tag{4.29}
$$

Multiplying this equation scalarly from the left with $\langle\Psi|$, yields a closed expression for the Lagrange multiplier:

$$
\mathscr{E}(t) = \frac{1}{\langle\Psi|\underline{\hat{\mathcal{O}}}|\Psi\rangle}\big(\,\langle\Psi|\underline{\hat{\mathcal{H}}}|\Psi\rangle - i\,\langle\Psi|\underline{\hat{\mathcal{T}}}\frac{\mathrm{d}}{\mathrm{d}t}|\Psi\rangle\,\big)\ . \tag{4.30}
$$

Reinsertion of this expression in Eq. (4.29), transforms the equation of motion to

$$
\underline{\hat{\mathsf{P}}\hat{\mathcal{H}}}\,|\Psi\rangle = \underline{\hat{\mathsf{P}}}i\underline{\hat{\mathcal{T}}}\,|\dot{\Psi}\rangle\ . \tag{4.31}
$$

The problem is, that the introduced operator $\underline{\hat{\mathsf{P}}} = (1 - \frac{1}{\langle\Psi|\underline{\hat{\mathcal{O}}}|\Psi\rangle}\underline{\hat{\mathcal{O}}}\,|\Psi\rangle\,\langle\Psi|)$ is a projector with $\underline{\hat{\mathcal{O}}}\,|\Psi\rangle$ as eigenstate with eigenvalue 0:

$$
\underline{\hat{\mathsf{P}}\hat{\mathcal{O}}}\,|\Psi\rangle = \left(1 - \frac{\underline{\hat{\mathcal{O}}}\,|\Psi\rangle\,\langle\Psi|}{\langle\Psi|\underline{\hat{\mathcal{O}}}|\Psi\rangle}\right)\underline{\hat{\mathcal{O}}}\,|\Psi\rangle = \underline{\hat{\mathcal{O}}}\,|\Psi\rangle - \underline{\hat{\mathcal{O}}}\,|\Psi\rangle\underbrace{\frac{\langle\Psi|\,\underline{\hat{\mathcal{O}}}\,|\Psi\rangle}{\langle\Psi|\underline{\hat{\mathcal{O}}}|\Psi\rangle}}_{=1} = 0\ , \tag{4.32}
$$

$$\underline{\hat{\mathsf{P}}}^2 = 1 - 2\frac{\underline{\hat{\mathcal{O}}}\,|\Psi\rangle\,\langle\Psi|}{\langle\Psi|\underline{\hat{\mathcal{O}}}|\Psi\rangle} + \frac{\underline{\hat{\mathcal{O}}}\,|\Psi\rangle\,\langle\Psi|\underline{\hat{\mathcal{O}}}|\Psi\rangle\,\langle\Psi|}{\langle\Psi|\underline{\hat{\mathcal{O}}}|\Psi\rangle^2} = \left(1 - \frac{\underline{\hat{\mathcal{O}}}\,|\Psi\rangle\,\langle\Psi|}{\langle\Psi|\underline{\hat{\mathcal{O}}}|\Psi\rangle}\right) = \underline{\hat{\mathsf{P}}}\,. \tag{4.33}$$

Thus $\underline{\hat{\mathsf{P}}}$ somehow blocks the *view* onto the sought after equation of motion. Fortunately, this problem can be fixed in a very similar way as in the GP case by demanding the time-derivative of $|\Phi\rangle$ to be orthogonal on $\langle\Phi|$:

$$0 \overset{!}{=} \langle\Phi|\frac{\mathrm{d}}{\mathrm{d}t}|\Phi\rangle = (N-1)!\,\langle\Psi|\underline{\hat{\mathcal{I}}}\frac{\mathrm{d}}{\mathrm{d}t}|\Psi\rangle\ . \tag{4.34}$$

Same as in the GP case, this equality can be obtained by multiplying the wave function with a time dependent phase.

Before going on with the development of a usable equation of motion for the spinor $|\Psi\rangle$, it is necessary to prove the validity of the last equal sign in Eq. (4.34). For this purpose, it is sufficient to show that

$$\langle n|\,\frac{1}{N!}\sum_{m=1}^{N}\hat{\mathcal{I}}_{nm}\frac{\mathrm{d}}{\mathrm{d}t}\,|m\rangle = \langle\Phi|\frac{\mathrm{d}}{\mathrm{d}t}|\Phi\rangle\ ,$$

which is the scalar product of the nth column of $\underline{\hat{\mathcal{I}}}\frac{\mathrm{d}}{\mathrm{d}t}\,|\Psi\rangle$ with $\langle n|$. So

$$\begin{aligned}\langle n|\,\frac{1}{N!}\sum_{m=1}^{N}\hat{\mathcal{I}}_{nm}\frac{\mathrm{d}}{\mathrm{d}t}\,|m\rangle &= \frac{1}{N!}\sum_{\pi\in S_N}\sum_{m=1}^{N}\delta_{n\pi^{-1}(m)}\ \underbrace{P_{\pi^{-1}(m)}\,\langle n|\frac{\mathrm{d}}{\mathrm{d}t}|m\rangle}_{\searrow P_{\pi^{-1}(m)}\langle\pi^{-1}(m)|\frac{\mathrm{d}}{\mathrm{d}t}|m\rangle}\\ &\quad + (1-\delta_{n\pi^{-1}(m)})\,\underbrace{P_{n\pi^{-1}(m)}\,\langle n|\pi(n)\rangle}_{P_{\pi^{-1}(m)}}\,\langle\pi^{-1}(m)|\frac{\mathrm{d}}{\mathrm{d}t}|m\rangle\\ = \frac{1}{N!}\sum_{\pi\in S_N}\sum_{m=1}^{N}P_{\pi^{-1}(m)}\,\langle\pi^{-1}(m)|\frac{\mathrm{d}}{\mathrm{d}t}|m\rangle &= \frac{1}{N!}\sum_{\pi\in S_N}\sum_{l=1}^{N}P_l\,\langle l|\frac{\mathrm{d}}{\mathrm{d}t}|\pi(l)\rangle \overset{(4.26)}{=} \langle\Phi|\frac{\mathrm{d}}{\mathrm{d}t}|\Phi\rangle\,.\end{aligned} \tag{4.35}$$

With

$$\langle\Psi|\underline{\hat{\mathcal{I}}}\frac{\mathrm{d}}{\mathrm{d}t}|\Psi\rangle = \sum_{n=1}^{N}\underbrace{\langle n|\,\frac{1}{N!}\sum_{m=1}^{N}\hat{\mathcal{I}}_{nm}\frac{\mathrm{d}}{\mathrm{d}t}\,|m\rangle}_{=\langle\Phi|\frac{\mathrm{d}}{\mathrm{d}t}|\Phi\rangle} = N\,\langle\Phi|\frac{\mathrm{d}}{\mathrm{d}t}|\Phi\rangle \tag{4.36}$$

the assertion is shown.

With the restriction given in Eq. (4.34), the Lagrange multiplier (see Eq. (4.30)) reads

$$\mathscr{E}(t) = \frac{\langle\Psi|\underline{\hat{\mathcal{H}}}|\Psi\rangle}{\langle\Psi|\underline{\hat{\mathcal{O}}}|\Psi\rangle} = \frac{\langle\Phi|\hat{H}|\Phi\rangle}{\langle\Phi|\Phi\rangle}\ , \tag{4.37}$$

and the reinsertion of this expression in Eq. (4.29) yields

$$\underline{\hat{\mathsf{P}}\hat{\mathcal{H}}}\,|\Psi\rangle = i\underline{\hat{\mathcal{I}}}\frac{\mathrm{d}}{\mathrm{d}t}\,|\Psi\rangle$$

$$\text{i.e.}\quad \boxed{\underline{\hat{\mathcal{H}}}\,|\Psi\rangle - \mathscr{E}(t)\underline{\hat{\mathcal{O}}}\,|\Psi\rangle = i\underline{\hat{\mathcal{I}}}\frac{\mathrm{d}}{\mathrm{d}t}\,|\Psi\rangle\ .} \tag{4.38}$$

The last equality follows directly from equations (4.21) and (4.22).

4.3.1 Resolving the equation of motion

Unfortunately equation (4.38) cannot be resolved. For the case of two particles, this can be seen by multiplying $\underline{\hat{\mathcal{I}}}$ with $(\langle 1|\,, -\langle 2|)^\dagger$:

$$\begin{pmatrix} |2\rangle\langle 2| + \langle 2|2\rangle & |1\rangle\langle 2| + \langle 2|1\rangle \\ |2\rangle\langle 1| + \langle 1|2\rangle & |1\rangle\langle 1| + \langle 1|1\rangle \end{pmatrix} \begin{pmatrix} |1\rangle \\ -|2\rangle \end{pmatrix} = 0\ . \tag{4.39}$$

Thus for two particles $\underline{\hat{\mathcal{I}}}$ has a vanishing eigenvalue. This singularity of $\underline{\hat{\mathcal{I}}}$ also arises in other approximations using the TDVP [40] and there are various propositions for solving this problem. In [41] it is proposed to make the transformation $\underline{A} \to \underline{A} + \varepsilon\underline{1}$ for the appearing noninvertible matrix [6] with a small parameter ε and hope that the new obtained operator is not singular. This solution could also work for this case, but lacks a good justification.

For the two particle case, practice has shown, that the additional equation

$$0 = \langle\Psi|\underline{\hat{\mathcal{I}}}|\dot{\Psi}\rangle\ (= \frac{1}{N}\langle\Psi|\underline{\hat{\mathcal{O}}}|\dot{\Psi}\rangle\,) \tag{4.40}$$

provides a solvable system of linear equations; though equation (4.40) follows directly from the main equation of motion (4.38).

4.4 Ambiguity of the spinor

The determining equations for the orbitals were derived by Romanovsky [39] in a slightly different fashion than in section 4.1. In his ansatz, he demanded all orbitals in the spinor to be normalized by introducing N further Lagrange multipliers. As this restriction does not provide any advantages for the numerical implementation, I avoided it. Furthermore it is possible to normalize the orbitals afterwards whenever needed. It is not even necessary, that all spinor orbitals have the same norm. In this section the transformation group of the spinor $|\Psi\rangle$ which leaves the resulting symmetrized product state $|\Phi(\Psi)\rangle$ (see Eq. (4.6)) unchanged, is introduced.

---

[6] In the mentioned literature, the noninvertibility of the equation of motion is usually due to a different kind of matrices.

Permutations

An arbitrary transposition of two orbitals

$$\pi_{ij}\begin{pmatrix}\vdots\\ |i\rangle\\ \vdots\\ |j\rangle\\ \vdots\end{pmatrix}=\begin{pmatrix}\vdots\\ |j\rangle\\ \vdots\\ |i\rangle\\ \vdots\end{pmatrix} \tag{4.41}$$

and combinations of such transpositions leave the symmetrized product invariant. Hence it is possible to arrange the orbitals in an order, that reflects the localization of the orbitals – see Fig. 5.1.

Equalizing the norm

Multiplying each spinor orbital $|k\rangle$ by a different factor $F_k \in \mathbb{C}\setminus\{0\}$ is equivalent to the multiplication of the symmetrized product state by $\prod_k F_k$. If this product values one, this transformation of the spinor does not have any effect on $|\Phi\rangle$. With the choice

$$F_k=\left(\prod_{s=1}^{N}\langle s|s\rangle\right)^{\frac{1}{2N}}\frac{1}{\sqrt{\langle k|k\rangle}} \tag{4.42}$$

for the factors, each spinor orbital has the same norm

$$\langle\tilde{k}|\tilde{k}\rangle=\langle k|F_kF_k|k\rangle=\left(\prod_{s=1}^{N}\langle s|s\rangle\right)^{\frac{1}{N}}\frac{\langle k|k\rangle}{\langle k|k\rangle}=\left(\prod_{s=1}^{N}\langle s|s\rangle\right)^{\frac{1}{N}}, \tag{4.43}$$

and the effect on $|\Phi\rangle$ equals the multiplication with the product of these factors

$$\prod_{k=1}^{N}F_k=\prod_{k=1}^{N}\left[\left(\prod_{s=1}^{N}\langle s|s\rangle\right)^{\frac{1}{2N}}\frac{1}{\sqrt{\langle k|k\rangle}}\right]=\left(\prod_{s=1}^{N}\langle s|s\rangle\right)^{\frac{N}{2N}}\left(\prod_{k=1}^{N}\frac{1}{\sqrt{\langle k|k\rangle}}\right)=1 \tag{4.44}$$

Thus, the transformation given by Eq. (4.42) yields a spinor with all components having the same norm. A priori, it is not necessary to transform the spinor such that all components have the same norm, but for the numerical implementation of UBHF, it is convenient to avoid some components having a norm near zero, while others have values near the upper limit of *double* numbers. Hence this transformation provides a numerical stability and should be performed after each iteration step of the scheme presented in section 4.2.

Multiplication by a phase factor

The multiplication of a quantum mechanical state by a phase factor $e^{i\phi}$ does not change any physical property. As the multiplication of a spinor component by a factor f equals a multiplication of $|\Phi\rangle$ by the same factor, it can be regarded as an additional symmetry. In the numerical implementation of the stationary UBHF, the spinor components are always considered to be real. This can also be explained by the fact, that for any generalized eigenvalue problem (4.16) with positive definite $\hat{O}$ has a real set of solutions.

All transformations presented here can be considered as gauge transformations of the spinor that make it possible to bring Ψ into a numerically more stable form and to order the components in a manner that reflects the position of the orbitals relative to each other.

4.5 The reduced one-body density matrix in UBHF

In contrast to fermionic Hartree-Fock, the self-consistent orbitals (spinor orbitals) obtained by UBHF are not equal to the natural orbitals. In section 2.1 the definition of the reduced one-body density matrix is given in the second quantization formalism. In the UBHF case, this formalism is not applicable in such a simple way, as the orbitals in Ψ are non-orthonormal. Hence it is convenient to express the operators in dyadic products of the single particle states:

$$\hat{a}_k^\dagger \hat{a}_l \longrightarrow |k\rangle \langle l| \ . \tag{4.45}$$

Analogously to the expectation value of any one-body operator of Φ, the expectation value of $|\vec{r}\rangle \langle \vec{r}'|$ is given by:

$$\mathfrak{g}(\vec{r},\vec{r}') = \frac{1}{N!} \sum_{\pi \in S_N} \sum_{l=1}^{N} P_l \langle l|\vec{r}\rangle \langle \vec{r}'|\pi(l)\rangle = \langle \vec{r}'| \left(\frac{1}{N!} \sum_{\pi \in S_N} \sum_{l=1}^{N} P_l |\pi(l)\rangle \langle l| \right) |\vec{r}\rangle \tag{4.46}$$

Thus the abstract form of the reduced one-body density matrix as introduced in section 2.1.1 is given by

$$\hat{\mathfrak{g}} = \frac{1}{N!} \sum_{\pi \in S_N} \sum_{l=1}^{N} P_l |\pi(l)\rangle \langle l| \ . \tag{4.47}$$

The action of this operator in the one-body Hilbert space can be divided into two regions. On the subspace of the one-body Hilbert space that is spanned by the set of spinor components $\mathscr{H}_\Psi = \mathrm{span}(|1\rangle, \ldots, |N\rangle)$ the action is, in general, nonzero. And on the subspace that is complementary to $\mathscr{H}_\Psi$ – the space where all vectors in it are orthogonal to all components of $|\Psi\rangle$ – the result of its action is zero. This means, that this complementary space to $\mathscr{H}_\Psi$ is an eigenspace of $\hat{\mathfrak{g}}$ with vanishing eigenvalues. Hence, $\hat{\mathfrak{g}}$ only has at most N eigenvectors (natural orbitals) with nonzero eigenvalues, as $\mathscr{H}_\Psi$ has dimension $\leq N$.

4.6 Minor permanent calculus

The sum over all permutations that arises in the previous sections makes the considered equations and expressions very cumbersome. The goal of this section is to bring the UBHF equations (4.14) into a much more simple form that provides the possibility for a less complex calculation of the terms than with the sum over all permutations.

4.6.1 Total energy expressed with permanents

For this purpose, the shorthand notation of the tensor product of the spinor components $|1\rangle \otimes \ldots \otimes |N\rangle =: |F)$ is needed. The vector that is obtained when the state $|i\rangle$ in $|F)$ is replaced by $|\eta\rangle$ is denoted by $|F_i^{|\eta\rangle})$. Using the representation given in Eq. (C.9) for the operator $\hat{h}$, yields the diagonal element

$$\langle\Phi|\hat{h}|\Phi\rangle = (F|\hat{S}_+ \sum_{ij} \langle i|\hat{h}|j\rangle\, \hat{o}\,|i\rangle\, \langle j|\, \hat{o}|F) = \sum_{ij} \langle i|\hat{h}|j\rangle\, (F|\hat{S}_+|F_j^{\hat{o}|i\rangle})\,. \tag{4.48}$$

Thus the calculation of the expectation value reduces to the calculation of the single particle matrix element of $\hat{h}$ and of $(F|\hat{S}_+|F_j^{\hat{o}|i\rangle})$ which has the following form

$$\begin{aligned}
(F|\hat{S}_+|F_j^{\hat{o}|i\rangle}) &= \frac{1}{N!} \sum_{\pi\in S_N} \underbrace{\langle\pi(j)|\hat{o}|i\rangle}_{=\delta_{i\pi(j)}} \prod_{s\neq j} \langle\pi(s)|s\rangle \\
&= \frac{1}{N!} \sum_{\substack{\pi\in S_N\\ \pi(j)=i}} \prod_{s\neq j} \langle\pi(s)|s\rangle = \frac{1}{N!}\mathrm{per}(\underline{G}_i^j)\,.
\end{aligned} \tag{4.49}$$

Here $\underline{G}_i^j$ is the matrix that is obtained after eliminating the jth row and the ith column from the Gramian matrix of the set of spinor components:

$$\underline{G}(|1\rangle, \ldots, |N\rangle) := \begin{pmatrix} \langle 1|1\rangle & \langle 1|2\rangle & \ldots\ldots & \langle 1|N\rangle \\ \langle 2|1\rangle & \langle 2|2\rangle & \ldots\ldots & \langle 2|N\rangle \\ \vdots & \vdots & \ddots & \vdots \\ \langle N|1\rangle & \langle N|2\rangle & \ldots\ldots & \langle N|N\rangle \end{pmatrix} \tag{4.50}$$

and is called minor of $\underline{G}$. With the notation Φ_i for the state that is a symmetrized product of all spinor components except the ith, $\frac{1}{N!}\mathrm{per}(\underline{G}_i^j)$ can be written as the scalar product $\frac{1}{N}\langle\Phi_i|\Phi_j\rangle$. Hence, the expectation value of $\hat{h}$ reads

$$\langle\Phi|\hat{h}|\Phi\rangle = \frac{1}{N}\sum_{ij} \langle i|\hat{h}|j\rangle\, \langle\Phi_i|\Phi_j\rangle \tag{4.51}$$

Of course, this equation holds for any one-body operator and with the unit operator $\hat{1}$, the Laplacian development (see Eq. (E.2)) for the permanent of the Gram matrix is obtained.

For two-body operators, an analogous calculation can be done:

$$\begin{aligned}
\langle\Phi|\hat{w}|\Phi\rangle &= (F|\hat{S}_+ \sum_{ijkl} (ij|w|kl)\, \hat{o}\,|i\rangle \otimes \hat{o}\,|j\rangle\, \langle k|\, \hat{o} \otimes \langle l|\, \hat{o}|F) \\
&= \sum_{ij,k<l} (ij|w|kl)(F|\hat{S}_+|F_{k,l}^{\hat{o}|i\rangle,\hat{o}|j\rangle})\,,
\end{aligned} \tag{4.52}$$

where the restriction of the summation to $k < l$ ensures, that the operator $\hat{w}$[7] acts only once on each pair of orbitals. In the two-fold subscripted and superscripted vector

---

[7] In this chapter, the two-particle integrals are denoted with $(ij|w|kl)$ instead of $w_{ij,kl}$. This is because with this notation, the two-particle integrals can be regarded as matrix elements of the interaction operator $\hat{w}$ with respect to not symmetrised tensor products. To avoid doubts: $(ij|w|kl) = w_{ij,kl}$.

$|F_{k,l}^{\hat{o}|i\rangle,\hat{o}|j\rangle})$ the orbital $|k\rangle$ was replaced by $\hat{o}\,|i\rangle$ and $|l\rangle$ by $\hat{o}\,|j\rangle$ – analogously to the above defined vector $|F_i^{|\eta\rangle})$. The appearing scalar products $(F|\hat{S}_+|F_{k,l}^{\hat{o}|i\rangle,\hat{o}|j\rangle})$ are calculated as follows:

$$\begin{aligned}(F|\hat{S}_+|F_{k,l}^{\hat{o}|i\rangle,\hat{o}|j\rangle}) &= \frac{1}{N!}\sum_{\pi\in S_N}\underbrace{\langle\pi(k)|\hat{o}|i\rangle}_{=\delta_{\pi(k),i}}\underbrace{\langle\pi(l)|\hat{o}|j\rangle}_{=\delta_{\pi(l),j}(1-\delta_{ij})}\prod_{s\neq k,l}\langle\pi(s)|s\rangle \\ &= (1-\delta_{ij})\frac{1}{N!}\sum_{\substack{\pi\in S_N\\ \pi(k)=i\\ \pi(l)=j}}\prod_{s\neq k,l}\langle\pi(s)|s\rangle = (1-\delta_{ij})\frac{1}{N!}\mathrm{per}(\underline{G}_{ij}^{kl})\ , \qquad (4.53)\end{aligned}$$

where $\underline{G}_{ij}^{kl}$ is the double-minor of $\underline{G}$ and is obtained after the elimination of the ith and jth row and kth and lth column of $\underline{G}$. The term $(1-\delta_{ij})$ emerges because of the inequality of k and l. Same as for the one-body case, this permanent can be expressed as the scalar product of symmetrized product states with removed orbitals:

$$\frac{1}{N!}\mathrm{per}(\underline{G}_{ij}^{kl}) = \frac{1}{N(N-1)}\langle\Phi_{ij}|\Phi_{kl}\rangle\ . \qquad (4.54)$$

Because of the identity $|\Phi_{kl}\rangle = |\Phi_{lk}\rangle$ and $(ij|w|kl) = (ji|w|lk)$ (see equation (A.5)), the summation over $k < l$ can be replaced by $k \neq l$ including a factor $\frac{1}{2}$. Then the expectation value of the total energy reads

$$\langle\Phi|\hat{H}|\Phi\rangle = \frac{1}{N}\sum_{ij}\langle i|\hat{h}|j\rangle\langle\Phi_i|\Phi_j\rangle + \frac{1}{2N(N-1)}\sum_{\substack{i\neq j\\ k\neq l}} w_{ij,kl}\langle\Phi_{ij}|\Phi_{kl}\rangle \qquad (4.55)$$

Using this term for the total energy, one can apply Ryser's formula for the calculation of the permanent of a matrix, which has a much lower complexity then the sum over S_N. Fortunately, the variational derivative of Eq. (4.55) can also be expressed with permanents of minor matrices of the Gram matrix of the spinor orbitals. Before going on to the calculation of the derivative of Eq. (4.55), a special restriction of the UBHF ansatz is proposed

4.6.2 Multi-occupied spinor orbitals (restricted UBHF)

In Chap. 5 it can be seen, that the natural orbital with the highest occupation number contains nearly the half of all particles, even for high coupling strength. This observation gives rise to the idea of restricting the UBHF ansatz by demanding some spinor orbitals to be equal. This equality of some orbitals can be used for the calculation of the permanents arising in the equations above in a way that is proposed in appendix E. For that purpose it is helpfull to introduce a tuple of natural numbers n_k, that tells how often the orbital $|k\rangle$ [8] appears in the spinor. This tuple is called partition of the spinor. The deterioration of the results due to this restriction should be small if

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[8] Actually this notation is a little bit misleading, because in the previous sections, the case that some spinor orbitals coincide was never excluded from the possible solutions. But in this case, the denotation of all orbital that are equal with the same number is obviously very practical.

the partition resembles the occupation numbers of the natural orbital obtained by the original UBHF approximation. Using the partition $(n_1, n_2 \ldots)$, the expression for the total energy (Eq. (4.55)) becomes

$$\begin{aligned}\langle\Phi|\hat{H}|\Phi\rangle = \frac{1}{N}\sum_{ij} n_i n_j \langle i|\hat{h}|j\rangle \langle\Phi_i|\Phi_j\rangle \\ + \frac{1}{2N(N-1)}\sum_{ijkl} w_{ij,kl} n_i(n_j - \delta_{ij}) n_k(n_l - \delta_{kl}) \langle\Phi_{ij}|\Phi_{kl}\rangle \ . \qquad (4.56)\end{aligned}$$

In this case, the summation in the interaction term does not restrict the *indices* i and j to be different, because some orbitals are many fold occupied. The sums run from 1 to ν – the number of different orbitals contained in $|\Phi\rangle$ – for each index. The Kronecker delta in the second factor ensures that for singly occupied orbitals the summand with $i = j$ vanishes.

4.6.3 A minor permanent version for the UBHF equations with multi-occupied orbitals

With this restriction of some orbitals being equal (characterized by the partition $\mathbf{n}$), the parameter set becomes smaller. As the product rule holds for the variational derivative (see appendix A), the full differentiation reduces to differentiations of the matrix elements of $\hat{h}$, the two-particle integrals, and permanents of minors of gramian matrices with some columns and rows being equal. The derivatives of the first two entities have already been performed in previous sections (see also appendix A). The differentiation of the permanents is performed in the following. For that purpose, consider the most general case of a scalar product of a symmetrized product state $\langle\Phi|$ of the components of the (dual) spinor $\langle\Psi|$, with the symmetrized product state $|\tilde{\Phi}\rangle$ of the spinor $|\tilde{\Psi}\rangle$ with the partitions $\mathbf{n}$ and $\tilde{\mathbf{n}}$ respectively. One way of representing such states is by giving the orbitals $|k\rangle$ and its related occupation number n_k. Another possibility is to give an N-tuple of orbitals $(\langle i_1|, \langle i_2|, \ldots)$ where $\langle i_1| = \langle i_2| = \ldots = \langle i_{n1}|$ $(=: \langle 1|)$ and $\langle i_{n_1+1}| = \langle i_{n_1+2}| = \ldots = \langle i_{n_1+n_2}|$ $(=: \langle 2|)$ and so on. With this notation ($\langle i_k|$ related to the state $\langle\Phi|$ and $|i_k\rangle$ related to the state $|\Phi\rangle$), the variational derivative with respect to $\langle l|$ reads

$$\begin{aligned}\frac{\delta}{\delta\left\langle l\right|}\left\langle\Phi|\tilde{\Phi}\right\rangle &= \frac{\delta}{\delta\left\langle l\right|}\frac{1}{N!}\sum_{\pi\in S_N}\prod_{s=1}^{N}\left\langle i_s|j_{\pi(s)}\right\rangle \\ &= \frac{1}{N!}\sum_{\pi\in S_N}\sum_{r=n_{l-1}+1}^{n_{l-1}+n_l}\left|j_{\pi(r)}\right\rangle\prod_{s\neq r}\left\langle i_s|j_{\pi(s)}\right\rangle \\ &= \sum_{r=n_{l-1}+1}^{n_{l-1}+n_l}\frac{1}{N!}\sum_{\pi\in S_N}\left|j_{\pi(r)}\right\rangle\prod_{s\neq r}\left\langle i_s|j_{\pi(s)}\right\rangle \\ &= \sum_{r=n_{l-1}+1}^{n_{l-1}+n_l}\sum_{q=1}^{N}\left|q\right\rangle\underbrace{\frac{1}{N!}\sum_{\substack{\pi\in S_N\\ \pi(r)=q}}\prod_{s\neq r}\left\langle i_s|j_{\pi(s)}\right\rangle}_{\frac{1}{N}\left\langle\Phi_{i_r}|\tilde{\Phi}_{j_q}\right\rangle} \\ &= \frac{1}{N}n_l\sum_{k=1}^{\tilde{\nu}}\tilde{n}_k\left\langle\Phi_l|\Phi_k\right\rangle\left|k\right\rangle\ , \qquad (4.57)\end{aligned}$$

where $\tilde{\nu}$ denotes the number of different orbitals contained in $|\tilde{\Psi}\rangle$ and $\tilde{n}_k$ denotes the occupation number of the orbital $|\tilde{k}\rangle$ in $|\tilde{\Psi}\rangle$. This relation can be applied for the calculation of the derivatives of $\langle\Phi|\Phi\rangle$, $\langle\Phi_i|\Phi_j\rangle$, and $\langle\Phi_{ij}|\Phi_{kl}\rangle$:

$$\frac{\delta}{\delta\left\langle s\right|}\left\langle\Phi|\Phi\right\rangle = \frac{1}{N}n_s\sum_{r=1}^{\nu}n_r\left\langle\Phi_s|\Phi_r\right\rangle\left|r\right\rangle \qquad (4.58)$$

$$\frac{\delta}{\delta\left\langle s\right|}\left\langle\Phi_i|\Phi_j\right\rangle = \frac{1}{N-1}(n_s-\delta_{si})\sum_{r=1}^{\nu}(n_r-\delta_{rj})\left\langle\Phi_{is}|\Phi_{jr}\right\rangle\left|r\right\rangle \qquad (4.59)$$

$$\frac{\delta}{\delta\left\langle s\right|}\left\langle\Phi_{ij}|\Phi_{kl}\right\rangle = \frac{1}{N-2}(n_s-\delta_{si}-\delta_{sj})\sum_{r=1}^{\nu}(n_r-\delta_{rk}-\delta_{rl})\left\langle\Phi_{ijs}|\Phi_{klr}\right\rangle\left|r\right\rangle \qquad (4.60)$$

The two-fold subscripted states Φ_{ij} are defined to be zero, if they are equal and if this orbital is singly occupied – similar to the two-fold application of an annihilation operator in second quantization formalism. With these formulas, the variational derivative of Eq. (4.11) can be performed easily:

$$\frac{\delta}{\delta\left\langle s\right|}\Big(\left\langle\Phi|\hat{H}|\Phi\right\rangle-\mathscr{E}\left\langle\Phi|\Phi\right\rangle\Big)\overset{!}{=}0$$

$$\begin{aligned}\Leftrightarrow\sum_r n_r\left\langle\Phi_s|\Phi_r\right\rangle\hat{h}\left|r\right\rangle &+ \frac{1}{N-1}\sum_{ijr}(n_i-\delta_{is})n_r(n_j-\delta_{rj})\left\langle\Phi_{is}|\Phi_{jr}\right\rangle\Big[\langle i|\hat{h}|j\rangle+\hat{J}_{ij}\Big]\left|r\right\rangle \\ &+ \frac{1}{2(N-1)(N-2)}\sum_{ijklr}(n_i-\delta_{si})(n_j-\delta_{sj}-\delta_{ij})n_k(n_l-\delta_{kl})(n_r-\delta_{rk}-\delta_{rl}) \\ &\qquad\cdot w_{ij,kl}\left\langle\Phi_{ijs}|\Phi_{klr}\right\rangle\left|r\right\rangle \\ &\qquad= \mathscr{E}\sum_r n_r\left\langle\Phi_s|\Phi_r\right\rangle\left|r\right\rangle \qquad \text{f.a. } s=1,\ldots,\nu\ , \qquad (4.61)\end{aligned}$$

which are the UBHF equations for the restriction of some orbitals being equal. These equations have not yet been tested, but a comparison with the (numerically) verified UBHF equations (4.14) shows that each term in this equation can be related with a therm in the other equations, what confirms this equation.

4.7 Gaussian type spinor orbitals

In contrast to fermionic Hartree-Fock, the self consistent spinor orbitals are, in general, not equal to the natural orbitals of the system. As will be seen in the simulation results (Chap. 5), the wave functions of the spinor orbitals have the shape of Gaussians in both cases (2D and 1D systems).

Thus, a possible restriction of UBHF that provides good numerical results, is to let all spinor orbitals be Gaussians. With this restriction the number of independent parameters decreases to two times the dimension (components of the mean value and the variance for each dimension) for each orbital. Furthermore, one can decrease the number of independent parameters by taking advantage of the symmetry of the given traps. E.g. in the 1D case for two particles, it turns out, that one orbital is just the mirrored of the other one:

$$|1\rangle = \hat{\mathfrak{p}}\,|2\rangle\,, \quad \hat{\mathfrak{p}} \rightarrow \text{parity operator.}$$

Thus, the mean value of the first orbital can be set as the negative of the mean value of the other one and the variances can be set to be equal. Thereby the number of independent orbitals has been reduced to two.

Summary

An extensive and deep description of the UBHF ansatz was presented in this chapter. A new approximation scheme, that takes advantage of the special structure of the UBHF equations is presented for the first time in this chapter. The proposition of a generalization of UBHF to an ansatz with some orbitals being equal is also new. The analysis of the ROBDO in UBHF gave more insight into this approximation.

Unfortunately, with the UBHF ansatz arise lots of expressions, that make it difficult to maintain an overview over the structure of this approximation. Also, the notation of the total energy in UBHF with minor permanents leads to difficultly manageable equations. Nevertheless, the numerical implementation of UBHF can be done within a few weeks and the capacity of this approximation is impressing, as will be shown in the following chapter.

5 Simulation results

> The purpose of computing is insight, not numbers.
>
> *(Richard Hamming)*

When a new approximation scheme is proposed, it is self-evident that its implementation has to be tested, before applying it for the analysis of the considered systems. Although UBHF was already presented and applied by Romanovsky [12, 39], solving the UBHF equations within a basis of single particle states was never done before. In this chapter, the analysis of UBHF is continued by regarding the simulation results obtained by the application to a certain bosonic system.

First it is necessary to see if the obtained results are reliable, or more precisely, which observables are reliable in which parameter regimes. The implementation and analysis of the obtained results are useful for a better understanding of the method. For example, it will be seen in this chapter that the wave functions of the spinor orbitals resemble Gaussians, what is totally different to the Hartree-Fock orbitals in the fermionic case. Another property of UBHF which will be discussed in this chapter is the breaking of the symmetries of the Hamiltonian, what is typical for Hartree-Fock type approximations.

The example system that will be used for the presentation of the simulation results consists of up to 8 Coulomb-interacting bosons trapped in a harmonic confinement.

5.1 System characterization (charged trapped bosons)

The Hamilton operator of a system consisting of N Coulomb interacting bosons with charge q and mass m in a harmonic trap of the frequency ω reads in coordinate space representation

$$\hat{H}_N = \sum_{i=1}^{N} \Big(-\frac{\hbar^2}{2m}\tilde{\Delta}_i + \frac{m\omega^2}{2}\vec{r}_i^{\,2} \Big) + \frac{q^2}{4\pi\varepsilon_0} \sum_{i<j} \frac{1}{\sqrt{|\vec{r}_i - \vec{r}_j|^2 + \tilde{\kappa}^2}} \,, \tag{5.1}$$

where the Laplacians $\tilde{\Delta}_i$ and the coordinate vectors $\vec{r}_i$ can be considered one- or two-dimensional. The shielding parameter $\tilde{\kappa}$ appearing in the square root of the interaction term is only needed for the 1D case to make the two-particle integrals (A.5) finite. It can be interpreted physically as a relict of the in fact higher dimensionality of the system (compare chapter 2.2). In the 1D case, the system is fermionized for $\tilde{\kappa} = 0$, and has thus exactly the same energy spectrum and ground state density as an analogous fermionic system. For higher dimensions, this parameter will be set to zero, as there arise no problems with the convergence of the two-particle integrals and two particles can pass each other in a 2D plane without having contact.

Entity	Symbol	Natural unit	Operator (expressed with creator and annihilator)
Energy	E	$E_0 = \hbar\omega$	$\hbar\omega \sum_i (a_i^\dagger a_i + \frac{1}{2})$
Spatial coordinate	x, y	$x_0 = \sqrt{\frac{\hbar}{m\omega}}$	$\frac{x_0}{\sqrt{2}}(a_i + a_i^\dagger), \quad i = x, y$
Momentum	p_x, p_y	$p_0 = \sqrt{\hbar m\omega}$	$\frac{p_0}{\sqrt{2}}(a_i - a_i^\dagger), \quad i = x, y$
Angular momentum	L	$L_0 = \hbar$	$-iL_0(a_x^\dagger a_y - a_y^\dagger a_x)$
Time	t	$t_0 = \frac{1}{\omega}$	
Inverse temperature	β	$\frac{1}{E_0}$	
Shielding parameter	κ	x_0	
Coupling parameter	λ	$\frac{q^2}{4\pi\varepsilon_0 x_0 \hbar\omega}$	

Table 5.1: *Overview of the quantities that are of interest in this work and their natural unit.*

The expression for the Hamiltonian given in (5.1) can be transformed into a form containing only two parameters

$$\hat{H}_N = \sum_{i=1}^{N} \Big(-\frac{1}{2}\Delta_i + \frac{1}{2}\vec{r}_i^{\,2} \Big) + \lambda \sum_{i<j} \frac{1}{\sqrt{|\vec{r}_i - \vec{r}_j|^2 + \kappa^2}} \;, \tag{5.2}$$

where the entities without the tilde are given in natural units (see Table 5.1). In second quantization, with the creation operator related to the orbitals of the ideal system, the Hamiltonian reads

$$\hat{H} = \sum_k \epsilon_k \hat{a}_k^\dagger \hat{a}_k + \frac{1}{2} \sum_{ijkl} w_{ij,lk} \hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_k \hat{a}_l \;, \tag{5.3}$$

with ϵ_k being the energy of the kth energy eigenstate of the ideal system.

5.2 Structure of the solutions

In contrast to fermionic Hartree-Fock, the obtained self-consistent orbitals in UBHF (spinor orbitals) do not coincide with the natural orbitals of the resulting many particle state. The spinor orbitals rather resemble displaced gaussians. In the 1D case, for even particle numbers, each of the spinor orbital can be transformed into another one by applying the parity operation (mirroring along the y-axis) to it. For odd particle numbers, there exist one orbital that has well defined positive parity. Although parity is in general not a good quantum number for interacting many body systems, the resulting density is mirror symmetric due to this paring of the spinor orbitals. This can be seen in Fig. 5.1. For small coupling (In Fig. 5.1 $\lambda = 0.2$), the resulting particle density cannot resolve the localization of the wave functions because of the strong mutual overlap. For higher interaction strengths, the density becomes wider and starts to exhibit N peaks at a certain value for λ. The resemblance of the spinor orbitals to gaussians increases with higher coupling.

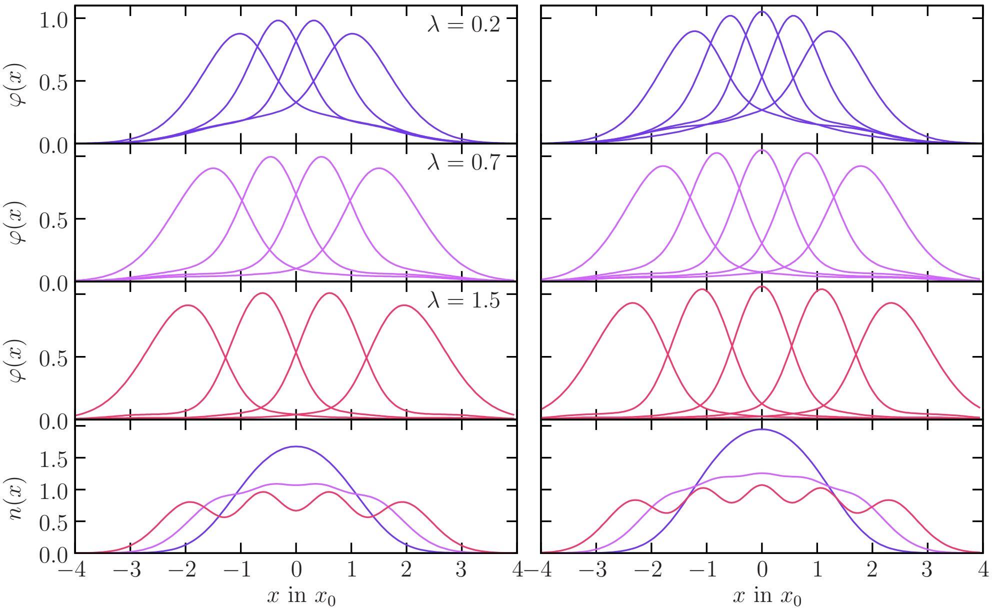


Figure 5.1: *Overview of the general form of the wave functions of the spinor orbitals for $N = 4$ (left column) and $N = 5$ (right column). The resulting density of each set of spinor orbitals is given in the lower row in the same color as the related set. The coupling strengths λ are given in the plots on the left and are the same in the plot on the right. The positivity of the wave functions is not an intrinsic property of the solution. They where rather transformed to be positive – by multiplying them with a factor – for better clarity. The number of basis functions for this calculation was $n_b = 30$.*

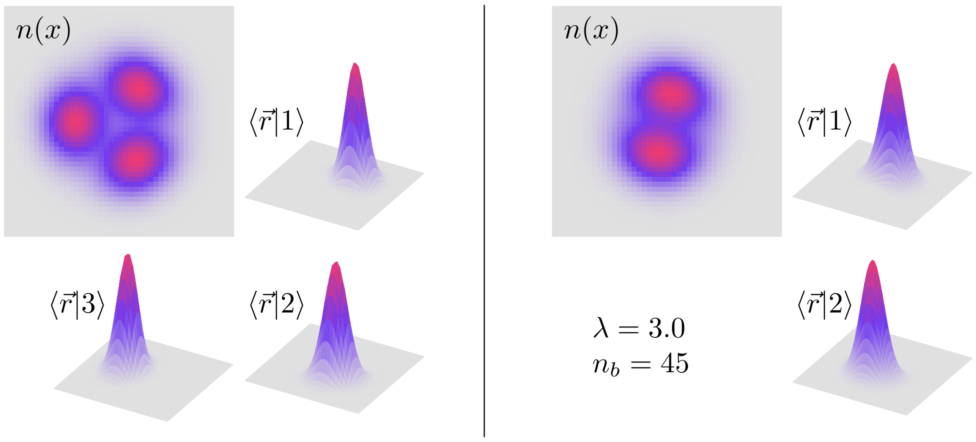


Figure 5.2: *Illustrative example of the localization of the spinor orbitals in 2D for two (left) and three (right) particles. The exact values of the densities are not important for this illustration, which is why no axis or colorbox is given in these plots. The coupling strength and basis number given in the picture is valid for both systems.*

For 2D systems, the structure of the resulting UBHF orbitals is similar. They resemble displaced two dimensional gaussians and the distance of the expectation value of the site increases for high coupling strength. Figure 5.2 shows how the total particle density is composed by the spinor orbitals in the 2D case.

5.3 Convergence of the algorithm

The results presented here are obtained by the implementation of the iterative algorithm proposed in Chap. 4. The computational effort of this algorithm is very high: a sum over S_N has to be performed $2N$ times in each step. Thus the complexity of this algorithm scales as $2N \cdot N!$. The computation of an 8-particle system with $n_b = 15$ and accuracy 10^{-6} requires circa twelve hours on a single CPU, if the initial spinor is created with a random number generator. In my implementation, the program seeks for results of former calculations with similar parameters – same particle number and a coupling strength close to the considered one. The final spinor of that calculation is used as initial spinor for the new one. In this case, a computation takes much less time if another system with the same particle number has already been calculated.

In Fig. 5.4 it can be seen that the energy and $D(\Psi^i, \Psi^{i+1})$ (see Eq. (4.25)) decrease exponentially. Both curves can be divided in two parts. At a certain iteration step (≈ 10), the curve changes the gradient and the decreasing becomes more slowly.

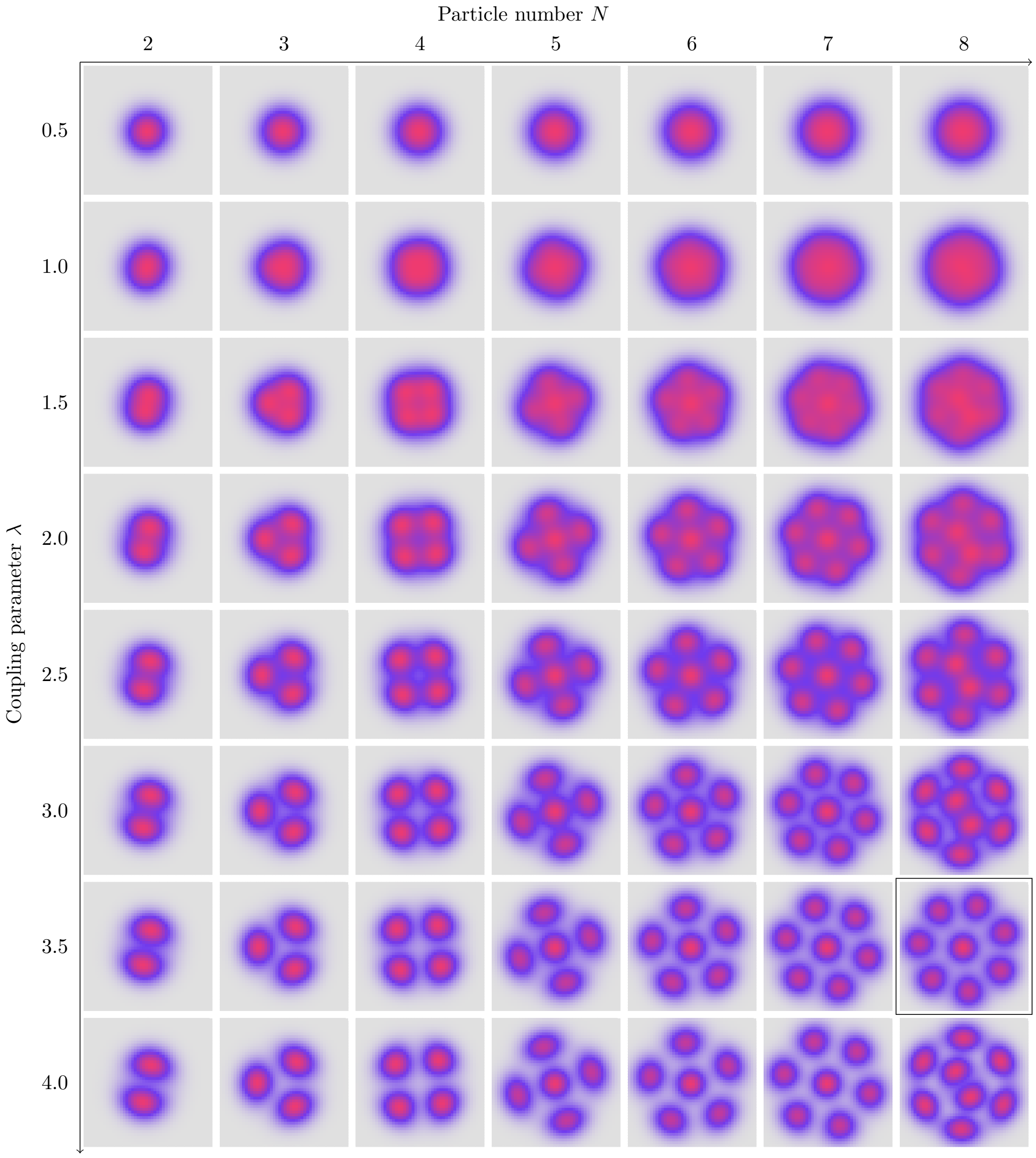
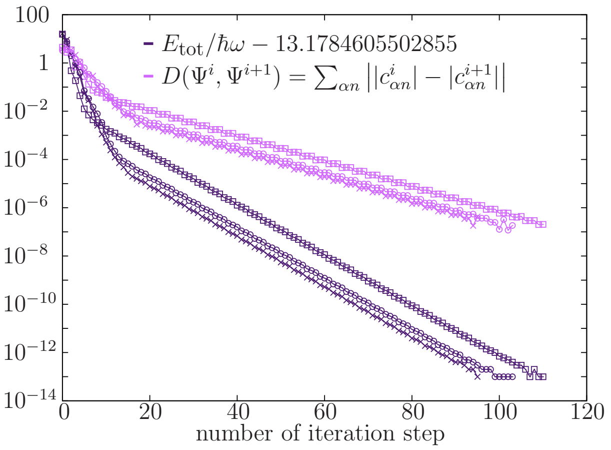


Figure 5.3: *Particle densities in the 2D case for different particle numbers and coupling strengths. The number of basis functions in this calculation was* $n_b = 45$.

5.4 Validity and quality of UBHF

For testing the validity of an approximation, it is favorable to use a method that is well known and where the origins of possibly arising differences can be localized. Path Integral Monte-Carlo (PIMC) is an exact method that can deal with systems with relatively high particle numbers, but it cannot consider systems at zero temperature, though the temperature can be chosen to be very low. Neither can be estimated which

Figure 5.4: *Convergence of the total energy and the quantity* $D(\Psi^i, \Psi^{i+1})$ *(Eq. (4.25)) representing the distance between the spinors of two iteration steps for a 1D 3-particle system and basis number* $n_b = 15$. *The different point types mark three iterations with different initial guesses for the spinor. The number that is subtracted from the total energy is the obtained ground state energy in UBHF approximation in natural units.*



differences between UBHF and PIMC arise from the limitation of the one particle basis in the UBHF implementation – so called basis effects. A very good benchmark for the UBHF approximation is configuration interaction (CI), which will be explained in the following.

5.4.1 Configuration Interaction (CI) as benchmark

Configuration Interaction is often referred to as an exact method. Strictly speaking, this is only true for Hilbert spaces with a finite dimension. It can be regarded as a variational method, where the trial wave function is a superposition of a fixed finite set of vectors. Thus the subset of all trial states that can be reached with this ansatz has the properties of a vector space and the hermiticity of all operators restricted to this space is conserved: $(\hat{\mathsf{P}}\hat{A}\hat{\mathsf{P}})^\dagger = \hat{\mathsf{P}}\hat{A}^\dagger\hat{\mathsf{P}}$; where $\hat{\mathsf{P}}$ is the projector into the subspace of the trial functions. In the CI method, the eigenstates of this projected Hamiltonian are the states that minimize the energy within this ansatz. Thus for the implementation of CI, one has to calculate all matrix elements of $\hat{\mathsf{P}}\hat{H}\hat{\mathsf{P}}$ with respect to the basis elements of the considered subspace and perform a matrix diagonalization.

For the so called full CI method, the considered basis consists of all symmetrised product states that can be created from a fixed ONS of single particle states [20]. The number of N-body Hilbert space states that can be created from a set of n_b single particle states is $\binom{N+n_b-1}{N}$ for bosons, and $\binom{n_b}{N}$ for fermions. This means, one has to diagonalize a matrix whose dimensionality increases with a binomial coefficient. It is evident that this method is not appropriate for systems with high particle numbers.

Nevertheless, it is well suited as a benchmark for UBHF results, because it can be used for ground state calculations and one can choose the same set of single particle orbitals as is used for the UBHF calculation, such that possible basis effects are blinded out.

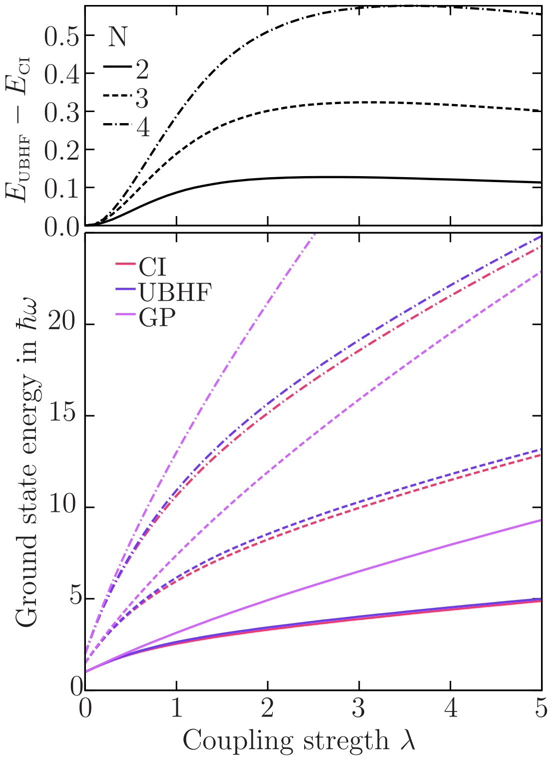


Figure 5.5: *Comparison of the ground state energies for* $2, 3$ *and* 4 *particles obtained by UBHF, CI and GP in dependence of the coupling strength* λ*. In the lower panel, the colours distinguish the related approximation method, and the particle numbers can be distinguished by the line type – see key in the upper panel. The number of basis states for this calculation is* $n_b = 12$*.*

5.4.2 Comparison of UBHF and CI

After the choice of the method for testing the UBHF method, there are many quantities that can be taken for comparison. As the trial wave function is the best approximation of the real ground state within a certain subset of the Hilbert space, one possible quantity for testing how good this approximation actually is would be the *distance*[1] of the approximating state Ψ_{UBHF} and the exact ground state Ψ_0. As this distance differs depending on the normalization of both states while expectation values do not, this is not a good indicator for the quality of the approximation. The most meaningful comparing quantities are those with a physical interpretation, such as the energy or the particle density.

In Fig. 5.5, it can be seen that the energy obtained by UBHF is very close to the CI result. For a certain value of λ – depending on the particle number – the difference between the UBHF and CI energy starts to decrease. The GP energy of the system is also given in the same plot and the graphs diverge strongly for high interaction strengths. This is a good indicator that GP is not appropriate for this parameter regime, while UBHF provides very good values for the total energy also for high coupling. The UBHF approximation also reflects very well the main behavior of the particle density – see Fig. 5.6. For high values of λ, the shape of the densities obtained by UBHF and CI differ quantitatively and qualitatively from the GP density. The density evinces N peaks for an N particle system. The GP approximation cannot by definition explain

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[1] With respect to the metric that is induced by the scalar product.

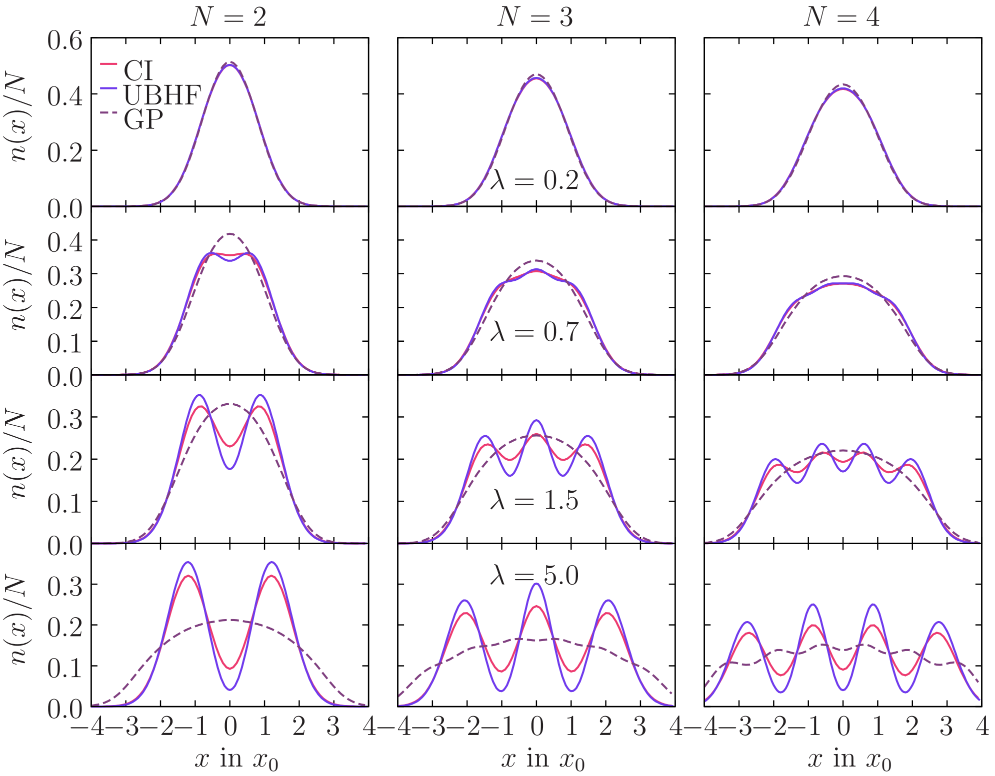


Figure 5.6: *Comparison of the particle densities obtained by UBHF, CI and GP for different coupling strength and particle numbers. The values for* λ *given in the middle graphs refer to the whole row and the particle numbers given on the top of each column refer to the whole column. To avoid big differences in the scaling of the values, all densities are normalized to* 1*. The number of basis states for this calculation is* $n_b = 12$*.*

this behavior of the density. This is due to the fact that the only dependency of the particle number in GP is as a factor in front of the Hartree term in the GP equation (3.24). The wavy form of the GP-density for $\lambda = 5.0$ in Fig. 5.6 is a pure finite basis effect. It can also be seen in the same graphic that the localization of the particles is slightly overestimated in the UBHF case.

In section 4.5 it was explained why the occupation numbers of the natural orbitals obtained in UBHF approximation for N particles are only nonzero for the first N natural orbitals. Figure 5.7 shows a comparison of the first N occupation numbers obtained by both methods. A qualitatively different behavior is that in the UBHF case one of the graphs crosses the $\langle n_i \rangle = 1$ line. It can be seen in this figure that for the exact method (CI) the occupation numbers of higher natural orbitals is nonzero. The kink in some curves in the left column of Fig. 5.7 is a pure numerical effect. Although, for high coupling one would expect all occupation numbers to be 1 in UBHF approximation, because in the extreme case of $\lambda \longrightarrow \infty$, the overlap of the spinor orbitals vanishes. Thus in this case, the spinor orbitals form an ONS and the natural orbitals of the symmetrised

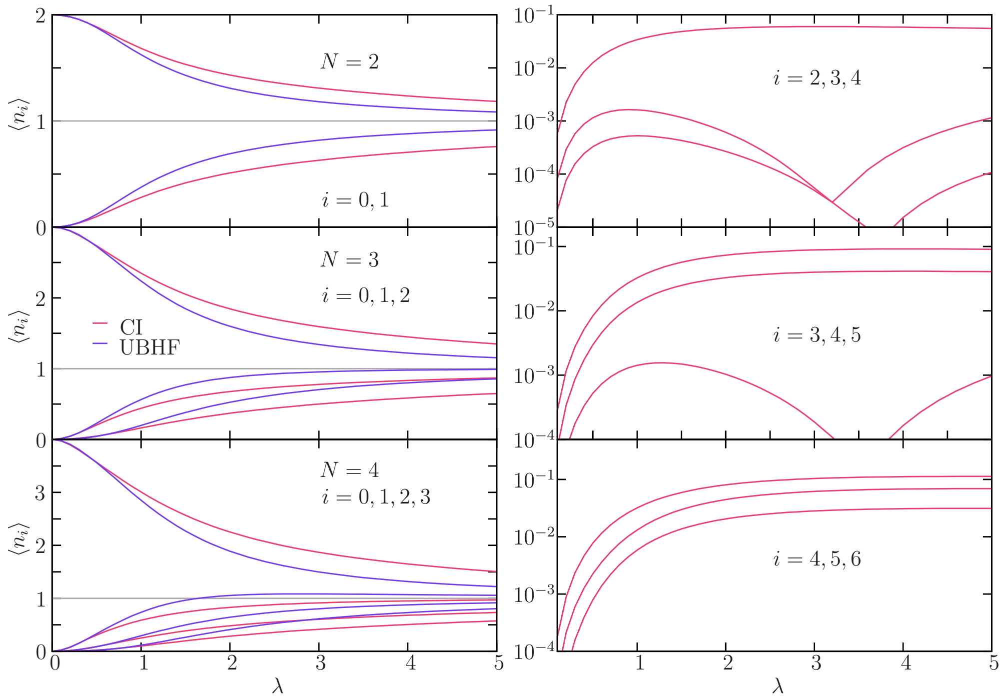


Figure 5.7: *Comparison of the ground state energies for* $2, 3$ *and* 4 *particles obtained by UBHF and CI in dependence of the coupling strength* λ*. The number of basis states for this calculation is* $n_b = 12$*. The occupation numbers given on the right are zero in the UBHF case.*

product state are the spinor orbitals themselves with occupation number 1. The graphs of the occupation numbers of the $(N + 1)$th, $(N + 2)$th and $(N + 3)$th natural orbital obtained by CI – also given in Fig. 5.7 – show that they are actually nonzero, but their highest values lies at about 0.1.

5.5 Metastable solutions

It is not unusual that the results obtained by a variational method are not the absolute minimum of the total energy within the considered ansatz. Just as the diagonal elements of the full Hamiltonian, the energy functional of an approximating ansatz can have many local minima.

The configurations of the particle densities in Fig. 5.3 for $N = 5$ and $N = 8$ (except the density with $\lambda = 3.5$) particles suggest that the obtained results are metastable solutions, because classically one would expect a $(0, 5)$ configuration for the 5-particle case and a $(1, 7)$ configuration for the 8-particle case [42]. For 5 particles, the $(1, 4)$ configuration is classically a metastable solution with an energy very close to the classical one, but for 8 particles, the $(2, 6)$ configuration as in Fig. 5.3 (execpt for $\lambda = 3.5$) is not mentioned as metastable configuration in the classical case in [42]. I tried to find other

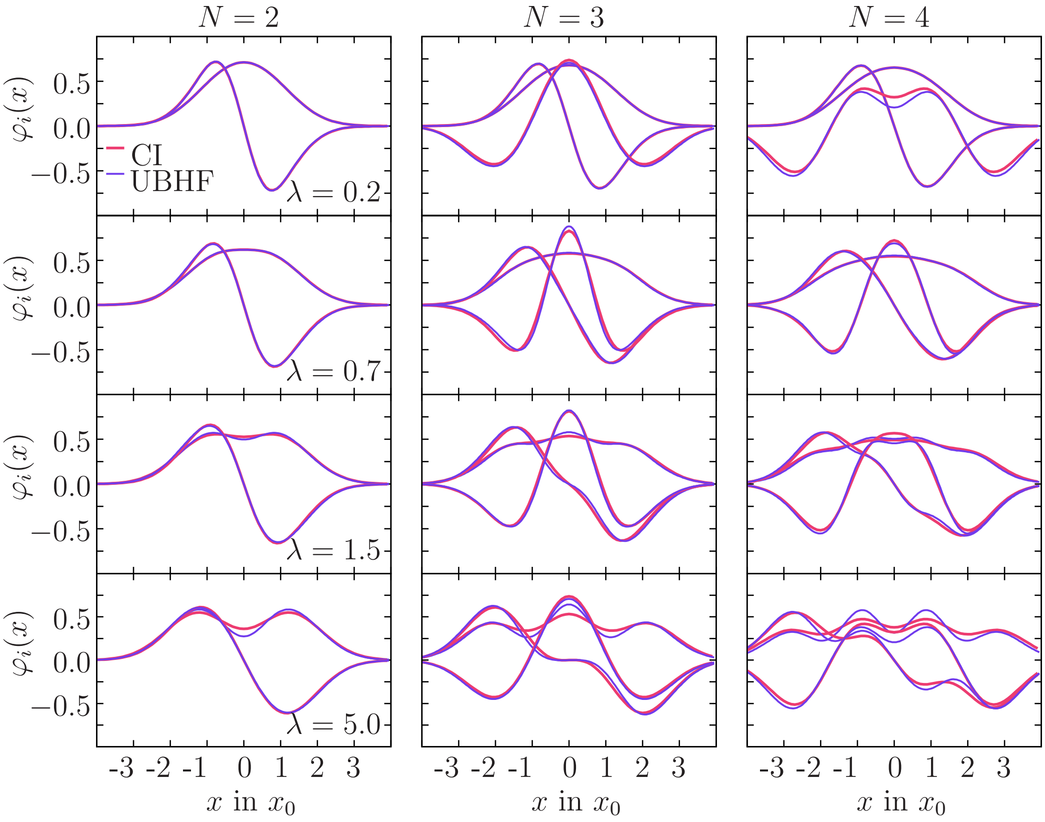


Figure 5.8: *Comparison of the natural orbitals. For the four-particle system, a comparison of the fourth orbital would also be of interest, but would worsen the overview.*

configurations for $N = 5$ particles in 2D by changing the initial guess for the spinor, but always obtained the same configurations as in Fig. 5.3. It is still possible that there exist other configurations with lower energies, but it seems that they have at least a smaller basin of attraction than the configurations with the absolute minimum. The depicted density with $N = 8$ and $\lambda = 3.5$ in Fig. 5.3 has the configuration that is expected for 8 particles according to [42].

In the one dimensional case, a metastable solution for a two-particle system is obtained if the first spinor orbital of the initial spinor is the ground state of the one-body Hamiltonian and the second spinor orbital the first exited state. Figure 5.9 shows that the metastable state obtained by this initialization of the spinor can be interpreted as an excited state of the system. The UBHF energies coincide very well with the energies of the first excited state of the system obtained with CI. In this solution, the spinor orbitals are orthogonal and singly occupied. Thus in this case, the spinor orbitals of the UBHF result are also the natural orbitals of the system. In Fig. 5.10 it is shown that the shape of the natural orbitals (spinor orbitals) of the metastable solution coincide very well with the natural orbitals of the first excited state of the exact solution.

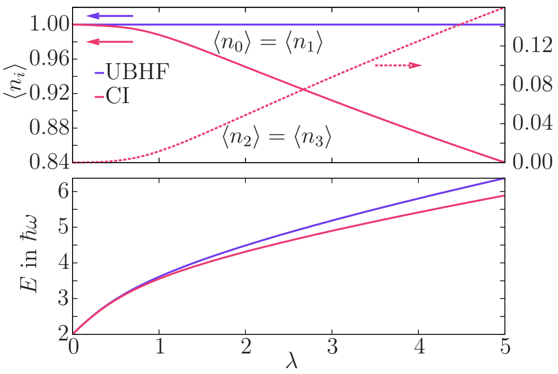


Figure 5.9: *Comparison of the energies (lower panel) and occupation numbers (upper panel) of a metastable state obtained with UBHF with the first exited state in CI for different λ. The CI results yield degenerated occupation numbers of the first and second (solid line) and third and fourth (dotted line) natural orbital. In UBHF, both occupation numbers are constant 1. The scale on the right in the upper panel refer to the solid line and the scale on the left to the dotted one. The basis number was $n_b = 12$.*

5.6 Rotational symmetry breaking for 2D systems

As the full many body Hamiltonian of the considered 2D isotropic harmonic oscillator with Coulomb interaction commutes with the operator of total angular momentum, the density of the ground state should be rotational invariant if the ground state is not degenerate. The densities obtained with UBHF however show a lower symmetry (see Fig. 5.3). For instance for six particles, the density is invariant under a rotation of the system with an angle of integer multiples of $\frac{2\pi}{5}$. This is very typical for the Hartree-Fock approximation [43, 44] and is still a topic of current investigation. In [45] a very efficient method for the restoration of the symmetries of the Hamiltonian is presented. The spin is another observable that is typically not conserved in Hartree-Fock approximations, but the here discussed particles have zero spin anyway.

While Romanovsky forced the symmetry breaking of the UBHF result by restricting the spinor orbitals to be displaced gaussians, in the implementation presented here, the

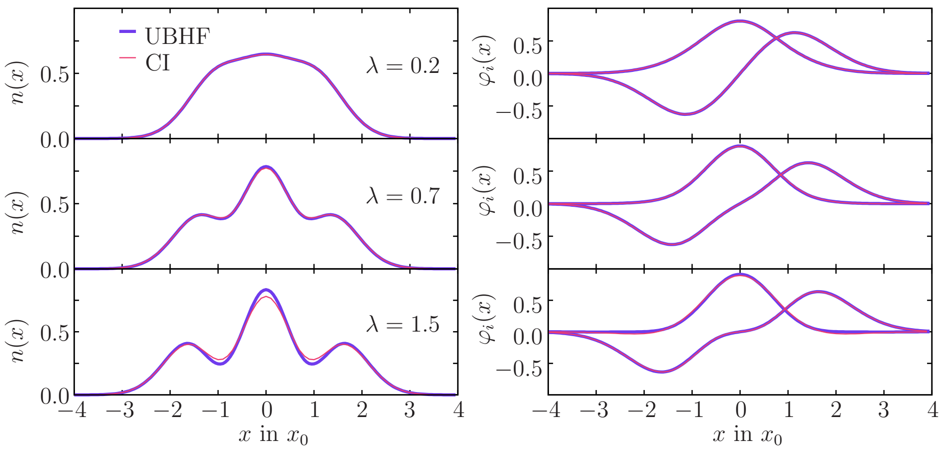


Figure 5.10: *Comparison of the shape of the particle density (left) and natural orbitals (right) of the metastable state in UBHF approximation with the first excited state obtained with CI.*

breaking of the rotational symmetry is spontaneous. Note that in Fig. 5.3, the number of the basis set is chosen such that the orbitals can *fill* an energy shell. E.g. for 45 basis functions, all orbitals of the 9th energy shell are included, hence no spatial direction is preferred.

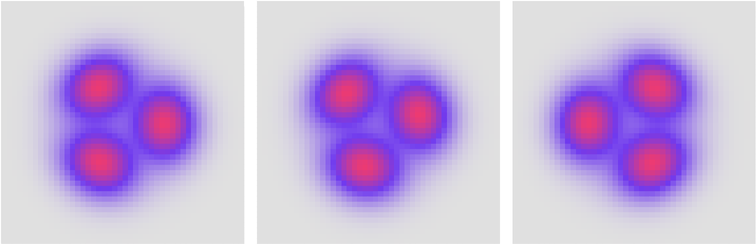


Figure 5.11: *Example for three equivalent UBHF results with coupling strength* $\lambda = 3.0$.

Fig. 5.11 shows UBHF densities that are obtained with three different initial guesses for the spinor. All densities shown are related by the same total energy of the underlying many particle state. It is important to keep in mind that it is absolutely possible to obtain a UBHF state which is rotationally symmetric; e.g. by choosing the initial state in an appropriate way, but the resulting energy is usually higher than the energy of the states with broken symmetry [46].

In Fig. 5.12 it is shown that the natural orbitals also reflect the rotationally broken symmetry. The depicted orbitals for the six-particle system are very similar to the analog fermionic system (see [47]).

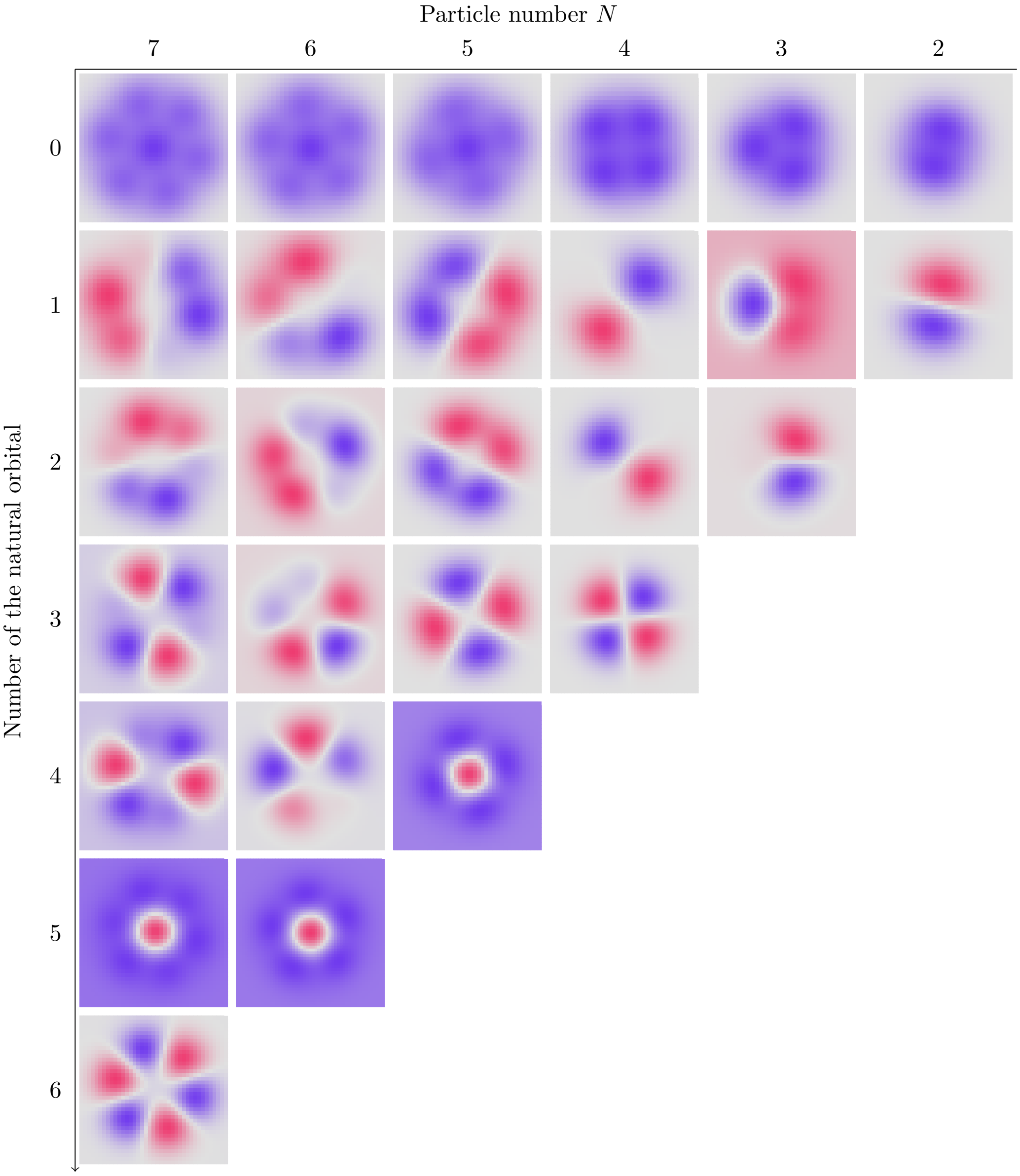


Figure 5.12: *Natural orbitals in UBHF approximation for 2D systems. The interaction strength is* $\lambda = 3.0$ *for all particle numbers. For the related spatial particle densities see figure 5.3.*

5.7 High coupling limit

As can be seen in Fig. 5.5, for high values of λ, the difference of the total energies obtained with UBHF and CI decreases. This is because for high coupling, the system transits to the classical limit [16]. In the classical case all particles are localized points and their statistic is equivalent to the Boltzmann statistic of distinguishable particles.

In UBHF the overlap of the spinor orbitals vanishes for high λ. In that case, the expectation value of a one-body operator $\hat{A}$ is given by

$$\langle \hat{A} \rangle = \sum_k \langle k|\hat{A}|k\rangle \ ,$$

because all terms in the sum over all permutations vanish, except for the identical permutation. Thus the formula for the expectation value is equal to the expectation value of an operator with respect to a Slater permanent. Hence in this case the statistic of the particles is not important.

A good indicator for how strong the orbitals are separated is the determinant of the gramian matrix (gramian determinant $\det(\underline{G})$), given in (4.50). For spatially totally separated orbitals, the gramian matrix is the unit matrix and its determinant is one. Thus this quantity is a good indicator for the classical behavior of the system. A graph of the gramian determinant as a function of λ is given in Fig. 5.13. There it is also shown that the decreasing of the values for $\det(\underline{G})$ is correlated with a stronger fragmentation of the system.

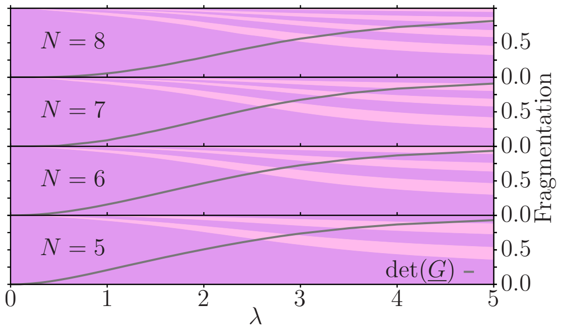


Figure 5.13: *Fragmentation of the relative occupation numbers for a two dimensional systems with different particle numbers. The broadness of each line represents the value of the relative occupation number of the related orbital. The graph of the gramian determinant depending on λ is given within each plot.*

5.8 Nonequilibrium

In quantum mechanics, every measurement of a system is also a perturbation that brings the considered system out of equilibrium. On the other hand, in computational simulations, one has to explicitly implement a perturbation of the system by making the Hamiltonian time dependent. In this section, the time-development of two Coulomb-interacting one dimensional bosons is compared with an exact method. Of special interest are of course those excitations that describe the interaction of the particles with the electromagnetic field. In classical mechanics, the so called normal modes are important to characterize a system. Not all of these modes have a quantum mechanical analog. Some normal mode excitations are common in trapped systems. In this section, the excitation to the quantum breathing mode is considered.

The main goal of this section is to show that the equations of motion in TDUBHF derived in Chap. 4 are correct and solvable. As these equations are new, this testing is a very important part for the further development of the UBHF approximation.

The results presented here are obtained by solving the TDUBHF equations (4.38) and (4.40) with the fourth order Runge-Kutta method. The time step was set fix to the value $\delta t = 0.005\omega$. As in the equilibrium results, the calculation was performed in the basis of the ideal system with $n_b = 12$. The time derivatives of the spinor $|\dot{\Psi}\rangle$ were calculated in each step by the inversion of the equations (4.38) and (4.40) with the linear algebra package LAPACK. Because the routine I used for solving the mentioned linear equations required a square matrix, I simply replaced the first line of the coefficient matrix by equation (4.40). By this replacement an invertible set of $N \cdot n_b$ equations is obtained.

5.8.1 Quantum breathing mode

Classically, the breathing mode is a normal mode excitation of trapped systems with an isotropic external confinement, where the deviation of the particles from their rest position is radial for all particles and the amplitudes are proportional to their distance to the center [48]. In [48] is also shown that the classical breathing mode exists for all harmonic trapped systems with particle interactions of the form $|\vec{r}|^\gamma (\gamma \in \mathbb{R}_{\neq 0})$.

Quantum mechanically, the breathing mode cannot be defined in this way. In [16], the quantum breathing mode is defined as the excitation that is obtained when the confining trap is switched off for a short time. In the classical case, the frequency of the breathing mode for coulomb interacting particles is $\sqrt{3}\omega$ – where ω is the frequency of the harmonic confinement – and for ideal quantum mechanical systems it is 2ω. For harmonically trapped systems, the motion of the many body wave function can be factorized into a center of mass part and a part only depending on the relative coordinates of the particles [49] and the Hamiltonian of the center of mass part is identical to the Hamiltonian of a single particle trapped in a harmonic confinement. Due to this separation, the normal mode spectrum also has at least two parts. One can be related with the motion of the center of mass wave function and the other one with the wave function of the relative coordinates. A good quantity for the analysis of the *breathing* motion of the system is the potential energy of the confinement. It turns out that the time evolution of the potential energy (in breathing mode excitation) for two interacting particles evinces exactly two frequencies: One for the center of mass wave function and one for the relative coordinates wave function [16]. Thus the time evolution of E_{pot} can be fitted with the following beat:

$$E_{\text{pot}} = a \sin(\omega_r t + \varphi_r) + b \sin(\omega_R t + \varphi_R) + c \ . \tag{5.4}$$

Because the Hamiltonian for the center of mass wave function has no interaction part, the frequency of the center of mass part is $\omega_R = 2\omega$ – the breathing mode frequency of ideal quantum systems. Unfortunately this cannot be reflected in UBHF. Figure 5.14 shows the time evolution of $E_{\text{pot}}(t)$ in TDUBHF. A comparison with the time evolution obtained by solving the time-dependent Schrödinger equation directly on a coordinate mesh (performed by Sebastian Bauch, see [16]) is also plotted in Fig. 5.14. The fit parameters for the fit plotted within the same figure (dashed line) are listed in table 5.2. Both graphs have very similar values until $t\omega \approx 25$ and in the narrowest area of the beat the difference of the two time evolutions is very notable. It seems that the behavior of the system changes abruptly, but note that this difference is also reflected in the beats which overlay perfectly the curves for both methods. Thus the difference of both curves

	$a/\hbar\omega$	ω_r/ω	$\varphi_r\omega$	$b/\hbar\omega$	ω_R/ω	$\varphi_R\omega$	$c/\hbar\omega$
TDSE	0.0161	1.8917	-0.1108	0.0132	1.9997	-0.1248	0.5450
TDUBHF	0.0098	1.8635	-0.0399	0.0181	1.9762	-0.0742	0.5447

Table 5.2: *Fit parameters for* E_{pot} (5.4) *of the excitation shown in Fig. 5.14.*

is already present for earlier times, but is not notable (with bare eyes) until $t\omega \approx 25$. The temporal energy fluctuation is negligible, as it only fluctuates at the fifth digit after the comma, what can be considered numerically constant. Unfortunately, the conservation of the norm is not very good but also numerically acceptable.

In summary, TDUBHF reflects the main behavior of the time evolution in the breathing mode excitation and also provides acceptable values for the quantities. In contrast to the exact methods, TDUBHF provides the possibility to consider higher particle numbers. Unfortunately, with the current implementation, the program aborts after a few time steps for $N > 2$, but with a further developement of the code it should be possible to consider systems with about 7 particles and calculate the time evolution within a few days on a single CPU. The consideration of systems with a higher dimensionality should also be possible for this range of particle numbers.

Summary

Many aspects of the results obtained in UBHF were shown in this chapter. A rigorous comparison of the energies and the ROBDM of UBHF and CI were performed and it turned out that this approximation provides very good values for the energies also for high particle interactions, while GP has only a small validity regime respective to the coupling. Also the ROBDM obtained with UBHF resembles the exact solution. This implies that all single particle observables yield very similar values for both methods.

Furthermore, the existence of metastable UBHF solutions that can be interpreted as an excited state of the system was shown. It was seen that in the 2D case, the rotational symmetry is not conserved. This is a property of UBHF that is supposed and used by Romanovsky, but he did not show that this symmetry breaking happens spontaneously. An important feature of this section is the test of the implementation of TDUBHF by considering the breathing mode excitation of a bosonic system.

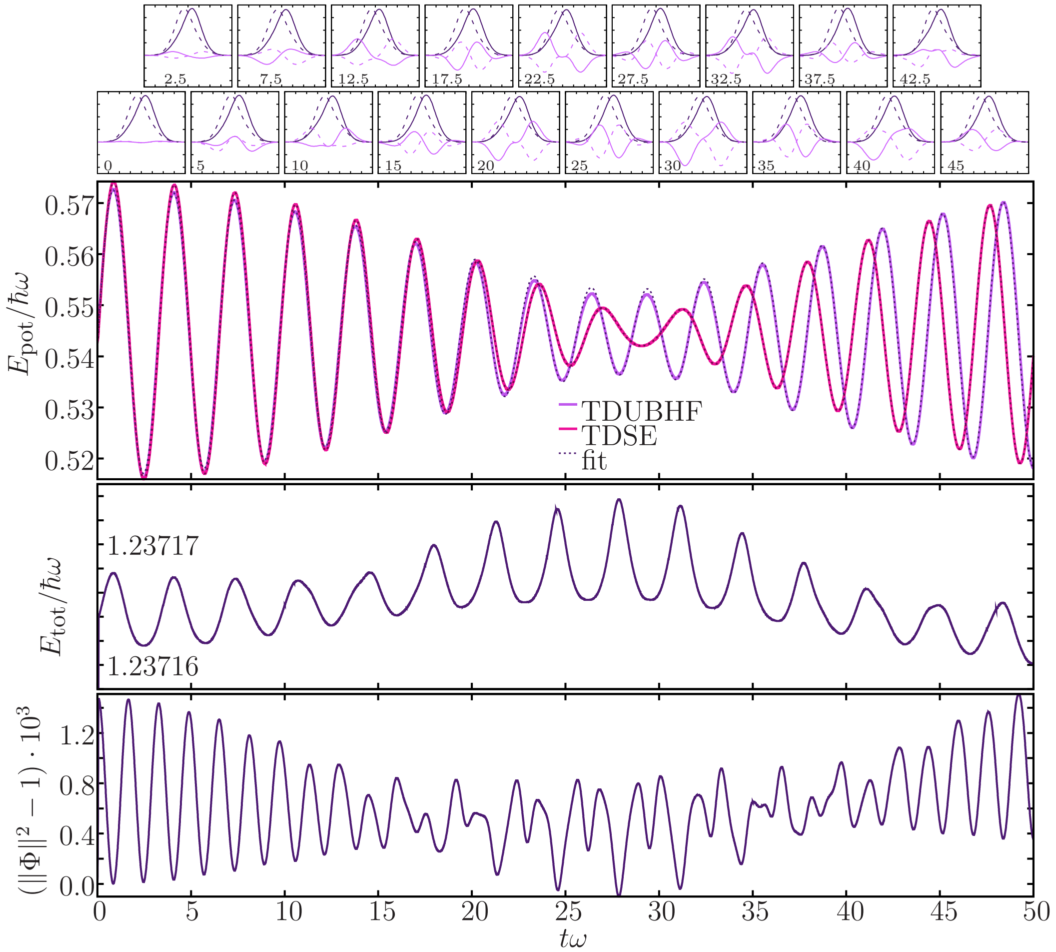
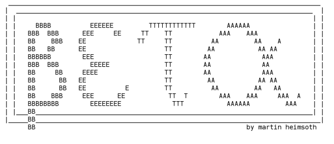


Figure 5.14: *Breathing mode excitation of a one dimensional two particle system with* $\lambda = 0.1, \kappa = 0.1$, *and* $n_b = 12$. *For this excitation, the confining potential was switched off for the time interval* $[t\omega = 0.00, t\omega = 0.05]$, *for both, the TDSE and the TDUBHF. The form of the fit is given in equation* (5.4) *and the fit parameters are listed in 5.2. Atop are plotted some snapshots of the time evolution. The blue lines are the real part of the wave function and the violet lines are the imaginary part multiplied by a factor* 10. *The related times are given within the snapshots in natural units. The solid lines refer to the first spinor orbital and the dashed line to the second. The TDSE calculation that is used for comparison in this section was performed by Sebastian Bauch [16].*

6 Structure of the computational implementation



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      BB                                                      by martin heimsoth
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(Shell output when starting the program)

The computational implementation of the presented scheme for solving the UBHF equations is a time consuming challenge. A large program for the performance of the GP and UBHF approximation was developed during the time of my diploma work. As it is the case for nearly all computer software it is under persistent construction and it is my hope, that this program will be used or even further developed by others. For that reason, an overview of the structure of this program and an auxiliary program that is needed for the analysis of the output is given in this chapter. I will start with the main program called *beta* [1]. Afterwards, an overview of the features of the pythonscript *scs.py* [2] that was used for further processing of the output provided by *beta* is given. All versions of these programs are administrated with the revision control system *subversion (svn)*. The repository is located under the url

`svn://134.245.67.14/programs/negf/heimsoth/beta`.

The repository is organized, such that it can be checked out as an eclipse [3] project. But it is also possible to do the checkout directly on the shell and compile the code with the makefile in the folder `src`. The code is designed for a LINUX operating system and requires the libraries GSL and LAPACK. This chapter refers to the revision number 361 of the repository given above. A HTML documentation for this program is planned to be done in June 2009.

6.1 The program *beta*

The main program *beta* solves the UBHF equations in basis representation. Furthermore it can perform different approximation schemes determined by a shell parameter. The

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[1] The name is historically related. The first computational realizations of UBHF where implemented in the source code of the program *hfmbeta* by K. Balzer [50]. Until later a separated program with a new structure was developed that still contains parts of its *mother* program.

[2] For a detailed tutorial of the python programming language, see the webpage `http://docs.python.org/tutorial/`.

[3] An integrated development environment available under `http://www.eclipse.org/platform`.

possible procedures and the related values of the shell parameters are listed in the following.

0/1 Hartree-Fock type approximation pursuant to the ansatz proposed by P. C. Martin and J. Schwinger [38, 51]. The results obtained by this approximation are of poor quality for the systems I considered. Furthermore, the iteration scheme is quite unstable in the mode 0. A better stability is obtained with mode 1 (damping mode procedure [52]).

2 Solves the GP equation by imaginary time stepping (see 3.2.2).

3 Solves the UBHF ansatz with the iteration scheme presented in 4.1.

4 In this mode *beta* starts performing the same procedure as in 3, and uses the obtained results for a subsequent time evolution of the system (see 4.3).

This list is also printed on the shell, if the option `--help` is passed. The calculation of the wave functions, matrix elements of important operators and the two-particle integrals with respect to the chosen basis are provided by a separated program developed by K. Balzer and stored in extra files. All further parameters can be modified via an initialization file `beta.ini`. The parameters that are accessible in this file and their meaning in the program are given in Table 6.1.

beta is written in the C++ [4] programming language and the code applies many features of object oriented programming paradigm. Each of the approximation schemes and procedures provided by *beta* is performed by a separated class. As all approximations are solved iteratively, many class members with very similar functionality are contained in each class. For that reason, they are all derived from an abstract base class called `solvable`. It contains an increment operator (`++`) that executes an iteration step when it is called. Also it has a member function called `renew`, that calculates the needed entities in each step. For instance the UBHF variant of the method `renew` calculates the operators $\hat{\mathcal{H}}_n$ and $\hat{\mathcal{O}}_n$ for each n. An important member, that is contained in `solvable` and hence in all derived classes is an object of the class `parameters`, where all parameters that are accessible with `beta.ini`, some matrix elements and the two-particle integrals are administrated. When the constructor of an object of `parameters` is called, it reads the values for the parameters given in `beta.ini`.

After the iteration has finished, an object of the class `output` is instantiated. It contains an object of the type `solvable` and hence has also access to the members of the instantiation of `parameters` contained in `solvable`. Its central function is `print` whose assignment is to store the results in ASCII datafiles. The relationships and tasks of the afore mentioned classes are summarized in Fig. 6.1.

6.2 Analysis of the primary output (scs.py)

The datafiles, that are created with `output` only contain the most important information, such as the chosen parameters, the resulting total energy (`eval.dat`), the spinor

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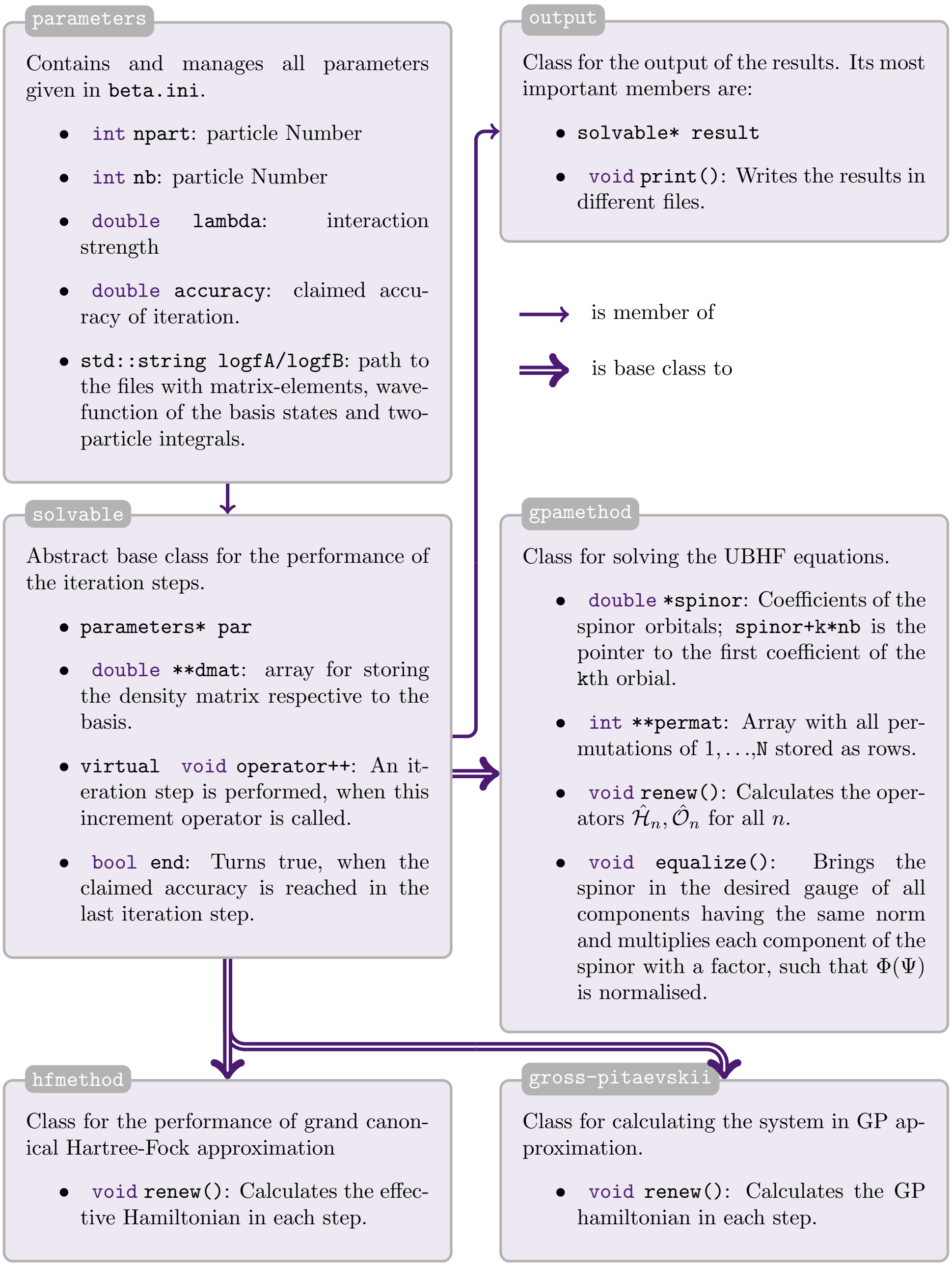
[4] For an introduction to this language, I recommend the web tutorial `http://www.cplusplus.com/doc/tutorial/`.



parameters

Contains and manages all parameters given in `beta.ini`.

- `int npart`: particle Number
- `int nb`: particle Number
- `double lambda`: interaction strength
- `double accuracy`: claimed accuracy of iteration.
- `std::string logfA/logfB`: path to the files with matrix-elements, wavefunction of the basis states and two-particle integrals.

output

Class for the output of the results. Its most important members are:

- `solvable* result`
- `void print()`: Writes the results in different files.

→ is member of

⇒ is base class to

solvable

Abstract base class for the performance of the iteration steps.

- `parameters* par`
- `double **dmat`: array for storing the density matrix respective to the basis.
- `virtual void operator++`: An iteration step is performed, when this increment operator is called.
- `bool end`: Turns true, when the claimed accuracy is reached in the last iteration step.

gpamethod

Class for solving the UBHF equations.

- `double *spinor`: Coefficients of the spinor orbitals; `spinor+k*nb` is the pointer to the first coefficient of the `k`th orbial.
- `int **permat`: Array with all permutations of 1,...,`N` stored as rows.
- `void renew()`: Calculates the operators $\hat{\mathcal{H}}_n, \hat{\mathcal{O}}_n$ for all n.
- `void equalize()`: Brings the spinor in the desired gauge of all components having the same norm and multiplies each component of the spinor with a factor, such that $\Phi(\Psi)$ is normalised.

hfmethod

Class for the performance of grand canonical Hartree-Fock approximation

- `void renew()`: Calculates the effective Hamiltonian in each step.

gross-pitaevskii

Class for calculating the system in GP approximation.

- `void renew()`: Calculates the GP hamiltonian in each step.

Figure 6.1: *Schematic overview of the classes in the code of beta . The class* `gpamethod` *performs the UBHF approximation.*

Parameter name and type of variable		Meaning and value range
`char stat`	0^*	Statistic of the considered system. Can only take on the values 'f' and 'b'.
`int npart`	1	Particle number N
`int nb`	2	Number of basis functions n_b
`double lambda`	3	Coupling strength λ.
`double beta`	4^*	Inverse temperature β.
`std::string logfA`	5	Path to the file with the matrix elements of the Hamiltonian and the wave functions of the basis states.
`std::string logfB`	6	Path to the file with the two-particle integrals.
`double accuracy`	7	Claimed accuracy of the iteration.
`int nitmax`	8	If this iteration number is reached, the procedure is forced to stop.
`double delta`	9^*	Acceptance fraction in damping-mode-procedure).
`double deltat`	10	Length of the time step for the time evolution.
`int xc`	11^*	Exchange term.
`char ensemble`	12^*	'g' for grand canonical ensemble, 'c' for canonical ensemble.
`bool bt`	13^*	Bose term.
`int g`	14^*	Spin degeneracy.
`double tmax`	15	Upper limit for the length of the time evolution.
`int partition`	16	Set partition for multi-occupied UBHF.

Table 6.1: *Parameters that can be controlled by editing the initialization file* `beta.ini` *and their meaning. The numbers in the central column refer to the number of the parameter in the initialization file. The parameters marked with* **have only an effect on the procedure in the modes 0 or 1 and are not further explained here (for more information see [50]).*

components (`spincomps.dat`), and the components of the ROBDM (`dmat.dat`). In fact the spinor orbitals is all the information, that is needed, because they determine the whole N-body wave function and with it all interesting expectation values can be calculated. Anyway, with this pure data it is not possible to plot the wave functions of the spinor orbitals or the natural orbitals. For that purpose, a python script called `scs.py` [5] was developted, that produces plotable data, or any other needed information to analyse the results – such as occupation numbers of the natural orbitals. Unfortunately, the current version of `scs.py` is only applicable to results, that where calculated in the basis of the energy eigenstates of the harmonic oscillator. The exact task of `scs.py` is determined by passing adequate shell parameters. The mode (passed by `-m [number of the mode]`) is a parameter, that always has to be passed. It determines what type of entity shall be calculated. Depending on the mode, other shell parameters are required. In the following, the possible values for the mode and the related tasks are listed:

0 Print the n-th natural orbital of the ROBDM stored in `dmat.dat`. The required number of the desired orbital is passed with `-n [number of the orbital]`, where the orbital with the highest occupation number has the number 0 in the enumeration of the orbitals.

1 Print the one-particle-part of the total energy of the system.

2 Print the occupation numbers of the natural orbitals.

3 Print the spatial particle-density.

4 Print the wave function of the desired spinor orbital. The number of the spinor orbital, that shall be printed is passed with `-s [number of the orbital]`.

This script uses the *numpy* programming library, for solving the eigenvalue problem of the ROBDM .

---

[5] The name of this program stands for "self consistent spinor", because it was created at a time, when I was not sure how to call this approximation method. Later I found out with the help of Karsten Balzer, that Romanovsky had already proposed this ansatz and named it UBHF

7 Conclusion and outlook

A rigorous and extensive analysis of the UBHF approximation was presentend in this work. Its relationship to the GP and other approximations proposed by Cederbaum et al. was discussed. In chapter 2, it was emphasized that for the considered systems with fixed particle number, the grand canonical description, as it is used in the Keldysh formalism does not yield acceptable results.

UBHF is the only single Slater permanent ansatz, which is capable to describe the depletion of the condensate for increasing relative interaction strength. It provides energies that are impressively close to the energies obtained by exact methods, and also the arising peaks in the particle densities for high coupling show up in this approximation. This is not included within GP. The current numerical implementation is capable to handle systems consisting of 8 particles within acceptable time ranges. The performance is better than CI, where for similar calculations, one is limited to a small basis size, what would worsen the quality of the results.

The unfortunately bad scaling of the simulation time with increasing particle number within the current implementation inhibits a consideration of systems with more than 8 bosons. The alternative representation of the UBHF equations with minor permanents of the gramian matrix opens the possibility to clearly improve the algorithm. Hence, it should be possible to apply the UBHF approximation to systems with up to 15 particles by using the Ryser algorithm for the calculation of the minor permanents. A C++ routine for the calculation of such minor permanents is already developed, but the implementation of this routine in a UBHF scheme did not yet work out fine. In addition, the generalization of UBHF to multi occupied UBHF (proposed in section 4.6.2) should further decrease the simulation time.

The TDUBHF approximation has so far only successfully been applied to two-particle systems. For larger particle numbers, the current implementation aborts after very few time steps. The comparison of the TDUBHF results with an exact method indicate, that this ansatz is indeed reasonable and there is no reason, why it should not work for larger particle numbers. The applicability of TDUBHF to higher particle numbers could be considered as a great and important success, as approximations, that are capable to describe the nonequilibrium of bosonic systems with such a good quality are very few.

For bosonic systems, it is pretty unsatisfactory to restrict to the consideration of the ground state, as for low temperatures such systems can undergo very interesting phase transitions, being connected with BEC, superfluidity or supersolidity. An extension of the Ritz principle to finite temperatures does not exist. One possibility would be to find all metastable states within the considered ansatz and raise a statistical approach with these solutions. However, this idea already fails at the problem of detecting all metastable states. And it is not guaranteed, that all metastable states refer to a real excited state of the system or that all excited states have an analog local minimum in the regarded ansatz. A suggestive extension of UBHF to finite temperature systems would be to use the UBHF orbitals as basis for a subsequent (full) CI calculation. The UBHF orbitals (spinor orbitals) are supposed to be especially suitable for representing the considered system.

The abstract notation of the ROBDO in Eq. (2.10), the Hartree and Fock mean-field terms (A.8), the GP equation (3.24), and the variational derivative with respect to single-particle states in appendix A is not used in the usual literature, thus, parts of this work can be used as an introduction for handling this notation.

During the time of this work, a publication with some here presented ideas and results did emerge [53].

A Variational derivative with respect to abstract Hilbert space vectors

In Chap. 3 and 4 variational derivatives of functionals containing only matrix-elements, scalar products and two-particle integrals are performed. To avoid an anticipated choice of the basis in which the calculation shall be done, it is useful to derive some rules for the derivative of such functionals with respect to an abstract Hilbert space state, such that the choice of the basis can be done afterwards.

Some differentiation rules that are needed to obtain equation (4.14) are deduced in this section. In the following, $\varphi_n(x)$ denotes the wavefunction of the nth orbital of a given set (like the components of the spinor (4.1) or a CONS). Consider now the variational derivative of the matrix element of an arbitrary operator $\hat{A}$:

$$\begin{aligned}\frac{\delta}{\delta\varphi_n^*(x)}\langle i|\hat{A}|j\rangle &= \frac{\delta}{\delta\varphi_n^*(x)}\int \varphi_i^*(z)A(z,y)\varphi_j(y)\,\mathrm{d}z\,\mathrm{d}y \\ &= \delta_{in}\int A(x,y)\varphi_j(y)\,\mathrm{d}y = \delta_{in}\langle x|\hat{A}|j\rangle = \langle x|\left(\frac{\delta}{\delta\langle n|}\langle i|\hat{A}|j\rangle\right). \end{aligned} \tag{A.1}$$

The latter transformation can be considered as a definition for the abstract derivative with respect to an abstract Hilbert space vector:

$$\frac{\delta}{\delta\langle n|}\langle i|\hat{A}|j\rangle := \delta_{in}\hat{A}|j\rangle \tag{A.2}$$

To point out that this definition makes sense, consider the *same* derivative but in an arbitrary discrete representation. Henceforth Greek letters will denote the quantum numbers of the fix but arbitrarily chosen CONS, which is used as basis:

$$\langle n| = \sum_\gamma c_{n\gamma}^*\langle\gamma| \qquad \text{and} \qquad |k\rangle = \sum_\alpha c_{k\alpha}|\alpha\rangle\ . \tag{A.3}$$

The differentiation of the matrix element $\langle i|\hat{A}|j\rangle$ with respect to $c_{n\gamma}^*$ – the γth expansion coefficient of the nth dual vector $\langle n|$ reads

$$\begin{aligned}\frac{\partial}{\partial c_{n\gamma}^*}\langle i|\hat{A}|j\rangle &= \frac{\partial}{\partial c_{n\gamma}^*}\sum_{\alpha\beta}c_{i\alpha}^*A_{\alpha\beta}c_{j\beta} = \sum_{\alpha\beta}\underbrace{\frac{\partial c_{i\alpha}^*}{\partial c_{n\gamma}^*}}_{=\delta_{in}\delta_{\alpha\gamma}}A_{\alpha\beta}c_{j\beta} = \delta_{in}\sum_\beta A_{\gamma\beta}c_{j\beta} \\ &= \delta_{in}\langle\gamma|\hat{A}|j\rangle = \langle\gamma|\left(\frac{\delta}{\delta\langle n|}\langle i|\hat{A}|j\rangle\right).\end{aligned}$$

Thus in general one can write for the differentiation with respect to an expansion coefficient with respect to an arbitrary basis

$$\boxed{\frac{\partial}{\partial c^*_{n\gamma}} \langle i|\hat{A}|j\rangle = \langle\gamma| \left(\frac{\delta}{\delta \langle n|} \langle i|\hat{A}|j\rangle\right) .} \tag{A.4}$$

This formula also includes differentiations of simple scalar products by taking the special case $\hat{A} = \hat{1}$.

For the differentiation of the two-particle integrals, the same ideas can be used. In this work, the convention

$$w_{ij,kl} := \int \mathrm{d}x\,\mathrm{d}y\; \varphi^*_i(x)\varphi^*_j(y)w(x,y)\varphi_k(x)\varphi_l(y) \qquad \Rightarrow \hat{W} = \frac{1}{2}\sum_{ijkl} w_{ij,kl}\hat{a}^\dagger_i\hat{a}^\dagger_j\hat{a}_l\hat{a}_k \tag{A.5}$$

for the two-particle integrals is used. The arguments in the wave function can be composed of spatial coordinates and inner degrees of freedom such as spin or isospin. Then the integral is actually a combination of an integral in coordinate space and a sum over all remaining quantum numbers. A two particle integral can be expressed in terms of two-particle integrals with respect to the vectors of the chosen CONS:

$$\text{(A.3)} \qquad \Rightarrow w_{ij,kl} = \sum_{\alpha\beta\kappa\lambda} c^*_{i\alpha}c^*_{j\beta}c_{k\kappa}c_{l\lambda}w_{\alpha\beta,\kappa\lambda} \tag{A.6}$$

Analog to the one-body operator case, in this discrete representation a differentiation with respect to the expansion coefficient $c^*_{n\gamma}$ reduces to a simple partial derivative:

$$\begin{aligned} \frac{\partial}{\partial c^*_{n\gamma}} w_{ij,kl} &= \sum_{\alpha\beta\kappa\lambda} \Big(\delta_{in}\delta_{\alpha\gamma}\, c^*_{j\beta}c_{k\kappa}c_{l\lambda} + \delta_{jn}\delta_{\beta\gamma}\, c^*_{i\alpha}c_{k\kappa}c_{l\lambda}\Big) w_{\alpha\beta,\kappa\lambda} \\ &= \langle\gamma| \left(\delta_{in}\hat{J}_{jl}\,|k\rangle + \delta_{jn}\hat{J}_{ik}\,|l\rangle\right) = \langle\gamma| \left(\delta_{in}\hat{K}_{jk}\,|l\rangle + \delta_{jn}\hat{K}_{il}\,|k\rangle\right) \end{aligned} \tag{A.7}$$

Thus we have a bit more liberties to define the remaining term. The names and the definitions of the appearing operators are

$$\boxed{\begin{aligned} &\text{Hartree (direct)}: && \hat{J}_{ij} = \int \mathrm{d}x\ \mathrm{d}y\, \varphi^*_i(y)w(x,y)\varphi_j(y)\,|x\rangle\,\langle x| \\ &\text{Fock (exchange)}: && \hat{K}_{ij} = \int \mathrm{d}x\ \mathrm{d}y\, \varphi^*_i(x)w(x,y)\varphi_j(y)\,|y\rangle\,\langle x|\ . \end{aligned}} \tag{A.8}$$

With these definitions and equation (A.7) the abstract variational derivative of a two-particle integral reads

$$\frac{\delta}{\delta\langle n|} w_{ij,kl} = \delta_{in}\hat{J}_{jl}\,|k\rangle + \delta_{jn}\hat{J}_{ik}\,|l\rangle = \delta_{in}\hat{K}_{jk}\,|l\rangle + \delta_{jn}\hat{K}_{il}\,|k\rangle\ . \tag{A.9}$$

It was shown here that all functional derivatives of matrix elements or two-particle integrals can be regarded as a comprehension of simple and well known partial differentiations, thus the usual differentiation rules like product or chain rule still hold for functionals that only depend on scalar products, matrix elements or two-particle integrals of the considered Hilbert space states. As this is the case for all considered functionals in chapters 3 and 4, all the differentiation rules needed are given in this chapter.

B Detailed derivations for the UBHF equations

The derivations of the operators $\underline{\hat{\mathcal{H}}}$ and $\underline{\hat{\mathcal{O}}}$ that are needed to bring equation (4.14) into the form of a self consistent eigenvalue problem (4.16), were not done in Chap. 4, as such derivations need lots of long equations and would worsen the overview.

Both, the derivation of the first introduced pair of spinor operators Eq. (4.15) and of the second ones Eq. (4.19) is given in this chapter. The notations of both pairs of operators only differs in the number of subscripts. I start with the derivation of the operators given in equation (4.15).

$$N!\frac{\delta}{\delta\left\langle n\right|}\left\langle\Phi|\Phi\right\rangle=\sum_{\pi\in S_N}P_n\left|\pi(n)\right\rangle=\sum_{m=1}^{N}\underbrace{\left(\sum_{\substack{\pi\in S_N\\ \pi(n)=m}}P_n\right)}_{\hat{\mathcal{O}}_{nm}}\left|m\right\rangle\ , \tag{B.1}$$

where the the last transformation simply arises from the equality of the sum $\sum_{\pi\in S_N}$ and the sum $\sum_{m=1}^{N}\sum_{\substack{\pi\in S_N\\ \pi(n)=m}}$. This can also be used for the derivation of the operator $\hat{\mathcal{H}}_{nm}$:

$$\begin{aligned}
&N!\frac{\delta}{\delta\left\langle n\right|}\langle\Phi|\hat{H}|\Phi\rangle\\
&=\sum_{\pi\in S_N}\Bigg\{\overset{\text{(T1)}}{P_n\hat{h}\left|\pi(n)\right\rangle}+\overset{\text{(T2)}}{\sum_{l\neq n}P_{nl}\langle l|\hat{h}|\pi(l)\rangle\left|\pi(n)\right\rangle}+\overset{\text{(T3)}}{\sum_{l\neq n}P_{nl}\hat{J}_{l\pi(l)}\left|\pi(n)\right\rangle}+\overset{\text{(T4)}}{\frac{1}{2}\sum_{\substack{k,l\neq n\\ k\neq l}}P_{nlk}w_{kl,\pi(k)\pi(l)}\left|\pi(n)\right\rangle}\Bigg\}\\
&=\sum_{\pi\in S_N}\Bigg\{P_n\hat{h}+\sum_{l\neq n}\Big(P_{nl}\langle l|\hat{h}|\pi(l)\rangle+\hat{J}_{l\pi(l)}\Big)+\frac{1}{2}\sum_{\substack{k,l\neq n\\ k\neq l}}P_{nlk}w_{kl,\pi(k)\pi(l)}\Bigg\}\left|\pi(n)\right\rangle\\
&=\sum_{m=1}^{N}\underbrace{\left(\sum_{\substack{\pi\in S_N\\ \pi(n)=m}}\Bigg\{P_n\hat{h}+\sum_{l\neq n}\Big(P_{nl}\langle l|\hat{h}|\pi(l)\rangle+\hat{J}_{l\pi(l)}\Big)+\frac{1}{2}\sum_{\substack{k,l\neq n\\ k\neq l}}P_{nlk}w_{kl,\pi(k)\pi(l)}\Bigg\}\right)}_{\hat{\mathcal{H}}_{nm}}\left|m\right\rangle\ .
\end{aligned} \tag{B.2}$$

The designation of the terms with (T1)…(T4) in the second line of this chain of equations is needed now for the calculation of the singly subscripted operators $\hat{\mathcal{H}}_n$ and $\hat{\mathcal{O}}_n$. These operators are obtained by expressing the derivatives in (B.1) and (B.2) as the action of an operator on $\left|n\right\rangle$. For the calculation of $\hat{\mathcal{O}}_n$ one has to distinguish only the cases $\pi(n)=n$ and $\pi(n)\neq n$ under the sum:

$$\sum_{\pi\in S_N}P_n\left|\pi(n)\right\rangle=\sum_{\pi\in S_N}\Big\{\delta_{n\pi(n)}P_n+(1-\delta_{n\pi(n)})P_{n\pi^{-1}(n)}\left|\pi(n)\right\rangle\left\langle\pi^{-1}(n)\right|\Big\}\left|n\right\rangle=\hat{\mathcal{O}}_n\left|n\right\rangle \tag{B.3}$$

If this transformation is not clear to the reader, I recommend to reproduce this transformation backwards or perform this calculation for the two-particle case, where the sum over all permutations has only two summands[1].

For the calculation of $\hat{\mathcal{H}}_n$, regard each of the terms (T1)...(T4) separately. For the term (T1), one has to consider the same cases as in (B.3):

$$\sum_{\pi\in S_N} P_n\hat{h}\,|\pi(n)\rangle = \sum_{\pi\in S_N}\left\{\delta_{n\pi(n)}P_n\hat{h} + (1-\delta_{n\pi(n)})P_{n\pi^{-1}(n)}\hat{h}\,|\pi(n)\rangle\,\langle\pi^{-1}(n)|\right\}|n\rangle\ . \tag{B.4}$$

For the term (T2) and (T3), one has to additionally consider the case $\pi(l) = n$. The cases $\pi(l) = n$ and $\pi(n) = n$ are exclusive, because the sum runs over $l \neq n$. In the following, the calculation of the terms that arise from (T2) is done:

$$\begin{aligned}
&\sum_{\pi\in S_N}\sum_{l\neq n} P_{nl}\,\langle l|\hat{h}|\pi(l)\rangle\,|\pi(n)\rangle \\
&= \sum_{\pi\in S_N}\sum_{l\neq n}\Bigg\{\delta_{n\pi(n)}P_{nl}\,\langle l|\hat{h}|\pi(l)\rangle + \Big(1-\delta_{n\pi(n)}\Big)\Big[\underbrace{\delta_{n\pi(l)}}_{\delta_{\pi^{-1}(n)l}}P_{nl}\,|\pi(n)\rangle\,\langle l|\,\hat{h} \\
&\qquad + \Big(1-\delta_{n\pi(l)}\Big)P_{n\pi^{-1}(n)l}\,\langle l|\hat{h}|\pi(l)\rangle\,|\pi(n)\rangle\,\langle\pi^{-1}(n)|\Big]\Bigg\}|n\rangle \\
&= \sum_{\pi\in S_N}\Bigg\{\delta_{n\pi(n)}\sum_{l\neq n}P_{nl}\,\langle l|\hat{h}|\pi(l)\rangle + \Big(1-\delta_{n\pi(n)}\Big)\Big[P_{n\pi^{-1}(n)}\,|\pi(n)\rangle\,\langle\pi^{-1}(n)|\,\hat{h} \\
&\qquad + \sum_{\substack{l\neq n\\ l\neq\pi^{-1}(n)}} P_{n\pi^{-1}(n)l}\,\langle l|\hat{h}|\pi(l)\rangle\,|\pi(n)\rangle\,\langle\pi^{-1}(n)|\Big]\Bigg\}|n\rangle
\end{aligned} \tag{B.5}$$

For the treatment of (T3), the relation $\hat{J}_{jl}\,|k\rangle = \hat{K}_{jk}\,|l\rangle$ is needed (see Eq. (A.9)).

$$\begin{aligned}
&\sum_{\pi\in S_N}\sum_{l\neq n} P_{nl}\hat{J}_{l\pi(l)}\,|\pi(n)\rangle \\
&= \sum_{\pi\in S_N}\sum_{l\neq n}\Bigg\{\delta_{n\pi(n)}P_{nl}\hat{J}_{l\pi(l)} + \Big(1-\delta_{n\pi(n)}\Big)\Big[\delta_{n\pi(l)}P_{nl}\hat{K}_{l\pi(n)} \\
&\qquad + \Big(1-\delta_{n\pi(l)}\Big)P_{n\pi^{-1}(n)l}\hat{J}_{l\pi(l)}\,|\pi(n)\rangle\,\langle\pi^{-1}(n)|\Big]\Bigg\}|n\rangle \\
&= \sum_{\pi\in S_N}\Bigg\{\delta_{n\pi(n)}\sum_{l\neq n}P_{nl}\hat{J}_{l\pi(l)} + \Big(1-\delta_{n\pi(n)}\Big)\Big[P_{n\pi^{-1}(n)}\hat{K}_{\pi^{-1}(n)\pi(n)} \\
&\qquad + \sum_{\substack{l\neq n\\ l\neq\pi^{-1}(n)}} P_{nl\pi^{-1}(n)}\hat{J}_{l\pi(l)}\,|\pi(n)\rangle\,\langle\pi^{-1}(n)|\Big]\Bigg\}|n\rangle
\end{aligned} \tag{B.6}$$

Finally, for the last term (T4), one additionally has to consider the case $\pi(k) = n$.

---

[1] For that purpose, the footnote 5 in Chap. 4 may helps.

Therefore the equation $w_{ij,kl} = \langle i|\hat{J}_{jl}|k\rangle$ is needed.

$$
\begin{aligned}
&\sum_{\pi\in S_N} \frac{1}{2} \sum_{\substack{k,l\neq n\\ k\neq l}} P_{nlk} w_{kl,\pi(k)\pi(l)} \left|\pi(n)\right\rangle \\
&= \sum_{\pi\in S_N} \frac{1}{2} \sum_{\substack{k,l\neq n\\ k\neq l}} \Bigg\{ \delta_{n\pi(n)} P_{nlk} w_{kl,\pi(k)\pi(l)} + \Big(1-\delta_{n\pi(n)}\Big) \Big[\delta_{n\pi(l)} \left|\pi(n)\right\rangle \left\langle l\right| \hat{J}_{k\pi(k)} + \delta_{n\pi(k)} \left|\pi(n)\right\rangle \left\langle k\right| \hat{J}_{l\pi(l)} \\
&\qquad\qquad + \Big(1-\delta_{n\pi(l)} - \delta_{n\pi(k)}\Big) w_{kl,\pi(k)\pi(l)} P_{n\pi^{-1}(n)kl} \left|\pi(n)\right\rangle \left\langle \pi^{-1}(n)\right| \Big] \Bigg\} \left|n\right\rangle \\
&= \sum_{\pi\in S_N} \Bigg\{ \delta_{n\pi(n)} \frac{1}{2} \sum_{\substack{k,l\neq n\\ k\neq l}} P_{nlk} w_{kl,\pi(k)\pi(l)} + \Big(1-\delta_{n\pi(n)}\Big) \Big[\sum_{\substack{l\neq n\\ l\neq \pi^{-1}(n)}} P_{nl\pi^{-1}(n)} \left|\pi(n)\right\rangle \left\langle \pi^{-1}(n)\right| \hat{J}_{l\pi(l)} \\
&\qquad\qquad + \frac{1}{2} \sum_{\substack{k,l\neq n,\pi^{-1}(n)\\ k\neq l}} P_{kln\pi^{-1}(n)} w_{kl,\pi(k)\pi(l)} \left|\pi(n)\right\rangle \left\langle \pi^{-1}(n)\right| \Big] \Bigg\} \left|n\right\rangle \ . \qquad \text{(B.7)}
\end{aligned}
$$

In order to obtain the sought after operator $\hat{\mathcal{H}}_n$, one has to bring all the here calculated terms together and obtains:

$$
\begin{aligned}
N! \frac{\delta}{\delta \left\langle n\right|} \langle\Phi|\hat{H}|\Phi\rangle &= \sum_{\pi\in S_N} \Bigg\{ \delta_{n\pi(n)} \Big[P_n \hat{h} + \sum_{l\neq n} P_{ln} (\langle l|\hat{h}|\pi(l)\rangle + \hat{J}_{l\pi(l)}) + \frac{1}{2} \sum_{\substack{k,l\neq n\\ k\neq l}} P_{kln} w_{kl,\pi(k)\pi(l)} \Big] \\
&\quad + (1-\delta_{\pi(n)n}) \Big[P_{n\pi^{-1}(n)} \Big(\hat{h} \left|\pi(n)\right\rangle \left\langle \pi^{-1}(n)\right| + \left|\pi(n)\right\rangle \left\langle \pi^{-1}(n)\right| \hat{h} + \hat{K}_{\pi^{-1}(n)\pi(n)} \Big) \\
&+ \sum_{\substack{l\neq \pi^{-1}(n)\\ l\neq n}} P_{ln\pi^{-1}(n)} \Big(\langle l|\hat{h}|\pi(l)\rangle \left|\pi(n)\right\rangle \left\langle \pi^{-1}(n)\right| + \hat{J}_{l\pi(l)} \left|\pi(n)\right\rangle \left\langle \pi^{-1}(n)\right| + \left|\pi(n)\right\rangle \left\langle \pi^{-1}(n)\right| \hat{J}_{l\pi(l)} \Big) \\
&\qquad + \frac{1}{2} \sum_{\substack{k,l\neq n\pi^{-1}(n)\\ k\neq l}} P_{kln\pi^{-1}(n)} w_{kl,\pi(k)\pi(l)} \left|\pi(n)\right\rangle \left\langle \pi^{-1}(n)\right| \Big] \Bigg\} \left|n\right\rangle = \hat{\mathcal{H}}_n \left|n\right\rangle \ .
\end{aligned}
$$

C Relativity of orthonormality

It is well known that one can create a set of orthonormal vectors out of an arbitrary set of linearly independent vectors $|1\rangle, \dots, |N\rangle$ such that both sets expand the same vector space; e.g. via the Gram-Schmidt process. Orthonormality of a set of vectors is not at all an intrinsic property of the vectors but is rather inseparably connected to the choice of the scalar product. Keeping this fact in mind, one may ask if it is also possible to create an orthonormal set of vectors not by changing the vectors, but by a change of the scalar product. I.e. if a linearly independent set of vectors $|1\rangle, \dots, |N\rangle$ is given; does there exist a (hermitian – with respect to the present scalar product) positive definite operator $\hat{o}$ such that

$$\langle i|\hat{o}|j\rangle = \delta_{ij} \quad \text{for all } i, j \text{ ?} \tag{C.1}$$

In this chapter it is shown that this is actually the case and a closed expression for the operator $\hat{o}$ is given. For that purpose consider each vector of the given set represented as an N-tuple (columns) $\mathbf{v}_1, \dots, \mathbf{v}_N$ that contains the expansion coefficients with respect to an arbitrary but fix chosen ONS that spans the same space as the original vectors – for which it is already known that this is always possible to find. As the vectors are linearly independent, the determinant of the matrix that has the tuples $\mathbf{v}_1, \dots, \mathbf{v}_N$ as columns is nonzero

$$\det(\mathbf{v}_1, \dots, \mathbf{v}_N) \neq 0 \; . \tag{C.2}$$

For the calculation of the partial derivative of this determinant with respect to the kth component of the ith vector[1] one can make use of the defining properties of the determinant:

$$\begin{aligned}\frac{\partial}{\partial v_{ik}} \det(\mathbf{v}_1, \dots, \mathbf{v}_N) &= \lim_{h \to 0} \frac{1}{h} \big(\det(\mathbf{v}_1, \dots, \mathbf{v}_i + h\hat{\mathbf{e}}_k, \dots, \mathbf{v}_N) - \det(\mathbf{v}_1, \dots, \mathbf{v}_i, \dots, \mathbf{v}_N) \big) \\ &= \det(\mathbf{v}_1, \dots, \hat{\mathbf{e}}_k, \dots, \mathbf{v}_N) \; ,\end{aligned} \tag{C.3}$$

where $\hat{\mathbf{e}}_k$ denotes the tuple with the kth component being 1 and the others being 0. The determinant of the matrix that is obtained by replacing the ith column by an arbitrary vector $\mathbf{v}'$ can be expressed as dyadic product of the gradient $\nabla_i \det(\mathbf{v}_1, \dots, \mathbf{v}_N)$ and $\mathbf{v}'$:

$$\det(\mathbf{v}_1, \dots, \mathbf{v}_N)|_{\mathbf{v}_i \leftrightarrow \mathbf{v}} = \sum_k \frac{\partial}{\partial v_{ik}} \det(\mathbf{v}_1, \dots, \mathbf{v}_N)\, v'_k \; . \tag{C.4}$$

Thus the dyadic product $\nabla_i \det(\mathbf{v}_1, \dots, \mathbf{v}_N)^{\mathsf{T}} \mathbf{v}_j$ is only nonvanishing if $i = j$, because otherwise it would be the determinant of a matrix with two vectors being equal. An

---

[1] As the basis to which the expansion coefficients (contained as components in the tuples) is fixed during this calculation, it is allowed to identify the tuples $\mathbf{v}_1, \dots, \mathbf{v}_N$ with the vectors $|1\rangle, \dots, |N\rangle$.

analogous calculation holds for the complex conjugated of the determinant and the derivatives with respect to the dual vectors $\mathbf{v}_1^\dagger, \dots, \mathbf{v}_N^\dagger$:

$$\begin{aligned}\Big(\nabla_i \det(\mathbf{v}_1, \dots, \mathbf{v}_N)\Big)^{\mathsf{T}} \mathbf{v}_j &= \delta_{ij} \det(\mathbf{v}_1, \dots, \mathbf{v}_N) \\ \mathbf{v}_j^\dagger \Big(\nabla_i \det(\mathbf{v}_1, \dots, \mathbf{v}_N)\Big)^* &= \delta_{ij} \det(\mathbf{v}_1, \dots, \mathbf{v}_N)^*\end{aligned}$$

These two equations can be merged to yield the following equation

$$\mathbf{v}_i^\dagger \left(\nabla_n \det(\mathbf{v}_1, \dots, \mathbf{v}_N)\right)^* \left(\nabla_n \det(\mathbf{v}_1, \dots, \mathbf{v}_N)\right)^{\mathsf{T}} \mathbf{v}_j = \delta_{in}\delta_{jn} |\det(\mathbf{v}_1, \dots, \mathbf{v}_N)|^2 \,, \tag{C.5}$$

which leads directly to the definition of the sought after operator

$$\hat{o} = \frac{1}{|\det(\mathbf{v}_1, \dots, \mathbf{v}_N)|^2} \sum_n \nabla_n^\dagger \nabla_n |\det(\mathbf{v}_1, \dots, \mathbf{v}_N)|^2 \,. \tag{C.6}$$

This notation for $\hat{o}$ – with the derivatives $\nabla_n^\dagger \nabla_n$ acting on the same term – only holds if the components of the tuples are considered as variables independent of their complex conjugated. The squared absolute value of a determinant is the determinant of the Gramian matrix of its columns (or its rows). Thus, for the abstract vectors $|1\rangle, \dots, |N\rangle$ given at the beginning of this chapter, this is just the norm of the antisymmetrized product state Φ^F of $|1\rangle, \dots, |N\rangle$, and the operator given in (C.6) can be expressed in an abstract way as follows

$$\begin{gathered}\hat{o} = \frac{1}{\langle \Phi^F | \Phi^F \rangle} \sum_n \frac{\delta}{\delta\, |n\rangle} \frac{\delta}{\delta\, \langle n|} \langle \Phi^F | \Phi^F \rangle \;, \qquad \text{with} \\ \frac{\delta}{\delta\, |n\rangle} \frac{\delta}{\delta\, \langle n|} \langle \Phi^F | \Phi^F \rangle = \sum_{\pi \in S_N} (-1)^\pi \Big\{ \delta_{n\pi(n)} P_n + (1 - \delta_{\pi(n)n}) P_{n\pi^{-1}(n)} \, |\pi(n)\rangle \langle \pi^{-1}(n)| \Big\}\end{gathered} \tag{C.7}$$

With this operator $\hat{o}$, one can give an expression of $\hat{1}$ (in the subspace of the expansion of the considered set of vectors) that is well connected to the set of vectors one has to deal with:

$$\hat{1} = \sum_n |n\rangle \langle n| \, \hat{o} = \sum_n \hat{o} \, |n\rangle \langle n| \;. \tag{C.8}$$

The first equality can be derived by regarding the action of the sum on one of the vectors $|1\rangle, \dots, |N\rangle$, and the second follows from the hermiticity of $\hat{1}$. Hence, the action of an arbitrary one-body operator $\hat{A}$ within the expansion of the vectors $|1\rangle, \dots, |N\rangle$ can be expressed as

$$\hat{A} = \hat{1}\hat{A}\hat{1} = \sum_{ij} \langle i|\hat{A}|j\rangle \, \hat{o} \, |i\rangle \langle j| \, \hat{o} \,. \tag{C.9}$$

A two body operator $\hat{w}$ can be expressed in an analog way:

$$\hat{w} = \sum_{ijkl} w_{ij,kl} \; \hat{o} \, |i\rangle \otimes \hat{o} \, |j\rangle \, \langle k| \, \hat{o} \otimes \langle l| \, \hat{o} \,. \tag{C.10}$$

This can easily be seen, by calculating the matrix elements $\langle k'| \otimes \langle l'| \, \hat{w} \, |i'\rangle \otimes |j'\rangle$, which yields the two-particle integrals.

D Hartree-Fock for the grand canonical ensemble

In literature the Hartree-Fock approximation for finite temperature systems is usually introduced as an expansion of the two-particle Green's function in terms of products of the one-particle Green's function that complies with the conditions due to the quantum statistics of the particles [38, 50, 54, 55]. The resulting reduced one-body density matrix, can be regarded as the one-body density matrix of an ideal system with an effective Hamiltonian.

In this chapter a different derivation of the well known Hartree-Fock equations is presented. The starting point is the assumption that all energy eigenstates of the many body system are symmetrized product states of a set of self-consistent one particle states and that each of these orbitals is related to an energy that additionally contributes to the total energy of the many body state.

D.1 Fermions

With this assumption, the total energy in the grand canonical ensemble has the form

$$\begin{aligned}\langle \hat{H} \rangle = \frac{1}{Z} \sum_{n_1=0,1} \sum_{n_2=0,1} \dots e^{-\beta \sum_{k=1} n_k(\varepsilon_k - \mu)} \\ \cdot \ \langle n_1 n_2 \dots | \sum_{k_1 k_2 = 1} h_{k_1 k_2} a^\dagger_{k_1} a_{k_2} + \frac{1}{2} \sum_{k_1 k_2 k_3 k_4} w_{k_1 k_2, k_3 k_4} \hat{a}^\dagger_{k_1} \hat{a}^\dagger_{k_2} \hat{a}_{k_3} \hat{a}_{k_4} | n_1 n_2 \dots \rangle \ . \end{aligned} \tag{D.1}$$

The two-particle integrals $w_{k_1 k_2, k_3 k_4}$ are defined in Eq. (A.5). The creation and annihilation operators refer to the Hartree-Fock orbitals. For the computation of this expectation value consider the diagonal elements of the following operator products

$$\begin{aligned}\langle n_1 n_2 \dots | \hat{a}^\dagger_{k_1} \hat{a}^\dagger_{k_2} \hat{a}_{k_3} \hat{a}_{k_4} | n_1 n_2 \dots \rangle &= (1 - \delta_{k_1 k_2})(1 - \delta_{k_3 k_4}) n_{k_1} n_{k_2} (\delta_{k_2 k_3} \delta_{k_1 k_4} - \delta_{k_2 k_4} \delta_{k_1 k_3}) \\ &= (\delta_{k_2 k_3} \delta_{k_1 k_4} - \delta_{k_2 k_4} \delta_{k_1 k_3}) n_{k_1} n_{k_2} \end{aligned} \tag{D.2}$$

$$\langle n_1 n_2 \dots | \hat{a}^\dagger_{k_1} \hat{a}_{k_2} | n_1 n_2 \dots \rangle = \delta_{k_1 k_2} n_{k_1} \tag{D.3}$$

The sum over the occupation numbers can be executed by introducing the averages of the occupation numbers and their products:

$$\begin{aligned}\langle\hat{H}\rangle &= \sum_{k_1k_2} h_{k_1k_2}\delta_{k_1k_2}\langle n_{k_1}\rangle + \frac{1}{2}\sum_{k_1k_2k_3k_4} w_{k_1k_2,k_3k_4}(\delta_{k_2k_3}\delta_{k_1k_4} - \delta_{k_2k_4}\delta_{k_1k_3})\langle n_{k_1}n_{k_2}\rangle \\ &= \sum_k h_{kk}\langle n_k\rangle + \frac{1}{2}\sum_{k_1k_2}[w_{k_1k_2,k_2k_1} - w_{k_1k_2,k_1k_2}]\langle n_{k_1}n_{k_2}\rangle \\ &= \langle h\rangle + \langle W\rangle \end{aligned} \tag{D.4}$$

Fortunately, for $i \neq j$ the replacement $\langle n_in_j\rangle = \langle n_i\rangle\langle n_j\rangle$ can be done. This equality is only valid for $i \neq j$, but it is allowed to make the same replacement also for equal indices, since these terms annul each other because of the minus sign that appears in the fermionic case in the exchange term.

For further calculation, the basis of the ideal system is chosen to represent the Hartree-Fock orbitals. The basis states of the ideal system will be denoted with the index l. Both the Hartree-Fock orbitals and the basis orbitals form a CONS. Thus, the transformation is notably easy

$$A_{kl} := \langle k|l\rangle \tag{D.5}$$

$$\Rightarrow \qquad \hat{a}_k^\dagger = \sum_l A_{kl}\hat{a}_l^\dagger \qquad\qquad \hat{a}_l^\dagger = \sum_k A_{kl}^*\hat{a}_k^\dagger \tag{D.6}$$

Especially the two-fold subscripted entities transform as follows

$$\langle\hat{a}_{l_1}^\dagger\hat{a}_{l_2}\rangle = \sum_{k_1k_2} A_{k_1l_1}^*A_{k_2l_2}\langle\hat{a}_{k_1}^\dagger\hat{a}_{k_2}\rangle = \sum_k A_{kl_1}^*A_{kl_2}\langle n_k\rangle \tag{D.7}$$

$$|k_1k_2) = \sum_{l_1l_2} A_{k_1l_1}A_{k_2l_2}|l_1l_2)\ , \tag{D.8}$$

where $|l_1l_2) := |l_1\rangle \otimes |l_2\rangle$ denotes the tensor product of the vectors $|l_1\rangle$ and $|l_2\rangle$. In the following equation, the two-particle integrals are regarded as matrix elements of these tensor products (according to [14]). These transformations can be used for the calculation of the expectation values within the basis of the ideal system

$$\langle h\rangle = \sum_k h_{kk}\langle n_k\rangle = \sum_k \underbrace{\sum_{l_1l_2} A_{kl_1}A_{kl_2}^*\langle l_1|h|l_2\rangle}_{=\langle k|h|k\rangle}\langle n_k\rangle = \sum_l \varepsilon_l^0 \underbrace{\sum_k A_{kl}A_{kl}^*\langle n_k\rangle}_{=\langle a_l^\dagger a_l\rangle=:\langle n_l\rangle}$$

The expectation values for the interaction $\langle W\rangle$ in Eq. (D.4) part is a little bit more awkward to calculate

$$\sum_{k_1k_2}\langle n_{k_1}\rangle\langle n_{k_2}\rangle w_{k_1k_2,k_1k_2} = \sum_{k_1k_2}\sum_{l_1l_2} A_{k_1l_1}^*A_{k_2l_2}^*(l_1l_2|w\sum_{l_3l_4} A_{k_1l_3}A_{k_2l_4}|l_3l_4)\langle n_{k_1}\rangle\langle n_{k_2}\rangle \tag{D.9}$$

$$= \sum_{l_1\ldots l_4} w_{l_1l_2,l_3l_4}\underbrace{\sum_{k_1}\langle n_{k_1}\rangle A_{k_1l_1}^*A_{k_1l_3}}_{=\langle a_{l_1}^\dagger a_{l_3}\rangle}\underbrace{\sum_{k_2}\langle n_{k_2}\rangle A_{k_2l_2}^*A_{k_2l_4}}_{=\langle\hat{a}_{l_2}^\dagger\hat{a}_{l_4}\rangle}$$

$$= \sum_{l_1\ldots l_4} w_{l_1l_2,l_3l_4}\langle\hat{a}_{l_1}^\dagger\hat{a}_{l_3}\rangle\langle\hat{a}_{l_2}^\dagger\hat{a}_{l_4}\rangle \tag{D.10}$$

Analogously, the other summand of the interaction part in (D.4) reads:

$$\sum_{k_1 k_2} \langle n_{k_1} \rangle \langle n_{k_2} \rangle w_{k_1 k_2, k_2 k_1} = \sum_{l_1 \dots l_4} w_{l_1 l_2, l_4 l_3} \langle \hat{a}^\dagger_{l_1} \hat{a}_{l_3} \rangle \langle \hat{a}^\dagger_{l_2} \hat{a}_{l_4} \rangle \tag{D.11}$$

In total, the following expression for the expectation value of the energy is obtained

$$\begin{aligned} \langle H \rangle &= \sum_l \varepsilon^0_l \langle n_l \rangle + \frac{1}{2} \sum_{l_1 \dots l_4} \left[w_{l_1 l_2, l_4 l_3} - w_{l_1 l_2, l_3 l_4} \right] \langle \hat{a}^\dagger_{l_1} \hat{a}_{l_3} \rangle \langle \hat{a}^\dagger_{l_2} \hat{a}_{l_4} \rangle \\ &= \left\langle \sum_l \varepsilon^0_l \hat{a}^\dagger_l \hat{a}_l + \frac{1}{2} \sum_{l_1 \dots l_4} \left[w_{l_1 l_2, l_4 l_3} - w_{l_1 l_2, l_3 l_4} \right] \langle \hat{a}^\dagger_{l_1} \hat{a}_{l_3} \rangle \hat{a}^\dagger_{l_2} \hat{a}_{l_4} \right\rangle \end{aligned} \tag{D.12}$$

Hence, by extracting one averaging, the outer averaging can be regarded as an average over an effective Hamiltonian. In second quantization this effective Hamiltonian deduced here reads

$$\hat{H}_{\text{eff}} = \sum_l \varepsilon^0_l \hat{a}^\dagger_l \hat{a}_l + \frac{1}{2} \sum_{l_1 \dots l_4} \left[w_{l_1 l_2, l_4 l_3} - w_{l_1 l_2, l_3 l_4} \right] \langle \hat{a}^\dagger_{l_1} \hat{a}_{l_3} \rangle \hat{a}^\dagger_{l_2} \hat{a}_{l_4} \tag{D.13}$$

As it is an effective one-particle Hamiltonian it is sufficient to calculate the matrix elements with respect to one-body Hilbert space states to know the action of this operator in Fock space. With the relation $\langle l_5 | \hat{a}^\dagger_{l_2} \hat{a}_{l_4} | l_6 \rangle = \delta_{l_4 l_6} \delta_{l_5 l_2}$ the matrix element

$$\langle l_5 | H | l_6 \rangle = \delta_{l_5 l_6} \varepsilon^0_{l_5} + \frac{1}{2} \sum_{l_1 l_3} \left[w_{l_1 l_5, l_6 l_3} - w_{l_1 l_5, l_3 l_6} \right] \langle \hat{a}^\dagger_{l_1} \hat{a}_{l_3} \rangle \tag{D.14}$$

is obtained. In [50] [1] , the factor $\frac{1}{2}$ does not appear at the interaction part, but there the total energy is calculated by

$$\begin{aligned} \langle \hat{H}^{[50]} \rangle &= \frac{1}{2} \sum_k f(\varepsilon_k - \mu) \varepsilon_k + \frac{1}{2} \sum_{k_1 k_2} h^0_{k_1 k_2} \langle a^\dagger_{k_1} a_{k_2} \rangle = \frac{1}{2} \sum_k H^{[50]}_{kk} \cdot \langle n_k \rangle + \frac{1}{2} \sum_k h^0_{kk} \langle n_k \rangle \\ &= \frac{1}{2} \langle H^{[50]} \rangle + \frac{1}{2} \langle h^0 \rangle = \frac{1}{2} \big(\langle h^0 \rangle + \langle W^{[50]} \rangle + \langle h^0 \rangle \big) = \langle h^0 \rangle + \frac{1}{2} \langle W^{[50]} \rangle \end{aligned} \tag{D.15}$$

The superscripted index [50] shall suggest that this is the calculation of the energy according to [50] where the factor $\frac{1}{2}$ is included in the calculation of the energy afterwards. The function f in the first term denotes the Fermi-Dirac distribution.

D.2 Bosons

Equation (D.1) holds as well for the calculation of the total energy of a bosonic system, but with the summations of the occupation numbers running from 0 to ∞. The expectation values of the products of creation and annihilation operators (D.2) differ from

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[1] For a comparison with [50] note the different conventions in the notation of the two-particle integrals: $w^{[50]}_{kl,ij} = w_{ik,jl}$.

the fermionic case [56]

$$\begin{aligned}\langle n_1 n_2 \ldots | \, \hat{a}^\dagger_{k_1} \hat{a}^\dagger_{k_2} \hat{a}_{k_3} \hat{a}_{k_4} \, | n_1 n_2 \ldots \rangle &= \delta_{k_3 k_4} \delta_{k_3 k_2} \delta_{k_2 k_1} n_{k_1} (n_{k_1} - 1) \\ &\quad + (1 - \delta_{k_1 k_2}) n_{k_1} n_{k_2} (\delta_{k_1 k_3} \delta_{k_2 k_4} + \delta_{k_1 k_4} \delta_{k_2 k_3}) \qquad \text{(D.16)} \\ \langle n_1 n_2 \ldots | \, \hat{a}^\dagger_{k_1} a_{k_2} \, | n_1 n_2 \ldots \rangle &= \delta_{k_1 k_2} n_{k_1} \qquad \text{(D.17)}\end{aligned}$$

Inserting these relations in equation (D.1) and gathering the thermal average to the products of creators and annihilators, the following expression for the total energy is obtained

$$\langle H \rangle = \sum_{k_1} h_{k_1 k_2} \langle n_{k_1} \rangle + \frac{1}{2} \sum_{k_1 \neq k_2} \underbrace{\langle n_{k_1} n_{k_2} \rangle}_{\langle n_{k_1} \rangle \langle n_{k_2} \rangle} [w_{k_1 k_2, k_2 k_1} + w_{k_1 k_2, k_1 k_2}] + \frac{1}{2} \sum_k (\langle n_k^2 \rangle - \langle n_k \rangle) w_{kk,kk}$$

In order to make the same transformation into the basis of the ideal system for the first two terms in the interaction part, it is necessary that the sums run over all k_1 and k_2. The error that arises by replacing the sum over $k_1 \neq k_2$ by a sum over all k_1, k_2 needs to be countervailed by subtracting the term $\sum_k \langle n_k \rangle^2 w_{kk,kk}$. Additionally the second moment of the bosonic occupation numbers in the grand canonical ensemble has to be replaced by a term consisting of the first moment of the occupation numbers. For that purpose, the following calculation is done:

$$\begin{aligned}\langle n_k \rangle &= \frac{1}{e^{\beta(\varepsilon_k - \mu)} - 1} &\Rightarrow\qquad & e^{\beta(\varepsilon_k - \mu)} = 1 + \frac{1}{\langle n_k \rangle} \\ < n_k^2 > &= \frac{e^{\beta(\varepsilon_k - \mu)} + 1}{(e^{\beta(\varepsilon_k - \mu)} - 1)^2} &\Rightarrow\qquad & < n_k^2 > = 2 < n_k >^2 + < n_k > \ . \qquad \text{(D.18)}\end{aligned}$$

This can be inserted in the expression for $\langle H \rangle$. Expressing the matrix elements with respect to eigenstates of $\hat{h}$ yields the following term for the total energy:

$$\begin{aligned}\langle H \rangle &= \sum_l \varepsilon_l^0 \langle n_l \rangle + \frac{1}{2} \sum_{l_1 \ldots l_4} [w_{l_1 l_2, l_4 l_3} + w_{l_1 l_2, l_3 l_4}] \langle \hat{a}^\dagger_{l_1} \hat{a}_{l_3} \rangle \langle \hat{a}^\dagger_{l_2} \hat{a}_{l_4} \rangle \\ &+ \frac{1}{2} \sum_k (\langle n_k^2 \rangle - \langle n_k \rangle - 2 \langle n_k \rangle^2) w_{kk,kk} \\ &= \sum_l \varepsilon_l^0 \langle n_l \rangle + \frac{1}{2} \sum_{l_1 \ldots l_4} [w_{l_1 l_2, l_4 l_3} + w_{l_1 l_2, l_3 l_4}] \langle \hat{a}^\dagger_{l_1} \hat{a}_{l_3} \rangle \langle \hat{a}^\dagger_{l_2} \hat{a}_{l_4} \rangle \\ &+ \frac{1}{2} \sum_k ((2 \langle n_k \rangle^2 + \langle n_k \rangle) - \langle n_k \rangle - 2 \langle n_k \rangle^2) w_{kk,kk} \\ &= \sum_l \varepsilon_l^0 \langle n_l \rangle + \frac{1}{2} \sum_{l_1 \ldots l_4} [w_{l_1 l_2, l_4 l_3} + w_{l_1 l_2, l_3 l_4}] \langle \hat{a}^\dagger_{l_1} \hat{a}_{l_3} \rangle \langle \hat{a}^\dagger_{l_2} \hat{a}_{l_4} \rangle \qquad \text{(D.19)}\end{aligned}$$

The additional term is canceled, and the same effective Hamiltonian as for the fermionic case is obtained (see Eq. (D.12)), but with a changed sign of the exchange term.

D.2.1 Problems for Bose systems

In practice, one can obtain the effective Hamilton operator $\hat{H}_{\text{eff}}$ by iteratively finding its eigensystem. Effects that arise from the particle number fluctuation in the grand canonical ensemble are negligible for fermions. For bosons this is not the case (see section 2.4). Another calculation is done here that emphasizes the fact that a grand canonical treatment is not suitable for Bose systems with fixed particle number N even if the mean value of N coincides with the particle number of the considered system.

The effective one-body Hamiltonian $\hat{H}_{\text{eff}}$ can also be obtained by an approximate expansion of the two-body density in terms of the reduced one-body density matrix:

$$\mathbf{n}(x,y) = n(x)n(y) + |\mathfrak{g}(x,y)|^2 \tag{D.20}$$

For a system with fixed particle number N, the two-body density should be normalized by

$$\int \mathrm{d}x\,\mathrm{d}y\;\mathbf{n}(x,y) = N(N-1)\;, \tag{D.21}$$

whereas the expansion in (D.20) gives

$$\begin{aligned}\int \mathrm{d}x\,\mathrm{d}y\; n(x)n(y) + &\underbrace{|\mathfrak{g}(x,y)|^2}_{=|\sum_i n_i\varphi_i^*(x)\varphi_i(y)|^2} \\ = N^2 + \sum_{ij} n_i n_j &\underbrace{\int \varphi_i^*(x)\varphi_j(x)\,\mathrm{d}x}_{=\delta_{ij}}\underbrace{\int \varphi_i(y)\varphi_j^*(y)\,\mathrm{d}y}_{=\delta_{ij}} \\ &= N^2 + \sum_i n_i^2\;. \end{aligned}\tag{D.22}$$

Which can impossibly be equal to the term in (D.21). Meanwhile, for fermions the last term in the latter equation would be signed with a minus and, for all occupation numbers being either one or zero, it coincides exactly with (D.21). This difference in the normalization of the two-body density is another explanation for the high difference of the Energy values with this Hartree-Fock approximation for bosons and an exact method (CI or PIMC).

E Computing the permanent of a matrix with Ryser's algorithm

As well as the determinant, the permanent of a Matrix is a special case of the so called immanent. Even though the definitions of both mappings are closely related to each other, the complexity of their computation differs substantially. While the determinant can be calculated in polynomial time[1] by Gaussian elimination, for the permanent, it is still uncertain, if an algorithm for its calculation in polynomial time even exists. The existence of such an algorithm would imply $P = NP$ in computational complexity theory, which is one of the Millennium Prize Problems [36][1]. In the analytical calculations for the UBHF-Method, the Leibniz-formula for the calculation of the permanent of an $m \times m$-matrix was used:

$$\mathrm{per}(\underline{A}) = \sum_{\pi \in S_m} \prod_{i=1}^{m} a_{i\pi(i)} \ . \tag{E.1}$$

This formula serves as the definition of the permanent and its complexity is given by the term $(m-1)m!$, which grows even faster than any exponential function. Moreover, there is an algorithm that is analog to the Laplacian expansion of a determinant:

$$\mathrm{per}(\underline{A}) = \sum_{i=1}^{m} a_{ij} \mathrm{per}(A_{ij}) \qquad \text{for all } j. \tag{E.2}$$

The minor matrix A_{ij} is the matrix that is obtained by removing the jth column and the ith row from A. As this algorithm is still super-exponential it is not suitable for computational implementation.

The best known algorithm for the computation of the permanent of an arbitrary matrix was developed 1963 by H.J. Ryser and is named after him [57]. The Ryser formula can be written in the following, compact way:

$$\mathrm{per}(\underline{A}) = \sum_{P \subseteq \{1,\ldots,m\}} (-1)^{m-|P|} \prod_{i=1}^{m} \sum_{j \in P} a_{ij} \ , \tag{E.3}$$

where $|P|$ denotes the cardinality of the set P. The set of all subsets of $\{1,\ldots,m\}$ is called the power set of $\{1,\ldots,m\}$ and has 2^m elements. Thus, the complexity of Ryser's formula is $m^2 \cdot 2^m$.

One possibility to reach larger particle numbers in UBHF is to set a certain number of particles in the same orbital (see section 4.6.3). For the calculation of the related permanents, this would mean that some columns and some rows of the matrix $\underline{A}$ are the same. The frequency of each column (row) vector can be expressed by a ν_c-tuple

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[1] For more explanations see the footnotes in section 3.4.

(ν_r-tuple) $\mathbf{n}_c$ ($\mathbf{n}_r$) of integer numbers – where ν_c (ν_r) denotes the number of different columns (rows). In this case it is sufficient to store the matrix by just dealing with the columns that differ from each other. E.g. let $\tilde{a}_{ij}$ denote the matrix component with frequency n_{cj} in column direction and n_{ri} in row direction. With this notation, the sum over all subsets in (E.3) can be replaced by a sum over all partitions $\mathbf{n}'$, with the property

$$n'_i \leq n_{ci} \qquad \text{for all } i \ , \tag{E.4}$$

which will be denoted with $\mathbf{n}' \prec \mathbf{n}_c$ and called a subpartition of $\mathbf{n}_c$. This is because the sum over all subsets would contain many summands that are equal, e.g. if the first and the second column of $\underline{A}$ are equal, then the subsets that are obtained by removing the element 1 or the element 2 of $\{1, \ldots, m\}$ yield the same summand in (E.3). The set of all subsets of $\{1, \ldots, m\}$ has, in general, a higher cardinality than the set of all subpartitions of a tuple with the sum of all components equal to m. Thus, in addition to replacing the sum over all subsets by a sum over all subpartitions, one has to build in a combinatorial factor, that takes into account how many possibilities exist to obtain the partition $\mathbf{n}'$ by removing a certain number of columns from a matrix with $\mathbf{n}_c$ as partition for its columns. The factor is composed as a product of factors for each component of the tuple $\mathbf{n}'$. As there are $\binom{n_{cl}}{n'_l}$[1] ways to select n'_l indistinguishable objects from n_{cl}, the total factor for each summand is $\prod_{l=1}^{\nu_c} \binom{n_{cl}}{n'_l}$. Thus, by considering matrices with some rows or columns to be equal, one obtains the following formula from the Ryser formula:

$$\mathrm{per}(\underline{A}) = \sum_{\mathbf{n}' \prec \mathbf{n}_c} \prod_{l=1}^{\nu_c} \binom{n_{cl}}{n'_l} (-1)^{m-|\mathbf{n}'|} \prod_{i=1}^{\nu_c} \left(\sum_{j=1}^{\nu_r} n_{rj} \tilde{a}_{ij} \right)^{n'_i} . \tag{E.5}$$

In this case $|\mathbf{n}'|$ denotes the sum of all components of the partition $\mathbf{n}'$. This variant of the Ryser formula is not present in the literature, but its correctness has been (positively) tested by comparing its numerical implementation with an implementation of the original version (E.3).

A good tutorial for the implementation of the Ryser algorithm is given on the web site `http://www.codeproject.com/KB/applications/RyserPermanent.aspx` .

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[1] binomial coefficient

F Occupation numbers in the canonical ensemble

The mean occupation numbers of ideal systems in equilibrium for both particle types fermions and bosons are well known in the case of a grand canonical ensemble

$$\langle n_k \rangle = \frac{1}{e^{\beta(\epsilon_k - \mu)} - \zeta} \qquad \text{with } \zeta = \begin{cases} +1 & \text{, for bosons} \\ -1 & \text{, for fermions} \end{cases} , \tag{F.1}$$

with ϵ_k being the energy of the kth orbital and μ the chemical potential of the system. Unfortunately, it is not possible to give a closed expression for the occupation numbers in the canonical ensemble. In this appendix a recursion relation for the canonical partition function $Z(N, \beta)$, the occupation numbers $\langle n_k \rangle (N, \beta)$, and the correlations of the occupation numbers $\langle n_k n_l \rangle (N, \beta)$ dependent upon the inverse temperature β and particle number N is derived for both particle types[1].

Two common ways exist to represent symmetrized product states. One way is the so called occupation number representation, which is usually used in literature. The other possibility to represent a (anti-)symmetrized product state is by only giving the orbitals that are occupied. E.g. $|i_1, i_2, \ldots, i_N\rangle$ means that one particle is in orbital i_1, another is in orbital i_2 and so on. For fermions, all orbitals $i_1, \ldots, i_N$ have to be different, while for bosons they don't. If a summation over all these states is performed – as is needed for the trace, a double counting of the states has to be avoided by introducing an ordering of these states. Note that e.g. the states $|i_1, i_2, \ldots, i_N\rangle$ and $|i_2, i_1, \ldots, i_N\rangle$ differ at most by a phase factor. A double counting is avoided by considering only states that fulfill

$$i_N \underset{(-)}{<} i_{N-1} \underset{(-)}{<} \cdots \underset{(-)}{<} i_2 \underset{(-)}{<} i_1 \tag{F.2}$$

with

$$\underset{(-)}{<} \quad = \quad \begin{cases} \leqslant & \text{, for bosons} \\ < & \text{, for fermions} \end{cases} \tag{F.3}$$

This ordering is used in the following expression of the occupation number $\langle n_k \rangle_N (\beta)$ of a N-particle system (multiplied by the partition $Z_N(\beta)$ function of the system)

$$Z_N(\beta) \langle n_k \rangle_N (\beta) = \sum_{i_N \underset{(-)}{<} i_{N-1}} \cdots \sum_{i_2 \underset{(-)}{<} i_1} e^{-\beta \sum_{s=1}^{N} \epsilon_{i_s}} \underbrace{n_k(i_1, \ldots, i_N)}_{:= \sum_{s=1}^{N} \delta_{k i_s}} \tag{F.4}$$

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[1] Even though fermions are not the topic of this thesis, I take the freedom and present this in my opinion beautiful calculation that I have never seen in literature.

For a simpler notation of the sums, the sum over a multi-index in introduced by

$$\sum_{i_N \underset{(-)}{\leq} i_{N-1}} \cdots \sum_{i_2 \underset{(-)}{\leq} i_1} \cdots = \sum_{\mathbf{i}\in I_{N,\zeta}} \cdots \,, \tag{F.5}$$

where the index set $I_{N,\zeta}$ fulfills the ordering given in Eq. (F.2), in compliance to the value of ζ.

The summand in (F.4) vanishes if none of the summation indices $i_1, \ldots, i_N$ equals k. Thus it is convenient to pick out one index i_N and fix it to k. For bosons, the remaining sum runs over the same range of indices but with one index fewer and the occupation counter n_k has to be incremented by 1. For fermions it is the same, but if one of the remaining indices equals k, the summand has to vanish due to the Pauli principle. This is guaranteed by replacing $n_k(\mathbf{i})$ with $\zeta n_k(\mathbf{i}) + 1$. Thus,

$$Z_N(\beta)\left\langle n_k\right\rangle_N(\beta) = e^{-\beta\epsilon_k} \sum_{\mathbf{i}\in I_{N-1,\zeta}} e^{-\beta\sum_{s=1}^{N-1}\epsilon_{i_s}}\left(\zeta n_k(i_1,\ldots,i_{N-1})+1\right)\,, \tag{F.6}$$

with ζ given in (F.1). The last expression can be further simplified:

$$\begin{aligned} & e^{-\beta\epsilon_k}\zeta \underbrace{\sum_{\mathbf{i}\in I_{N-1,\zeta}} e^{-\beta\sum_{s=1}^{N-1}\epsilon_{i_s}} n_k(\mathbf{i})}_{=Z_{N-1}(\beta)\langle n_k\rangle_{N-1}(\beta)} + e^{-\beta\epsilon_k}\underbrace{\sum_{\mathbf{i}\in I_{N-1,\zeta}} e^{-\beta\sum_{s=1}^{N-1}\epsilon_{i_s}}}_{=Z_{N-1}(\beta)} \\ &\qquad = e^{-\beta\epsilon_k} Z_{N-1}(\beta)(\left\langle n_k\right\rangle_{N-1}(\beta)+\zeta) \end{aligned} \tag{F.7}$$

$$\Longrightarrow \boxed{Z_N(\beta)\left\langle n_k\right\rangle_N(\beta) = e^{-\beta\epsilon_k} Z_{N-1}(\beta)\Big(\zeta\left\langle n_k\right\rangle_{N-1}(\beta)+1\Big)\,.} \tag{F.8}$$

This equation coincides with the one given in [18]. E.g. for two particles, one obtains

$$Z_2(\beta)\left\langle n_k\right\rangle_2(\beta) = e^{-\beta\epsilon_k}(\zeta\underbrace{Z_1(\beta)\left\langle n_k\right\rangle_1(\beta)}_{e^{-\beta\epsilon_k}} + Z_1(\beta)) = \zeta e^{-2\beta\epsilon_k} + e^{-\beta\epsilon_k} Z_1(\beta) \tag{F.9}$$

Inserting this expression in the equation for $N = 3$ and so on, leads to

$$\boxed{Z_N(\beta)\left\langle n_k\right\rangle_N(\beta) = \sum_{n=1}^{N}\zeta^{n+1} Z_{N-n}(\beta) e^{-\beta n\epsilon_k}\,,} \tag{F.10}$$

with the definition

$$Z_0(\beta) \equiv 1\,. \tag{F.11}$$

In the canonical ensemble, the particle number is fixed. Thus the sum over the occupation numbers of all orbitals equals N. This identity can be used for the determination of the occupation numbers, by summing equation (F.10) over all k.

$$\underbrace{Z_N(\beta)\sum_k\left\langle n_k\right\rangle_N(\beta)}_{N} = \sum_{n=1}^{N}\zeta^{n+1} Z_{N-n}(\beta)\underbrace{\sum_k e^{-\beta n\epsilon_k}}_{Z_1(n\beta)} \tag{F.12}$$

$$\Longrightarrow \boxed{Z_N(\beta)N = \sum_{n=1}^{N} \zeta^{n+1} Z_{N-n}(\beta) Z_1(n\beta)\ .} \tag{F.13}$$

This relation is also given for the special case of only bosonic particles in [13]. The equations (F.13) and (F.10) are sufficient to calculate all occupation numbers of a given system.

For the derivation of a recursion relation for the correlation of the occupation numbers $\langle n_k n_l \rangle_N(\beta)$, consider its definition given by the sum

$$Z_N(\beta)\langle n_k n_l \rangle_N(\beta) = \sum_{\mathbf{i}\in I_{N,\zeta}} e^{-\beta\sum_{s=1}^{N}\epsilon_{i_s}} n_k(\mathbf{i}) n_l(\mathbf{i}) \tag{F.14}$$

Just as for the derivative of equation (F.8), one component of the multyindex i_N can be fixed to the value k and the occupation counter n_k can be replaced by $\zeta n_k + 1$. For the remaining sum it is necessary to factor in that in the case $k = l$, i_N is also fixed to l, hence, n_l has to be replaced by $n_l + \delta_{kl}$:

$$\begin{aligned} Z_N(\beta)\langle n_k n_l \rangle_N(\beta) &= e^{-\beta\epsilon_k} \sum_{\mathbf{i}\in I_{N-1,\zeta}} e^{-\beta\sum_{s=1}^{N-1}\epsilon_{i_s}} (\zeta n_k(\mathbf{i}) + 1)(n_l(\mathbf{i}) + \delta_{kl}) \\ &= e^{-\beta\epsilon_k} \sum_{\mathbf{i}\in I_{N-1,\zeta}} e^{-\beta\sum_{s=1}^{N-1}\epsilon_{i_s}} \Big(\zeta \underset{\to\langle n_k n_l\rangle_{N-1}(\beta)}{n_k(\mathbf{i}) n_l(\mathbf{i})} \\ &\qquad + \underset{\to\langle n_l\rangle_{N-1}(\beta)}{n_l(\mathbf{i})} + \zeta \underset{\to\langle n_k\rangle_{N-1}(\beta)}{\delta_{kl} n_k(\mathbf{i})} + \delta_{kl}\Big) \end{aligned}$$

$$\Longrightarrow \boxed{Z_N\langle n_k n_l \rangle_N = e^{-\beta\epsilon_k} Z_{N-1}\Big(\zeta\langle n_k n_l\rangle_{N-1} + \langle n_l\rangle_{N-1} + \delta_{kl}(\zeta\langle n_k\rangle_{N-1} + 1)\Big)\ .} \tag{F.15}$$

For a better overview, the β dependence has been omitted, since all quanities in this equation depend on the same temperature. This equation allows to calculate efficiently the correlations of the occupation numbers $\langle n_k n_l \rangle$, which are needed for calculating e.g. the heat capacity c_V of the system. I haven't found this equation in the literature, but it has been positively tested by comparing the results obtained by this equation with results obtained by Eq. (F.14).

G List of (frequently) used abbreviations and symbols

Abbreviation	Explanation
UBHF	Unrestrestricted bosonic Hartree-Fock
GP	Gross-Pitaevskii (Approximation)
MOMF	Multi orbital mean-field
CI	Configuration interaction
MCHB	Multi configurational Hartree for bosons
ROBDM	Reduced one-body density matrix
ROBDO	Reduced one-body density operator
ONS	Orthonormal set (of vectors, with respect to the considered scalarproduct)
CONS	Complete orthonormal set (of vectors, with respect to the considered scalarproduct)
BEC	Bose-Einstein condensation
PIMC	Path integral Monte-Carlo
TDSE	Time-dependent Schrödinger equation
TDUBHF	Time-dependent unrestricted Bosonic Hartree-Fock
TDVP	Time-dependent variational principle

Table G.1: List of abbreviations used in this work.

Symbol	Explanation
$\mathfrak{g}(x, y)$	One-body density matrix
$\mathbf{n}(x, x')$	Two-body density (probability density of finding one particle at site x and another at x')
$n(x)$	One-body density (probability density of finding a particle at x)
$\hat{1}$	Unit operator of the considered vector space
$\|\Psi\rangle$	Vector built by a Cartesian product of single particle orbitals
$\|\Phi\rangle$	Symmetrised product state of the orbitals contained as components in $\|\Psi\rangle$
$\|\Phi_{i_1 i_2 \dots}\rangle$	Symmetrised product state of the orbitals contained as components in $\|\Psi\rangle$ except the orbitals $\|i_1\rangle, \|i_2\rangle \dots$
$w_{ij,kl}$	Two-particle integrals (A.5)
$\hat{A}$	Abstract operator
$\underline{A}$	Matrix
$\underline{\hat{A}}$	Operator compound of blocks of operators arranged in a matrix, acting on a spinor.
$\vec{r}$	Vector in coordinate space
$\mathbf{k}$	A tuple of entities
S_N	Symmetric group of the numbers $1, \dots, N$ (set of all permutations)
$\|1\rangle \otimes \|2\rangle$	Tensor product of the vectors $\|1\rangle$ and $\|2\rangle$. In some literature, the operation symbol $\otimes$ is omitted.
$\|i_1 \dots i_n)$	Short notation for the tensor product $\|i_1\rangle \otimes \dots \otimes \|i_n\rangle$.
$\binom{n}{k}$	Binomial coefficient

Table G.2: Explanation of the symbols used in this work.

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Die vorliegende Arbeit ist von mir selbständig und nur unter Zuhilfenahme der angegebenen Quellen und Hilfsmittel angefertigt worden.

Kiel, den

(Ort) (Datum) (Unterschrift)