Foundations of Configuration Path Integral Monte Carlo Methods in the Grand Canonical Ensemble

Christian-Albrechts University
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Bachelor's Thesis

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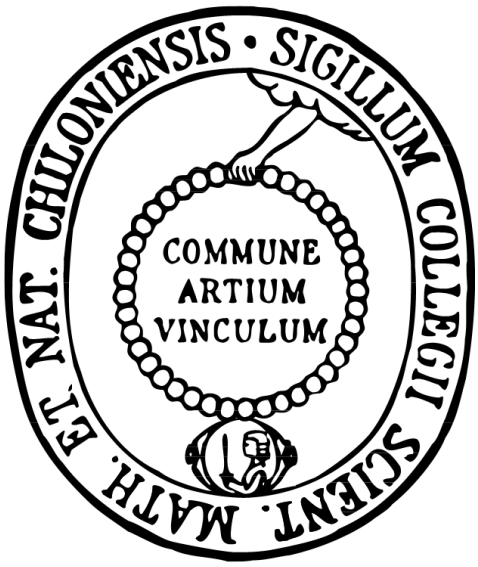

November, 2019

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Abstract

The Configuration Path Integral Monte Carlo (CPIMC) method constitutes an efficient approach for the computation of thermodynamic equilibrium quantities of warm dense matter states. A restraining factor of this method is the fermion sign problem. This problem is NP-hard, thus generally cannot be resolved, so one has to indirectly bypass it. This thesis lays the foundation for such an endeavour, by conducting a higher order Taylor expansion in the high temperature approximation for discrete numbers of M. It is expected that this may lead to a lower mean sign $\langle s \rangle'$, therefore reducing the sign problem. For the case of the uniform electron gas estimators and Monte Carlo steps are calculated, providing the theoretical foundations for a possible implementation.

Zusammenfassung

Die Configuration Path Integral Monte Carlo (CPIMC) Methode stellt eine effiziente Möglichkeit der Berechnung von thermodynamischen Eigenschaften warmer, dichter Materiezustände dar. Ein Beitrag der die Effizienz der Methode verringert, ist das fermionische Vorzeichenproblem. Da dieses NP-Schwer ist, deshalb nicht konventionell vereinfacht werden kann, muss man Methoden finden, um dieses indirekt zu verringern. Diese Arbeit stellt die Grundlage für eine solche Verbesserung dar. Durch einen, im Vergleich zu vorherigen Arbeiten, niedrigeren Fehler in der Hochtemperaturnäherung wird sich eine schnellere Konvergenz versprochen. Im Testsystem des homogenen Elektronengases werden Estimatoren und Monte Carlo Schritte vorgestellt, welche den Grundbaustein einer zukünftigen Implementierung legen.

Contents

1 Introduction

The investigated topic of this thesis is the description of warm dense matter. Matter in such a state is characterized by certain configurations of temperatures and densities, which lie between hot plasma and condensed matter. (Dornheim et al., 2018)
The description of warm dense matter states is of increasing interest, because it enables the possibility of studying important physical systems, such as the core of certain stars and planets or matter that is created in the inertial confinement fusion context.

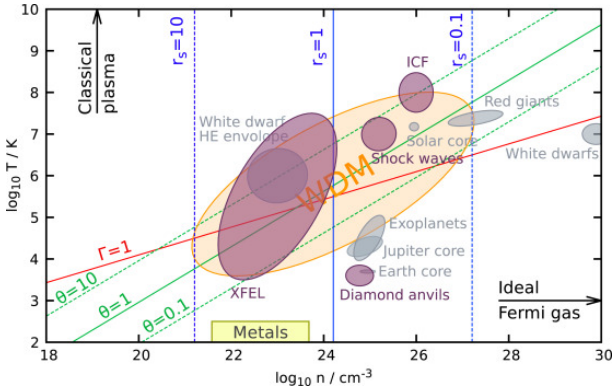


Figure 1: Warm dense matter (Dornheim et al., 2018)

However, there are difficulties in finding a suitable description of matter in such a state, because it is affected by quantum- and strong coupling effects. Thus the configuration path integral Monte Carlo (CPIMC) method was introduced which enables the calculating of properties in such a regime.
Since the introductory paper in 2011 (Schoof, Bonitz, Filinov, Hochstuhl, & Dufty, 2011) the method was further developed by Prof. Bonitz *et al.*. The current algorithm has successfully produced numerous measurements, which advanced the understanding of systems such as the uniform electron gas at warm dense matter conditions (Dornheim et al., 2018). In its current form, it is already highly optimized in for example utilizing the worm algorithm (Schoof, 2016) for the reduction of statistical variance of estimators or using parallelized code for the computation on the HLRN the computation of complex systems is achieved. The notorious bottleneck of the fermion sign problem, that is especially severe for weakly to moderately coupled systems and highly degenerated systems, still is limiting its efficiency.

Reducing the sign problem is important, but not easily feasible. The problem is NP-hard, thus cannot be generically solved (Troyer, Matthias & Wiese, Uwe-Jens, 2005). Hence the need for an indirect reduction of the problem arises. The main innovation of this thesis starts with the transition from

continuous time-slices to discrete times. This, of course, imposes an error. To then compensate this error, a higher order Taylor expansion in the high temperature approximation is applied.

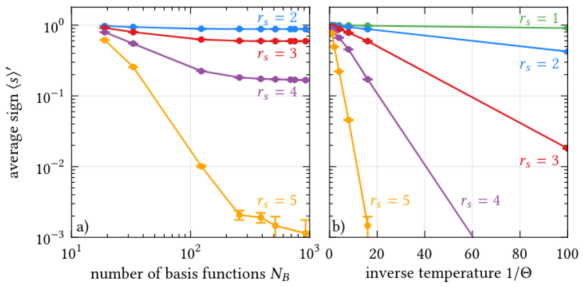


Figure 2: Sign problem (Schoof, 2016)

It is expected that this procedure has a positive impact on the sign problem. The smaller error in the Taylor-expansion translates to a smaller number of M that are necessary for the same accuracy of the simulation. Furthermore, fewer M directly implies a reduction of the sign problem, because the sign of different contributions in the sum, that is, to evaluate numerically, oscillates less. This thesis develops the theoretical principles of a higher order expansion in deriving the estimators of thermodynamic quantities and Monte Carlo steps in the test-system of the uniform electron gas. Thereby, the foundation for a possible implementation is set.

The literature that was used for this thesis focuses on the work that was done by Prof. Bonitz, Dr. Simon Groth, Dr. Tim Schoof, and lectures from Prof. Pehlke. It is also important to note that parts of this thesis were developed in collaboration with Jakob Nazarenus. The differences in the two works lie in e.g. the considered ensemble and the Monte Carlo steps. Complimentary results that are derived in the other thesis can be found in the appendix.

2 Theory

In this chapter, an introduction to the basic theory that is necessary for the understanding of this bachelor thesis is presented. First, the occupation number representation is introduced, since it is the formalism that is used for the description of quantum many-body systems in this thesis. Operators in this formalism are briefly outlined, and the Slater-Condon rules that describe the effect of a two-particle operator on an arbitrary state are introduced. For a more comprehensive overview of the formalism see (Schwabl, 2008), and (Schoof, 2011).
Following that, the density operator and the concept of the Grand canonical ensemble are introduced. Moreover, different realizations of systems in the Grand canonical ensemble are presented, and important correlations for the calculation of thermodynamic expectation values are provided.

2.1 Second quantization

Second quantization is a formalism that is used to efficiently describe quantum many-body systems. In this approach, a many-body state is represented in the Fock state basis, which can be constructed by assigning a number of identical particles to a single-particle state. An arbitrary quantum many-body state can then be expressed as a linear combination of aforementioned Fock states.
This description of a state through an occupation number is an important distinction from the first-quantization many-body wave function description. The occupation number formalism changes the required information for the sufficient description of a many-body state from "which particle is in which state" to "how many particles are in each state", thus eliminating redundancy that arises through the indistinguishability of quantum particles. This is demonstrated in the following chapters.

2.1.1 Slater determinants

Starting point for the derivation is the Hamiltonian of an ideal, N particle system.

$$\hat{H} = \sum_{\alpha=1}^{N} \hat{h}_\alpha \tag{1}$$

Here $\hat{h}_\alpha = \frac{\hat{p}_\alpha^2}{2m} + \hat{v}_\alpha$ denotes the single-particle Hamiltonian that consists of the kinetic energy operator $\frac{\hat{p}_\alpha^2}{2m}$ and the potential energy operator $\hat{v}_\alpha$ of the particle α. The wave function of the particle can be expressed as $\langle \mathbf{r}\sigma|\alpha\rangle = \psi_\alpha(\mathbf{r},\sigma) = \psi_\alpha(x)$. And, each particle is characterized by its position $\mathbf{r}$ as well as its spin σ. Therefore, both position- and spin coordinates are combined into the x coordinate. It is also important to note that in this thesis the natural units $\hbar = k_B = 1$ are used.

The N-particle eigenvalue problem $\hat{H}|\Psi\rangle = E|\Psi\rangle$ can be resolved by utilizing a solution that uses a product state of single-particle states $|i\rangle$. This is possible, because the Hamiltonian in (1) is separated into a sum of single-particle Hamiltonians.
One can express $|\Psi\rangle$ as a product state:

$$|\Psi\rangle = |i_1 i_2 \dots i_N\rangle = |i_1\rangle_1 |i_2\rangle_2 \dots |i_N\rangle_N$$

Where $|i_n\rangle_n$ denotes the n-th particle in the n-th orbital, the orbitals are labeled according to increasing energy eigenvalues, $\epsilon_1 \leq \epsilon_2 \leq \epsilon_3 \leq \dots$ and are assumed to form a complete orthonormal basis, $\langle i|j\rangle = \delta_{ij}$. Thus, the N-particle eigenvalue problem can be expressed in terms of the single-particle eigenvalue problem.

$$\hat{h}_\alpha|\alpha\rangle = \epsilon_\alpha|\alpha\rangle$$

This leads to a product state that is an eigenstate of the ideal Hamiltonian (1).

$$\sum_{\alpha=1}^{N} \hat{h}_\alpha |i_1\rangle_1 |i_2\rangle_2 \dots |i_N\rangle_N = \sum_{\alpha=1}^{N} \epsilon_{i_\alpha} |i_1\rangle_1 |i_2\rangle_2 \dots |i_N\rangle_N$$

Up until now, the assumption of indistinguishability of particles has not been accounted for. When considering the indistinguishability of quantum particles, one has to correctly anti-symmetrize states[1]. Anti-symmetry in states manifests itself in a sign change under particle exchange:

$$|\dots, i_\alpha, \dots, i_\beta, \dots\rangle_- = -|\dots, i_\beta, \dots, i_\alpha, \dots\rangle \tag{2}$$

[1]This is the case for fermions. When considering bosons, states have to be symmetric under particle exchange.

This can be implemented through the superposition of $N!$ permuted product states. The resulting anti-symmetric state has to fulfil the prerequisite that it remains an eigenstate of the Hamiltonian (1).

$$|i_1 i_2 \dots i_N\rangle_- = \frac{1}{\sqrt{N!}} \sum_{\mathcal{P}} (-1)^{\mathcal{P}} \ \hat{\mathcal{P}}(|i_1\rangle_1 \dots |i_N\rangle_N) \tag{3}$$

Here $\hat{\mathcal{P}}$ is the permutation operator, and $\mathcal{P}$ is the number of particle exchanges in $\hat{\mathcal{P}}$. This leads to the Slater determinant, which is the expression that describes the wave function of a multi-fermionic system.

$$\langle x_1 x_2 \dots x_N | i_1 i_2 \dots i_N\rangle_- = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_{i_1}(x_1) & \psi_{i_2}(x_1) & \dots & \psi_{i_N}(x_1) \\ \psi_{i_1}(x_2) & \psi_{i_2}(x_2) & \dots & \psi_{i_N}(x_2) \\ \vdots & \vdots & \vdots & \vdots \\ \psi_{i_1}(x_N) & \psi_{i_2}(x_N) & \dots & \psi_{i_N}(x_N) \end{vmatrix}$$

It is apparent that the structure of a determinant prohibits the occurrence of two or more particles with the same quantum number, because the determinant would disappear. This is also known as the Pauli principle.

2.1.2 Occupation number representation

The anti-symmetrization procedure in (3) results in the loss of information about which particle is in which single-particle state. A system is now uniquely defined by the number of occupied states and the number of particles they contain. The quantity n_i (that denotes the latter) is called an occupation number. Therefore, one can express an anti-symmetric state fully via occupation numbers:

$$|i_1 \dots i_N\rangle_- := |n_0 n_1 n_2 \dots\rangle := |\{n\}\rangle$$

With $|\{n\}\rangle$ as the occupation number vector[2]. For fermions these occupation numbers are either one or zero, i.e. $n_i \in \{0, 1\}$.

Additionally, important properties of the occupation number vectors are the completeness relation,

[2]These occupation number vectors are also called Fock states.

$$\sum_{\{n\}} |\{n\}\rangle\langle\{n\}| = \hat{1} \quad \text{with } \sum_{\{n\}} = \sum_{n_0=0}^{1} \sum_{n_1=0}^{1} \dots \tag{4}$$

as well as the orthogonality relation

$$\langle\{n\}|\{\tilde{n}\}\rangle = \delta_{\{n\},\{\tilde{n}\}} \tag{5}$$

2.1.3 Fermion creation and annihilation operators

The fermion creation- and annihilation operators are introduced below, along with their effects on an arbitrary Fock states.
The creation operator creates a particle in the orbital α, raising its occupation number n_α.

$$\hat{a}_\alpha^\dagger |\dots, n_\alpha, \dots\rangle = (1 - n_\alpha)(-1)^{\phi(0,\alpha,\{n\})} |\dots, n_\alpha + 1, \dots\rangle \tag{6}$$

The annihilation operator removes a particle from the orbital α.

$$\hat{a}_\alpha |\dots, n_\alpha, \dots\rangle = n_\alpha (-1)^{\phi(0,\alpha,\{n\})} |\dots, n_\alpha - 1, \dots\rangle \tag{7}$$

The prefactors $(n_\alpha - 1)$ in (6) and n_α in (7) ensure that the Pauli exclusion principle is always met, i.e. that an orbital can only be occupied by either no fermion or a single fermion. The phase factor

$$\phi(\beta, \alpha, \{n\}) = \sum_{\beta<\alpha} n_\beta \tag{8}$$

may cause a sign change, which depends on the occupation numbers of the preceding orbitals.
The occupation number operator can be expressed in terms of these operators

$$\hat{a}_\alpha^\dagger \hat{a}_\alpha |n_\alpha\rangle := \hat{n}_\alpha |n_\alpha\rangle = n_\alpha |n_\alpha\rangle$$

and is used for the introduction of the particle number operator $\hat{N} := \sum_\alpha \hat{n}_\alpha$.
Lastly, the transition of a particle from orbital α to orbital β is introduced.

$$\hat{a}_\beta^\dagger \hat{a}_\alpha |\dots, 1_\alpha, 0_\beta, \dots\rangle = |\dots, 0_\alpha, 1_\beta \dots\rangle$$

This transition can also be displayed using the following abbreviation:

$$\hat{a}_\beta^\dagger \hat{a}_\alpha |\{n\}\rangle = |\{n\}_\alpha^\beta\rangle$$

Using this simplified notation, multi-particle excitations are also able to be displayed. For example, a two-particle excitation can be described as:

$$\hat{a}_\beta^\dagger \hat{a}_\alpha \hat{a}_\gamma^\dagger \hat{a}_\delta |\{n\}\rangle = |\{n\}_{\alpha<\delta}^{\beta<\gamma}\rangle$$

2.1.4 Single-particle operators in second quantization

In second quantization, operators are expressed in terms of creation and annihilation operators. The expression for a single-particle operator in first quantization is of the form $\hat{A} = \sum_\alpha \hat{a}_\alpha$. Transitioning to the representation in second quantization leads to the following expression:

$$\hat{A} = \sum_{i,j=1}^{\infty} a_{ij} \hat{a}_i^\dagger \hat{a}_j$$

with $a_{ij} := \langle i|\hat{a}|j\rangle = \int \psi_i^*(x) a(x) \psi_j(x) dx$ as the single-particle integral. Note that the computation of a_{ij} requires the summation over σ and integration over $\mathbf{r}$.
For the computation of the matrix elements of $\hat{A}$, one can compute the matrix elements of the product of creation and annihilation operators, to then trace the result back to the initial problem.

$$\langle\{n\}|\hat{a}_\alpha^\dagger \hat{a}_\beta|\{\tilde{n}\}\rangle = \begin{cases} n_\alpha \delta_{\{n\},\{\tilde{n}\}}, & \text{if } \alpha = \beta \\ (-1)^{\phi(0,\alpha,\{n\})+\phi(0,\beta,\{\tilde{n}\})} \delta_{n_\alpha,1} \delta_{\tilde{n}_\alpha,0} \delta_{n_\beta,0} \delta_{\tilde{n}_\beta,1} \delta_{\{n\},\{\tilde{n}\}}^{\beta\alpha}, & \text{if } \alpha \neq \beta \end{cases}$$

With $\delta_{\{n\},\{\tilde{n}\}}^{\beta\alpha} := \prod_{\substack{i=0 \\ i\neq\alpha\neq\beta}}^{\infty} \delta_{n_i,\tilde{n}_i}$ as the generalized Kronecker delta. This then leads to the matrix element of an arbitrary single-particle operator in second quantization:

$$\langle\{n\}|\hat{A}|\{\tilde{n}\}\rangle := A_{\{n\},\{\tilde{n}\}} = \begin{cases} \sum_{i=0}^{\infty} a_{ii} n_i, & \text{if } \{n\} = \{\tilde{n}\} \\ a_{pq} (-1)^{\sum_{i=min(p,q)+1}^{max(p,q)-i} n_i}, & \text{if } \{n\} = \{\tilde{n}\}_q^p \\ 0, & \text{else} \end{cases}$$

The case structure of the matrix element shows that only certain combinations of states lead to a contribution. If $\{n\}$ and $\{\tilde{n}\}$ are identical, a

contribution to the diagonal matrix elements occurs. If $\{n\}$ and $\{\tilde{n}\}$ differ in exactly one orbital or two occupation numbers, then a contribution to the off-diagonal matrix elements occurs. This case can be described as a single-particle excitation.

To give the reader an example on how to utilise this information, matrix elements of the kinetic energy operator in the system of the uniform electron gas are computed in the following passage. It is important to note that the UEG[3] is described in the basis of k-space.
Starting point, of course, is the representation of the kinetic energy operator in second quantization.

$$\hat{T} = \sum_{i,j} t_{ij}\, \hat{a}^\dagger_{\mathbf{k}_j\sigma_j} \hat{a}_{\mathbf{k}_i\sigma_i}\,.$$

The single-particle integral t_{ij} is easily computable, because the momentum operator is diagonal.

$$t_{ij} = \left\langle \mathbf{k}_j\sigma_j \left| \frac{\hat{p}^2}{2} \right| \mathbf{k}_i\sigma_i \right\rangle = \frac{\mathbf{k}_i^2}{2} \langle \mathbf{k}_j\sigma_j | \mathbf{k}_i\sigma_i \rangle = \frac{\mathbf{k}_i^2}{2} \delta_{\mathbf{k}_j\mathbf{k}_i} \delta_{\sigma_j\sigma_i}\,,$$

With the momentum eigenvalues $\mathbf{p}_i = \hbar\mathbf{k}_i$. This yields the kinetic energy operator in occupation number representation:

$$\hat{T} = \sum_{i,j} \frac{\mathbf{k}_i^2}{2} \delta_{\mathbf{k}_j\mathbf{k}_i} \delta_{\sigma_j\sigma_i} \hat{a}^\dagger_{\mathbf{k}_j\sigma_j} \hat{a}_{\mathbf{k}_i\sigma_i} = \sum_i \frac{\mathbf{k}_i^2}{2} \hat{a}^\dagger_{\mathbf{k}_i\sigma_i} \hat{a}_{\mathbf{k}_i\sigma_i} = \sum_i \epsilon_i \hat{n}_i\,,$$

where $\epsilon_i := \frac{\mathbf{k}_i^2}{2}$ denotes the free electron energy.

Now, the matrix elements of $\hat{T}$ are computed. The occupation number operator is diagonal, hence one can replace the operator with its eigenvalues:

$$T_{\{n\},\{\tilde{n}\}} = \sum_{i=0}^{\infty} \epsilon_i n_i \langle n|\tilde{n}\rangle = \begin{cases} \sum_i \epsilon_i\, n_i, & \text{if } \{n\} = \{\tilde{n}\} \\ 0, & \text{else} \end{cases} \tag{9}$$

[3] A more comprehensive overview of the UEG is given in chapter (2.5)

2.1.5 Two-particle operators in second quantization

The expression for a two-particle operator in first quantization is of the form $\hat{W} = \frac{1}{2}\sum_{i\neq j=1}\hat{w}_{i,j}$, with $\hat{w}_{i,j}$ as the interaction operator of particle i and j. Transitioning to the representation in second quantization leads to the following expression

$$\hat{W} = \frac{1}{2}\sum_{i,j,k,l=0} w_{ijkl}\hat{a}_i^\dagger\hat{a}_j^\dagger\hat{a}_l\hat{a}_k$$

With the two-particle integrals $w_{ijkl} = \langle ij|\hat{w}|kl\rangle$. For the case of the Coulomb interaction the matrix element w_{ijkl} in the plain wave basis is given by the Fourier transform of the Coulomb potential.

$$w_{ijkl} = \frac{4\pi e^2}{L^3}\frac{\delta_{\mathbf{k}_i+\mathbf{k}_j,\mathbf{k}_k+\mathbf{k}_l}}{(\mathbf{k}_i-\mathbf{k}_k)^2} \tag{10}$$

The Kronecker delta $\delta_{\mathbf{k}_i+\mathbf{k}_j,\mathbf{k}_k+\mathbf{k}_l}$ enforces momentum conservation. Furthermore, the anti-symmetrized two-particle integrals $w^-_{ijkl} = w_{ijkl} - w_{ijlk}$ enables the rewriting of the pair-interaction operator.

$$\hat{W} = \sum_{i=0}^{\infty}\sum_{j=i+1}^{\infty}\sum_{k=0}^{\infty}\sum_{l=k+1}^{\infty} w^-_{ijkl}\hat{a}_i^\dagger\hat{a}_j^\dagger\hat{a}_l\hat{a}_k$$

The matrix elements of the two-particle operator in the N-particle Fock state basis can be compactly displayed via the Slater-Condon rules:

$$W_{\{n\},\{\tilde{n}\}} = \begin{cases} W^I = \sum_{i=0}^{\infty}\sum_{j=i+1}^{\infty} w^-_{ijij} n_i n_j, & \text{if } \{n\} = \{\tilde{n}\} \quad (11) \\ W^{II} = \sum_{\substack{i=0 \\ i\neq p,q}} w^-_{ipiq}(-1)^{\sum_{l=min(p,q)+1}^{max(p,q)-1} n_l} n_i, & \text{if } \{n\} = \{\tilde{n}\}^p_q \quad (12) \\ W^{III} = w^-_{pqrs}(-1)^{\sum_{l=p+1}^{q-1} n_l + \sum_{l=r+1}^{s-1}\tilde{n}_l}, & \text{if } \{n\} = \{\tilde{n}\}^{p<q}_{r<s} \\ 0, & \text{else .} \end{cases}$$

When comparing the matrix elements of a single-particle operator with those of the two-particle operator, it can be seen that there are additional contributions in the latter. This occurs, if the two states $\{n\}$ and $\{\tilde{n}\}$ differ in two orbitals. This case can be described as a two particle excitation.

2.2 Density operator and the Grand canonical ensemble

The Grand canonical ensemble(GCE) is a statistical ensemble that represents all possible states of a mechanical system that is in thermodynamic equilibrium and in contact with a reservoir. The system can exchange energy as well as particles with the reservoir, thus the particle number of the system is not fixed. The GCE is dependent on the two thermodynamic variables chemical potential μ and temperature T as well as the mechanical variable volume V. (Fließbach, 2018)
The thermodynamic properties of a system are determined by the density operator, which can be defined as the sum over all possible microstates with their respective probabilities

$$\hat{\rho} = \sum_{\alpha} P(|\Psi_\alpha\rangle)|\Psi_\alpha\rangle\langle\Psi_\alpha|$$

The index α denotes every possible state in the system and $P(|\Psi_\alpha\rangle)$ denotes the corresponding probability of observing such state. In the case of a system in the GCE, one can express the density operator as

$$\hat{\rho} = \frac{1}{Z}\exp(-\beta(\hat{H} - \mu\hat{N})) \qquad Tr(\hat{\rho}) = 1 \tag{13}$$

with

$$Z = Tr(\exp(-\beta(\hat{H} - \mu\hat{N}))) \tag{14}$$

as the grand canonical partition function that follows from the normalization of $\hat{\rho}$ and $\beta = 1/T$ as the inverse temperature. The trace is over all Fock states, i.e. includes states with arbitrary particle numbers N.

Of further interest is whether altering the considered statistical ensemble to the canonical ensemble influences the calculations in the following chapters. In the canonical ensemble the number of particles in the system is fixed and the contribution from the chemical potential μ is omitted. Thus, the diagonal contributions of the matrix elements change, the Monte Carlo steps in chapter (3.3) change, and the estimators of thermodynamic quantities change. An example for the latter change is the expectation value of the occupation number operator of an ideal Fermi gas. In the case of the GCE this quantity is easily computable, which changes in the canonical ensemble.

2.3 Ideal Fermi gas

The ideal Fermi gas is the quantum mechanical analogy of the ideal gas. It describes a number of non-interacting fermions, i.e. particles with a spin of $\frac{1}{2}$. For this chapter the "Theoretische Physik IV" lecture from Prof. Pehlke was used as a source. This chapter is included, because it demonstrates that non-interacting systems can be described rather easily. Furthermore, the derived expressions for the observables are later used in chapter (4), for the comparison with numerically computed results.

2.3.1 Partition function

As introduced in the previous chapter, the partition function (14) of a system describes its statistical properties. For the case of the ideal Fermi gas, the partition function can be calculated analytically.
Starting point of the computation is the consideration of the Hamiltonian of the system. The Hamiltonian of an ideal system $\hat{H}_0$ is undisturbed, hence its corresponding eigenvalue problem is trivial:

$$\hat{H}_0|\{n\}\rangle = \sum_\alpha \epsilon_\alpha n_\alpha |\{n\}\rangle$$

The partition function can now be calculated:

$$\begin{aligned}
Z(T,V,\mu) &= Tr(exp(-\beta(\hat{H}-\hat{N}\mu))) \\
&= \sum_{\{n\}} \langle\{n\}|exp(-\beta(\hat{H}-\hat{N}\mu))|\{n\}\rangle \\
&= \sum_{\{n\}} exp(-\beta(H_{\{n\},\{n\}} - N_{\{n\},\{n\}}\mu))\langle\{n\}|\{n\}\rangle \\
&= \sum_{\{n\}} exp(-\beta \sum_{i=0}^{\infty}(\epsilon_i - \mu)n_i) \\
&= \prod_{i=0}^{\infty} \sum_{n_1=0}^{1} \dots exp(-\beta \sum_{i=0}^{\infty}(\epsilon_i - \mu)n_i) \\
&= \prod_{i=0}^{\infty} (1 + exp(-\beta(\epsilon_i - \mu)))
\end{aligned}$$

The computation is analytically possible, because the matrix elements of the operators are entirely diagonal. Thus, the operators simply can be replaced with their eigenvalues.

2.3.2 Observables

The thermodynamic relations that are used for the calculation of observables can be derived from the general expression:

$$\begin{aligned}
\langle \hat{n}_j \rangle &= Tr(\hat{\rho}\ \hat{n}_j) \\
&= \sum_{\{n\}} \langle \{n\} | \hat{n}_j exp(-\beta(\hat{H} - \hat{N}\mu)) | \{n\} \rangle \\
&= \sum_{\{n\}} n_j exp(-\beta \sum_{i=0}^{\infty} (\epsilon_i - \mu) n_i) \\
&= -\frac{1}{\beta} \frac{\partial}{\partial \epsilon_j} \sum_{\{n\}} exp(-\beta \sum_{i=0}^{\infty} (\epsilon_i - \mu) n_i) \\
&= -\frac{1}{\beta} \frac{\partial}{\partial \epsilon_j} ln(Z) \Big|_{\beta,\mu,V} \\
&= \frac{1}{1 + exp(\beta(\epsilon_j - \mu))}
\end{aligned} \tag{15}$$

This quantity is also known as the Fermi distribution, which denotes the mean occupation number of a state with the energy ϵ_j. Additional observables can be calculated similarly. The fluctuation of the mean occupation number is given by the following expression:

$$\langle (\Delta \hat{n}_j)^2 \rangle = \frac{exp(\beta(\epsilon_i - \mu))}{(1 + exp(\beta(\epsilon_i - \mu)))^2} \tag{16}$$

The mean occupation number of the system can be calculated by considering the occupation number of each energy state.

$$\langle \hat{N} \rangle = \sum_{i=0}^{\infty} n_i = \sum_{i=0}^{\infty} \frac{1}{1 + exp(\beta(\epsilon_i - \mu))} \tag{17}$$

2.4 Non-ideal systems

The considered system now changes to one of interacting fermions. In contrast to the ideal Fermi gas in chapter (2.3), the Hamiltonian in this model contains contributions from particle interactions.

$$\hat{H} = \hat{T} + \hat{V} = \hat{H}_0 + \hat{W}$$

In this case the Hamiltonian and the interaction operator do not commute, $[\hat{H}_0, \hat{W}] \neq 0$. Therefore, the density operator $\hat{\rho}$ cannot be directly computed, as previously seen in (2.3.1). In the following chapters a method for approximating the density matrix is introduced, which will lead to the so-called Feynman path integral formulation of quantum mechanics. (Feynman, 1965) As a preliminary, the argument of the exponential function is assorted by diagonal and off-diagonal contributions:

$$\begin{aligned}
\hat{\rho} &= Tr(\exp(-\beta(\hat{H} - \hat{N}\mu))) \\
&= Tr(\exp(-\beta(\hat{D} + \hat{Y}))) \\
\hat{D} &= \hat{H}_0 + \hat{W}^I - \hat{N}\mu, && (18) \\
\hat{Y} &= \hat{W}^{II} + \hat{W}^{III} && (19)
\end{aligned}$$

The three contributions of the interaction potential, $\hat{W} = \hat{W}_I + \hat{W}_{II} + \hat{W}_{III}$, follow from the Slater-Condon rules (12). The matrix element of the diagonal part (18) contains kinetic energy as already seen in chapter (2.3), a mean field contribution from the interaction in the first Slater-Condon equation (11) as well as a contribution due to the chemical potential.

2.4.1 High temperature approximation

Now, the density matrix is transformed. The goal is to approximate the matrix, but such an endeavour introduces an error. This error providentially disappears with increasing temperatures, thus the temperature is artificially increased.

$$
\begin{aligned}
\rho_{\{n\},\{\tilde{n}\}} &= \frac{1}{Z}\langle\{n\}|\exp(-\beta(\hat{D}+\hat{Y}))|\{\tilde{n}\}\rangle \\
&= \frac{1}{Z}\langle\{n\}|(\exp(-\tilde{\beta}(\hat{D}+\hat{Y})))^M|\{\tilde{n}\}\rangle) \\
&= \frac{1}{Z}\sum_{\{n^{(1)}\}}\cdots\sum_{\{n^{(M-1)}\}}\langle\{n\}|\exp(-\tilde{\beta}(\hat{D}+\hat{Y}))|\{n^{(1)}\}\rangle\ldots \\
&\ldots\langle\{n^{(M-1)}\}|\exp(-\tilde{\beta}(\hat{D}+\hat{Y}))|\{\tilde{n}\}\rangle
\end{aligned} \tag{20}
$$

This is implemented with the introduction of the inverse of the M times higher temperature, $\tilde{\beta} = \beta/M$. The original exponent is expressed as a product of $M \in 2, 3, \ldots$ exponents. Between two successive factors, using the completeness relation (4), a set of new states is inserted. This procedure will result in the path integral representation in Fock space.

Furthermore, the partition function(14) can be transformed analogous to the density matrix.

$$
\begin{aligned}
Z &= \sum_{\{n\}}\langle\{n\}|exp(-\beta(\hat{D}+\hat{Y}))|\{n\}\rangle \\
&= \sum_{\{n\}}\langle\{n\}|\left[\exp(-\tilde{\beta}(\hat{D}+\hat{Y}))\right]^M|\{n\}\rangle \\
&= \sum_{\{n\}}\sum_{\{n^{(1)}\}}\cdots\sum_{\{n^{(M-1)}\}}\langle\{n\}|\exp(-\tilde{\beta}(\hat{D}+\hat{Y}))|\{n^{(1)}\}\rangle\ldots \\
&\ldots\langle\{n^{(M-1)}\}|\exp(-\tilde{\beta}(\hat{D}+\hat{Y}))|\{n\}\rangle
\end{aligned} \tag{21}
$$

For the calculation of the M matrix elements, a Taylor expansion up to second order is applied:

$$
\exp(-\tilde{\beta}(\hat{D}+\hat{Y})) = \hat{1} - \tilde{\beta}(\hat{D}+\hat{Y}) + \frac{1}{2}\tilde{\beta}^2(\hat{D}+\hat{Y})^2 + \mathcal{O}\left(\tilde{\beta}^3\right) \tag{22}
$$

This approximation introduces an error of $\mathcal{O}(\tilde{\beta}^3)$ for each expanded factor and an error of $\mathcal{O}(\tilde{\beta}^2)$ for the product of M factors (20). These errors are one magnitude smaller than in predecessing models, e.g. (Schoof, 2011), thus constituting the main innovation of this thesis. For the calculation of

the matrix element of the operator (22), the definition of the off-diagonal operators of the Hamiltonian (19) is applied and the term is expanded.

$$\begin{aligned}\exp(-\tilde{\beta}\hat{H}) &= \hat{1} - \tilde{\beta}(\hat{D} + \hat{W}^{II} + \hat{W}^{III}) \\ &+ \frac{1}{2}\tilde{\beta}^2(\hat{D}^2 + \hat{D}\hat{W}^{II} + \hat{W}^{II}\hat{D} + \hat{D}\hat{W}^{III} + \hat{W}_{III}\hat{D}) \\ &+ \frac{1}{2}\tilde{\beta}^2((\hat{W}^{II})^2 + \hat{W}^{II}\hat{W}^{III} + \hat{W}^{III}\hat{W}^{II} + (\hat{W}^{III})^2)\end{aligned}$$

The second order terms of the expansion contribute an expression, where two operators are successively applied. The evaluation of mixed states containing a diagonal operator is easily feasible:

$$\begin{aligned}(D^2)_{\{n\},\{\tilde{n}\}} &= \sum_{\{\bar{n}\}} \langle\{n\}|\hat{D}\{\bar{n}\}\rangle\langle\{\bar{n}\}|\hat{D}\{\tilde{n}\}\rangle = \left(D_{\{n\}}\right)^2 \delta_{\{n\},\{\tilde{n}\}} \\ (W^{II,III}D)_{\{n\},\{\tilde{n}\}} &= \sum_{\{\bar{n}\}} \langle\{n\}|\hat{W}^{II,III}\{\bar{n}\}\rangle\langle\{\bar{n}\}|\hat{D}\{\tilde{n}\}\rangle = W^{II,III}_{\{n\},\{\tilde{n}\}} D_{\{\tilde{n}\}} \\ \left(DW^{II,III}\right)_{\{n\},\{\tilde{n}\}} &= \sum_{\{\bar{n}\}} \langle\{n\}|\hat{D}\{\bar{n}\}\rangle\langle\{\bar{n}\}|\hat{W}^{II,III}\{\tilde{n}\}\rangle = D_{\{n\}} W^{II,III}_{\{n\},\{\tilde{n}\}}\end{aligned}$$

The computation of matrix elements with strictly non-diagonal operators cannot be done easily. The successive application of operators that alter the orbitals of a state enables the possibility for multiple contributions to a matrix element.
The computation of the matrix element $(W^{II})^2_{\{n\},\{\tilde{n}\}}$ was done in detail, for more insights on the calculation of the matrix elements, a graphical representation can be found in the appendix.

$$(W^{II})^2_{\{n\},\{\tilde{n}\}} = \begin{cases} \sum\limits_{\substack{p\neq q \\ p,q<N_B}} |\langle\{\tilde{n}\}^p_q|\hat{W}^{II}|\{\tilde{n}\}\rangle|^2, & \text{if } \{n\} = \{\tilde{n}\}, \\ \sum\limits_{\substack{i<N_B \\ i\neq p,q}} \langle\{n\}|\hat{W}^{II}|\{\tilde{n}\}^i_q\rangle\langle\{\tilde{n}\}^i_q|\hat{W}^{II}|\{\tilde{n}\}\rangle, & \text{if } \{n\} = \{\tilde{n}\}^p_q, \\ \sum\limits_{\substack{x\in\{r,s\} \\ y\in\{p,q\}}} \langle\{n\}|\hat{W}^{II}|\{\tilde{n}\}^y_x\rangle\langle\{\tilde{n}\}^y_x|\hat{W}^{II}|\{\tilde{n}\}\rangle, & \text{if } \{n\} = \{\tilde{n}\}^{p<q}_{r<s}, \\ 0, & \text{else.} \end{cases}$$

In the diagonal case, there is an excitation into an intermediate orbital from the first single-particle excitation, which is then undone. In the calculation of this specific contribution, every physically feasible[4] excitation into intermediate states has to be considered, hence the sum over all p, q. A constraint on the calculation is N_b, which denotes the threshold number of orbitals that are to be considered. This constraint is set to enable a more efficient numerical calculation of such a sum.
The next matrix element was computed likewise. $(W^{II}W^{III})_{\{n\},\{\tilde{n}\}} =$

$$\begin{cases} \sum\limits_{\substack{i,j<N_B \\ i\neq j \\ i,j\notin\{p,q\}}} \langle\{n\}|\hat{W}^{II}|\{\tilde{n}\}^{p,i}_{q,j}\rangle\langle\{\tilde{n}\}^{p,i}_{q,j}|\hat{W}^{III}|\{\tilde{n}\}\rangle, & \text{if } \{n\} = \{\tilde{n}\}^{p}_{q}, \\ \sum\limits_{\substack{i<N_B \\ x\in\{p,q\} \\ i\notin\{p,q,r,s\}}} \langle\{n\}|\hat{W}^{II}|\{\tilde{n}\}^{x,i}_{r,s}\rangle\langle\{\tilde{n}\}^{x,i}_{r,s}|\hat{W}^{III}|\{\tilde{n}\}\rangle, & \text{if } \{n\} = \{\tilde{n}\}^{p<q}_{r<s}, \\ \sum\limits_{\substack{a<b\in\{p,q,r\} \\ c<d\in\{s,t,u\}}} \langle\{n\}|\hat{W}^{II}|\{\tilde{n}\}^{a,b}_{c,d}\rangle\langle\{\tilde{n}\}^{a,b}_{c,d}|\hat{W}^{III}|\{\tilde{n}\}\rangle, & \text{if } \{n\} = \{\tilde{n}\}^{p<q<r}_{s<t<u}, \\ 0, & \text{else.} \end{cases}$$

Again, the matrix element was computed likewise. $(W^{III}W^{II})_{\{n\},\{\tilde{n}\}} =$

$$\begin{cases} \sum\limits_{\substack{i,j<N_B \\ i\neq j \\ i,j\notin\{p,q\}}} \langle\{n\}|\hat{W}^{III}|\{\tilde{n}\}^{i}_{j}\rangle\langle\{\tilde{n}\}^{i}_{j}|\hat{W}^{II}|\{\tilde{n}\}\rangle, & \text{if } \{n\} = \{\tilde{n}\}^{p}_{q}, \\ \sum\limits_{\substack{i<N_B \\ x\in\{r,s\} \\ i\notin\{p,q,r,s\}}} \langle\{n\}|\hat{W}^{III}|\{\tilde{n}\}^{i}_{x}\rangle\langle\{\tilde{n}\}^{i}_{x}|\hat{W}^{II}|\{\tilde{n}\}\rangle, & \text{if } \{n\} = \{\tilde{n}\}^{p<q}_{r<s}, \\ \sum\limits_{\substack{x\in\{s,t,u\} \\ y\in\{p,q,r\}}} \langle\{n\}|\hat{W}^{III}|\{\tilde{n}\}^{y}_{x}\rangle\langle\{\tilde{n}\}^{y}_{x}|\hat{W}^{II}|\{\tilde{n}\}\rangle, & \text{if } \{n\} = \{\tilde{n}\}^{p<q<r}_{s<t<u}, \\ 0, & \text{else.} \end{cases}$$

[4]Contributions that contain invalid intermediate states, e.g. excitation from an empty orbital, excitation into an occupied orbital, etc., are 0.

Lastly, the resulting matrix element is of the following form. $(W^{III})^2_{\{n\},\{\tilde{n}\}} =$

$$\begin{cases} \sum\limits_{\substack{r<s<N_B \\ p<q<N_B}} |\langle\{\tilde{n}\}^{p<q}_{r<s}|\hat{W}^{III}|\{\tilde{n}\}\rangle|^2, & \text{if } \{n\} = \{\tilde{n}\}\,, \\ \sum\limits_{\substack{i,j,k<N_B \\ i\neq j\neq k \\ j<k}} \langle\{n\}|\hat{W}^{III}|\{\tilde{n}\}^{j,k}_{q,i}\rangle\langle\{\tilde{n}\}^{j,k}_{q,i}|\hat{W}^{III}|\{\tilde{n}\}\rangle, & \text{if } \{n\} = \{\tilde{n}\}^{p}_{q}\,, \\ \sum\limits_{i<j<N_B} \langle\{n\}|\hat{W}^{III}|\{\tilde{n}\}^{i<j}_{r<s}\rangle\langle\{\tilde{n}\}^{i<j}_{r<s}|\hat{W}^{III}|\{\tilde{n}\}\rangle, & \text{if } \{n\} = \{\tilde{n}\}^{p<q}_{r<s}\,, \\ \sum\limits_{\substack{i<N_B \\ i\notin\{p,q,r,s,t,u\} \\ z\in\{p,q,r\} \\ x<y\in\{s,t,u\}}} \langle\{n\}|\hat{W}^{III}|\{\tilde{n}\}^{i,z}_{x,y}\rangle\langle\{\tilde{n}\}^{i,z}_{x,y}|\hat{W}^{III}|\{\tilde{n}\}\rangle, & \text{if } \{n\} = \{\tilde{n}\}^{p<q<r}_{s<t<u}\,, \\ \sum\limits_{\substack{c<d\in\{p,q,r,s\} \\ a<b\in\{t,u,v,w\}}} \langle\{n\}|\hat{W}^{III}|\{\tilde{n}\}^{c<d}_{a<b}\rangle\langle\{\tilde{n}\}^{c<d}_{a<b}|\hat{W}^{III}|\{\tilde{n}\}\rangle, & \text{if } \{n\} = \{\tilde{n}\}^{p<q<r<s}_{t<u<v<w}\,, \\ 0, & \text{else.} \end{cases}$$

With these results, it is now possible to compute all contributions to the matrix element of one factor of the approximated partition function. However, in order to obtain an actually useful representation, further efforts are necessary. This includes sorting the contributions of the matrix elements according to their order of excitation.

$$\Big(\exp(-\tilde{\beta}(D+Y))\Big)_{\{n\},\{\tilde{n}\}} \approx \begin{cases} A^{0T}_{\{n\},\{\tilde{n}\}}, & \text{if } \{n\} = \{\tilde{n}\}\,, \\ A^{1T}_{\{n\},\{\tilde{n}\}}, & \text{if } \{n\} = \{\tilde{n}\}^{p}_{q}\,, \\ A^{2T}_{\{n\},\{\tilde{n}\}}, & \text{if } \{n\} = \{\tilde{n}\}^{p<q}_{r<s}\,, \\ A^{3T}_{\{n\},\{\tilde{n}\}}, & \text{if } \{n\} = \{\tilde{n}\}^{p<q<r}_{s<t<u}\,, \\ A^{4T}_{\{n\},\{\tilde{n}\}}, & \text{if } \{n\} = \{\tilde{n}\}^{p<q<r<s}_{t<u<v<w}\,, \\ 0, & \text{else.} \end{cases} \tag{23}$$

Here A^{nT} denotes an excitation of n-th order, e.g. A^{1T} describes a single-particle excitation. The sorted contributions are specified in the following.

$$
\begin{aligned}
A^{0T}_{\{n\}} = \; & 1 - \tilde{\beta} D_{\{n\}} + \frac{1}{2}\tilde{\beta}^2 \Bigg[(D_{\{n\}})^2 + \underbrace{\sum_{\substack{p \neq q \\ p,q<N_B}} |\langle \{n\}^p_q | \hat{W}^{II} | \{n\} \rangle|^2}_{D^{II}_{\{n\}}} \\
& + \underbrace{\sum_{\substack{r<s<N_B \\ p<q<N_B}} |\langle \{n\}^{p<q}_{r<s} | \hat{W}^{III} | \{n\} \rangle|^2}_{D^{III}_{\{n\}}} \Bigg] \\
= \; & 1 - \tilde{\beta} D_{\{n\}} + \frac{1}{2}\tilde{\beta}^2 \left[(D_{\{n\}})^2 + D^{II}_{\{n\}} + D^{III}_{\{n\}} \right] \\
= \; & 1 - \tilde{\beta} \left[D_{\{n\}} - \frac{\tilde{\beta}}{2} D^{II}_{\{n\}} - \frac{\tilde{\beta}}{2} D^{III}_{\{n\}} \right] + \frac{1}{2}\tilde{\beta}^2 (D_{\{n\}})^2 \\
= \; & 1 - \tilde{\beta} \left[D_{\{n\}} - \frac{\tilde{\beta}}{2} D^{II}_{\{n\}} - \frac{\tilde{\beta}}{2} D^{III}_{\{n\}} \right] + \frac{1}{2}\tilde{\beta}^2 \left[D_{\{n\}} - \frac{\tilde{\beta}}{2} D^{II}_{\{n\}} - \frac{\tilde{\beta}}{2} D^{III}_{\{n\}} \right]^2 + \mathcal{O}\left(\tilde{\beta}^3\right) \\
= \; & \exp\left(-\tilde{\beta} \left[D_{\{n\}} - \frac{\tilde{\beta}}{2} D^{II}_{\{n\}} - \frac{\tilde{\beta}}{2} D^{III}_{\{n\}} \right] \right) + \mathcal{O}\left(\tilde{\beta}^3\right) \qquad (24)
\end{aligned}
$$

In the case of the no-particle excitation it is possible to reverse the Taylor expansion. The error in equation (24) that arises in the reversing process is of the same order as the error in the Taylor expansion of each factor of the density operator in (22). Thus, it won't be repeated in the further expressions.

All contributions to the matrix element of the single-particle excitations can be written as:

$$
\begin{aligned}
A^{1T}_{\{n\},\{\tilde{n}\}} \; = \; & -\tilde{\beta}\, W^{II}_{\{n\},\{\tilde{n}\}} + \frac{1}{2}\tilde{\beta}^2 \Bigg[\left(D_{\{n\}} + D_{\{\tilde{n}\}} \right) W^{II}_{\{n\},\{\tilde{n}\}} \\
& + \sum_{\substack{i<N_B \\ i \neq p,q}} \langle \{n\} | \hat{W}^{II} | \{\tilde{n}\}^i_q \rangle \langle \{\tilde{n}\}^i_q | \hat{W}^{II} | \{\tilde{n}\} \rangle \\
& + \sum_{\substack{i,j<N_B \\ i \neq j \\ i,j \notin \{p,q\}}} \langle \{n\} | \hat{W}^{III} | \{\tilde{n}\}^i_j \rangle \langle \{\tilde{n}\}^i_j | \hat{W}^{II} | \{\tilde{n}\} \rangle
\end{aligned}
$$

$$
\begin{aligned}
&+ \sum_{\substack{i,j<N_B \\ i\neq j \\ i,j\notin\{p,q\}}} \langle\{n\}|\hat{W}^{II}|\{\tilde{n}\}^{p,i}_{q,j}\rangle\langle\{\tilde{n}\}^{p,i}_{q,j}|\hat{W}^{III}|\{\tilde{n}\}\rangle \\
&+ \sum_{\substack{i,j,k<N_B \\ i\neq j\neq k \\ j<k}} \langle\{n\}|\hat{W}^{III}|\{\tilde{n}\}^{j,k}_{q,i}\rangle\langle\{\tilde{n}\}^{j,k}_{q,i}|\hat{W}^{III}|\{\tilde{n}\}\rangle\Bigg]
\end{aligned}
$$

Likewise, the contributions from two-particle excitations can be written as:

$$
\begin{aligned}
A^{2T}_{\{n\},\{\tilde{n}\}} &= -\tilde{\beta}\, W^{III}_{\{n\},\{\tilde{n}\}} + \frac{1}{2}\tilde{\beta}^2\Bigg[\left(D_{\{n\}} + D_{\{\tilde{n}\}}\right) W^{III}_{\{n\},\{\tilde{n}\}} \\
&+ \sum_{\substack{x\in\{r,s\} \\ y\in\{p,q\}}} \langle\{n\}|\hat{W}^{II}|\{\tilde{n}\}^{y}_{x}\rangle\langle\{\tilde{n}\}^{y}_{x}|\hat{W}^{II}|\{\tilde{n}\}\rangle \\
&+ \sum_{\substack{i<N_B \\ x\in\{p,q\} \\ i\notin\{p,q,r,s\}}} \langle\{n\}|\hat{W}^{II}|\{\tilde{n}\}^{x,i}_{r,s}\rangle\langle\{\tilde{n}\}^{x,i}_{r,s}|\hat{W}^{III}|\{\tilde{n}\}\rangle \\
&+ \sum_{\substack{i<N_B \\ x\in\{r,s\} \\ i\notin\{p,q,r,s\}}} \langle\{n\}|\hat{W}^{III}|\{\tilde{n}\}^{i}_{x}\rangle\langle\{\tilde{n}\}^{i}_{x}|\hat{W}^{II}|\{\tilde{n}\}\rangle \\
&+ \sum_{i<j<N_B} \langle\{n\}|\hat{W}^{III}|\{\tilde{n}\}^{i<j}_{r<s}\rangle\langle\{\tilde{n}\}^{i<j}_{r<s}|\hat{W}^{III}|\{\tilde{n}\}\rangle\Bigg]
\end{aligned}
$$

The contributions from three-particle excitations can be written as:

$$
\begin{aligned}
A^{3T}_{\{n\},\{\tilde{n}\}} &= \frac{1}{2}\tilde{\beta}^2\Bigg[\sum_{\substack{a<b\in\{p,q,r\} \\ c<d\in\{s,t,u\}}} \langle\{n\}|\hat{W}^{II}|\{\tilde{n}\}^{a,b}_{c,d}\rangle\langle\{\tilde{n}\}^{a,b}_{c,d}|\hat{W}^{III}|\{\tilde{n}\}\rangle \\
&+ \sum_{\substack{x\in\{s,t,u\} \\ y\in\{p,q,r\}}} \langle\{n\}|\hat{W}^{III}|\{\tilde{n}\}^{y}_{x}\rangle\langle\{\tilde{n}\}^{y}_{x}|\hat{W}^{II}|\{\tilde{n}\}\rangle \\
&+ \sum_{\substack{i<N_B \\ i\notin\{p,q,r,s,t,u\} \\ z\in\{p,q,r\} \\ x<y\in\{s,t,u\}}} \langle\{n\}|\hat{W}^{III}|\{\tilde{n}\}^{i,z}_{x,y}\rangle\langle\{\tilde{n}\}^{i,z}_{x,y}|\hat{W}^{III}|\{\tilde{n}\}\rangle\Bigg]
\end{aligned}
$$

Lastly, the contributions from four-particle excitations can be written as:

$$A^{4T}_{\{n\},\{\tilde{n}\}} = \frac{1}{2}\tilde{\beta}^2 \sum_{\substack{c<d\in\{p,q,r,s\}\\ a<b\in\{t,u,v,w\}}} \langle\{n\}|\hat{W}^{III}|\{\tilde{n}\}^{c<d}_{a<b}\rangle\langle\{\tilde{n}\}^{c<d}_{a<b}|\hat{W}^{III}|\{\tilde{n}\}\rangle$$

For later calculations the introduction of the off-diagonal term is needed

$$A^{\text{off}}_{\{n\},\{\tilde{n}\}} := A^{1T}_{\{n\},\{\tilde{n}\}} + A^{2T}_{\{n\},\{\tilde{n}\}} + A^{3T}_{\{n\},\{\tilde{n}\}} + A^{4T}_{\{n\},\{\tilde{n}\}}$$

2.4.2 Path integral

The derived results in the previous chapters allow for the so-called Feynman path integral formulation of the partition function. (Feynman, 1965)

$$Z = \sum_{\{n^{(0)}\}} \sum_{\{n^{(1)}\}} \cdots \sum_{\{n^{(M-1)}\}} \prod_{i=0}^{M-1} A_{\{n^i\},\{n^{i+1}\}} \tag{25}$$

In this representation, the classical notion of a single, unique trajectory for a system is replaced with a sum over all quantum-mechanically possible trajectories. Using the already derived expression for the partition function (25), the sum over all trajectories or paths can be described by the sum over all configuration of states $c = \{\{n^{(0)}\}, \cdots, \{n^{(M)}\}\}$.

This representation can be further enhanced. Another possibility of representing a configuration of states c is the kink-representation, which describes the change of states at given points in the path, rather than specifying each intermediate state. (Prokof'ev, Svistunov, & Tupitsyn, 1998) This allows all factors in which the state does not change to be summarised and therefore be calculated more efficiently. A path in kink-representation is defined by a 3-tuple $c_{\text{kink}} = \{K, (\{n^{(0)}\}, \ldots, \{n^{(K-1)}\}), (l_1, \ldots, l_K)\}$, where K is the number of kinks (i.e. changes of states in the path), l_i defines the position of the kink in the path, and $\{n^{(i)}\}$ denotes the state following the i-th kink. This leads to the following representation of the partition function:

$$
\begin{aligned}
Z &= \sum_{\substack{K=0 \\ K\neq 1}}^{M} \sum_{\substack{\{n^{(0)}\} \\ =\{n^{(K)}\}}} \sum_{\substack{\{n^{(1)}\} \\ \neq\{n^{(0)}\}}} \cdots \sum_{\substack{\{n^{(K-1)}\} \\ \neq\{n^{(K-2)}\} \\ \neq\{n^{(0)}\}}} \sum_{l_1=1}^{M-K+1} \sum_{l_2=l_1+1}^{M-K+2} \cdots \sum_{l_K=l_{K-1}+1}^{M} \\
&\quad \left(\prod_{i=0}^{K} (A^{0T}_{\{n^{(i)}\}})^{(l_{i+1}-l_i-1)} \right) \cdot \left(\prod_{i=0}^{K-1} A^{\text{off}}_{\{n^{(i)}\}\{n^{(i+1)}\}} \right) \\
&= \sum_{c_{\text{kink}}} w(c_{\text{kink}})
\end{aligned}
$$

with $\{n^{(0)}\} = \{n^{(M)}\}$. The exponential expression (24) can be inserted for A^{0T}. This allows for further simplifications.

$$
\begin{aligned}
w(c_{\text{kink}}) &= \exp\left(-\tilde{\beta} \sum_{i=0}^{K} (l_{i+1} - l_i - 1) \left[D_{\{n^{(i)}\}} - \frac{\tilde{\beta}}{2} D^{II}_{\{n^{(i)}\}} - \frac{\tilde{\beta}}{2} D^{III}_{\{n^{(i)}\}} \right] \right) \\
&\quad \cdot \prod_{i=0}^{K-1} A^{\text{off}}_{\{n^{(i)}\}\{n^{(i+1)}\}} \qquad (26)
\end{aligned}
$$

This formulation of the partition function, with the sum over all weights of configurations, is used in chapter (2.5.3) for the calculation of estimators and allows for the application of Monte Carlo methods in chapter (3).

2.5 Uniform electron gas

In the following, the results of the previous chapters are applied to a special case of many-fermion systems; the uniform electron gas (UEG). As the source for this chapter (Dornheim et al., 2018) was used. The UEG describes electrons in a cell with open boundary conditions, where the main simulation cell is periodically repeated in all directions. This is particularly important for the case of Coulomb interaction, due to its slow decay with the particle distance. This requires to take into account that not only do particles interact within the main simulation cell, but also with the periodic images of their partners. In the second quantization representation, this so-called Ewald interaction solely manifests itself in an addend in the Hamiltonian, which is called the Madelung constant ζ_M. An efficient realization of this

longe-range interaction is the Ewald summation. This approach leads to a modification of the Coulomb potential, this was studied in e.g. (Schoof, Groth, Vorberger, & Bonitz, 2015; Dornheim et al., 2018). In addition to this electron-electron Coulomb interaction, the interaction of the electrons with the positively charged background is also considered. This interaction leads to overall charge neutrality in the system.

The boundary conditions have implications on the wave function of a particle inside the box. A particle can be realised as a plane wave, which can be derived by solving the Schrödinger equation for this case. In coordinate representation (Dornheim et al., 2018):

$$\Psi_{\mathbf{k}\sigma}(\mathbf{r}, s) = \langle \mathbf{r}s|\mathbf{k}\sigma\rangle = \frac{1}{\sqrt{V}} e^{i\mathbf{k}\cdot\mathbf{r}}\, \delta_{s\sigma}$$

together with periodic boundary conditions. For any fixed box length L, this leads to a quantization of the of the wavenumbers, $\mathbf{k} \in \{\frac{2\pi}{L}\mathbf{n}; n \in \mathbb{Z}^3\}$. The particle in the orbital i is characterized by its momentum $\mathbf{k}_i$ as well as its spin projection σ_i. Each state is normalized to 1 whereas different orbitals are mutually orthogonal. Furthermore, it is important to note that momentum conservation has to be considered in this system[5].

2.5.1 Hamiltonian

The Hamiltonian of the system consists of the kinetic energy of the electrons, electron-electron interaction energy given by the Coulomb interaction as well as the Madelung constant:

$$\hat{H} = \sum_{i=1}^{N} \frac{\hat{p}_i^2}{2m} + \frac{e^2}{2} \sum_{i\neq j}^{N} \frac{1}{|\hat{\mathbf{r}}_i - \hat{\mathbf{r}}_j|} + \frac{\hat{N}}{2}\zeta_M = \hat{T} + \hat{W} + \frac{\hat{N}}{2}\zeta_M$$

The transformation of the Hamiltonian to the second quantization formalism using creation and annihilation operators, was done in chapter (2.1.4) and (2.1.5), where the momentum conservation now imposes a restriction on the matrix elements, hence single-particle excitations, e.g. $\hat{W}^{II}$ can be omitted.

[5] See the δ in (10)

$$H_{\{n\},\{\tilde{n}\}} = \begin{cases} \sum_i \epsilon_i n_i + \sum_{i=0}^{\infty} \sum_{j=i+1}^{\infty} w^-_{ijij} n_i n_j + \frac{\zeta_M}{2} \sum_i n_i, & \text{if } \{n\} = \{\tilde{n}\} \\ 0, & \text{if } \{n\} = \{\tilde{n}\}_p^q \,, \\ w^-_{pqrs}(-1)^{\alpha(p,q)+\alpha(r,s)}, \quad \alpha(p,q) = \sum_{l=p+1}^{q-1} n_l, & \text{if } \{n\} = \{\tilde{n}\}_{r<s}^{p<q} \,, \\ 0, & \text{else} \,. \end{cases}$$

To include the Madelung constant, the diagonal contribution to the density operator $\hat{D}$ (18) is modified.

$$\hat{D} := \hat{H}_0 + \hat{W}^I + \hat{N}(\frac{\zeta_M}{2} - \mu)$$

2.5.2 Simplification of matrix elements

As stated above, an important distinction from the general partition function is that, in the UEG, there are no single-particle excitations. Hence, these excitations are omitted in the Hamiltonian of the system. These changes are transitive, so the derived representation of the partition function (26) is affected. Applying the modified Hamiltonian yields:

$$A^{0T}_{\{n\}} = exp(-\tilde{\beta} \left[D_{\{n\}} - \frac{\tilde{\beta}}{2} D^{III}_{\{n\}} \right]) \tag{27}$$

$$A^{1T}_{\{n\},\{\tilde{n}\}} = \frac{\tilde{\beta}^2}{2} \sum_{\substack{i,j,k<N_B \\ i\neq j\neq k \\ j<k}} \left\langle \{n\}|\hat{W}^{III}|\{\tilde{n}\}^{j,k}_{q,i} \right\rangle \left\langle \{\tilde{n}\}^{j,k}_{q,i}|\hat{W}^{III}|\{\tilde{n}\} \right\rangle = 0 \,, \tag{28}$$

$$\begin{aligned} A^{2T}_{\{n\},\{\tilde{n}\}} = & -\tilde{\beta}\, W^{III}_{\{n\},\{\tilde{n}\}} + \frac{\tilde{\beta}^2}{2} \Big[\left(D_{\{n\}} + D_{\{\tilde{n}\}} \right) W^{III}_{\{n\},\{\tilde{n}\}} \\ & + \sum_{i<j<N_B} \left\langle \{n\}|\hat{W}^{III}|\{\tilde{n}\}^{i<j}_{r<s} \right\rangle \left\langle \{\tilde{n}\}^{i<j}_{r<s}|\hat{W}^{III}|\{\tilde{n}\} \right\rangle \Big] \,, \end{aligned} \tag{29}$$

$$A^{3T}_{\{n\},\{\tilde{n}\}} = \frac{\tilde{\beta}^2}{2} \sum_{\substack{i<N_B \\ i\notin\{p,q,r,s,t,u\} \\ z\in\{p,q,r\} \\ x<y\in\{s,t,u\}}} \left\langle \{n\}|\hat{W}^{III}|\{\tilde{n}\}^{i,z}_{x,y} \right\rangle \left\langle \{\tilde{n}\}^{i,z}_{x,y}|\hat{W}^{III}|\{\tilde{n}\} \right\rangle \,, \tag{30}$$

$$A^{4T}_{\{n\},\{\tilde{n}\}} = \frac{\tilde{\beta}^2}{2} \sum_{\substack{c<d\in\{p,q,r,s\}\\ a<b\in\{t,u,v,w\}}} \left\langle \{n\}|\hat{W}^{III}|\{\tilde{n}\}^{c<d}_{a<b}\right\rangle \left\langle \{\tilde{n}\}^{c<d}_{a<b}|\hat{W}^{III}|\{\tilde{n}\}\right\rangle . \quad (31)$$

The restriction of momentum conversation also effects the matrix element $\left\langle \{\tilde{n}\}^{j,k}_{q,i}|\hat{W}^{III}|\{\tilde{n}\}\right\rangle$ in (28). It can be shown that this expression vanishes by formulating the momentum balance:

$$\begin{aligned} & \mathbf{k}_i + \mathbf{k}_p = \mathbf{k}_j + \mathbf{k}_k = \mathbf{k}_i + \mathbf{k}_q \\ \Leftrightarrow\ & \mathbf{k}_i + \mathbf{k}_p = \mathbf{k}_i + \mathbf{k}_q \\ \Leftrightarrow\ & \mathbf{k}_p = \mathbf{k}_q \\ \Leftrightarrow\ & p = q \quad \lightning \end{aligned}$$

The matrix elements of equations (27), (29) as well as (30) all contain sums over all orbitals, which can be restricted to intermediate states that conserve momentum. Likewise, between the final state $\langle\{n\}|$ and the initial state $|\{\tilde{n}\}\rangle$ the momentum has to be conserved. For the sake of further simplification, a function o is defined as $o(\mathbf{k}_i) = i$. Furthermore, let $\{n\}_o$ be the set of occupied orbitals in the state $\{n\}$.

$$\begin{aligned} A^{0T}_{\{n\}} &= \exp\left(-\tilde{\beta} D_{\{n\}} + \frac{\tilde{\beta}^2}{2} \sum_{\substack{r<s\in\{n\}_o\\ p<q<N_b\\ q=o(\mathbf{k}_r+\mathbf{k}_s-\mathbf{k}_p)}} \left| \left\langle \{n\}^{p<q}_{r<s}|\hat{W}^{III}|\{n\}\right\rangle \right|^2 \right) , \\ A^{2T}_{\{n\},\{\tilde{n}\}} &= -\tilde{\beta}\, W^{III}_{\{n\},\{\tilde{n}\}} + \frac{\tilde{\beta}^2}{2}\Big[\left(D_{\{n\}} + D_{\{\tilde{n}\}}\right) W^{III}_{\{n\},\{\tilde{n}\}} \\ &\quad + \sum_{\substack{i<j<N_B\\ j=o(\mathbf{k}_r+\mathbf{k}_s-\mathbf{k}_i)}} \left\langle \{n\}|\hat{W}^{III}|\{\tilde{n}\}^{i<j}_{r<s}\right\rangle \left\langle \{\tilde{n}\}^{i<j}_{r<s}|\hat{W}^{III}|\{\tilde{n}\}\right\rangle \Big] , \\ A^{3T}_{\{n\},\{\tilde{n}\}} &= \frac{\tilde{\beta}^2}{2} \sum_{\substack{z\in\{p,q,r\}\\ x<y\in\{s,t,u\}\\ i=o(\mathbf{k}_x+\mathbf{k}_y-\mathbf{k}_z)\\ i\notin\{p,q,r,s,t,u\}}} \left\langle \{n\}|\hat{W}^{III}|\{\tilde{n}\}^{i,z}_{x,y}\right\rangle \left\langle \{\tilde{n}\}^{i,z}_{x,y}|\hat{W}^{III}|\{\tilde{n}\}\right\rangle , \\ A^{4T}_{\{n\},\{\tilde{n}\}} &= \frac{\tilde{\beta}^2}{2} \sum_{\substack{c<d\in\{p,q,r,s\}\\ a<b\in\{t,u,v,w\}}} \left\langle \{n\}|\hat{W}^{III}|\{\tilde{n}\}^{c<d}_{a<b}\right\rangle \left\langle \{\tilde{n}\}^{c<d}_{a<b}|\hat{W}^{III}|\{\tilde{n}\}\right\rangle . \end{aligned}$$

In this representation of the matrix elements the run time for the computation of each sum is reduced. While the sums in $A^{3T}_{\{n\},\{\tilde{n}\}}$ and $A^{4T}_{\{n\},\{\tilde{n}\}}$ can now be computed in constant time, the sum in $A^{2T}_{\{n\},\{\tilde{n}\}}$ is now computed with $\mathcal{O}(N_b)$ addends. For the sum in $A^{0T}_{\{n\}}$ each of the $\binom{N}{2} \in \mathcal{O}(N^2)$ pairs of occupied orbitals r and s has to be considered. Additionally, i runs over all basis orbitals, which leads to a run time of $\mathcal{O}(N^2 \cdot N_b)$.

2.5.3 Estimators

The protruding goal of this thesis is the computation of thermodynamic expectation values with a Monte Carlo procedure. This requires the expectation value of an observable $\hat{O}$ to be of the form (Schoof, 2011)

$$\langle \hat{O} \rangle = \frac{1}{Z} \sum_c O(c) w(c) \tag{32}$$

in order to use these methods for the computation. Here $O(c)$ only depends on the configuration and is called estimator for the observable $\hat{O}$.

In the following chapters, examples of the conversion of expectation values of quantities from their known thermodynamic representation, into a form that can be used for numerical simulations are presented. For the following chapters the diploma thesis (Schoof, 2011) was used as a source

2.5.4 Mean occupation number

The mean occupation number describes the average number of particles in a given system. It can be calculated by differentiating the partition function with respect to the chemical potential μ.

$$\begin{aligned}
\langle \hat{N} \rangle &= \frac{\beta}{Z} \frac{\partial}{\partial \mu} Z \\
&= \frac{\beta}{Z} \sum_c \left\{ \frac{\partial exp(x)}{\partial \mu} \cdot \prod_{i=0}^{K-1} A^{off}_{\{n^{(i)}\}\{n^{(i+1)}\}} + exp(x) \frac{\partial}{\partial \mu} \prod_{i=0}^{K-1} A^{off}_{\{n^{(i)}\}\{n^{(i+1)}\}} \right\} \\
&= \frac{\beta}{Z} \sum_c \left\{ \prod_{i=0}^{K-1} A^{off}_{\{n^{(i)}\}\{n^{(i+1)}\}} \cdot exp(x) \frac{\partial}{\partial \mu} x \right\}
\end{aligned}$$

The derivative of x can be expressed as :

$$\begin{aligned}\frac{\partial}{\partial\mu}x &= \frac{\partial}{\partial\mu}\left\{ -\tilde{\beta}\sum_{i=0}^{K}\Delta l_i\left[D_{\{n^{(i)}\}}-\frac{\tilde{\beta}}{2}D^{III}_{\{n^{(i)}\}}\right]\right\} \\ &= -\tilde{\beta}\sum_{i=0}^{K}\Delta l_i\frac{\partial}{\partial\mu}D_{\{n^{(i)}\}} \\ &= \tilde{\beta}\sum_{i=0}^{K}\Delta l_i\ N_{\{n^{(i)}\}}\end{aligned} \tag{33}$$

Here $N_{\{n^{(i)}\}} = \sum_{j=0}^{\infty} n_j^{(i)}$ denotes the particle number of system in a given configuration, with $n_j^{(i)}$ as the occupation number of the orbital j in the configuration $\{n^{(i)}\}$. Furthermore, the abbreviation $\Delta l_i = l_{i+1} - l_i - 1$ was introduced. This yields the following estimator:

$$N(c) = \tilde{\beta}^2 M\sum_{i=0}^{K}\Delta l_i\ N_{\{n^{(i)}\}}$$

This result was then compared with the estimator of the occupation number $N'(c)$ in the first order Taylor expansion. As was to be expected, the estimators did not differ. Despite the difference in in the Taylor expansions, both systems generally are expected to maintain the same number of particles.

2.5.5 Mean orbital occupation number

In the second quantization representation, the mean occupation number of the orbital i is given by $n_i = \langle a_i^\dagger a_i\rangle$. The expectation value for the mean orbital occupation number $\langle n_i\rangle$ can be derived via differentiation of the partition function with respect to ϵ_i, see (Schoof, Groth, & Bonitz, 2014):

$$\langle\hat{n}_i\rangle = \mathrm{Tr}(\hat{n}_i\hat{\rho}) = -\frac{1}{\beta}\frac{\partial}{\partial\epsilon_i}\ln(Z)$$

This yields the following expression for the expectation value[6]:

[6]For more insigths on the calculation, see chapter (6.5)

$$\langle n_x \rangle = \frac{1}{Z} \sum_c \Bigg[n_x^{eff} - \sum_{\substack{i<K \\ \Delta(\{n^{(i)}\},\{n^{(i+1)}\})=4}} \frac{\tilde{\beta}}{2M} \cdot \frac{(n_x^{(i)} + n_x^{(i+1)}) W^{III}_{\{n^{(i)}\}\{n^{(i+1)}\}}}{A^{2T}_{\{n^{(i)}\}\{n^{(i+1)}\}}} \Bigg] \cdot w(c)$$

Here, n_x^{eff} has been defined as: $n_x^{eff} := \frac{1}{M} \sum_{j=0}^{K} \Delta l_j \; n_x^{(j)}$ and the definition of x was introduced in (33).
The estimator of the mean orbital occupation number is given by:

$$n_x(c) = n_x^{eff} - \sum_{\substack{i<K \\ \Delta(\{n^{(i)}\},\{n^{(i+1)}\})=4}} \frac{\tilde{\beta}}{2M} \frac{(n_x^{(i)} + n_x^{(i+1)}) W^{III}_{\{n^{(i)}\}\{n^{(i+1)}\}}}{A^{2T}_{\{n^{(i)}\}\{n^{(i+1)}\}}}$$

This result was then compared to the estimator of a system with a lower Taylor expansion.

$$n'_x(c) = n_x^{eff}$$

This procedure reveals that the higher order expansion introduces additional contributions to the estimator.

2.5.6 One-particle density matrix

The one-particle density matrix describes the transition of particles from orbital i to j, thus constitutes a generalization of the occupation number operator. It is defined as $\hat{n}_{ij} = \hat{a}_i^\dagger \hat{a}_j$, with the expectation value

$$n_{ij} = \langle \hat{n}_{ij} \rangle = \mathrm{Tr}\, \hat{a}_i^\dagger \hat{a}_j \, \hat{\rho}$$

Diagonal matrix elements of the one-particle density matrix are the mean orbital occupation numbers $\langle \hat{n}_i \rangle$, which were introduced in the previous chapter. The estimator allows for an alternative formulation of the expectation value of an arbitrary single-particle operator, as introduced in (32)

$$\langle \hat{O} \rangle = \sum_{i,j=0}^{\infty} o_{ij} n_{ij}$$

If the Hamiltonian contains a single-particle potential[7], the matrix element can be computed through derivation of the partition function.

$$n_{ij} = \frac{1}{Z}\mathrm{Tr}\,\hat{a}_i^\dagger \hat{a}_j exp(-\beta(\hat{D}+\hat{Y}+\hat{V})) = -\frac{1}{\beta}\frac{\partial}{\partial v_{ij}}\ln Z \tag{34}$$

Here, $\hat{V}$ is the newly introduced single-particle potential.

$$\hat{V} = \sum_{i,j=0}^{\infty} v_{ij}\hat{a}_i^\dagger \hat{a}_j$$

In the following, the density matrix in the case of the UEG is calculated. As a preliminary, one can identify which contributions to the matrix elements are altered by the modified Hamiltonian. The matrix elements of a single-particle operator were already calculated in chapter (2.1.4).

$$V_{\{n\},\{\tilde{n}\}} = \begin{cases} V_I = \sum_{m=0}^{\infty} v_{mm} n_m, & \text{if } \{n\} = \{\tilde{n}\} \\ V^{II} = v_{pq}(-1)^{\alpha(p,q)}, & \text{if } \{n\} = \{\tilde{n}\}_q^p \\ 0, & \text{else .} \end{cases} \tag{35}$$

The matrix element has diagonal as well as single-particle excitation contributions, thus the external potential breaks the translation symmetry of the UEG.[8]
The computation of the density matrix has to be redone. The matrix elements of the single-particle potential (35) are added to their respective contributions to the density matrix (36). This yields the following expression:

[7] After computing the differentiation in equation (34), one can perform the limit $v_{ij} \to 0$ for the amplitude. Therefore, it is not necessary to perform simulations with an off-diagonal potential $\hat{V}$ included.

[8] This was studied e.g. in Ref. (Groth, Dornheim, & Bonitz, 2017).

$$\Big(\exp(-\tilde{\beta}(D+Y+V))\Big)_{\{n\},\{\tilde{n}\}} \approx \begin{cases} A^{0T}_{\{n\},\{\tilde{n}\}}, & \text{if } \{n\} = \{\tilde{n}\}\,, \\ A^{1T}_{\{n\},\{\tilde{n}\}}, & \text{if } \{n\} = \{\tilde{n}\}^{p}_{q}\,, \\ A^{2T}_{\{n\},\{\tilde{n}\}}, & \text{if } \{n\} = \{\tilde{n}\}^{p<q}_{r<s} \\ A^{3T}_{\{n\},\{\tilde{n}\}}, & \text{if } \{n\} = \{\tilde{n}\}^{p<q<r}_{s<t<u}\,, \\ A^{4T}_{\{n\},\{\tilde{n}\}}, & \text{if } \{n\} = \{\tilde{n}\}^{p<q<r<s}_{t<u<v<w}\,, \\ 0, & \text{else.} \end{cases} \tag{36}$$

The different contributions of the matrix element are specified in the appendix (6.3). With these results, one can rewrite the partition function to the path integral representation, as shown in chapter (2.3).

$$Z = \sum_{c} \exp(x) \cdot \prod_{m=0}^{K-1} A^{\text{off}}_{\{n^{(m)}\}\{n^{(m+1)}\}}$$

Here, x is the abbreviation for the expression below:

$$\begin{aligned} x &= -\tilde{\beta} \sum_{m=0}^{K} \Delta l_m \Bigg[D_{\{n^{(m)}\}} + V^{I}_{\{n^{(m)}\}} \\ &- \frac{\tilde{\beta}}{2} \sum_{\substack{p \neq q \\ p,q<N_B}} \langle \{n\} | \hat{V}^{II} | \{n\}^{p}_{q} \rangle \cdot \langle \{n\}^{p}_{q} | \hat{V}^{II} | \{\tilde{n}\} \rangle - \frac{\tilde{\beta}}{2} D^{III}_{\{n^{(m)}\}} \Bigg] \end{aligned}$$

The one-particle matrix is then calculated by derivation of the partition function (34).

$$\begin{aligned}
n_{ij} &= -\frac{1}{\beta}\frac{1}{Z}\frac{\partial}{\partial v_{ij}}Z \\
&= -\frac{1}{\beta}\frac{1}{Z}\sum_{c}\prod_{m=0}^{K-1}A^{\text{off}}_{\{n^{(m)}\}\{n^{(m+1)}\}}\frac{\partial}{\partial v_{ij}}exp(x) + exp(x)\frac{\partial}{\partial v_{ij}}\prod_{m=0}^{K-1}A^{\text{off}}_{\{n^{(m)}\}\{n^{(m+1)}\}} \\
&= -\frac{1}{\beta}\frac{1}{Z}\sum_{c}\prod_{m=0}^{K-1}A^{\text{off}}_{\{n^{(m)}\}\{n^{(m+1)}\}}\cdot exp(x)\frac{\partial}{\partial v_{ij}}x \\
&- \frac{1}{\beta}\frac{1}{Z}\sum_{c}exp(x)\sum_{m=0}^{K-1}\frac{\partial}{\partial v_{ij}}A^{\text{off}}_{\{n^{(m)}\}\{n^{m+1)}\}}\prod_{b\neq m}A^{\text{off}}_{\{n^{(b)}\}\{n^{(b+1)}\}}
\end{aligned}$$

The derivatives of x, and the off-diagonal contributions are now calculated separately. This procedure is not easily feasible, because one has to consider different combinations of measured orbitals i, j and orbitals that change from $\{n^{m+1}\}$ to $\{n^{m}\}$.

$$\begin{aligned}
\frac{\partial}{\partial v_{ij}}x &= -\tilde{\beta}\sum_{m=0}^{K}\Delta l_m\frac{\partial}{\partial v_{ij}}\Bigg[D_{\{n^{(m)}\}} + V^{I}_{\{n^{(m)}\}} \\
&- \frac{\tilde{\beta}}{2}\sum_{\substack{p\neq q\\ p,q<N_B}}\langle\{n\}|\hat{V}^{II}|\{n\}^{p}_{q}\rangle\cdot\langle\{n\}^{p}_{q}|\hat{V}^{II}|\{\tilde{n}\}\rangle - \frac{\tilde{\beta}}{2}D^{III}_{\{n^{(m)}\}}\Bigg] \\
&= \sum_{m=0}^{K}\Delta l_m\frac{\partial}{\partial v_{ij}}\left(-\tilde{\beta}V^{I}_{\{n^{(m)}\}} + \frac{\tilde{\beta}^2}{2}\sum_{\substack{p\neq q\\ p,q<N_B}}\langle\{n\}|\hat{V}^{II}|\{n\}^{p}_{q}\rangle\cdot\langle\{n\}^{p}_{q}|\hat{V}^{II}|\{\tilde{n}\}\rangle\right) \\
&= \sum_{m=0}^{K}\Delta l_m\frac{\partial}{\partial v_{ij}}\left(-\tilde{\beta}\sum_{\alpha}v_{\alpha\alpha}n_{\alpha} + \frac{\tilde{\beta}^2}{2}\sum_{\substack{p\neq q\\ p,q<N_B}}v_{pq}v_{qp}\right) \\
&= \sum_{m=0}^{K}\Delta l_m\left(-\tilde{\beta}n_i\delta_{ij} + \frac{\tilde{\beta}^2}{2}v_{ji}(1-\delta_{ij})\right)
\end{aligned}$$

For the computation of the derivative of x, one has to identify which matrix elements may contain a contribution. In the case of x, there are only two possibilities for this to occur, because of the prerequisite that the equation $\{n^m\} = \{n^{m+1}\}$ has to be fulfilled. First, in the case of equal orbital indices $i = j$, the matrix element of $\hat{V}^I$ contributes to the derivative. Following that, in the case that the orbital indices are not equal $i \neq j$, the matrix element of $\hat{V}^{II}$ may contribute. In the expression

$$\sum_{\substack{p \neq q \\ p,q<N_B}} \langle \{n\} | \hat{V}^{II} | \{n\}_q^p \rangle \cdot \langle \{n\}_q^p | \hat{V}^{II} | \{\tilde{n}\} \rangle$$

a particle is excited from orbital q to p, to then be de-excited to its starting orbitals. This yields the following expression:

$$\sum_{\substack{p \neq q \\ p,q<N_B}} v_{pq} v_{qp}$$

In the case of matching i,j and p,q, there is a contribution to the derivative. The same procedure is used for the computation of the derivatives of the off-diagonal matrix elements.

$$\frac{\partial}{\partial v_{ij}} A^{off}_{\{n^{(m)}\},\{n^{(m+1)}\}} = \frac{\partial}{\partial v_{ij}} \left(A^{1T}_{\{n^{(m)}\},\{n^{(m+1)}\}} + A^{2T}_{\{n^{(m)}\},\{n^{(m+1)}\}} + A^{3T}_{\{n^{(m)}\},\{n^{(m+1)}\}} \right)$$

First, the derivative of the single-particle excitation contributions are computed. Effectively, a particle is excited from orbital q to p, but different intermediate states in the excitation process impose a challenge in the calculation of the derivative.

$$
\begin{aligned}
\frac{\partial}{\partial v_{ij}} A^{1T}_{\{n\},\{\tilde{n}\}} &= -\tilde{\beta}\frac{\partial}{\partial v_{ij}} V^{II}_{\{n\},\{\tilde{n}\}} + \frac{1}{2}\tilde{\beta}^2 \frac{\partial}{\partial v_{ij}} \Bigg[\left(D_{\{n\}} + D_{\{\tilde{n}\}}\right) V^{II}_{\{n\},\{\tilde{n}\}} \\
&+ \sum_{\substack{x<N_B \\ x\neq p,q}} \langle \{n\}|\hat{V}^{II}|\{\tilde{n}\}^x_q\rangle\langle\{\tilde{n}\}^x_q|\hat{V}^{II}|\{\tilde{n}\}\rangle \\
&+ \sum_{\substack{x,y<N_B \\ x\neq y \\ x,y\notin\{p,q\}}} \langle \{n\}|\hat{W}^{III}|\{\tilde{n}\}^x_y\rangle\langle\{\tilde{n}\}^x_y|\hat{V}^{II}|\{\tilde{n}\}\rangle \\
&+ \sum_{\substack{x,y<N_B \\ x\neq y \\ x,y\notin\{p,q\}}} \langle \{n\}|\hat{V}^{II}|\{\tilde{n}\}^{p,x}_{q,y}\rangle\langle\{\tilde{n}\}^{p,x}_{q,y}|\hat{W}^{III}|\{\tilde{n}\}\rangle \Bigg],
\end{aligned}
$$

The different cases of non-disappearing derivatives are listed below:

Case 1 There is a contribution if $\hat{V}^{II}$ leads to a direct excitation. This can be described as $\{n\} = \{\tilde{n}\}^p_q = \{\tilde{n}\}^i_j$.

Case 2 In the expression $\sum_{\substack{x<N_B \\ x\neq p,q}} \langle \{n\}|\hat{V}^{II}|\{\tilde{n}\}^x_q\rangle\langle\{\tilde{n}\}^x_q|\hat{V}^{II}|\{\tilde{n}\}\rangle$, $\hat{V}^{II}$ excites a particle from orbital j to i. This state is then further excited into the final state q. This procedure can be written as $\{n\} = \{\tilde{n}\}^p_q = \{\tilde{n}\}^p_j$.

Case 3 Another possibility is that in $\sum_{\substack{x<N_B \\ x\neq p,q}} \langle \{n\}|\hat{V}^{II}|\{\tilde{n}\}^x_q\rangle\langle\{\tilde{n}\}^x_q|\hat{V}^{II}|\{\tilde{n}\}\rangle$, $\hat{V}^{II}$ excites a particle from orbital q into j, to then further excite it into orbital i. This can be written as $\{n\} = \{\tilde{n}\}^p_q = \{\tilde{n}\}^i_q$.

Case 4 In $\sum_{\substack{x,y<N_B \\ x\neq y \\ x,y\notin\{p,q\}}} \langle \{n\}|\hat{W}^{III}|\{\tilde{n}\}^x_y\rangle\langle\{\tilde{n}\}^x_y|\hat{V}^{II}|\{\tilde{n}\}\rangle$, $\hat{V}^{II}$ excites a particle from orbital j to i. This excitation is then undone by $\hat{W}^{III}$, which also excites a particle from orbital q to p.
In $\sum_{\substack{x,y<N_B \\ x\neq y \\ x,y\notin\{p,q\}}} \langle \{n\}|\hat{V}^{II}|\{\tilde{n}\}^{p,x}_{q,y}\rangle\langle\{\tilde{n}\}^{p,x}_{q,y}|\hat{W}^{III}|\{\tilde{n}\}\rangle$, $\hat{W}^{III}$ excites two particles into the orbitals p and j. The $\hat{V}^{II}$ operator then de-excites the

particle from orbital j to i. Both of these possibilities are characterized by contributions that stem from entirely intermediate states.

Lastly, the derivative can be compactly expressed in a case structure:
$\frac{\partial}{\partial v_{ij}} A^{1T}_{\{n^{(m)}\},\{n^{(m+1)}\}} =$

$$X' + (1-\delta_{ij}) \begin{cases} -\tilde{\beta}(-1)^{\alpha(i,j)} + \dfrac{\tilde{\beta}^2}{2}\left(D_{\{n^{(m)}\}} + D_{\{n^{(m+1)}\}}\right)(-1)^{\alpha(i,j)}, & \text{if case 1} \\ \dfrac{\tilde{\beta}^2}{2} v_{pi}(-1)^{\alpha(i,j)}(-1)^{\alpha(p,i)}, & \text{if case 2} \\ \dfrac{\tilde{\beta}^2}{2} v_{qj}(-1)^{\alpha(q,j)}(-1)^{\alpha(i,j)}, & \text{if case 3} \\ \dfrac{\tilde{\beta}^2}{2}(-1)^{\alpha(i,j)}\left(W^{III}_{\{n^p_q\},\{n^i_j\}} + W^{III}_{\{n^{p,j}_{q,i}\},\{n\}}\right), & \text{if case 4} \\ 0, & \text{else.} \end{cases}$$

The abbreviation $X' = \frac{\tilde{\beta}^2}{2} V^{II}_{\{n^{(m)}\},\{n^{(m+1)}\}}(n_i^{(m)} + n_i^{(m+1)})\delta_{ij}$ denotes the offset in all 4 cases. The reason for this offset can can be seen in the expression $V^{II}_{\{n^{(m)}\},\{n^{(m+1)}\}} \frac{\partial}{\partial v_{ij}}(V^I_{\{n^{(m)}\}} + V^I_{\{n^{(m+1)}\}})$ that is a result from the product rule in the derivation. Here, the sum in the matrix element of the $\hat{V}^I$ operator guarantees a contribution to the derivative while the $\hat{V}^{II}$ operator can match any case of excitation.
The derivative of the two-particle excitation contributions is computed likewise.

$$\begin{aligned} \frac{\partial}{\partial v_{ij}} A^{2T}_{\{n\},\{\tilde{n}\}} &= \frac{1}{2}\tilde{\beta}^2 \frac{\partial}{\partial v_{ij}} \Bigg[(D_{\{n\}} + D_{\{\tilde{n}\}}) W^{III}_{\{n\},\{\tilde{n}\}} \\ &+ \sum_{\substack{x\in\{r,s\} \\ y\in\{p,q\}}} \langle\{n\}|\hat{V}^{II}|\{\tilde{n}\}^y_x\rangle\langle\{\tilde{n}\}^y_x|\hat{V}^{II}|\{\tilde{n}\}\rangle \\ &+ \sum_{\substack{z<N_B \\ x\in\{p,q\} \\ z\notin\{p,q,r,s\}}} \langle\{n\}|\hat{V}^{II}|\{\tilde{n}\}^{x,z}_{r,s}\rangle\langle\{\tilde{n}\}^{x,z}_{r,s}|\hat{W}^{III}|\{\tilde{n}\}\rangle \end{aligned}$$

$$+ \sum_{\substack{z<N_B \\ x\in\{r,s\} \\ z\notin\{p,q,r,s\}}} \langle\{n\}|\hat{W}^{III}|\{\tilde{n}\}_x^z\rangle\langle\{\tilde{n}\}_x^z|\hat{V}^{II}|\{\tilde{n}\}\rangle \Bigg]$$

Here, there are 4 different cases for contributions:

Case 5 There is a contrribution if $\hat{W}^{III}$ excites into a state $\{n\} = \{\tilde{n}\}_q^p$, with $i, j \neq p, q$. Here, the matrix element of the $\hat{V}^I$ operator creates a contribution.

Case 6 In $\sum_{\substack{x\in\{r,s\} \\ y\in\{p,q\}}} \langle\{n\}|\hat{V}^{II}|\{\tilde{n}\}_x^y\rangle\langle\{\tilde{n}\}_x^y|\hat{V}^{II}|\{\tilde{n}\}\rangle$, one of the $\hat{V}^{II}$ operators excites a particle from orbital j to i, while the other operator excites a particle from orbital b to a. This can be written as $\{n\} = \{\tilde{n}\}_{j,b}^{i,a}$. With this simplified description of non-contributing orbitals $a := y \setminus i$ and $b := x \setminus j$, the problem of the indistinguishability of the particles is bypassed.

Case 7 In $\sum_{\substack{z<N_B \\ x\in\{p,q\} \\ z\notin\{p,q,r,s\}}} \langle\{n\}|\hat{V}^{II}|\{\tilde{n}\}_{r,s}^{x,z}\rangle\langle\{\tilde{n}\}_{r,s}^{x,z}|\hat{W}^{III}|\{\tilde{n}\}\rangle$, the $\hat{W}^{III}$ operator excites into the orbital x (either p or q) and an intermediate state j. The particle in the intermediate orbital j is then further excited into the orbital a that was not affected in the initial excitation.

Case 8 In $\sum_{\substack{z<N_B \\ x\in\{r,s\} \\ z\notin\{p,q,r,s\}}} \langle\{n\}|\hat{W}^{III}|\{\tilde{n}\}_x^z\rangle\langle\{\tilde{n}\}_x^z|\hat{V}^{II}|\{\tilde{n}\}\rangle$, $\hat{V}^{II}$ excites a particle from orbital j into an intermediate orbital i. The $\hat{W}^{III}$ operator then further excites this particle from i to either p or q. Furthermore, a particle is excited from orbital $b := x \setminus j$ to either p or q.

These contributions yield the case structure:

$$\frac{\partial}{\partial v_{ij}} A^{2T}_{\{n^{(m)}\},\{n^{(m+1)}\}} = X + (1-\delta_{ij}) \begin{cases} 0, & \text{if case 5} \\ \frac{\tilde{\beta}^2}{2} v_{ab} (-1)^{\alpha(a,b)} (-1)^{\alpha(i,j)}, & \text{if case 6} \\ \frac{\tilde{\beta}^2}{2} (-1)^{\alpha(i,j)} W^{III}_{\{\tilde{n}\}^{j,x}_{r,s},\{\tilde{n}\}}, & \text{if case 7} \\ \frac{\tilde{\beta}^2}{2} (-1)^{\alpha(i,j)} W^{III}_{\{\tilde{n}\}^{p,q}_{i,b},\{\tilde{n}\}^{i}_{j}}, & \text{if case 8} \\ 0, & \text{else.} \end{cases}$$

Again, the offset $X = \frac{\tilde{\beta}^2}{2} W^{III}_{\{n^{(m)}\},\{n^{(m+1)}\}} (n_i^{(m)} + n_i^{(m+1)}) \delta_{ij}$ is introduced.

The matrix element of the three-particle excitation contributions is computed likewise.

$$\begin{aligned} \frac{\partial}{\partial v_{ij}} A^{3T}_{\{n\},\{\tilde{n}\}} &= \frac{1}{2} \tilde{\beta}^2 \Bigg[\sum_{\substack{a<b\in\{p,q,r\} \\ c<d\in\{s,t,u\}}} \langle \{n\} | \hat{V}^{II} | \{\tilde{n}\}^{a,b}_{c,d} \rangle \langle \{\tilde{n}\}^{a,b}_{c,d} | \hat{W}^{III} | \{\tilde{n}\} \rangle \\ &+ \sum_{\substack{x\in\{s,t,u\} \\ y\in\{p,q,r\}}} \langle \{n\} | \hat{W}^{III} | \{\tilde{n}\}^{y}_{x} \rangle \langle \{\tilde{n}\}^{y}_{x} | \hat{V}^{II} | \{\tilde{n}\} \rangle \Bigg], \end{aligned}$$

Case 9 In this case, the only contributions stem from direct excitations. In each $\sum_{\substack{a<b\in\{p,q,r\} \\ c<d\in\{s,t,u\}}} \langle \{n\} | \hat{V}^{II} | \{\tilde{n}\}^{a,b}_{c,d} \rangle \langle \{\tilde{n}\}^{a,b}_{c,d} | \hat{W}^{III} | \{\tilde{n}\} \rangle$ and $\sum_{\substack{x\in\{s,t,u\} \\ y\in\{p,q,r\}}} \langle \{n\} | \hat{W}^{III} | \{\tilde{n}\}^{y}_{x} \rangle \langle \{\tilde{n}\}^{y}_{x} | \hat{V}^{II} | \{\tilde{n}\} \rangle$, $\hat{W}^{III}$ excites into random orbitals a from b and c from d. This can be written as $a, c, i \in \{p, q, r\}$ from $b, d, j \in \{s, t, u\}$

The derivative can be expressed in the following case structure: $\frac{\partial}{\partial v_{ij}} A^{3T}_{\{n^{(m)}\},\{n^{(m+1)}\}} =$

$$(1-\delta_{ij}) \begin{cases} \frac{\tilde{\beta}^2}{2} (-1)^{\alpha(i,j)} \left(W^{III}_{\{n^{a,c}_{b,d}\},\{\tilde{n}\}} + W^{III}_{\{n^{a,c}_{b,d}\},\{n^{i}_{j}\}} \right), & \text{if case 9} \\ 0, & \text{else.} \end{cases}$$

Now, the limit $v_{ij} \to 0$ is performed, leading to the following expressions:

$$\frac{\partial}{\partial v_{ij}} x \Big|_{v_{ij}=0} = \sum_{m=0}^{K} \Delta l_m \left(-\tilde{\beta} n_i \delta_{ij} \right)$$

The derivatives of the off-diagonal matrix elements maintain contributions. Performing the limit on the derivative of the one-particle excitations leads to: $\frac{\partial}{\partial v_{ij}} A^{1T}_{\{n^{(m)}\},\{n^{(m+1)}\}} \Big|_{v_{ij}=0} =$

$$(1-\delta_{ij}) \begin{cases} -\tilde{\beta}(-1)^{\alpha(i,j)} + \frac{\tilde{\beta}^2}{2} \Big(D_{\{n^{(i)}\}} + \ D_{\{n^{(i+1)}\}} \Big) (-1)^{\alpha(i,j)}, & \text{if case 1} \\ \frac{\tilde{\beta}^2}{2} (-1)^{\alpha(i,j)} \Big(W^{III}_{\{n^p_q\},\{n^i_j\}} + \ W^{III}_{\{n^{p,j}_{q,i}\},\{n\}} \Big), & \text{if case 4} \\ 0, & \text{else.} \end{cases}$$

Performing the limit on the derivative of the two-particle excitations leads to: $\frac{\partial}{\partial v_{ij}} A^{2T}_{\{n^{(m)}\},\{n^{(m+1)}\}} \Big|_{v_{ij}=0} =$

$$X + (1-\delta_{ij}) \begin{cases} 0, & \text{if case 5} \\ 0, & \text{if case 6} \\ \frac{\tilde{\beta}^2}{2} (-1)^{\alpha(i,j)} W^{III}_{\{\tilde{n}\}^{j,x}_{r,s},\{\tilde{n}\}}, & \text{if case 7} \\ \frac{\tilde{\beta}^2}{2} (-1)^{\alpha(i,j)} W^{III}_{\{\tilde{n}\}^{p,q}_{i,b},\{\tilde{n}\}^i_j}, & \text{if case 8} \\ 0, & \text{else.} \end{cases}$$

Lastly, performing the limit on the derivative of the three-particle excitations leads to: $\frac{\partial}{\partial v_{ij}} A^{3T}_{\{n^{(m)}\},\{n^{(m+1)}\}} \Big|_{v_{ij}=0} =$

$$(1-\delta_{ij}) \begin{cases} \frac{\tilde{\beta}^2}{2} (-1)^{\alpha(i,j)} \left(W^{III}_{\{n^{a,b}_{c,d}\},\{\tilde{n}\}} + W^{III}_{\{n^{a,b}_{c,d}\},\{n^i_j\}} \right), & \text{if case 9} \\ 0, & \text{else.} \end{cases}$$

These results show that the addition of an external potential leads to non-disappearing contributions, even after the amplitude of the potential was

omitted $v_{ij} \to 0$. This is particularly interesting for the A^{1T} contributions, considering the prerequisite of no single-particle excitations.
Lastly, the results can be used to obtain the estimator $n_{ij}(c)$:

$$n_{ij}(c) \;=\; \frac{1}{M}\sum_{m=0}^{K}\Delta l_m n_i\delta_{ij} - \frac{1}{\beta}\sum_{m=0}^{K-1}\frac{\left(\frac{\partial}{\partial v_{ij}}A^{off}_{\{n^{(m)}\},\{n^{(m+1)}\}}\right)}{A^{\text{off}}_{\{n^{(m)}\},\{n^{(m+1)}\}}}$$

The comparison of this result to the estimator of a lower Taylor expansion $n'_{ij}(c)$

$$n'_{ij}(c) = (-\tilde{\beta})^K\left[\frac{1}{M}\sum_{m=0}^{K}\Delta l_m n_i\delta_{ij} \;-\frac{1}{\beta}\sum_{m=0}^{K-1}\frac{(-1)^{\alpha(i,j)}(1-\delta_{ij})}{W^{III}_{\{n^{(m)}\},\{n^{(m+1)}\}}}\right]$$

shows that both estimators take on similar expression. The higher order Taylor expansion introduces several new contributions to the estimator.
This result was then validated by considering the estimator for matching orbital indices $i = j$ and comparing it to the estimator of the mean occupation number in the previous chapter.

$$n_{ii}(c) = \frac{1}{M}\sum_{m=0}^{K}\Delta l_m n_i - \frac{1}{\beta}\sum_{m=0}^{K-1}\frac{X}{A^{\text{2T}}_{\{n^{(m)}\},\{n^{(m+1)}\}}}$$

Thus, this demonstrates that the special case of $i = j$ can be derived from the one-particle density matrix.

3 Monte Carlo

In general, the sum (32) that denotes the calculation of an expectation value is high-dimensional, because numerous particles are to be considered in a given system. Therefore, a trivial approach of evaluating the sum is not efficient. Numerical methods, such as Monte Carlo approximations, are used to bypass this problem of the calculation, because their computation time does not scale with the dimensionality of the approximated sum (Bonitz & Semkat, 2006).

The expectation value of an arbitrary observable $\hat{O}$, that is in thermodynamic equilibrium, is defined as

$$\langle \hat{O} \rangle = \sum_x O(x) p(x) \tag{37}$$

with $p(x)$ as the probability distribution[9] and x as an arbitrary multi-variable. Applying a Monte Carlo scheme for the evaluation of the sum leads to

$$\langle \hat{O} \rangle = \frac{1}{N_{MC}} \sum_{i=0}^{N_{MC}} O(x_i) + \mathcal{O}(\frac{1}{\sqrt{N_{MC}}})$$

Here, a number of N_{MC} micro states x_i are sampled from $p(x)$. This so-called importance sampling ensures greater accuracy of the expectation value in comparison to a computation with the same number of N_{MC}, but with uniformly sampled micro states. This expression also presents one of the advantages of Monte Carlo approximations. The central limit theorem (Kwak, Sang Gyu & Kim, Jong Hae, 2017) states that the uncertainty of the quantity disappears with $N_{MC} \to \infty$. Therefore, one can virtually reach an arbitrary accuracy of the calculated observable, with sufficient computing power.

Substituting the probability with $p(c) = w(c)/Z$ leads to the representation of an expectation value that was introduced in (32).

$$\langle \hat{H} \rangle = \sum_c H(c) \frac{w(c)}{Z} \tag{38}$$

This representation imposes a new challenge, because the normalization Z is not necessarily known. A solution for this problem is presented in the following chapter.

[9] i.e. $p(x) \geqslant 0$ and $\sum_x p(x) = 1$

3.1 Metropolis–Hastings algorithm

In 1953, Metropolis *et al.* introduced an algorithm, which was later generalised by Hastings, that generates a sequence of random samples from a given distribution function without the knowledge of its normalization. (Metropolis, Arianna, Marshall, Rosenbluth, & A., 1953)
The creation of this so-called Markov chain $(C_0, \ldots, C_{N_{MC}})$ of samples can be illustrated via a simple framework:

- First the Markov chain has to be initiated with a randomly chosen initial state C_0
- For each iteration $i \in \{1, \ldots, N_{MC}\}$ that follows after C_0, preconditions such as the detailed balance equation[10] and ergodicty[11] have to be fulfilled:
  - Using the proposal density $Q(C_i \to C_i')$[12], a new possible configuration (Monte Carlo step) C_i' is generated
  - The probability of accepting such a configuration is computed
    $A(C_i \to C_i') = min\left[1, \frac{Q(C_i' \to C_i)w(C_i')}{Q(C_i' \to C_i)w(C_i)}\right]$
    In this step, the normalization disappears by using $p(x) = w(x)/Z$.
    $A(C_i \to C_i') = min\left[1, \frac{Q(C_i' \to C_i)p(C_i')}{Q(C_i' \to C_i)p(C_i)}\right]$
  - The proposed change is either accepted or rejected with a probability of $1 - A$:
    - Generate a random number $a \in [0, 1]$
    - Accept the change if $A(C_i \to C_i') > a$ and set $C_{i+1} = C_i'$
    - Reject the change if $A(C_i \to C_i') < a$ and set $C_{i+1} = C_i$
  - The framework is continued with the next iteration $i = i + 1$

When using this framework, it is important to note that a high number of samples leads to a better approximation of the desired distribution $p(x)$. One also has to consider the equilibrium time when using a Markov chain.

[10] The DBE is of the form $p(C_i)v(C_i \to C_i') = p(C_i')v(C_i' \to C_i)$ with $v(C_i \to C_i')$ as the transition probability from C_i to C_i'

[11] Every possible configuration has be reachable in a finite number of Monte Carlo steps

[12] In the implementation process an arbitrary proposal density may be chosen, with the prerequisite that the Monte Carlo steps are ergodic

Due to the randomly chosen initial state C_0, numerous iterations may be necessary to generate samples that are actually distributed according to the distribution $p(x)$. Therefore, an appropriate number of initial samples should be discarded from the Markov chain. It is also necessary to consider the autocorrelations between adjacent configurations. This correlation of samples can be compensated by only considering every n-th configuration.

3.2 Sign problem

A further aspect of the weight of a configuration $w(c)$ (38) that needs to be considered is that its sign is not necessarily positive. Therefore, it cannot be interpreted as a probability density. Different sources for these negative signs can be identified:
In the product of the off-diagonal matrix elements, the $\hat{W}^{III}$ [13] operator may induce a negative sign, depending on the configuration of $\{n^i\}$ and $\{n^{i+1}\}$.

To bypass this problem, one can ascribe the sign of the weight $s(x)$ to the estimator. This can be realized by changing the definition of an expectation value to:

$$\langle \hat{O} \rangle = \frac{\int O(x)s(x)p(x)'}{\int s(x)p(x)'} = \frac{\langle \hat{O}\hat{s} \rangle'}{\langle \hat{s} \rangle'}$$

Here, $\langle s \rangle'$ is the expectation value of the sign and $p(x)' = \frac{|p(x)|}{\int |p(x)|dx}$ is the probability that the configurations x are distributed in accordance with. In the case of an average sign $\langle \hat{s} \rangle'$ that is much smaller than 1, the expression $\langle \hat{O}\hat{s} \rangle'$ has to determined with a high accuracy in order to obtain a reliable result for $\langle \hat{O} \rangle$.
The expectation value of the mean sign $\langle s \rangle' = \frac{Z}{Z'} = exp(-\beta N(f - f'))$ is small in the case of large inverse temperatures β, large systems with a numerous particles N, and large differences in the free energy per particle of f and f'.
In this case, the relative error of the observable (Schoof, 2011) can be expressed as:

$$\frac{\Delta O}{\bar{O}} \sim \frac{\Delta s}{\bar{s}} \approx \frac{1}{\sqrt{N_{MC}}} exp(\beta N \Delta f)$$

This relation illustrates the fermion sign problem. The reduction of the relative error of the observable is severely inefficient in comparison to the scaling

[13] This can be seen in the Slater Condon rules in (12)

of the system.

In the past, there were numerous approaches for bypassing this problem, for example the permutation-blocking method (Dornheim, Groth, Filinov, & Bonitz, 2015). In this thesis, the approach of reformulating the partition function to a discrete time representation, with a lower error in the Taylor expansion (22), is taken. This procedure shows promise in reducing the sign problem, because a smaller number of time slices M (21) have to be used in order to obtain a similar accuracy in comparison with previous works. This is the case, because the error in (22) is lower by default. A smaller number of M should then affirmatively affect the mean sign $\langle s \rangle'$, because the individual signs of the different contributions oscillate less.

An additional, but more ambiguous, motivation for the chosen approach is the modification of the weight that a higher order expansion introduces. In previous works (Schoof, 2011), the weight $w'(c)$ was of the following form:

$$w'(c) = (-\tilde{\beta})^K exp(x') \prod_{i=0}^{K-1} W^{III}_{\{n^i\},\{n^{i+1}\}}$$

In the higher order Taylor expansion (26) the expression changes to

$$w(c) = exp(x) \prod_{i=0}^{K-1} A^{off}_{\{n^i\},\{n^{i+1}\}}$$

The comparison shows that the main difference of these two expressions is in the product of the matrix elements. In the latter weight, the off-diagonal contributions consist of three matrix elements that each introduce successive application of the $\hat{W}^{III}$ operator. This characteristic is a new feature of the algorithm, therefore further research will show if it impacts the effectiveness of the algorithm.

3.3 Monte Carlo steps

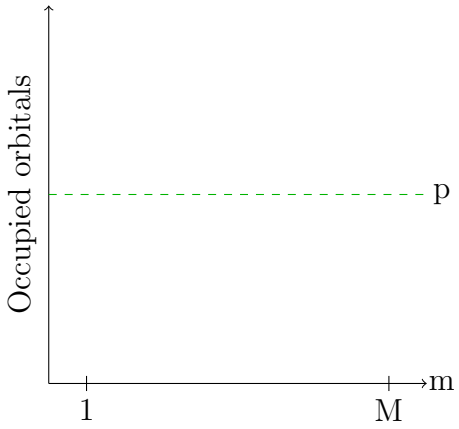
As introduced in the framework in chapter (3.1), a Monte Carlo step denotes a specific transition from a given configuration C to the next configuration C' in the Markov chain. The possible Monte Carlo steps will be determined by applying one of the seven steps listed below as well as in the appendix. The new configuration C' will be proposed with the probability $p(C \to C')$ and, eventually, be accepted with an acceptance probability $A(C \to C')$ which satisfies the detailed balance equation. For each of the steps there is a corresponding probability to be applied:

- Create stationary orbital: p_{cs}
- Remove stationary orbital: p_{rs}
- Add two kinks: p_{a2k}
- Remove two kinks: p_{r2k}
- Appendix: Shift one kink: p_{shift}
- Appendix: Add one kink: p_{a1k}
- Appendix: Remove one kink: p_{r1k}

If it is known that, for a given configuration, one of the steps cannot be applied (for example adding one kink if there is none in C) then its proposal probability is set to 0, and the other probabilities are scaled accordingly so they still add up to 1.
Furthermore, there are two different ways to implement this algorithm. As all excitations need to fulfil momentum conservation each new kink will be created by choosing an excitation vector. In the naive approach, these excitation vectors are chosen completely randomly. This allows for an easy computation of proposal probabilities and finding each of those vectors in constant time. But it might also result in vectors that produce invalid new states, for example by exciting into an orbital that is already occupied or by exciting into an orbital $i > N_b$. In the algorithm above, this is dealt with by allowing these vectors nevertheless and, therefore, producing invalid states, which will then always lead to configurations with $W(C') = 0$. These configurations will then always have an acceptance probability of $A(C \to C') = 0$. Therefore, these proposals are never accepted and those configurations never

appear in the Markov chain.
The second approach is to only consider valid vectors. This has the advantage of never proposing a new configuration C' where one knows beforehand that the acceptance probability will be zero. There are two disadvantages to consider. The first is that every valid option has to be counted, which leads to longer run times for finding the excitation vectors and for the computation of the acceptance probability. The second problem is that it might happen, that, in a certain situation, there is no valid option for an excitation vector. This would then require to propose an invalid configuration, which will be guaranteed to be rejected.
This approach is going to be used for this algorithm. To allow the computation of the acceptance probability, the number of valid options has to be tracked in every decision made in the algorithm.

3.3.1 Create stationary orbital



The left figure shows the creation of an occupied stationary orbital p from an empty orbital p. The x-axis parameter m describes the individual factors of the path.

Let $n_{sf}(C)$ be the number of stationary free orbitals in a configuration C. Furthermore, let C_{fail} be a configuration with $w(C_{fail}) = 0$ which leads to an acceptance probability of $A(C_{fail}) = 0$. Then the following algorithm is used to propose the next configuration C':

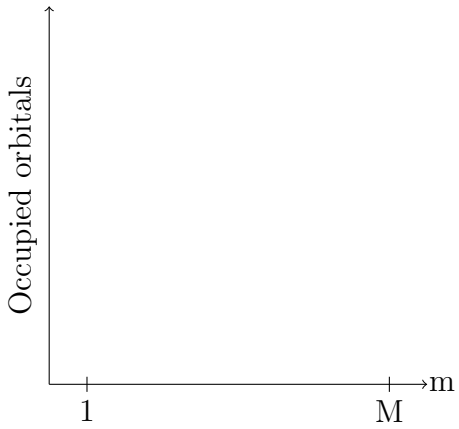
Precondition for creation : $n_{sf}(C) > 0$

1. Count the number of stationary free orbitals $n_{sf}(C)$.
2. Choose one of the $n_{sf}(C)$ free orbitals p.

3. Propose C' which results from inverting the occupation numbers of the orbitals p in every state $\{n^i\}$ in C.

$$\begin{aligned} p(C \to C') &= p_{cs} \cdot \frac{1}{n_{sf}(C)} = p_{cs} \cdot \frac{1}{n_{sf}(C')} = p(C' \to C) \\ A(C \to C') &= min\left[1, \frac{W(C')}{W(C)} \frac{p(C \to C')}{p(C' \to C)}\right] = min\left[1, \frac{W(C')}{W(C)}\right] \end{aligned}$$

3.3.2 Remove stationary orbital



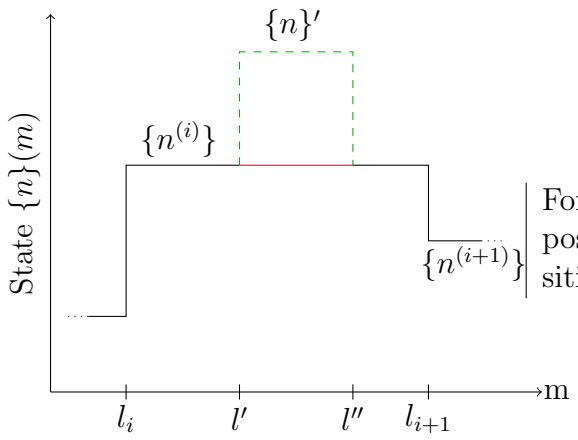
The left figure shows the removal of an occupied stationary orbital p.

Let $n_{so}(C)$ be the number of stationary occupied orbitals in a configuration C. Then the following algorithm is used to propose the next configuration C':
Precondition for removal : $n_{so}(C) > 0$

1. Count the number of stationary occupied orbitals $n_{so}(C)$.
2. Choose one of the $n_{so}(C)$ occupied orbitals p.
3. Propose C' which results from inverting the occupation numbers of the orbitals p in every state $\{n^i\}$ in C.

$$\begin{aligned} p(C \to C') &= p_{rs} \cdot \frac{1}{n_{so}(C)} = p_{rs} \cdot \frac{1}{n_{so}(C')} = p(C' \to C) \\ A(C \to C') &= min\left[1, \frac{W(C')}{W(C)} \frac{p(C \to C')}{p(C' \to C)}\right] = min\left[1, \frac{W(C')}{W(C)}\right] \end{aligned}$$

3.3.3 Add two kinks



For a randomly chosen kink at the position l_i two new kinks at the positions $l', l'' \in (l_i.l_{i+1})$ are created.

Let n_{a2k} be the number of different $i \in [0, K]$ with $\Delta l := l_{i+1} - l_i - 1 \geq 2$.

Precondition: $n_{a2k} > 0$

1. Choose one of the n_{a2k} valid positions i.
2. Choose two new kink positions $l' < l'' \in (l_i, l_{i+1})$.
3. Decide for new T4, T6, or T8 kinks with the according probabilities p_{T4}, p_{T6} and p_{T8}.
   (a) New T4 kinks:
      i. Choose two occupied orbitals r, s in the state $\{n^{(i)}\}$.
      ii. Count the number $n_{\mathbf{k}}$ of all $\mathbf{k}$ that satisfy $\mathbf{k} \neq 0$, $\mathbf{k}^2 \leq \mathbf{k}^2_{max}$ and $o(\mathbf{k}_r - \mathbf{k})$, $o(\mathbf{k}_s + \mathbf{k})$ are unoccupied orbitals.
      iii. If $n_{\mathbf{k}} = 0$, then propose C_{fail}, else continue.
      iv. Randomly choose one of the $n_{\mathbf{k}}$ vectors as an excitation vector $\mathbf{k}$.
      v. Calculate $r' := o(\mathbf{k}_r - \mathbf{k})$ and $s' := o(\mathbf{k}_s + \mathbf{k})$.
      vi. Propose new configuration C' with two new T4 kinks. The first is at position l' with the state $\{n^{(i)}\}^{r',s'}_{r,s}$ and the second kink at position l'' with the state $\{n^{(i)}\}$.

(b) New T6 kinks:

i. Choose three non-identical occupied orbitals p, q, r in the state $\{n^{(i)}\}$.

ii. Count the number $n_{\mathbf{k}}$ of all pairs of vectors $\mathbf{k}^{(1)}$, $\mathbf{k}^{(2)}$ that satisfy $(\mathbf{k}^{(1)}), (\mathbf{k}^{(2)}) \neq 0$, $(\mathbf{k}^{(1)})^2, (\mathbf{k}^{(2)})^2 \leq \mathbf{k}^2_{max}$ and $o(\mathbf{k}_p - \mathbf{k}^{(1)})$, $o(\mathbf{k}_q + \mathbf{k}^{(1)} + \mathbf{k}^{(2)})$, $o(\mathbf{k}_r - \mathbf{k}^{(2)})$ are unoccupied orbitals.

iii. If $n_{\mathbf{k}} = 0$, then propose C_{fail}, else randomly choose one of the $n_{\mathbf{k}}$ pairs $\mathbf{k}^{(1)}$, $\mathbf{k}^{(2)}$.

iv. Calculate $p' := o(\mathbf{k}_p - \mathbf{k}^{(1)})$, $q' := o(\mathbf{k}_q + \mathbf{k}^{(1)} + \mathbf{k}^{(2)})$ and $r' := o(\mathbf{k}_r - \mathbf{k}^{(2)})$.

v. If $|\{p, q, r\} \setminus \{p', q', r'\}| \neq 3$, then propose C_{fail}.

vi. Else, propose new configuration C' with two new T6 kinks. The first is at position l' with the state $\{n^{(i)}\}^{p',q',r'}_{p,q,r}$ and the second at position l'' with the state $\{n^{(i)}\}$.

(c) New T8 kinks:

i. Choose four non-identical occupied orbitals p, q, r, s in the state $\{n^{(i)}\}$.

ii. Count the number $n_{\mathbf{k}}$ of all pairs of vectors $\mathbf{k}^{(1)}$, $\mathbf{k}^{(2)}$ that satisfy $(\mathbf{k}^{(1)}), (\mathbf{k}^{(2)}) \neq 0$, $(\mathbf{k}^{(1)})^2, (\mathbf{k}^{(2)})^2 \leq \mathbf{k}^2_{max}$, $o(\mathbf{k}_p - \mathbf{k}^{(1)})$, $o(\mathbf{k}_q + \mathbf{k}^{(1)})$, $o(\mathbf{k}_r - \mathbf{k}^{(2)})$ and $o(\mathbf{s}_s + \mathbf{k}^{(2)})$ are unoccupied orbitals.

iii. If $n_{\mathbf{k}} = 0$, then propose C_{fail}, else continue.

iv. Choose one of these $n_{\mathbf{k}}$ pairs of excitation vectors $\mathbf{k}^{(1)}$, $\mathbf{k}^{(2)}$.

v. Calculate $p' := o(\mathbf{k}_p - \mathbf{k}^{(1)})$, $q' := o(\mathbf{k}_q + \mathbf{k}^{(1)})$, $r' := o(\mathbf{k}_r - \mathbf{k}^{(2)})$ and $s' := o(\mathbf{s}_s + \mathbf{k}^{(2)})$.

vi. If $|\{p, q, r, s\} \setminus \{p', q', r', s'\}| \neq 4$, then propose C_{fail}.

vii. Else, propose new configuration C' with two new T8 kinks. The first is at position l' with the state $\{n^{(i)}\}^{p',q',r',s'}_{p,q,r,s}$ and the second at position l'' with the state $\{n^{(i)}\}$.

As before, in the case of no valid options for excitation vectors, an alternative configuration C_{fail} is proposed which is guaranteed to have a zero acceptance probability. In all other cases, the probability for proposing a specific new configuration is determined by the options to choose the orbitals which will be excited and the number of possible excitation vectors $n_{\mathbf{k}}$:

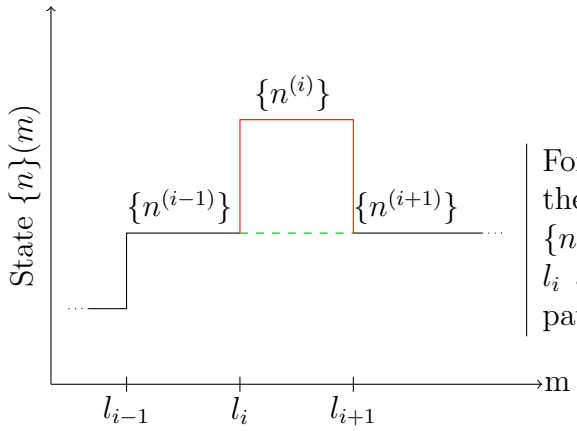
$$p(C \to C') = \frac{p_{a2k}}{n_{\mathbf{k}} \cdot n_{a2k}} \binom{\Delta l}{2}^{-1} \cdot \begin{cases} \frac{p_{T4}}{N(N-1)}, & \text{if case } a \\ \frac{p_{T6}}{N(N-1)(N-2)}, & \text{if case } b \\ \frac{p_{T8}}{N(N-1)(N-2)(N-3)}, & \text{if case } c \end{cases}$$

With the proposal probabilities for removing two kinks from below, this yields the following acceptance probabilities:

$$A(C \to C') = min\left[1, \frac{W(C')}{W(C)} \frac{p(C \to C')}{p(C' \to C)}\right] = min\left[1, \frac{W(C')}{W(C)}\ p(C \to C')\ \frac{n_{r2k}(C)+1}{p_{r2k}}\right]$$

$$A(C \to C') = \begin{cases} min\Big[1, \frac{W(C')}{W(C)}\ \frac{p_{a2k}}{n_{\mathbf{k}} \cdot n_{a2k}} \binom{\Delta l}{2}^{-1} \\ \cdot \frac{n_{r2k}(C)+1}{p_{r2k}}\ \frac{p_{T4}}{N(N-1)}\Big], & \text{if case } a \\ min\Big[1, \frac{W(C')}{W(C)}\ \frac{p_{a2k}}{n_{\mathbf{k}} \cdot n_{a2k}} \binom{\Delta l}{2}^{-1} \\ \cdot \frac{n_{r2k}(C)+1}{p_{r2k}}\ \frac{p_{T6}}{N(N-1)(N-2)}\Big], & \text{if case } b \\ min\Big[1, \frac{W(C')}{W(C)}\ \frac{p_{a2k}}{n_{\mathbf{k}} \cdot n_{a2k}} \binom{\Delta l}{2}^{-1} \\ \cdot \frac{n_{r2k}(C)+1}{p_{r2k}}\ \frac{p_{T8}}{N(N-1)(N-2)(N-3)}\Big], & \text{if case } c \end{cases}$$

3.3.4 Remove two kinks



For a randomly chosen kink at the position l_i with $\{n^{(i-1)}\} = \{n^{(i+1)}\}$, the two kinks at positions l_i and l_{i+1} are removed from the path.

Let $n_{r2k}(C)$ be the number of kink positions i in the configuration C which satisfy $\{n^{(i-1)}\} = \{n^{(i+1)}\}$.

Precondition: $n_{r2k}(C) > 0$

1. Choose $i \in [1, K-1]$ with $\{n^{(i-1)}\} = \{n^{(i+1)}\}$.
2. Propose new Configuration C' which results from removing the two kinks with indices i and $i+1$ from the current configuration C.

Assuming a satisfied precondition, the probability for proposing a specific removal is only determined by the number of possible positions $n_{r2k}(C)$, which results in the following proposal probability:

$$p(C \to C') = \frac{p_{r2k}}{n_{r2k}(C)}$$

This leads to the following acceptance probability:

$$A(C \to C') = \begin{cases} min\Big[1, \dfrac{W(C')}{W(C)} \dfrac{p_{r2k}}{n_{r2k}(C)} \dfrac{n_{\mathbf{k}}(C')\ n_{a2k}(C')}{p_{a2k}} \binom{\Delta l}{2} \\ \cdot N(N-1)\Big], & \text{if case } a \\ min\Big[1, \dfrac{W(C')}{W(C)} \dfrac{p_{r2k}}{n_{r2k}(C)} \dfrac{n_{\mathbf{k}}(C')\ n_{a2k}(C')}{p_{a2k}} \binom{\Delta l}{2} \\ \cdot N(N-1)(N-2)\Big], & \text{if case } b \\ min\Big[1, \dfrac{W(C')}{W(C)} \dfrac{p_{r2k}}{n_{r2k}(C)} \dfrac{n_{\mathbf{k}}(C')\ n_{a2k}(C')}{p_{a2k}} \binom{\Delta l}{2} \\ \cdot N(N-1)(N-2)(N-3)\Big], & \text{if case } c \end{cases}$$

4 Results for the simulation of the ideal Fermi gas

In this chapter several statistically computed expectation values of thermodynamic quantities are compared with their analytically derived values. The considered system, the ideal Fermi gas, was introduced in chapter (2.3), hence only the implementation of the algorithm is presented in the following.

Omitting particle interaction simplifies the Monte Carlo algorithm used for the numerical approximation of the system. A configuration of the system can be described via the Fock state $|n_0, \ldots, n_{N_B}\rangle$ with n_i as the occupation numbers of single-particle states that are sorted by increasing energies $\epsilon_i \leq \epsilon_{i+1}$. For this algorithm a number of $N_B = 100$ basis orbitals was chosen. Furthermore, the construct, that is to evaluate numerically, is simplified, since the path solely consists of stationary orbitals. Hence, the only Monte Carlo steps that are considered are create- or remove stationary orbital.
The algorithm that is used for the computation of the expectation values of thermodynamic quantities can be displayed with the following framework:

- Initialize a randomly occupied Fock state $|n_0, \ldots, n_{N_B}\rangle$
- Choose random orbital n_i according to a normal distribution $p(x)$ with the chemical potential μ as the mean of the distribution
- Depending on the occupation status of the random orbital, chose a Monte Carlo step and calculate the acceptance probability $A(C_i \to C_i') = min\left[1, exp(-\beta(\Delta E - \mu) \cdot occ(n_i))\right]$[14]
- Accept or reject the proposed change with the probability $(1 - A)$
- Iterate N_{MC}-times
- Process the results for plotting

This algorithm was used for the computation of the following results.
The first observable that was computed is the mean orbital occupation number (15).

[14]The function $occ(n) := \begin{cases} -1, \text{if n=1} \\ 1, \text{else} \end{cases}$ may induce a sign change.

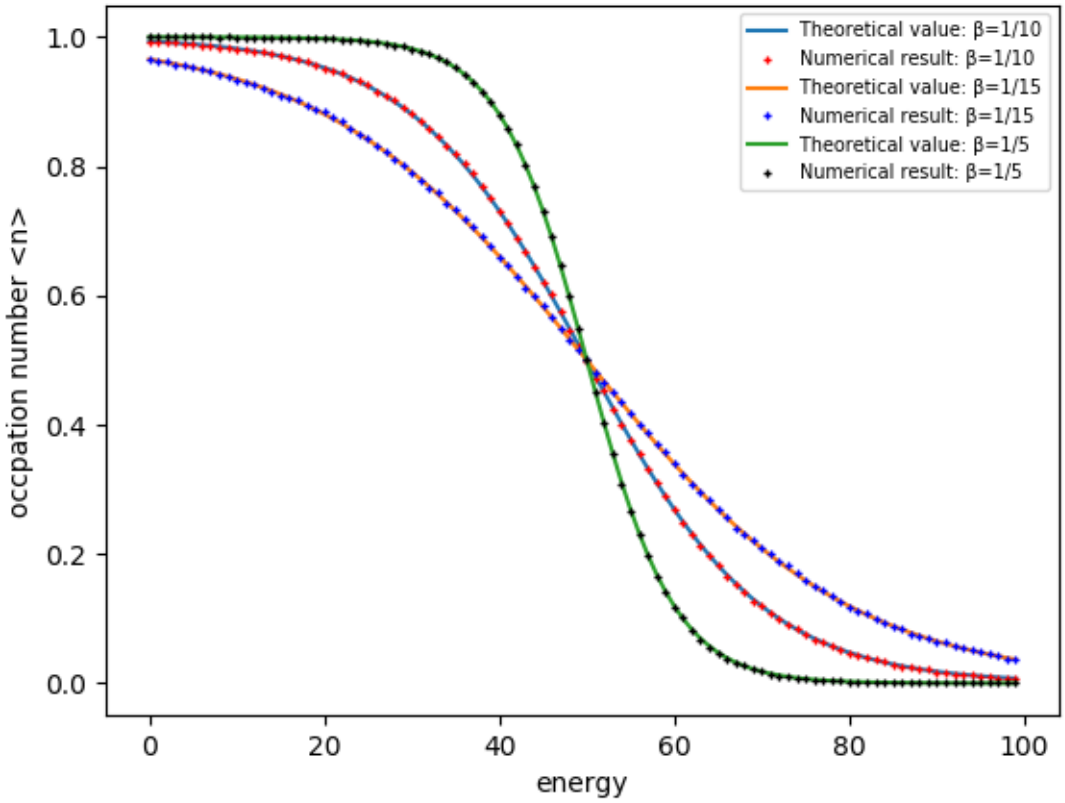


Figure 3: Mean occupation number at three inverse temperatures as a function of the energy. The chemical potential was set to $\mu = 50$ and $N_{MC} = 10^7$ Monte Carlo steps were used for the simulation.

This graph displays the so-called Fermi distribution. The mean occupation numbers decline with increasing energys. At energys at the chemical potential μ the occupation number is 0.5. With increasing inverse temperatures the slope of the distribution of occupied states increases. The case of $\beta \to \infty$ would result in the so-called Fermi edge.

Additionally, the fluctuation of the mean orbital occupation number (16) was computed.

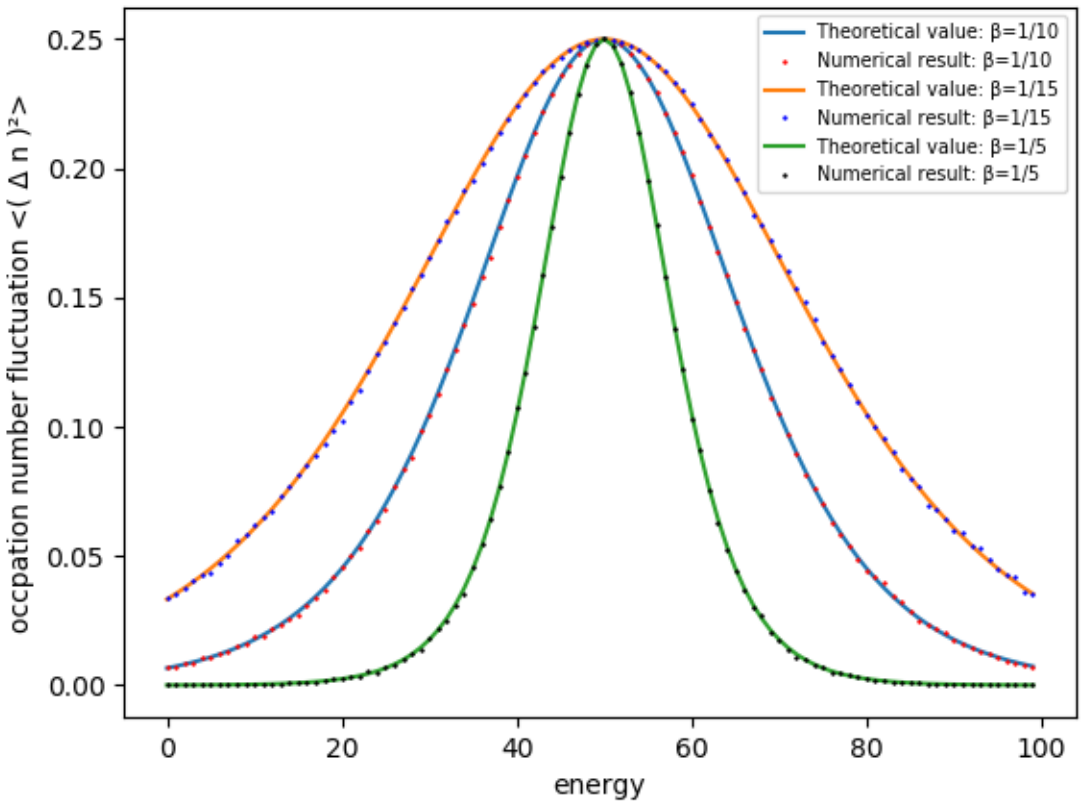


Figure 4: Fluctuation of the mean occupation number at three inverse temperatures as a function of the energy. The chemical potential was set to $\mu = 50$ and $N_{MC} = 10^7$ Monte Carlo steps were used for the simulation.

This result shows a peak of the fluctuation at the chemical potential and a decrease for higher/lower energys. For small temperatures the distribution is confined to energys near the chemical potential, because excitations to energys that strongly differ from the chemical potential are unlikely.

Lastly, the mean occupation number (17) was computed.

β	Theoretical value N	Numerical result N	Percentage deviation
$\frac{1}{10}$	50.492	50.483	-0.018
$\frac{1}{15}$	50.466	50.486	0.040
$\frac{1}{5}$	50.500	50.488	-0.024

These results demonstrates that the algorithm is successful in the numerical computation of thermodynamic quantities.

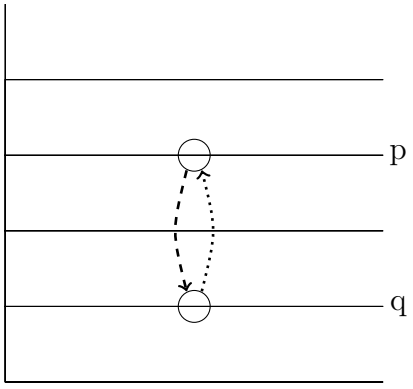
5 Outlook

The research presented in this thesis has opened a number of research opportunities that could be explored in the future. For instance, the test-case of the ideal Fermi gas may be further developed into the uniform electron gas. In particular, this would require the implementation of the 6 additional Monte Carlo steps that result from the consideration of particle interactions. The uniform electron gas also is a well researched system, so one could compare the measurement results with existing data to determine the effectiveness of the higher order expansion. If the developed algorithm proves to be reducing the sign problem, one could further lower the error in the Taylor expansion with a third-order expansion. An intrinsic problem of this higher order expansion method is that it is not entirely foreseeable which order of an expansion has an affirmative influence on the simulation. Furthermore, an even higher expansion would entail an increased time commitment, because of the number of new matrix elements that would have to be derived and computed.
Further possibilities of expanding the algorithm, with the prerequisite that the changes prove to be valuable, is the implementation of optimizing methods that were introduced in the CPMIC algorithm. This would include the worm algorithm which is an important tool in the case of the Grand canonical ensemble.

6 Appendix

6.1 Graphical representation of possible particle excitations in the computation of matrix elements

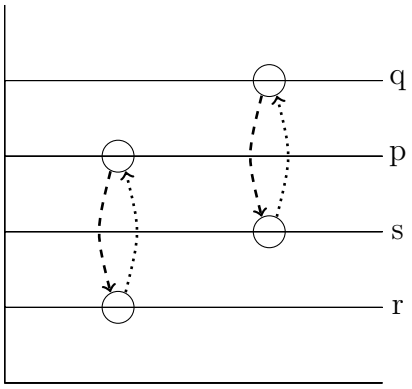
In the following, the matrix elements of the non-diagonal operators that arise from the second order Taylor expansion in chapter (2.4.1) are graphically displayed. In second quantization, particles are indistinguishable from one another, thus, in a multi-particle excitation, one cannot obtain information concerning which particle has been excited into which orbital.
Therefore, the following representation uses dotted lines to denote the first application of a given operator and dashed lines to denote the second application. Two arrows of the same type describe a two-particle excitation.
The white circles represent randomly chosen orbitals, which do not differ from $|\{n\}\rangle$ to $|\{\tilde{n}\}\rangle$.



$$W^2_{II\{n\},\{\tilde{n}\}} = \sum_{\substack{p\neq q \\ p,q<N_B}} |\langle\{\tilde{n}\}^p_q|\hat{W}_{II}|\{\tilde{n}\}\rangle|^2$$

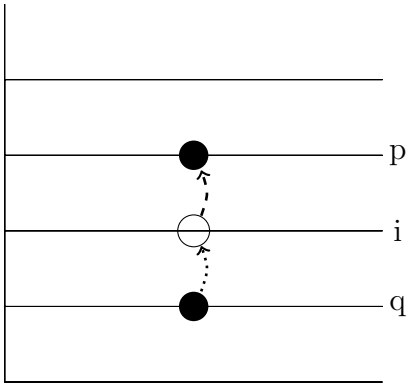
$$\text{if } \{n\} = \{\tilde{n}\}$$

The left figure shows the case of identical states before and after the two single-particle excitations. In the first step the particle in the randomly chosen orbital p is excited to a randomly chosen orbital q. In the second step, the excitation is reversed.

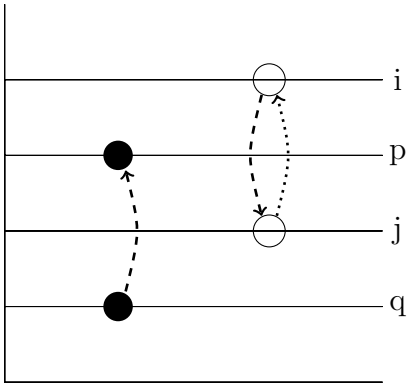


Two double excitations (up and down arrows, respectively) that are reversed.

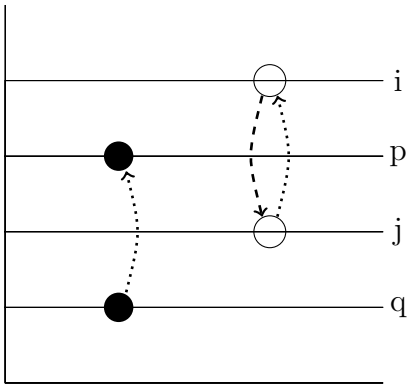
$W^2_{III\{n\},\{\tilde{n}\}}$ if $\{n\} = \{\tilde{n}\}$



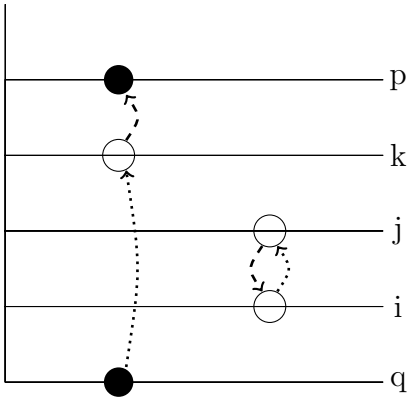
$W^2_{II\{n\},\{\tilde{n}\}}$ if $\{n\} = \{\tilde{n}\}^p_q$



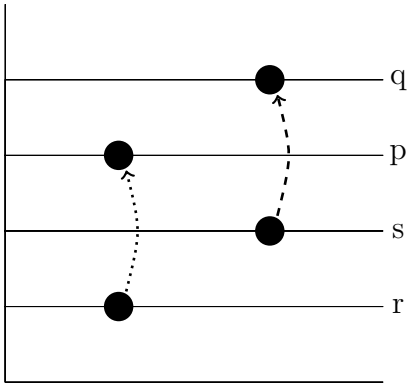
$(W_{III}W_{II})_{\{n\},\{\tilde{n}\}}$ if $\{n\} = \{\tilde{n}\}^p_q$



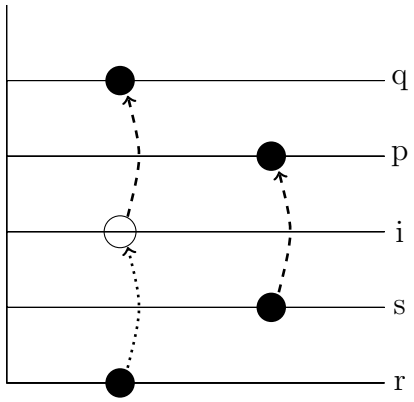
$(W_{II}W_{III})_{\{n\},\{\tilde{n}\}}$ if $\{n\} = \{\tilde{n}\}^{p}_{q}$



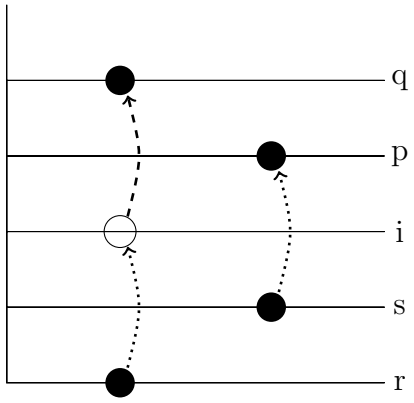
$(W^2_{III})_{\{n\},\{\tilde{n}\}}$ if $\{n\} = \{\tilde{n}\}^{p}_{q}$



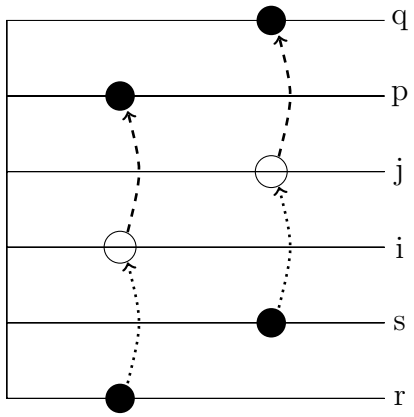
$(W^2_{II})_{\{n\},\{\tilde{n}\}}$ if $\{n\} = \{\tilde{n}\}^{p<q}_{r<s}$



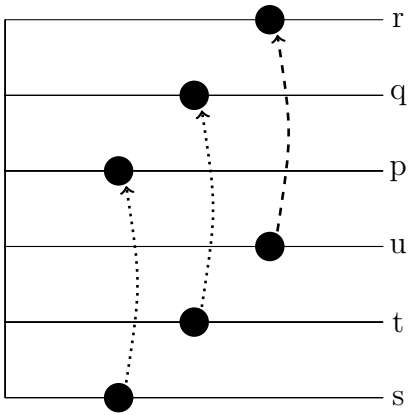
$(W_{III}W_{II})_{\{n\},\{\tilde{n}\}}$ if $\{n\} = \{\tilde{n}\}_{r<s}^{p<q}$



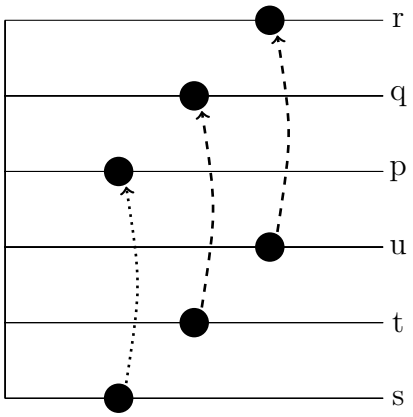
$(W_{II}W_{III})_{\{n\},\{\tilde{n}\}}$ if $\{n\} = \{\tilde{n}\}_{r<s}^{p<q}$



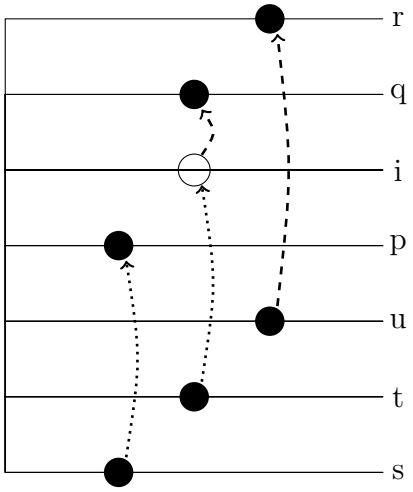
$W^2_{III\{n\},\{\tilde{n}\}}$ if $\{n\} = \{\tilde{n}\}_{r<s}^{p<q}$



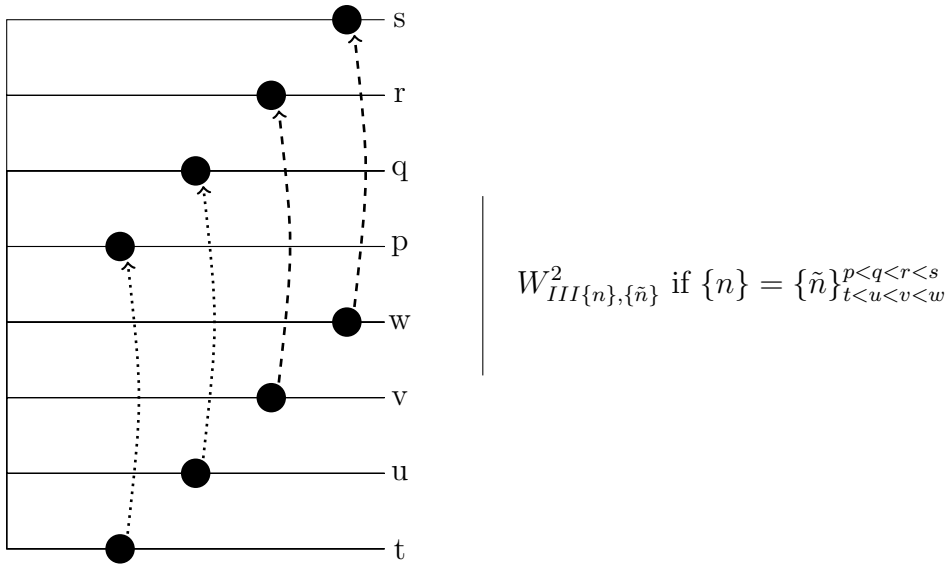
$(W_{II}W_{III})_{\{n\},\{\tilde{n}\}}$ if $\{n\} = \{\tilde{n}\}^{p<q<r}_{s<t<u}$



$(W_{III}W_{II})_{\{n\},\{\tilde{n}\}}$ if $\{n\} = \{\tilde{n}\}^{p<q<r}_{s<t<u}$



$W^2_{III\{n\},\{\tilde{n}\}}$ if $\{n\} = \{\tilde{n}\}^{p<q<r}_{s<t<u}$



6.2 Matrix elements in the one-particle density matrix

These are matrix elements in equation (36).

$$
\begin{aligned}
A^{0T}_{\{n\}} = \exp\Bigg(-\tilde{\beta}\Bigg[& D_{\{n\}} + V^I_{\{n\}} - \frac{\tilde{\beta}}{2} \sum_{\substack{p\neq q \\ p,q<N_B}} \langle\{n\}|\hat{V}^{II}|\{n\}^p_q\rangle \\
& \cdot \langle\{n\}^p_q|\hat{V}^{II}|\{\tilde{n}\}\rangle - \frac{\tilde{\beta}}{2} D^{III}_{\{n\}}\Bigg]\Bigg) \\
A^{1T}_{\{n\},\{\tilde{n}\}} = & -\tilde{\beta}\, V^{II}_{\{n\},\{\tilde{n}\}} + \frac{1}{2}\tilde{\beta}^2\Bigg[\left(D_{\{n\}} + D_{\{\tilde{n}\}}\right) V^{II}_{\{n\},\{\tilde{n}\}} \\
& + \sum_{\substack{i<N_B \\ i\neq p,q}} \langle\{n\}|\hat{V}^{II}|\{\tilde{n}\}^i_q\rangle\langle\{\tilde{n}\}^i_q|\hat{V}^{II}|\{\tilde{n}\}\rangle \\
& + \sum_{\substack{i,j<N_B \\ i\neq j \\ i,j\notin\{p,q\}}} \langle\{n\}|\hat{W}^{III}|\{\tilde{n}\}^i_j\rangle\langle\{\tilde{n}\}^i_j|\hat{V}^{II}|\{\tilde{n}\}\rangle
\end{aligned}
$$

$$
\begin{aligned}
&+ \sum_{\substack{i,j<N_B \\ i\neq j \\ i,j\notin\{p,q\}}} \langle\{n\}|\hat{V}^{II}|\{\tilde{n}\}^{p,i}_{q,j}\rangle\langle\{\tilde{n}\}^{p,i}_{q,j}|\hat{W}^{III}|\{\tilde{n}\}\rangle \\
&+ \sum_{\substack{i,j,k<N_B \\ i\neq j\neq k \\ j<k}} \langle\{n\}|\hat{W}^{III}|\{\tilde{n}\}^{j,k}_{q,i}\rangle\langle\{\tilde{n}\}^{j,k}_{q,i}|\hat{W}^{III}|\{\tilde{n}\}\rangle\Bigg], \\
A^{2T}_{\{n\},\{\tilde{n}\}} = &-\tilde{\beta}\, W^{III}_{\{n\},\{\tilde{n}\}} + \frac{1}{2}\tilde{\beta}^2\Bigg[\left(D_{\{n\}} + D_{\{\tilde{n}\}}\right) W^{III}_{\{n\},\{\tilde{n}\}} \\
&+ \sum_{\substack{x\in\{r,s\} \\ y\in\{p,q\}}} \langle\{n\}|\hat{V}^{II}|\{\tilde{n}\}^{y}_{x}\rangle\langle\{\tilde{n}\}^{y}_{x}|\hat{V}^{II}|\{\tilde{n}\}\rangle \\
&+ \sum_{\substack{i<N_B \\ x\in\{p,q\} \\ i\notin\{p,q,r,s\}}} \langle\{n\}|\hat{V}^{II}|\{\tilde{n}\}^{x,i}_{r,s}\rangle\langle\{\tilde{n}\}^{x,i}_{r,s}|\hat{W}^{III}|\{\tilde{n}\}\rangle \\
&+ \sum_{\substack{i<N_B \\ x\in\{r,s\} \\ i\notin\{p,q,r,s\}}} \langle\{n\}|\hat{W}^{III}|\{\tilde{n}\}^{i}_{x}\rangle\langle\{\tilde{n}\}^{i}_{x}|\hat{V}^{II}|\{\tilde{n}\}\rangle \\
&+ \sum_{i<j<N_B} \langle\{n\}|\hat{W}^{III}|\{\tilde{n}\}^{i<j}_{r<s}\rangle\langle\{\tilde{n}\}^{i<j}_{r<s}|\hat{W}^{III}|\{\tilde{n}\}\rangle\Bigg], \\
A^{3T}_{\{n\},\{\tilde{n}\}} = &\frac{1}{2}\tilde{\beta}^2\Bigg[\sum_{\substack{a<b\in\{p,q,r\} \\ c<d\in\{s,t,u\}}} \langle\{n\}|\hat{V}^{II}|\{\tilde{n}\}^{a,b}_{c,d}\rangle\langle\{\tilde{n}\}^{a,b}_{c,d}|\hat{W}^{III}|\{\tilde{n}\}\rangle \\
&+ \sum_{\substack{x\in\{s,t,u\} \\ y\in\{p,q,r\}}} \langle\{n\}|\hat{W}^{III}|\{\tilde{n}\}^{y}_{x}\rangle\langle\{\tilde{n}\}^{y}_{x}|\hat{V}^{II}|\{\tilde{n}\}\rangle \\
&+ \sum_{\substack{i<N_B \\ i\notin\{p,q,r,s,t,u\} \\ z\in\{p,q,r\} \\ x<y\in\{s,t,u\}}} \langle\{n\}|\hat{W}^{III}|\{\tilde{n}\}^{i,z}_{x,y}\rangle\langle\{\tilde{n}\}^{i,z}_{x,y}|\hat{W}^{III}|\{\tilde{n}\}\rangle\Bigg], \\
A^{4T}_{\{n\},\{\tilde{n}\}} = &\frac{1}{2}\tilde{\beta}^2 \sum_{\substack{c<d\in\{p,q,r,s\} \\ a<b\in\{t,u,v,w\}}} \langle\{n\}|\hat{W}^{III}|\{\tilde{n}\}^{c<d}_{a<b}\rangle\langle\{\tilde{n}\}^{c<d}_{a<b}|\hat{W}^{III}|\{\tilde{n}\}\rangle
\end{aligned}
$$

6.3 Number of allowed direct excitations for adding one kink

This table is used in the chapter (6.4.2).

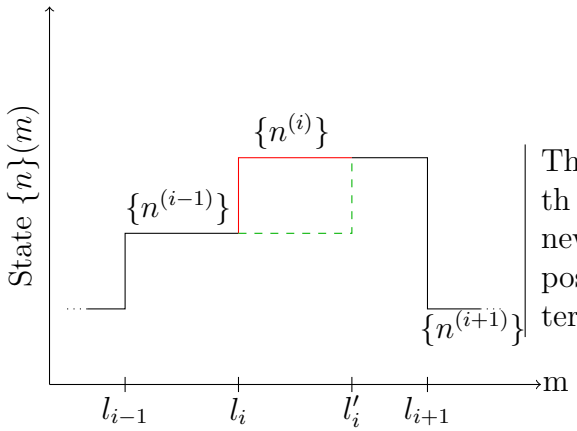
New kink	**Kink at l_i**	**Direct excitations**
T4	T4	0,1
T4	T6	0,1
T4	T8	0,1,2
T6	T4	0,1
T6	T6	0,1,2
T6	T8	0,1,2
T8	T4	0,1,2
T8	T6	0,1,2
T8	T8	0,1,2,3

Figure 5: When adding a single kink, an existing kink is replaced by a new kink and a changed kink. For example, a new T4 kink will be added to an existing T4 kink. In this case, the direct excitation of two particles to their final orbitals is prohibited, as it would already put the system into its final state, therefore making it impossible to perform any other excitation with the second kink.

6.4 Excluded Monte Carlo Steps

The Monte Carlo steps that are presented in the following were derived by Jakob Nazarenus. These results are indispensable in the implementation of the UEG, hence they are presented in the appendix.

6.4.1 Shift one kink



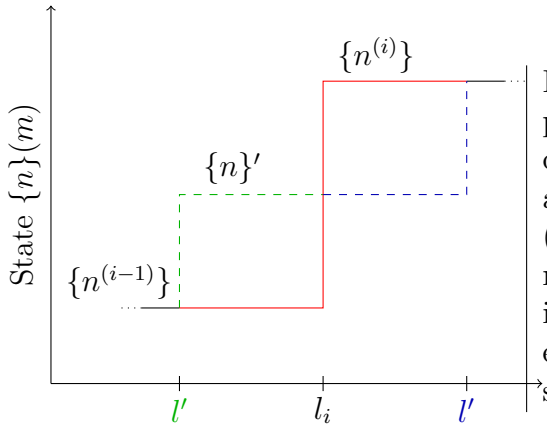
This figure shows the shift of the i-th kink from the position l_i to the new position at l'_i. Both of these positions have to lie within the interval (l_{i-1}, l_{i+1}).

Precondition: $K > 0$

1. Choose i as one of the K kink positions.
2. Choose a new kink position $l'_i \in (l_{i-1}, l_{i+1})$.
3. Propose new configuration C', which results from changing $l_i \to l'_i$ in the current configuration C.

$$p(C \to C') = p_{shift} \cdot \frac{1}{K} \frac{1}{(l_{i+1} - l_{i-1} - 1)} = p(C' \to C)$$
$$A(C \to C') = min\left[1, \frac{W(C')}{W(C)} \frac{p(C \to C')}{p(C' \to C)}\right] = min\left[1, \frac{W(C')}{W(C)}\right]$$

6.4.2 Add one kink



For a randomly chosen kink at the position l_i it has been randomly decided that one kink should be added at its left (green) or right (blue) side at the corresponding new position l'. In both cases, the introduction of the new kink will effect the existing kink at the position l_i.

Let $\Delta(\{n\},\{\tilde{n}\}) \in \mathbb{N}$ be the number of orbitals that differ in their occupation between $\{n\}$ and $\{\tilde{n}\}$.
Precondition: $K \geq 2$

1. Randomly choose a kink with index i.
2. Decide to add a right or a left kink.
   (a) If a left kink will be added, choose $l' \in (l_{i-1}, l_i)$ and set $\Delta l := l_i - l_{i-1} - 1$. If $l_i = l_{i-1} + 1$, propose C_{fail}. Furthermore, the intermediate state $\{n\}'$ will be created by exciting the state $\{n\}_{ex} := \{n^{(i-1)}\}$.
   (b) If a left kink will be added, choose $l' \in (l_i, l_{i+1})$ and set $\Delta l := l_{i+1} - l_i - 1$. If $l_{i+1} = l_i + 1$, propose C_{fail}. Furthermore, the intermediate state $\{n\}'$ will be created by exciting the state $\{n\}_{ex} := \{n^{(i)}\}$.
3. Decide to add a T4, T6 or T8 kink with the according probabilities p_{aT4}, p_{aT6} and p_{aT8}.
4. Determine the set of orbitals E which are excited from $\{n^{(i-1)}\}$ to $\{n^{(i)}\}$ for the left case and from $\{n^{(i)}\}$ to $\{n^{(i-1)}\}$ for the right case.
   (a) Adding a T4 kink:
      i. Choose two occupied orbitals r, s in $\{n\}_{ex}$.

ii. Count the number $n_{\mathbf{k}}$ of all $\mathbf{k}$ that satisfy $\mathbf{k} \neq 0$, $\mathbf{k}^2 \leq \mathbf{k}^2_{max}$ and $o(\mathbf{k}_r - \mathbf{k})$, $o(\mathbf{k}_s + \mathbf{k})$ are unoccupied orbitals in $\{n\}_{ex}$. Moreover, the number of direct excitations (to an orbital in E) must comply with the numbers given in the appendix at 6.3.

iii. If $n_{\mathbf{k}} = 0$, then propose C_{fail}, else continue.

iv. Randomly choose one of the $n_{\mathbf{k}}$ vectors as an excitation vector $\mathbf{k}$.

v. Calculate $r' := o(\mathbf{k}_r - \mathbf{k})$ and $s' := o(\mathbf{k}_s + \mathbf{k})$.

vi. Set $\{n\}' := (\{n\}_{ex})^{r',s'}_{r,s}$.

(b) Adding a T6 kink:

i. Choose three non-identical occupied orbitals p, q, r in the state $\{n\}_{ex}$.

ii. Count the number $n_{\mathbf{k}}$ of all pairs of vectors $\mathbf{k}^{(1)}$, $\mathbf{k}^{(2)}$ that satisfy $(\mathbf{k}^{(1)}), (\mathbf{k}^{(2)}) \neq 0$, $(\mathbf{k}^{(1)})^2, (\mathbf{k}^{(2)})^2 \leq \mathbf{k}^2_{max}$ and $o(\mathbf{k}_p - \mathbf{k}^{(1)})$, $o(\mathbf{k}_q + \mathbf{k}^{(1)} + \mathbf{k}^{(2)})$, $o(\mathbf{k}_r - \mathbf{k}^{(2)})$ are unoccupied orbitals in $\{n\}_{ex}$. Moreover, the number of direct excitations (to an orbital in E) must comply with the numbers given in the appendix at 6.3.

iii. If $n_{\mathbf{k}} = 0$, then propose C_{fail}, else randomly choose one of the $n_{\mathbf{k}}$ pairs $\mathbf{k}^{(1)}$, $\mathbf{k}^{(2)}$.

iv. Calculate $p' := o(\mathbf{k}_p - \mathbf{k}^{(1)})$, $q' := o(\mathbf{k}_q + \mathbf{k}^{(1)} + \mathbf{k}^{(2)})$ and $r' := o(\mathbf{k}_r - \mathbf{k}^{(2)})$.

v. If $|\{p, q, r\} \setminus \{p', q', r'\}| \neq 3$, then propose C_{fail}.

vi. Set $\{n\}' := (\{n\}_{ex})^{p',q',r'}_{p,q,r}$.

(c) Adding a T8 kink:

i. Choose four non-identical occupied orbitals p, q, r, s in the state $\{n^{(i)}\}$.

ii. Count the number $n_{\mathbf{k}}$ of all pairs of vectors $\mathbf{k}^{(1)}$, $\mathbf{k}^{(2)}$ that satisfy $(\mathbf{k}^{(1)}), (\mathbf{k}^{(2)}) \neq 0$, $(\mathbf{k}^{(1)})^2, (\mathbf{k}^{(2)})^2 \leq \mathbf{k}^2_{max}$, $o(\mathbf{k}_p - \mathbf{k}^{(1)})$, $o(\mathbf{k}_q + \mathbf{k}^{(1)})$, $o(\mathbf{k}_r - \mathbf{k}^{(2)})$ and $o(\mathbf{s}_s + \mathbf{k}^{(2)})$ are unoccupied orbitals in $\{n\}_{ex}$. Moreover, the number of direct excitations (to an orbital in E) must comply with the numbers given in the appendix at 6.3.

iii. If $n_{\mathbf{k}} = 0$, then propose C_{fail}, else continue.

iv. Choose one of these $n_{\mathbf{k}}$ pairs of excitation vectors $\mathbf{k}^{(1)}$, $\mathbf{k}^{(2)}$.

v. Calculate $p' := o(\mathbf{k}_p - \mathbf{k}^{(1)})$, $q' := o(\mathbf{k}_q + \mathbf{k}^{(1)})$, $r' := o(\mathbf{k}_r - \mathbf{k}^{(2)})$ and $s' := o(\mathbf{s}_s + \mathbf{k}^{(2)})$.

vi. If $|\{p,q,r,s\} \setminus \{p',q',r',s'\}| \neq 4$, then propose C_{fail}.

vii. Set $\{n\}' := (\{n\}_{ex})^{p',q,'r',s'}_{p,q,r,s}$.

5. For a left kink, propose a new configuration C' which is created by adding a new kink at the position l' with the state $\{n\}'$ in the previous configuration C.

6. For a right kink, propose a new configuration C' which is created by changing the state of the i-th kink to $\{n\}'$ and introducing a new kink at the position l' with the state $\{n^{(i)}\}$ in the previous configuration C.

Assuming a satisfied precondition and a successful proposal which is not C_{fail}, the proposal probability is as follows:

$$p(C \to C') = \frac{p_{a1k}}{2\ K\ \Delta l\ n_{\mathbf{k}}} \cdot \begin{cases} \dfrac{p_{aT4}}{N(N-1)}, & \text{for a T4 kink}, \\ \dfrac{p_{aT6}}{N(N-1)(N-2)}, & \text{for a T6 kink}, \\ \dfrac{p_{aT8}}{N(N-1)(N-2)(N-3)}, & \text{for a T8 kink}. \end{cases}$$

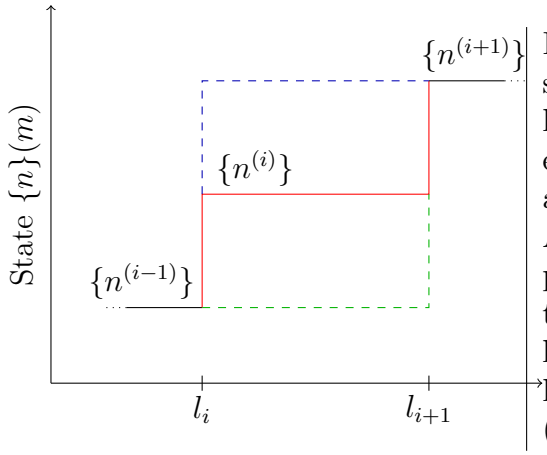
With the proposal probability for removing one kink from below, this yields the following acceptance probability:

$$A(C \to C') = min\left[1, \frac{W(C')}{W(C)} \frac{p(C \to C')}{p(C' \to C)}\right]$$

$$A(C \to C') = \begin{cases} min\Big[1, \dfrac{W(C')}{W(C)} \dfrac{p_{a1k}}{2\ K\ \Delta l\ n_{\mathbf{k}}} \dfrac{p_{aT4}}{N(N-1)} \\ \cdot\ \dfrac{2\ (n_{T4}+1)}{p_{r1k}\ p_{rT4}}\Big], & \text{if T4} \\ min\Big[1, \dfrac{W(C')}{W(C)} \dfrac{p_{a1k}}{2\ K\ \Delta l\ n_{\mathbf{k}}} \dfrac{p_{aT6}}{N(N-1)(N-2)} \\ \cdot\ \dfrac{2\ (n_{T6}+1)}{p_{r1k}\ p_{rT6}}\Big], & \text{if T6} \\ min\Big[1, \dfrac{W(C')}{W(C)} \dfrac{p_{a1k}}{2\ K\ \Delta l\ n_{\mathbf{k}}} \dfrac{p_{aT8}}{N(N-1)(N-2)(N-3)} \\ \cdot\ \dfrac{2\ (n_{T8}+1)}{p_{r1k}\ p_{rT8}}\Big], & \text{if T8} \end{cases}$$

6.4.3 Remove one kink

Removing one kink is essentially combining two kinks into a single new kink. For two T4 kinks, this is always possible, because in this representation, every kink arises from the combination of two T4 kinks. Thus, the removal would result in a new T4, T6 or T8 kink. In all other cases, one has to determine the number of orbitals that differ in their occupation between the left and the right state. If there are more than 8 differently occupied orbitals after two kinks, this can not be combined into a single new kink. Therefore, if a T4 kink has to be removed, one has to check if the previous and the following state of the one to be removed differ in 4, 6 or 8 orbitals. If this is the case, the kink can be removed, otherwise not.



Randomly, a kink at position i shall be removed from the path. It has been checked that the difference in orbitals between $\{n^{(i-1)}\}$ and $\{n^{(i+1)}\}$ is exactly $4, 6$ or 8. As it is indicated in the left example, there are two different ways to undo the creation of a single kink. It can either be removed as a left kink (green) or as a right kink (blue).

Precondition: $K > 2$

1. Decide to remove an x-Kink with $x \in \{T4, T6, T8\}$ with given probabilities $p_{rT4}, p_{rT6}, p_{rT8}$.

2. Count the number n_x of x-Kinks at their position i which satisfy $\Delta(\{n^{(i-1)}\}, \{n^{(i+1)}\}) \in \{4, 6, 8\}$.

3. If $n_x = 0$, then propose C_{fail}.

4. Choose one of the n_x kinks with its position i.

5. Decide whether to remove a left or a right kink.

(a) If a left kink will be removed, propose C' which is created by removing the kink at position i in C.

(b) If a right kink will be removed, propose C' which is created by removing the kink at position i in C and changing the kink at the position l_{i+1} to be at the former position l_i.

Assuming $K > 2$ and $n_x > 0$, the probability for proposing a specific removal is only determined by the number of possible positions N_x, which results in the following proposal probability:

$$p(C \to C') = \frac{p_{r1k}}{2} \cdot \begin{cases} \frac{p_{rT4}}{n_{T4}}, & \text{if T4} \\ \frac{p_{rT6}}{n_{T6}}, & \text{if T6} \\ \frac{p_{rT8}}{n_{T8}}, & \text{if T8} \end{cases}$$

With the proposal probability for adding one kink from above, this yields the following acceptance probability:

$$A(C \to C') = min\left[1, \frac{W(C')}{W(C)} \frac{p(C \to C')}{p(C' \to C)}\right]$$

$$A(C \to C') = \begin{cases} min\Big[1, \frac{W(C')}{W(C)} \frac{p_{r1k}\ p_{rT4}}{2\ n_{T4}} \\ \cdot \frac{2\ (K-1)\Delta l(C')\ n_{\mathbf{k}}(C')\ N(N-1)}{p_{a1k}\ p_{aT4}}\Big], & \text{if T4} \\ min\Big[1, \frac{W(C')}{W(C)} \frac{p_{r1k}\ p_{rT6}}{2\ n_{T6}} \\ \cdot \frac{2\ (K-1)\Delta l(C')\ n_{\mathbf{k}}(C')\ N(N-1)(N-2)}{p_{a1k}\ p_{aT6}}\Big], & \text{if T6} \\ min\Big[1, \frac{W(C')}{W(C)} \frac{p_{r1k}\ p_{rT8}}{2\ n_{T8}} \\ \cdot \frac{2\ (K-1)\Delta l(C')\ n_{\mathbf{k}}(C')\ N(N-1)(N-2)(N-3)}{p_{a1k}\ p_{aT8}}\Big], & \text{if T8} \end{cases}$$

6.5 Outsourced calculations

Computation of the estimator of the mean occupation number in chapter (2.5.5).

$$
\begin{aligned}
\langle n_x \rangle &= -\frac{1}{\beta}\frac{1}{Z}\sum_c \left[\left(\prod_{i=0}^{K-1} A^{off}_{\{n^{(i)}\}\{n^{(i+1)}\}} \right) \frac{\partial}{\partial \epsilon_x} \exp(x) \right. \\
&+ \left. \exp(x) \frac{\partial}{\partial \epsilon_x} \left(\prod_{i=0}^{K-1} A^{off}_{\{n^{(i)}\}\{n^{(i+1)}\}} \right) \right] \\
&= -\frac{1}{\beta}\frac{1}{Z}\sum_c \left[-\beta\ n_x^{eff} \right. \\
&+ \left. \sum_{\substack{i<K \\ \Delta(\{n^{(i)}\},\{n^{(i+1)}\})=4}} \frac{\tilde{\beta}^2 (n_x^{(i)} + n_x^{(i+1)}) W^{III}_{\{n^{(i)}\}\{n^{(i+1)}\}}}{2\ A^{2T}_{\{n^{(i)}\}\{n^{(i+1)}\}}} \right] \cdot w(c) \\
&= \frac{1}{Z}\sum_c \left[n_x^{eff} \right. \\
&- \left. \sum_{\substack{i<K \\ \Delta(\{n^{(i)}\},\{n^{(i+1)}\})=4}} \frac{\tilde{\beta} (n_x^{(i)} + n_x^{(i+1)}) W^{III}_{\{n^{(i)}\}\{n^{(i+1)}\}}}{2\ M\ A^{2T}_{\{n^{(i)}\}\{n^{(i+1)}\}}} \right] \cdot w(c)
\end{aligned}
$$

References for figures

Figure 1: (Dornheim et al., 2018)
Figure 2: (Schoof, 2016) Note from Author:" Average sign versus a) basis size and b) temperature for $N = 4$ particles and densities given by $r_s \in [1, 2, 3, 4, 5]$, indicated by colours green, blue, red, violet ,and orange respectively. In a), the temperature is $\Sigma = 0.0625$ and in b), $N_B = 515$ basis functions are used. Solid lines are guides to the eye. Note the different scales of abscissia."

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Erklärung

Hiermit erkläre ich, dass ich die vorliegende Arbeit selbständig und ohne fremde Hilfe angefertigt und keine anderen als die angegebenen Quellen und Hilfsmittel verwendet habe. Weiterhin versichere ich, dass diese Arbeit noch nicht als Abschlussarbeit an anderer Stelle vorgelegen hat.

Bonn, 14.11.2019
Ort, Datum

Unterschrift