

30 hp Master Thesis
June, 2018

Variational approach to the many-body problem with error estimation

Claes Rogius Svensson

Division of Mathematical Physics, Department of Physics, Lund University

Supervised by Gillis Carlsson



LUND
UNIVERSITY

Abstract

In this thesis a method for doing approximate calculations of the ground state of quantum mechanical many-body systems is developed and implemented. This method uses the Hartree-Fock method as a starting point and approximates the ground state as a linear combination of non-orthogonal Slater determinants. The Slater determinants are added consecutively by minimising their associated energy while keeping the previously found Slater determinants fixed. This method was tested on a quantum harmonic oscillator filled with interacting fermions and was found to give good approximations to the ground state of this system with only a few Slater determinants. Error estimation of the approximated ground state is done by calculating the energy variance. The energy variance was used in two different methods for improving upon the approximated energy, both of which was found to work well.

Contents

1	Introduction	4
2	Theory	5
2.1	Many-body quantum theory	5
2.1.1	Many-body states	5
2.1.2	Many-body operators	5
2.1.3	Solving the Schrödinger equation	7
2.2	Hartree-Fock method	7
2.2.1	Slater determinants	8
2.2.2	Calculation of energy	8
2.2.3	Variational principle	8
2.2.4	Mean field approximation	9
2.3	Quantum harmonic oscillator	9
2.3.1	Energies and eigenstates	9
2.3.2	Ground state with several particles	10
3	Method	11
3.1	Description of method	11
3.2	Numerical implementation	12
3.3	Error estimation	15
4	Results	17
4.1	Presentation of problem	17
4.2	Calculated energies	19
4.3	Variance	22
4.4	Standard deviation	24
4.5	Time	28
5	Outlook	29
5.1	Summary	29
5.2	Extensions	29
A	Gram-Schmidt Orthogonalization	32
B	Method of gradient descent	32

Acknowledgements

I would like to thank my supervisor Gillis Carlsson for his help and advice in producing this thesis. I would also like to thank David Gustafsson with whom i have discussed this work. Furthermore, i would like to thank my family for their support.

1 Introduction

Many interesting problems in physics involve more than one or two particles. These problems, known as many-body problems, appear in a wide range of applications of quantum mechanics, from nuclear structure theory to atomic physics to condensed matter theory. As the particles in these systems generally interact, solving these types of problems analytically is often not possible. Due to this, numerical methods have to be applied to these problems.

There exist several numerical methods for solving quantum mechanical many-body problems, both exact and approximative. These methods have in common that they become computationally more expensive when the number of interacting particles increase. This becomes an issue for exact methods where large systems become intractable to solve. An issue with approximative methods, although computationally cheaper than exact methods, is that they give less valid solutions as the number of interacting particles increase. A method that scales well with an increasing number of particles that can give valid solutions to many-body problems would therefore be desirable.

A way of accomplishing this would be to extend upon an approximative method, such as the Hartree-Fock method, which is a computationally cheap mean-field method. The Hartree-Fock method works by approximating the wave function as a single Slater determinant, an expression used in the description of anti-symmetric wave functions. A way of extending the Hartree-Fock method would be to use not one, but several Slater determinants. Finding the Slater determinants that approximate the wave function can be done in different ways, such as in Ref. [5] where a Monte-Carlo method is used. In this thesis a method is presented where the Slater determinants and their coefficients are found through minimisation of the energy that they yield.

Another issue is how to evaluate how well the calculated solutions approximate the actual wave functions. This is done by calculating the variance and standard deviation of the Hamilton operator, quantities which tend towards zero as the approximation improves. The calculated variances can also give an improvement upon the approximation of the energy through a novel extrapolation method proposed in Ref. [5].

The system which this approximation method is tested upon is the quantum harmonic oscillator filled with several interacting fermions. The quantum harmonic oscillator is an important system since it can be used to approximate potential wells and therefore is used in a wide variety of applications of quantum mechanics.

2 Theory

In this section the theory used in this thesis will be presented. Firstly, the necessary theory concerning many-body problems is presented. This includes the states used to describe many-body problems and the operators that will be used. Also, a method which can solve these types of problems exactly is described. Secondly, the Hartree-Fock method is introduced. This is an approximate method for solving many-body problems and will serve as the starting point for the method presented in the thesis. Lastly, the quantum harmonic oscillator is introduced as this is the problem which is the problem to which the many-body method is applied.

2.1 Many-body quantum theory

2.1.1 Many-body states

A quantum mechanical state with one particle is described by a vector in Hilbert space, \mathcal{H} . Such vectors describing quantum mechanical states are known as kets and are usually denoted as $|\psi\rangle$. These kets can be expressed as:

$$|\psi\rangle = \sum_i c_i |\phi_i\rangle, \quad (1)$$

where $\{|\phi_i\rangle\}$ is an orthonormal basis of single particle states that spans the Hilbert space and c_i is the amplitude of each basis element, calculated as $c_i = \langle\phi_i|\psi\rangle$. If a quantum mechanical system consists of N particles, the quantum state is represented by a vector in an N -particle Hilbert space \mathcal{H}_N . The particles that these many-body systems can consist of are either bosons or fermions, which are distinguished by the fact that the former has integer-valued spin while the latter has half-integer-valued spin. Further difference between these two classes of particles is that bosonic states are symmetric while fermionic states are anti-symmetric with respect to changing coordinates of two particles. In the case of fermions, which this thesis treats, the states in the space \mathcal{H}_N , are constructed as anti-symmetrised sums of product states. In the case of two fermions the anti-symmetrised state has the following appearance:

$$|\phi_1\phi_2\rangle = \frac{1}{\sqrt{2}}(|\phi_1\rangle|\phi_2\rangle - |\phi_2\rangle|\phi_1\rangle). \quad (2)$$

For the sake of brevity, the shorthand notation $|\phi_1\rangle|\phi_2\rangle = |\phi_1\rangle \otimes |\phi_2\rangle$ is used. One can from this expression conclude that if $|\phi_1\rangle = |\phi_2\rangle$, then $|\phi_1\phi_2\rangle = 0$. This shows that two fermions cannot occupy the same quantum mechanical state, which is a manifestation of the Pauli exclusion principle. The anti-symmetry of this state is easily verified:

$$|\phi_2\phi_1\rangle = \frac{1}{\sqrt{2}}(|\phi_2\rangle|\phi_1\rangle - |\phi_1\rangle|\phi_2\rangle) = -|\phi_1\phi_2\rangle. \quad (3)$$

This also generalises to states with N particles:

$$|\phi_1\phi_2\dots\phi_i\dots\phi_j\dots\phi_N\rangle = -|\phi_1\phi_2\dots\phi_j\dots\phi_i\dots\phi_N\rangle. \quad (4)$$

2.1.2 Many-body operators

Two operators often used while working with many-body states are the creation and annihilation operators. These operators, as their respective names suggest, create and annihilate particles within the state that they are applied to. They are also used to define other operators such as the one-body, two-body and the density operator. The action of a creation operator on a vacuum state is the following:

$$c_i^\dagger |0\rangle = |\phi_i\rangle. \quad (5)$$

The creation operator thus increase the number of particles in the state from zero to one. The action of the annihilation operator is the reversed:

$$c_i |\phi_i\rangle = |0\rangle. \quad (6)$$

These operators obey the following anti-commutation relations:

$$\{c_i^\dagger, c_j\} = \delta_{i,j}, \quad (7)$$

$$\{c_i^\dagger, c_j^\dagger\} = 0, \quad (8)$$

$$\{c_i, c_j\} = 0. \quad (9)$$

Using these relations, the action of creation and annihilation operators on many-body states can be deduced:

$$c_i^\dagger |\phi_1\phi_2\dots\phi_{i-1}\phi_{i+1}\dots\phi_N\rangle = |\phi_i\phi_1\phi_2\dots\phi_{i-1}\phi_{i+1}\dots\phi_N\rangle = f |\phi_1\phi_2\dots\phi_{i-1}\phi_i\phi_{i+1}\dots\phi_N\rangle. \quad (10)$$

In equation 10 the action of the creation operator c_i^\dagger is seen. Initially the state $|\phi_i\rangle$ is unoccupied. The creation operator then creates a particle in this state and by the use of the anti-commutations relations, the state is then reordered. This results in a factor f which is defined as:

$$f = (-1)^{i-1}. \quad (11)$$

The application of the creation operator has thereby increased the number of particles in the many-body state by one. If the operator c_i^\dagger is applied to a state where $|\phi_i\rangle$ is already occupied, the action of the operator is the following:

$$c_i^\dagger |\phi_1\phi_2\dots\phi_i\dots\phi_N\rangle = 0. \quad (12)$$

Application of the annihilation operator on many-body states has the effect of reducing the number of particles in a state by one:

$$c_i |\phi_1\phi_2\dots\phi_i\dots\phi_N\rangle = f |\phi_1\phi_2\dots\phi_N\rangle. \quad (13)$$

The factor f is here defined as previously. If the operator c_i is applied to a state where $|\phi_i\rangle$ is unoccupied, the action of the operator is the following:

$$c_i |\phi_1\phi_2\dots\phi_{i-1}\phi_{i+1}\dots\phi_N\rangle = 0. \quad (14)$$

The one-body operator, which is defined through creation and annihilation operators, is an operator which only acts on one particle. This operator is defined as follows:

$$\mathcal{T} = \langle i|T|j\rangle c_i^\dagger c_j. \quad (15)$$

A one-body operator thus works by taking a particle out of single particle state $|\phi_j\rangle$ and putting it into state $|\phi_i\rangle$ with amplitude $\langle i|T|j\rangle$. This amplitude is calculated as:

$$\langle i|T|j\rangle = \int \phi_i^*(x)T(x)\phi_j(x)dx. \quad (16)$$

A one-body operator which affects all particles in a state can be constructed simply as a sum of one-body operators:

$$\mathcal{T} = \sum_{ij} \langle i|T|j\rangle c_i^\dagger c_j. \quad (17)$$

The two-body operator depends on coordinates of two particles and is used for describing interactions between particles. Such an operator, affecting only a single pair of particles, is also defined using creation and annihilation operators and is stated as:

$$\mathcal{V} = \langle ij|V|kl\rangle c_i^\dagger c_j^\dagger c_l c_k. \quad (18)$$

The amplitude is calculated as:

$$\langle ij|V|kl\rangle = \int \int \phi_i^*(x)\phi_j^*(x')V(x,x')\phi_k(x)\phi_l(x')dx dx'. \quad (19)$$

A two-body operator which affects all possible pairs of particles can be written as a sum of two-body operators:

$$\mathcal{V} = \frac{1}{4} \sum_{ijkl} \langle ij|V|kl\rangle c_i^\dagger c_j^\dagger c_l c_k. \quad (20)$$

For a more thorough introduction to many-body states and many body operators consult refs. [2] and [3].

2.1.3 Solving the Schrödinger equation

To calculate the energies and wave-functions of many-body systems, one has to solve the time-independent Schrödinger equation:

$$H |\Psi\rangle = E |\Psi\rangle, \quad (21)$$

where H is the Hamiltonian of the system, $|\Psi\rangle$ is a many-body state and E is the energy associated with this state. The Hamiltonian is stated as a sum of the one- and two-body operators introduced in the previous section:

$$H = \mathcal{T} + \mathcal{V}. \quad (22)$$

It is generally not possible to solve this equation analytically for many-body systems, which is why numerical methods are usually used when doing many-body calculations. One numerical method for doing these kinds of calculations is full configuration interaction (CI). This method utilises the fact that the many-body state can be expressed as a sum of many-body basis states as:

$$|\Psi\rangle = \sum_i c_i |\Phi_i\rangle, \quad (23)$$

where $\{|\Phi_i\rangle\}$ is an orthonormal basis of many-body states and c_i are the respective amplitudes of the basis states, $c_i = \langle \Phi_i | \Psi \rangle$. These amplitudes are calculated by formulating the Schrödinger equation in the following way:

$$\begin{pmatrix} \langle \Phi_1 | H | \Phi_1 \rangle & \langle \Phi_1 | H | \Phi_2 \rangle & \dots \\ \langle \Phi_2 | H | \Phi_1 \rangle & \langle \Phi_2 | H | \Phi_2 \rangle & \dots \\ \vdots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ \vdots \end{pmatrix} = E \begin{pmatrix} c_1 \\ c_2 \\ \vdots \end{pmatrix}. \quad (24)$$

The Schrödinger equation is then solved by diagonalising this matrix. As this method does not introduce any approximations, it solves the Schrödinger equation exactly within the space that is spanned by the many-body states. The amount of many-body states that are considered thus dictates the accuracy of the solution which is obtained by this method. Due to numerical restrictions however, the amount of many-body states considered has to be restricted. This limits the applicability of this method as the number of many-body states needed to obtain an accurate solution to the Schrödinger equation grows very rapidly, thereby increasing the size of the matrix that has to be constructed and diagonalised. A system with N particles and dimensionality n would describe a state as sum of

$$i = \binom{n}{N} \quad (25)$$

orthogonal many-body states. More on the subject of configuration interaction can be found in [1].

2.2 Hartree-Fock method

The Hartree-Fock method is an approximative method for determining the wave-function and energy of a quantum mechanical many-body system. This is done by approximating the wave-function as a single Slater determinant and minimising the associated energy of the wave-function via the variational principle. Furthermore, the Hartree-Fock method employs the mean-field approximation. This method is computationally very cheap compared to the configuration interaction method.

2.2.1 Slater determinants

One of the important assumptions of the Hartree-Fock method is that an exact wave function can be approximated by a single Slater determinant. A Slater determinant is an anti-symmetrized wave function which is composed of several independent particle wave functions. The Slater determinant is used to describe the wave function of systems with several fermions and is written in the case of N particles, as a determinant, in the following way:

$$\psi(x_1, x_2, \dots, x_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(x_1) & \phi_2(x_1) & \cdots & \phi_N(x_1) \\ \phi_1(x_2) & \phi_2(x_2) & \cdots & \phi_N(x_2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1(x_N) & \phi_2(x_N) & \cdots & \phi_N(x_N) \end{vmatrix},$$

where the factor preceding the determinant ensures normalisation.

2.2.2 Calculation of energy

The energy of the wave function is calculated as the expectation value of the Hamiltonian:

$$E = \langle \psi | H | \psi \rangle. \quad (26)$$

An alternative formulation for calculating the energy relies on using the density matrix which contains information concerning the occupation of different states within the system. As a many-body Hamiltonian can be stated as a sum of one- and two-body operators, expressions for their respective density matrices are needed. The matrix elements for a one-body density matrix are stated as:

$$\rho_{ij} = \langle \psi | c_j^\dagger c_i | \psi \rangle, \quad (27)$$

and for the two-body density matrix they are stated as:

$$\rho_{ijkl} = \langle \psi | c_i^\dagger c_j^\dagger c_l c_k | \psi \rangle. \quad (28)$$

Using equation 28 and a matrix representation of the Hamiltonian, rewritten as a single two-body operator (this is done explicitly in sec 4.1):

$$H_{ijkl} = \langle ij | H | kl \rangle, \quad (29)$$

the energy can be calculated as the following sum:

$$E = \sum_{ijkl} H_{ijkl} \rho_{ijkl}. \quad (30)$$

With the aid of Wick's theorem [4], the density matrix in equation 28, can be rewritten in the following way:

$$\rho_{ijkl} = \rho_{il} \rho_{jk} - \rho_{ik} \rho_{jl}. \quad (31)$$

The energy can then be evaluated as:

$$E = \sum_{ijkl} H_{ijkl} (\rho_{il} \rho_{jk} - \rho_{ik} \rho_{jl}). \quad (32)$$

2.2.3 Variational principle

To find the wave-function which yields the lowest energy and thereby approximates the ground state of a system, the variational principle [2], which can be stated as follows:

$$\delta \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} = 0, \quad (33)$$

is employed. δ signifies the functional derivative. This method utilises the fact that any ket, other than the eigenket of the Hamiltonian, will yield a higher energy than the energy of the ground state. This can be stated as:

$$\tilde{E} \geq E_0, \quad (34)$$

where E_0 is the energy of the ground state and

$$\tilde{E} = \frac{\langle \tilde{0} | H | \tilde{0} \rangle}{\langle \tilde{0} | \tilde{0} \rangle}, \quad (35)$$

where $|\tilde{0}\rangle$ is a trial ket. The approximation of the ground state is done by guessing a trial ket and then minimising the energy via some optimisation method.

2.2.4 Mean field approximation

The Hartree-Fock method employs, as previously stated, a mean-field approximation. This approximation is based on averaging the interaction between the particles. By doing this, a mean-field is created that each individual particle experiences [8]. This is of course a simplification of the true nature of a many-body system, in which every particle affects every other particle in different ways. This restricts the accuracy which can be attained by the Hartree-Fock method. A way of circumventing this would be to express the many-body state as a sum of several Slater determinants. This would be more computationally demanding but could give a more accurate description of the many-body state.

2.3 Quantum harmonic oscillator

In this section some theory concerning the quantum harmonic oscillator is presented. In the tests of the new approximation method the eigenstates of the quantum harmonic oscillator will be used as basis states. The quantum harmonic oscillator is a very important system as it can be used to model many potentials in quantum mechanics. Examples of where the quantum harmonic oscillator finds its use are in the approximation of nuclear potentials, in the approximation of the potential created by magnetic traps in Bose-Einstein condensate experiments and in the modeling of phonons in solid state physics [3] [8].

2.3.1 Energies and eigenstates

The Hamiltonian for the one dimensional harmonic oscillator is:

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{m\omega^2 \hat{x}^2}{2}. \quad (36)$$

\hat{x} and \hat{p} are the position and momentum operators, respectively. m signifies the mass of a particle and ω the angular frequency of the harmonic oscillator. The Hamiltonian can be restated in terms of creation and annihilation operators expressed as:

$$\hat{a} = \sqrt{\frac{m\omega}{2\hbar}} \left(\hat{x} + \frac{i\hat{p}}{m\omega} \right), \hat{a}^\dagger = \sqrt{\frac{m\omega}{2\hbar}} \left(\hat{x} - \frac{i\hat{p}}{m\omega} \right). \quad (37)$$

These have the following effect on a state $|n\rangle$:

$$\hat{a} |n\rangle = \sqrt{n} |n-1\rangle, \hat{a}^\dagger |n\rangle = \sqrt{n+1} |n+1\rangle, \quad (38)$$

where n signifies what harmonic oscillator state that is being occupied. Combining these operators, the number operator can be defined:

$$\hat{N} = \hat{a}^\dagger \hat{a}. \quad (39)$$

Using equations 37 and 39 the following expression for the Hamiltonian can be deduced:

$$\hat{H} = \hbar\omega \left(\hat{N} + \frac{1}{2} \right). \quad (40)$$

By applying this Hamiltonian on an eigenstate $|n\rangle$, the energies of the different eigenstates become:

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega, \quad n = 0, 1, 2, \dots \quad (41)$$

The eigenfunctions of the harmonic oscillator in the spatial representation, $\langle x|\phi_n\rangle = \phi_n(x)$, are [2]:

$$\phi_n(x) = \frac{1}{\sqrt{2^n n!}} \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}}, H_n\left(\sqrt{\frac{m\omega}{\hbar}}x\right) \quad (42)$$

where H_n are the Hermite polynomials:

$$H_n(z) = -1^n e^{z^2} \frac{\partial^n}{\partial z^n} \left(e^{-z^2}\right). \quad (43)$$

As can be seen, the case of a one-dimensional harmonic oscillator with one particle is possible to solve analytically.

2.3.2 Ground state with several particles

The ground state for a quantum harmonic oscillator filled with several particles is also a problem for which there exists an analytic solution. In calculating the energy of such a state, the spin of the particles in question has to be considered. Fermions, which have half-integer spin, cannot share the same quantum mechanical state according to the Pauli principle. Two fermions can however occupy states with the same eigenenergies, given that they have different spin (up and down). The ground state will thus consist of particles occupying the lowest available eigenstates pairwise. The ground state of a harmonic oscillator containing N particles will thereby have the energy:

$$E_N = \frac{\hbar\omega}{2} \left\lceil \frac{N^2}{2} \right\rceil, \quad (44)$$

where $\lceil \cdot \rceil$ is the ceiling function [9] which returns the least integer greater than a real number. If an interaction is added between the particles confined in the oscillator potential and analytic solution is no longer possible to find and numerical methods have to be employed.

3 Method

In this section the approximation method this thesis concerns itself with is described. Firstly, some expressions concerning the evaluation of the energy of states is introduced and the methodology is described. Secondly, the numerical implementation (which has been done in FORTRAN), is described. Lastly, the error estimation of the states, which is done through calculation of variance, is introduced.

3.1 Description of method

A single Slater-determinant can in most cases not approximate the wave function of a ground state exactly. A way of improving the approximation is to express the wave function in terms of more than one Slater determinant, thereby going beyond the Hartree-Fock approximation. In this thesis the improvement on the approximation is done by using a linear combination of a finite number of non-orthogonal Slater-determinants

$$|\psi\rangle = c_1 |\psi_1\rangle + c_2 |\psi_2\rangle + \dots + c_N \cdot |\psi_N\rangle \quad (45)$$

As the different Slater-determinants in the expansion are non-orthogonal, the norm overlap between them is non-zero:

$$n_{ij} = \langle \psi_i | \psi_j \rangle \neq 0. \quad (46)$$

The overlap between an individual Slater-determinant and itself is one due to the normalisation of the states. Furthermore, the overlaps between the different Slater determinants are assumed to be real:

$$\langle \psi_i | \psi_j \rangle = \langle \psi_j | \psi_i \rangle. \quad (47)$$

The energy of the state in equation 45 is calculated as:

$$E^{(N)} = \sum_{ij}^N c_i c_j E_{ij}, \quad (48)$$

where:

$$E_{ij} = \langle \psi_i | H | \psi_j \rangle, \quad (49)$$

are calculated in the same way as the energy in the Hartree-Fock method (see sec. 2.2.2). The Slater determinants and their amplitudes in the expansion of the ground state will be chosen by minimisation of the energy that they yield. This will be done by adding more terms to the expansion consecutively, giving the energy of the approximations the following property:

$$E^{(1)} > E^{(2)} > \dots > E^{(N)} > E_0, \quad (50)$$

where E_0 is the energy of the exact ground state. The first term in this expression, $E^{(1)}$, is the the Hartree-Fock energy since it is calculated with only one Slater determinant and is thus calculated as described in section 2.2. The optimisation method used to do this is the method of gradient descent (described in appendix B). The following step consists in calculating $E^{(2)}$, where the ground state is approximated by two Slater determinants:

$$|\psi\rangle = c_1 |\psi_1\rangle + c_2 |\psi_2\rangle. \quad (51)$$

$|\psi_1\rangle$ in this expression is the state calculated by the Hartree-Fock method and c_1 is the amplitude for this state within the second approximation. This amplitude can be chosen as:

$$0 < c_1 < 1. \quad (52)$$

The second Slater determinant $|\psi_2\rangle$ and its amplitude c_2 is then found by minimisation of the energy $E^{(2)}$, which is also done through the gradient descent method. This is done while $|\psi_1\rangle$ and c_1 is kept fixed. During the minimisation the approximated ground state has to be normalised:

$$\langle \psi | \psi \rangle = c_1^2 + 2c_1 c_2 n_{12} + c_2^2 = 1. \quad (53)$$

This is done by continuously during the minimisation solving the quadratic equation:

$$c_2 = -c_1 n_{12} + \sqrt{c_1^2 n_{12}^2 - c_1^2 + 1}. \quad (54)$$

The extension from $N - 1$ to N Slater determinants in the description of the ground state, as in expression 45, is done in similar fashion. The amplitudes c_1, c_2, \dots, c_{N-1} in this expression are chosen as:

$$c_1 = A_1 c'_1, c_2 = A_2 c'_2, \dots, c_{N-1} = A_{N-1} c'_{N-1}, \quad (55)$$

where $c'_1, c'_2, \dots, c'_{N-1}$ are the amplitudes from the previous step in the approximation and A_1, A_2, \dots, A_{N-1} are chosen as:

$$0 < A_1, A_2, \dots, A_{N-1} < 1. \quad (56)$$

The N th Slater determinant and its amplitude are then chosen by minimisation of the energy $E^{(N)}$ while the previously chosen Slater determinants and amplitudes are kept fixed. During the minimisation (by gradient descent), the state is normalised:

$$\langle \psi | \psi \rangle = (c_1 \langle \psi_1 | + c_2 \langle \psi_2 | + \dots + c_N \langle \psi_N |) (c_1 | \psi_1 \rangle + c_2 | \psi_2 \rangle + \dots + c_N | \psi_N \rangle) = 1. \quad (57)$$

This is done by solving the quadratic equation:

$$c_N = -\frac{A}{2} + \sqrt{\frac{A^2}{4} - B}, \quad (58)$$

where:

$$A = \sum_{i=1}^{N-1} c_i n_{iN}, \quad (59)$$

and:

$$B = \sum_{i=1}^{N-1} c_i^2 + \sum_{i=1}^{N-2} \sum_{j=2}^{N-1} 2c_i c_j n_{ij} - 1. \quad (60)$$

More steps in the approximation can in this way be added until a desired accuracy has been achieved.

3.2 Numerical implementation

In this section, the numerical implementation of this method (done in FORTRAN), is presented. In numerical calculations the possible space of orbitals has to be restricted, and the Slater determinants used in the approximation can be expressed in discretised form as [4]:

$$|\psi\rangle = \prod_{i=1}^{N_p} a_i^\dagger |0\rangle, \quad (61)$$

where N_p is the number of particles considered and a_i^\dagger is a generalised creation operator. The generalised creation operators can be expressed as a sum of creation operators $c_1^\dagger, c_2^\dagger, \dots, c_{N_s}^\dagger$, which each are creation operators of a harmonic oscillator state labeled by l :

$$\phi_l(x) = \langle x | c_l^\dagger | 0 \rangle. \quad (62)$$

The creation operators are related through the following expression:

$$a_i^\dagger = \sum_l^{N_s} D_{li} c_l^\dagger. \quad (63)$$

D is a matrix of size $N_s \times N_p$ where $N_s > N_p$ and N_s is the number of single particles orbitals. This matrix characterises the many-body state. For this matrix to represent a Slater determinant, it has to be orthonormal, which is ensured through Gram-Schmidt orthogonalisation (described in appendix A). The density matrix is written as [4]:

$$\rho_{ij}^{ab} = \frac{\langle \psi^a | c_i^\dagger c_j | \psi^b \rangle}{\langle \psi^a | \psi^b \rangle} = [D^a (D^{b\dagger} D^a)^{-1} D^{b\dagger}]_{ij}, \quad (64)$$

where D^a and D^b refers to different Slater determinants. In the case of $D^a = D^b$ this reduces to

$$\rho_{ij}^{aa} = D^a D^{a\dagger}, \quad (65)$$

since:

$$D^{a\dagger} D^a = I, \quad (66)$$

if D^a is an orthonormal matrix. The density matrix has the dimensionality $N_s \times N_s$. The norm overlap between different Slater determinants is calculated as [4]:

$$n_{ab} = \langle \psi^a | \psi^b \rangle = \det(D^{b\dagger} D^a), \quad (67)$$

where the matrix $D^{b\dagger} D^a$ has the dimensionality $N_p \times N_p$. Energy is evaluated through the previously introduced expression:

$$E_{aa} = \sum_{ijkl}^{N_s} H_{ijkl} \rho_{ijkl}^{aa}. \quad (68)$$

The energy between two different Slater determinants is calculated through the same formula while also considering the overlap:

$$E_{ab} = n_{ab} \sum_{ijkl}^{N_s} H_{ijkl} \rho_{ijkl}^{ab}, \quad (69)$$

where:

$$\rho_{ijkl}^{ab} = \rho_{il}^{ab} \rho_{jk}^{ab} - \rho_{ik}^{ab} \rho_{jl}^{ab}. \quad (70)$$

The Hamiltonian and the density matrix are written as vectors of length N_s^4 :

$$H_{ijkl} = [H_{1111}, H_{1112}, \dots, H_{N_s N_s N_s N_s}], \quad (71)$$

$$\rho_{ijkl} = \rho_{il} \rho_{jk} - \rho_{ik} \rho_{jl} = [\rho_{11} \rho_{11} - \rho_{11} \rho_{11}, \dots, \rho_{N_s N_s} \rho_{N_s N_s} - \rho_{N_s N_s} \rho_{N_s N_s}], \quad (72)$$

and the energy is thus calculated as an inner product between these vectors. In the following figures the implementation is schematically described in detail.

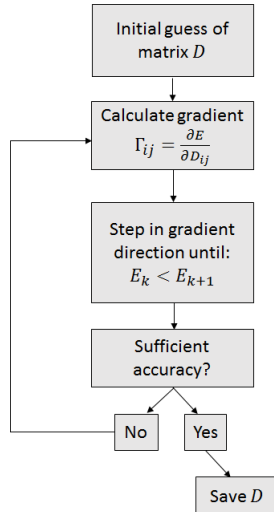


Figure 1: Schematic representation of implementation of the Hartree-Fock method.

Figure 1 describes the implementation of the first step in this approximation technique which is the Hartree-Fock method. Initially a guess of the ground state, represented by matrix D has to be made. The gradient is then calculated numerically and steps (as described in appendix B) are taken in the direction of the gradient. This is done until the energy in step $k + 1$ is higher than the energy in step k . A new gradient is then calculated from the point found by the previous calculation and the processes of minimisation is repeated. This is repeated until the difference in energy between consecutively found states is smaller than some chosen value. This process is then terminated and the matrix D is saved.

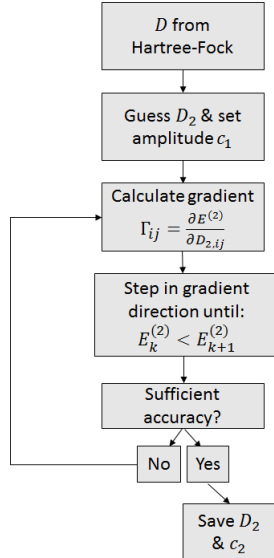


Figure 2: Schematic representation of implementation of the extension from the Hartree-Fock method to a two determinant approximation.

Figure 2 describes how the extension from the Hartree-Fock calculations to an expression containing two Slater determinants is done. The Slater determinant from the Hartree-Fock calculation is kept and used in this calculation. To initialise this procedure a guess for a second Slater determinant is done and an amplitude for the previously calculated Slater determinant is set. The gradient is calculated numerically

with respect to the second Slater determinant. The energy associated with the second Slater determinant is then minimised by stepping in the direction of the gradient until a minimum is found. During this minimisation the matrix representing the second Slater determinant is kept orthonormal by Gram-Schmidt orthogonalisation and the state is kept normalised. The Slater determinant calculated by the Hartree-Fock method and its amplitude is kept fixed during this minimisation. This procedure is repeated until sufficient accuracy is attained, which is decided in the same way as in the Hartree-Fock calculations. The Slater determinant and amplitude found by this procedure is then saved to be used in the next step of the calculation.

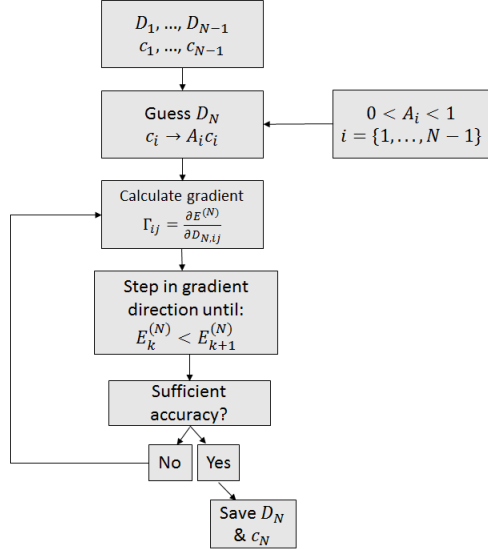


Figure 3: Schematic representation of implementation of the extension from an $N - 1$ to N determinant approximation.

Figure 3 describes how the extension from an expression containing $N - 1$ Slater determinants to an expression containing N Slater determinants is done. The previously calculated determinants and their associated amplitudes are kept from previous calculations and used in these calculations. To initialise these calculations a guess of a Slater determinant has to be done and the amplitudes associated with the previous determinants have to be decreased. A gradient is then calculated with respect to the new Slater determinant the energy associated with it is minimised by stepping in the direction of the gradient. This process is repeated until a sufficient accuracy is attained. More and more Slater determinants can be added using this technique. The basic assumption of the method is thus that the groundstate can be reached by only varying the latest Slater determinant and keeping the remaining ones fixed. With this assumption the number of variational parameters is kept small, thereby keeping the time for each variation small.

3.3 Error estimation

The error estimation is performed by calculating the energy variance of the states. Variance is defined as:

$$\langle \Delta H^2 \rangle = \langle \psi | H^2 | \psi \rangle - \langle \psi | H | \psi \rangle^2. \quad (73)$$

From this, the standard deviation can also be calculated:

$$\sigma = \sqrt{\langle \Delta H^2 \rangle}. \quad (74)$$

As the approximate state approaches the exact ground state, the value of this quantity decreases and tends towards zero. The exact ground state has energy variance of zero since it is an eigenstate of the

Hamiltonian:

$$\begin{aligned}\langle \Delta H^2 \rangle &= \langle \psi_0 | H^2 | \psi_0 \rangle - \langle \psi_0 | H | \psi_0 \rangle^2 = \\ &= E_0 \langle \psi_0 | H | \psi_0 \rangle - E_0^2 = E_0^2 - E_0^2 = 0.\end{aligned}\tag{75}$$

In calculating the energy variance of a state, the expectation value of H^2 has to be calculated. To this end, the following formulas [5], where $|\psi^a\rangle$ and $|\psi^b\rangle$ are different Slater determinants, are used:

$$\begin{aligned}g(\psi^a, \psi^b) &= \frac{\langle \psi^a | H^2 | \psi^b \rangle}{\langle \psi^a | \psi^b \rangle} = \sum_{i < j, \alpha < \beta} \left(\sum_{k < l} v_{ijkl} [(1 - \rho)_{k\alpha}^{ab} (1 - \rho)_{l\beta}^{ab} - (1 - \rho)_{l\alpha}^{ab} (1 - \rho)_{k\beta}^{ab}] \right) \times \\ &\times \left(\sum_{\gamma < \delta} (\rho_{\gamma i}^{ab} \rho_{\delta j}^{ab} - \rho_{\delta i}^{ab} \rho_{\gamma j}^{ab}) \right) + \text{Tr}[(t + \Gamma)(1 - \rho)^{ab}(t + \Gamma)\rho^{ab}] + \left(\text{Tr} \left[\rho^{ab} \left(t + \frac{1}{2} \Gamma \right) \right] \right)^2,\end{aligned}\tag{76}$$

$$\Gamma_{ik} = \sum_{jl} v_{ijkl} \rho_{lj}^{ab}.\tag{77}$$

In this expression v_{ijkl} denotes the interaction part of the Hamiltonian. As can be seen, the evaluation of the matrix elements consists of a sixfold summation over the indices of the one body density operators. This formula thus reduces the computing time needed to evaluate $\langle \psi^a | H^2 | \psi^b \rangle$ since it generally requires a eightfold summation over one body density operators if H^2 is regarded as a four-body operator. To illustrate how this function is used, in the case of two Slater determinants, the expression for the expectation value of the square of the Hamiltonian becomes:

$$\langle \psi | H^2 | \psi \rangle = c_1^2 g(\psi_1, \psi_1) + c_1 c_2 n_{12} g(\psi_1, \psi_2) + c_2 c_1 n_{21} g(\psi_2, \psi_1) + c_2^2 g(\psi_2, \psi_2).\tag{78}$$

As the approximation improves the energy variance will decrease:

$$\langle \Delta H^2 \rangle_1 > \langle \Delta H^2 \rangle_2 > \dots > \langle \Delta H^2 \rangle_N > 0.\tag{79}$$

A way of utilising this fact to improve upon the approximation of the calculated energy, would be to plot the calculated energies as a function of the calculated variances and extrapolating the energy towards $\langle \Delta H^2 \rangle = 0$. This can be done by fitting the values of energies and variances by a second order polynomial and evaluating this function at $\langle \Delta H^2 \rangle = 0$.

4 Results

In this section results concerning different aspects of this method are presented and discussed. Firstly, the physics problem considered is presented. Secondly the new method is tested and compared to exact results. This is followed by calculations of the variance and standard deviation of the approximated states. These quantities are then used to improve upon the approximation of the ground state energy.

4.1 Presentation of problem

The system considered in this thesis is a one-dimensional quantum harmonic oscillator. This oscillator is filled with four interacting fermions which interact through the delta potential. This potential is described as follows [10]:

$$V(x, x') = t_0 \delta(x - x'), \quad (80)$$

where t_0 dictates the strength of the interaction between the particles. This constant can assume either a positive or negative value, making the interaction either repulsive or attractive. In the case of $t_0 = 0$ there is no interaction between the particles. δ is the Dirac delta function which has the consequence that there is no interaction between particles with the same spin projection. The ground state of this problem will be calculated for 100 different interaction strengths with t_0 ranging from $t_0 = -4$ to $t_0 = 3.92$. The Hamiltonian for this problem looks as follows:

$$H = \sum_{il} t_{il} a_i^\dagger a_l + \frac{1}{4} \sum_{ijkl} V_{ijkl} a_i^\dagger a_j^\dagger a_k a_l. \quad (81)$$

It is practical to restate the first part of the Hamiltonian as a two-body operator. This is done with the use of a number operator in the following way:

$$\sum_{il} t_{il} a_i^\dagger a_l = \sum_{il} t_{il} a_i^\dagger \left(\frac{1}{N-1} \sum_{jk} a_j^\dagger a_k \delta_{jk} \right) a_l = \sum_{ijkl} \frac{t_{il} \delta_{jk}}{N-1} a_i^\dagger a_j^\dagger a_k a_l. \quad (82)$$

The Hamiltonian can thus be written as:

$$H = \sum_{ijkl} H_{ijkl} a_i^\dagger a_j^\dagger a_k a_l, \quad (83)$$

where:

$$H_{ijkl} = \frac{(n_i + \frac{1}{2})}{N-1} \delta_{il} \delta_{jk} + \frac{V_{ijkl}}{4}. \quad (84)$$

V_{ijkl} is calculated as in expression 19, N is the number of fermions in the oscillator and n_i refers to the different eigenenergies of the oscillator and runs as $\{0, 1, 2, \dots\}$. Neither \hbar nor ω appear in the expression of the Hamiltonian since for the sake of simplicity the value of these constants has been set as: $\hbar\omega = 1$. The number of allowed energy eigenstates of the oscillator has been restricted to 5, thereby restricting the dimension of the many-body states to 10 as each state can be occupied by two fermions with different spins. This gives the matrices which represent the Slater determinants dimensions 10×4 and the density matrices dimensions 10×10 . The ground state in the case of non-interacting fermions is known and can be written as one Slater determinant:

$$D = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}. \quad (85)$$

This yields the density matrix:

$$\rho = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}. \quad (86)$$

This represents a state where the first two levels of the harmonic oscillator are filled with two fermions each. This state has according to equation 44 energy $E = 4$. With interaction between particles a representation of the ground state with only one Slater determinant is not possible. As a benchmark for the approximation method, the energies of the exact groundstates in these cases have been calculated with the configuration interaction method.

4.2 Calculated energies

In the following figures the energies that have been calculated are presented together with the exact energies calculated with configuration interaction. The approximation method has been implemented to include seven Slater determinants. The amplitude c_1 when extending the expansion from one to two Slater determinants is chosen as $c_1 = \sqrt{0.9}$. The factor by which the amplitudes are decreased when extending the expansion from $N - 1$ to N Slater determinants is chosen as $A_i = \sqrt{0.9}$. This means that in each step 90% of the old wavefunction is kept and 10% can be replaced with something new. Since the states are allowed to be non-orthogonal the new Slater determinant found can have a large overlap with the old ones. In such a scenario, the method may partially add back what has been removed. When the new Slater determinant is added there is a new diagonal term in the energy and new crossterms. Because of the crossterms, a new lower energy can be found.

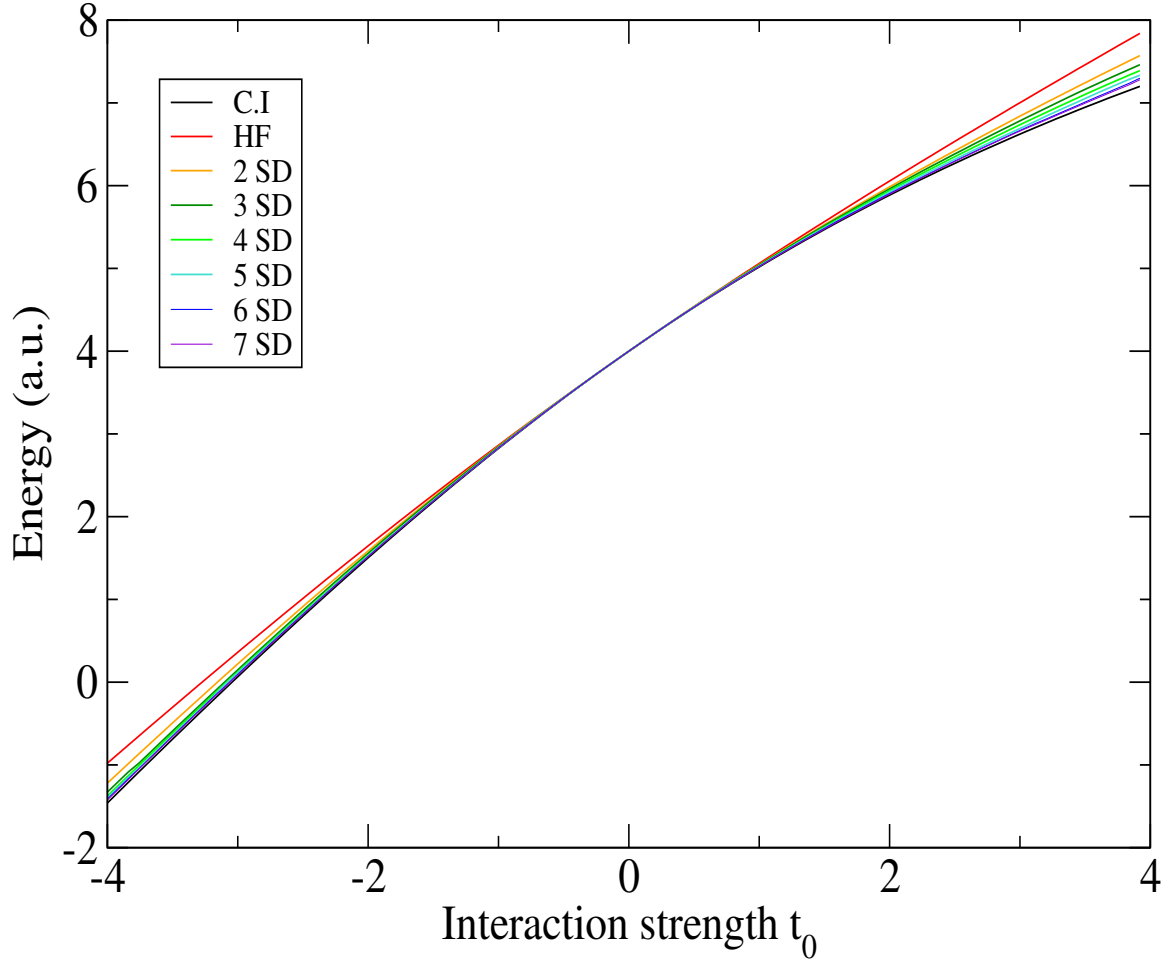


Figure 4: Calculated energies as function of interaction strength.

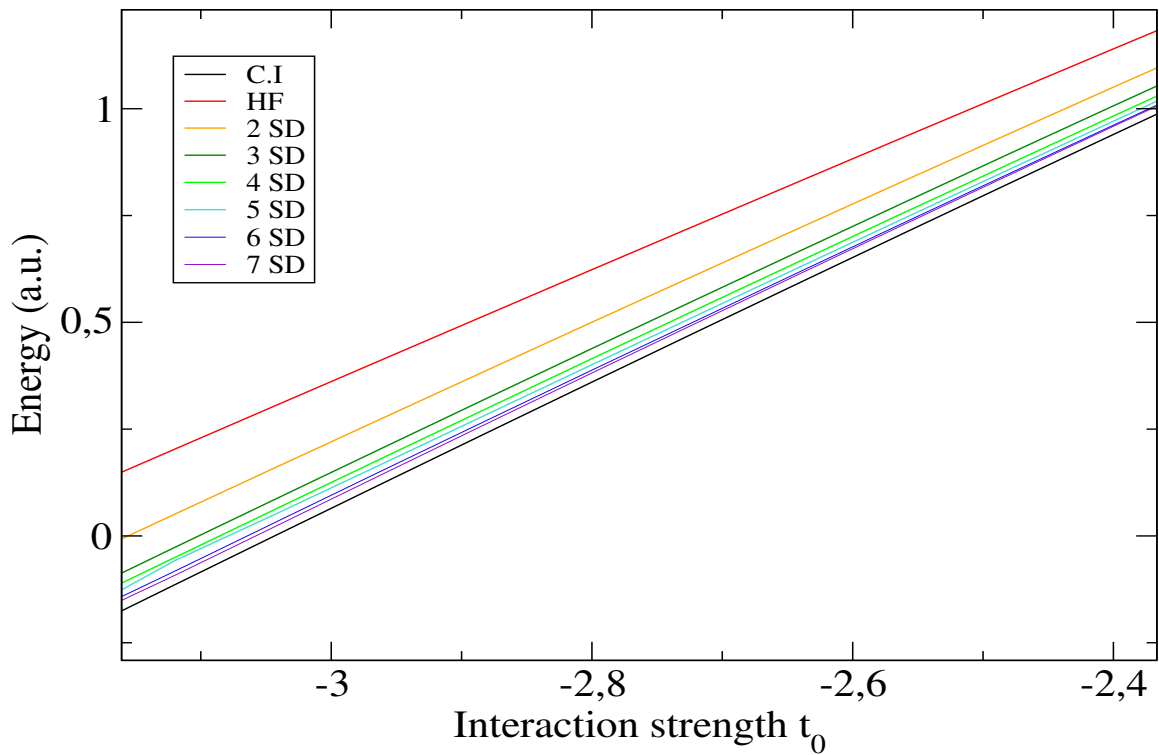


Figure 5: Zoomed in version of figure 4 on section with negative interaction.

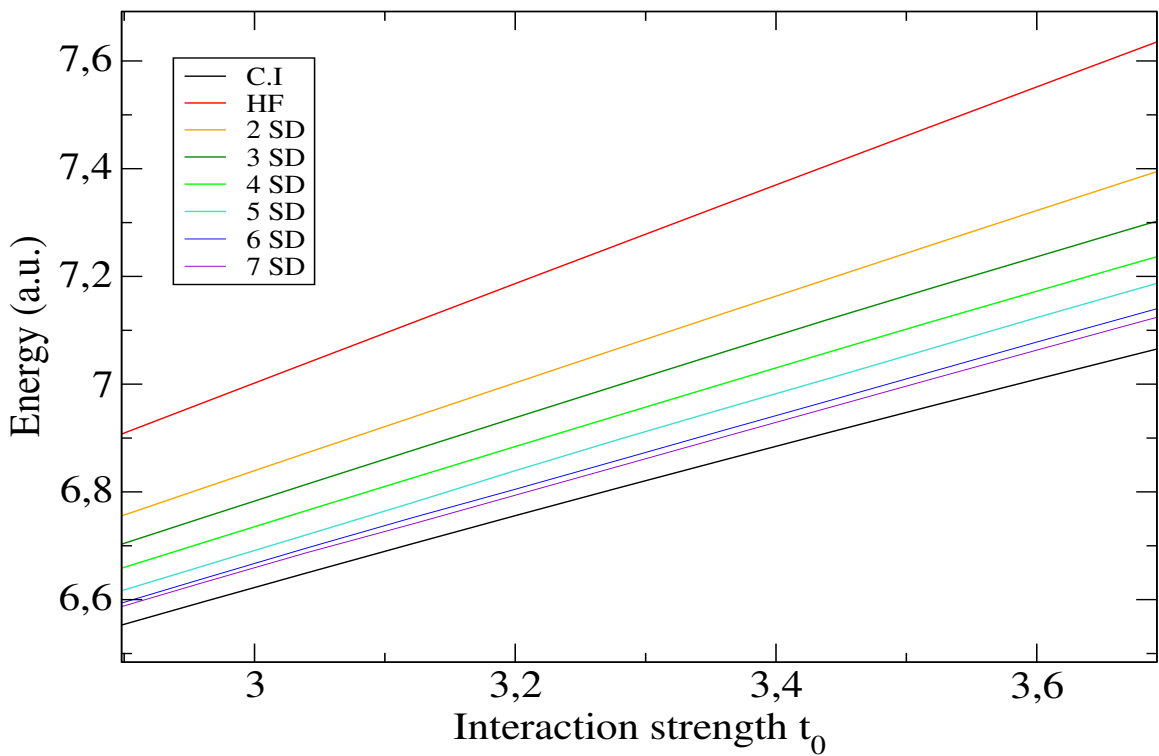


Figure 6: Zoomed in version of figure 4 on section with positive interaction.

In figure 4 the calculated energies are presented. This is accompanied by figures 5 and 6 which are zoomed in versions of figure 4. The configuration interaction method calculates the exact energy of the ground state. In the case of non-interacting particles this energy is $E = 4$. As the interaction becomes more repulsive (see fig. 6) the energy of the ground state increase. The ground state in these cases will not be the same as in the non-interacting case (see eq. 85 and 86). The exact ground state will here consist of a linear combination of orthogonal states (as described in sec. 2.1.3). Should the interaction strength be further increased the energy of the ground state would eventually stop increasing. This would happen when the energy of the ground state reached $E = 8$, since then the ground state would consist of the four lowest energy eigenstates being occupied by one particle each. This state can, as the ground state with non-interacting particles, also be described by a single Slater determinant. When the interaction strength becomes more attractive (see fig. 5), the energy of the ground state decrease. The exact ground states in these cases will also consist of a linear combination of orthogonal states.

The energies found by the Hartree-Fock method are in all cases but the non-interacting case, higher than the exact energies. This is expected since they are calculated through a variational principle. In the non-interacting case the Hartree-Fock and exact energies coincide since the Hartree-Fock method here also results in the exact ground state as it can be exactly described by a single Slater determinant. When the interaction is small, the Hartree-Fock energy is fairly close to the exact energies as in these cases the mean-field approximation is apt but as the interaction strength grows, the validity of this approximation falter. Should the interaction strength be increased to where the ground state would have energy $E = 8$, the Hartree-Fock energy would converge with the exact energy as in this case a single Slater determinant could again completely describe the ground state.

The energies calculated by the approximation method lie between the Hartree-Fock energies and the exact energies and get consecutively closer to the exact energies as more Slater determinants are added. In the non-interacting case, the energies from this method coincide with both the Hartree-Fock and the exact energies. As the Hartree-Fock method finds the exact ground state in this case, the later added Slater determinants will be the same as the one found in the first step. Going beyond Hartree-Fock calculations in this case is thus superfluous. With small interactions, where the Hartree-Fock method approximates the ground state well, only a few Slater determinants needs to be added for a good approximation to be achieved. In the cases where the interaction is large and the Hartree-Fock method does not give very accurate energies, this method requires more Slater determinants to approximate the exact energy well. In these cases the interaction is of large importance making the mean-field approximation less valid, thereby requiring the addition of more Slater determinants.

In the cases with most negative and most positive interaction, respectively, this method yields energies which are 99.1% and 98.0% correct with seven Slater determinants where the corresponding numbers for the Hartree-Fock method is 88.0% and 84.0%. This method can thus give a fairly accurate approximation of the ground state with only a few Slater determinants whereas the configuration interaction uses 210 Slater determinants.

4.3 Variance

In the following section the calculated variances are presented together with the interpolation method described in sec 3.3.

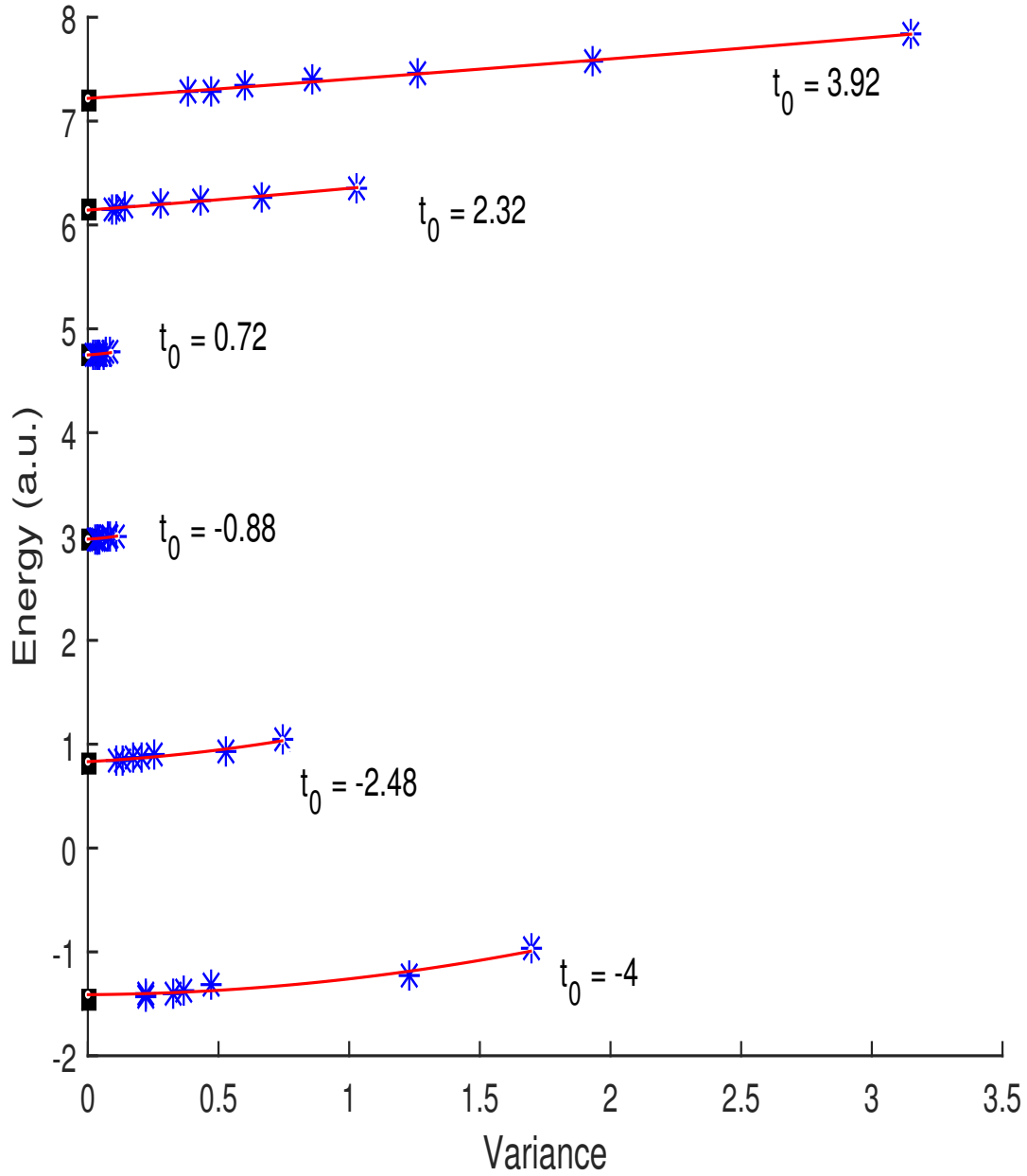


Figure 7: Energy as function of variance for six different interaction strengths. The blue stars represent the calculated energies and variances for consecutive approximations and the red line is a quadratic interpolation. The black squares are the exact energies.

In figure 7 the calculated variances are presented. The variances decrease as the approximation improves by addition of more Slater determinants. Differences between systems with different interaction strengths is clearly visible in this figure, where in the cases with large interaction the improvement in both variance and energy is large, and in the cases with small interaction this improvement is very small.

The interpolation of points by quadratic curves is shown as red lines in figure 7. In most of the cases these curves fit the points quite well and the extrapolation towards $\langle \Delta H^2 \rangle = 0$ does indeed give an improvement upon the calculated energies. For instance, in the case of interaction strength $t_0 = 3.92$, where the approximation through seven Slater determinants yields an energy which is 98.0% of the exact energy, the interpolation improves this figure to 99.5%. As this method can give an improvement upon the calculated energy, it can serve as an alternative to adding a few more Slater determinants, thereby shortening the time required to achieve a good approximation.

In certain cases however, this method does give worse approximations to the energy than the last point of the expansion. This is in figure 7 visible in the case of interaction strength $t_0 = -4$ where this method results in a higher energy than that of the seventh step in the expansion (an unreasonable results since the exact energy must be lower). Another place where this method falters is when the interaction is very weak. The improvement in both energy and variance are in these cases very small which makes extrapolation of points a highly uncertain procedure as points in the expansion lie very close to each other. This tendency stems in part from the gradient descent method used in the implementation, which can get stuck in local minima.

4.4 Standard deviation

The following section concerns the standard deviation of the calculated states and a discussion about the magnitude of the standard deviation.

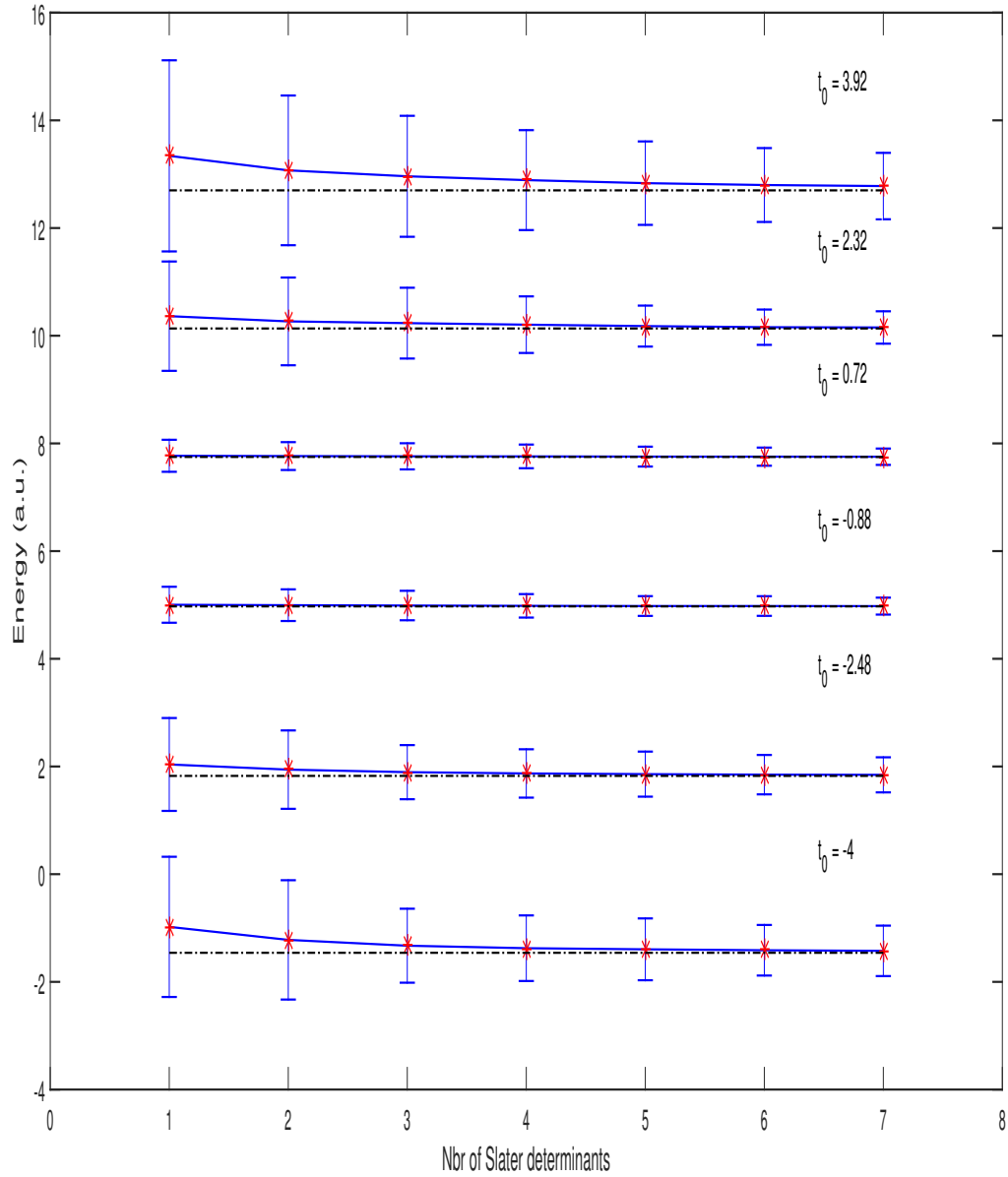


Figure 8: Energy as a function of the number of Slater determinants in the expansion. The red stars are the calculated energies, blue error bars are the standard deviation and the black dotted lines are the exact energies. To avoid overlaps between the error bars, the energies of the states has been shifted (compare with energies in figure 7).

As can be seen in figure 8 the standard deviation decrease for every consecutive approximation. However, the standard deviation does not decrease very much and does remain at fairly large values even for the last few points of the approximation. A way of interpreting these results is that the calculated state consists of the actual ground state and an excited state:

$$|\psi\rangle = \sin\theta|\psi_0\rangle + \cos\theta|\psi_1\rangle, \quad (87)$$

where $|\psi\rangle$ is the approximated ground state, $|\psi_0\rangle$ is the exact ground state and $|\psi_1\rangle$ is an assumed excited state. The assumed excited state could contribute to the large standard deviation. This can, however, be utilised to improve upon the calculated energy of the ground state. This state has the expectation value:

$$E = \langle H \rangle = \sin^2\theta E_0 + \cos^2\theta E_1, \quad (88)$$

where E_0 is the energy of the ground state and E_1 is energy associated with excited state $|\psi_1\rangle$. The expectation value of H^2 would be:

$$\langle H^2 \rangle = \sin^2\theta E_0^2 + \cos^2\theta E_1^2. \quad (89)$$

A shift of the energy scale with E_0 would yield the following expectation value of this state:

$$M = \langle H \rangle = \cos^2\theta E_x \quad (90)$$

and:

$$\langle H^2 \rangle = \cos^2\theta E_x^2. \quad (91)$$

E_x is now defined as the distance from the ground state to the excited state. The variance of this state is:

$$V = \langle H^2 \rangle - \langle H \rangle^2 = \cos^2\theta E_x^2 - \cos^4\theta E_x^2 = M E_x - M^2. \quad (92)$$

Since the energy scale is shifted with E_0 , M can be expressed as:

$$M = E - E_0. \quad (93)$$

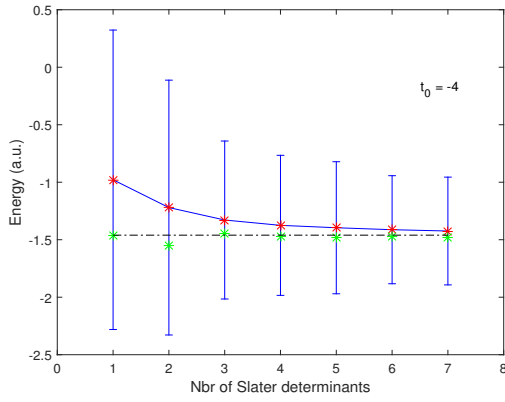
This yields the following expression for the variance:

$$V = E_x(E - E_0) - (E - E_0)^2. \quad (94)$$

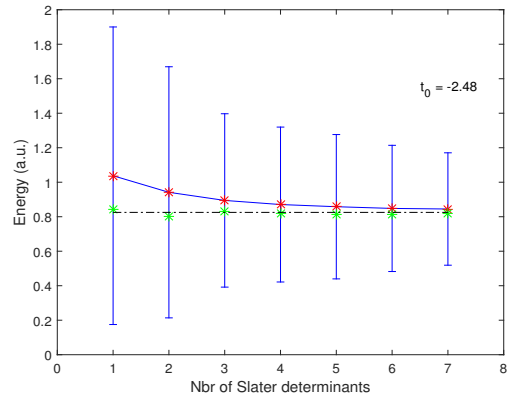
From this expression the ground state energy E_0 can be calculated given that E_x is guessed. E_0 is calculated as:

$$E_0 = E - \frac{E_x}{2} + \sqrt{\frac{E_x^2}{4} - V}, \quad (95)$$

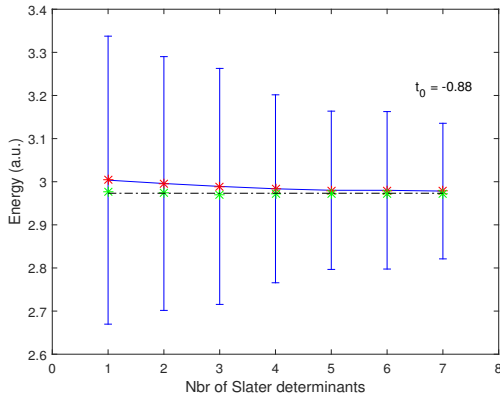
where E_0 is the energy of the ground state, E_x is the guessed energy, V is the calculated variance and E is the energy calculated through the approximation method.



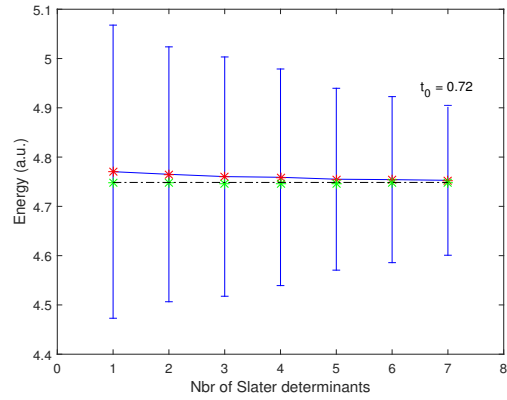
(a)



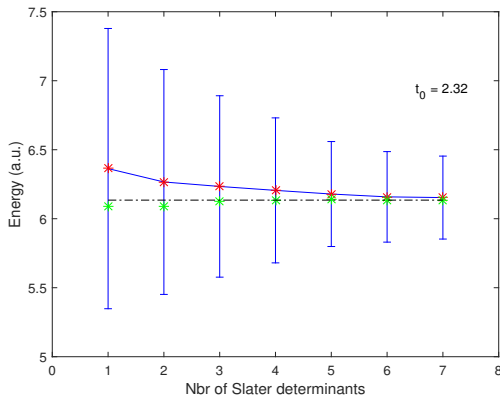
(b)



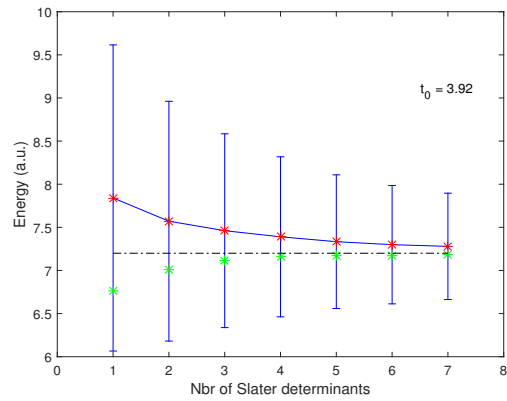
(c)



(d)



(e)



(f)

Figure 9: Energy plotted as function of the number of Slater determinants with same notation as in figure 8. The green stars are energies calculated through equation 95 with $E_x = 4$.

In figure 9 the results of this method are presented. This method is used on the same cases as in figure 8, and for all different interaction strengths the guess $E_x = 4$ is used. This method works well and gives energies closer to the exact ground state energy than the interpolation method does. Where the interpolation method falters, such as in for example the case of interaction strength $t_0 = -4$, this improves the approximation. In that case, where seven Slater determinants achieves an approximation of the exact energy 99.1% correct, this method improves that figure to 99.5%. This method also works well when the interaction strengths are small as the uncertainty of the interpolation is avoided.

An issue with this method is that the value of E_x somehow has to be guessed. $E_x = 4$ has been chosen here as it worked well for all interaction strengths, though this could be done since the exact ground state energy was known. The choice of E_x will in conjunction with the energy variance influence the value of the calculated ground state energy according to equation 95. If E_x is chosen as a large value, this expression will yield an energy close to the energy given by the approximation method, though slightly lower. The lowest E_x could be guessed as is $E_x = 2\sqrt{V}$. This would result in the energy:

$$E_0 = E - \sqrt{V}, \tag{96}$$

a result lower than the exact energy since the standard deviation is fairly large. This method can thereby give energies both higher and lower than the exact energy which can be seen in figure 8. In 8f and 8e the resulting energies lie lower than the exact energies and in 8b, the resulting energies are both lower and higher than the exact ground state energy. The different cases do have in common that the resulting energy is quite close to the exact energy in the last few points, where the variance is small. This method will always result in an energy lower than the one given by the approximation method which is fitting since the exact energy is also lower than the approximated energy.

4.5 Time

The time that this method requires to do calculations was recorded and these results are presented in this section.

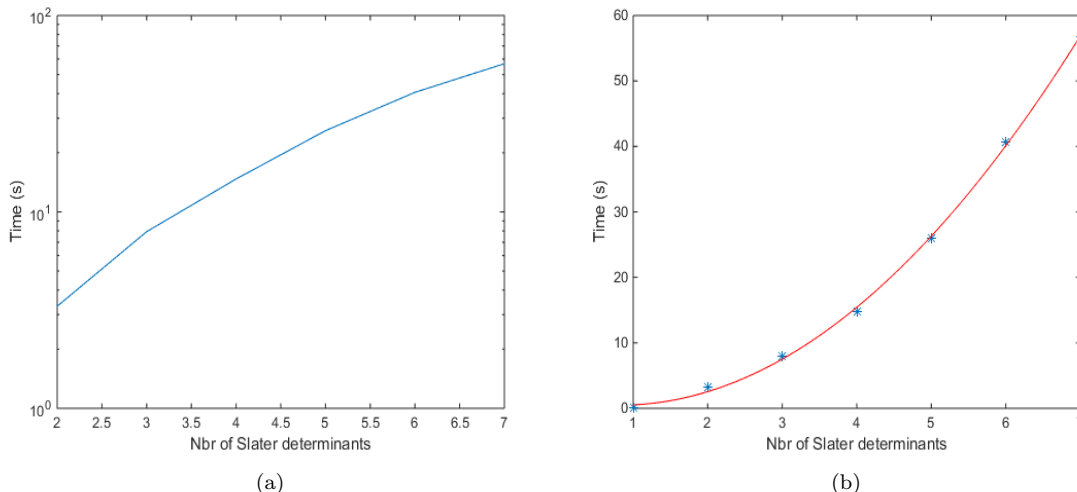


Figure 10: The total time required for consecutive approximations. In (a) time for approximations 2 to 7 plotted (logarithmic y-axis). In (b) time for approximations 1 to 7, plotted alongside a fitted quadratic curve.

In figures 10a and 10b the total time required for the consecutive approximations is presented. These times have been calculated as a mean between time required for the 100 different cases of interaction strength. In figure 10a these times are plotted with a logarithmic y-axis which shows that the increase of time, as more steps are added in the approximation, is less than exponential. Figure 10b shows the times fitted with a quadratic equation, indicating that time for consecutive approximations increase polynomially. The increasing time each step requires comes from the fact that more energies have to be evaluated as more steps are added. Evaluation of the total energy in the N th step requires N calculations of different energies which adds time required to perform minimisation and to calculate gradients. Since the time required for each step increases in this way (and not for instance exponentially) quite a few Slater determinants could be added without the time required becoming unpractical.

As this method in each step only relies on minimisation dependent on a $N_s \times N_p$ matrix, this method could be useful in systems with a large number of particles. When the number of particles and considered orbitals increase, configuration interaction quickly become too computationally expensive to use, as the matrix which has to be diagonalised grows very quickly, limiting this method to be used in only small systems. An increasing amount of particles and orbitals would for this method only mean a larger matrix which the energy depends on. The computational effort required by this method would thereby scale much better with an increasing number of particles and orbitals, which can make this method a viable option for calculations on systems where configuration interaction is not possible to use.

5 Outlook

5.1 Summary

In this thesis an approximate method for calculating the ground state of a quantum mechanical system was developed. This was done by approximating the ground state as a linear combination of non-orthogonal Slater determinants. These Slater determinants and their coefficients were found by minimisation of their associated energy while keeping the previously calculated Slater determinants and coefficients frozen.

The method was tested on a one-dimensional quantum harmonic oscillator filled with interacting fermions for which the interaction strength was varied. The energies found by this method do approach the energies calculated with an exact method as the approximation is improved. Also, where the Hartree-Fock method give reasonable results, this method also gives reasonable results with only a few Slater determinants in the expansion. Moreover, where the Hartree-Fock is not particularly exact, more Slater determinants are needed to attain a good approximation. Even so, with only a few Slater determinants, in this case seven, approximations of a high accuracy have been found for all interaction strengths.

Furthermore, the variance and standard deviation of the calculated wave functions was calculated. These quantities did decrease as the approximation improved. Also, the method of improving the calculated energies by extrapolation did give improvement of the energy in most cases. However in some cases this method gave a worse approximation. The calculated standard deviations was quite large. This was interpreted as that the calculated ground state was a linear combination of the actual ground state and some excited state. Using this assumption another way of improving the calculated energy was developed that worked well.

The time this method requires was also measured. This seems to grow polynomially (at least less than exponentially), which suggests that it could be used when large systems are concerned where more determinants would be needed.

Some more analysis concerning the results and possible extensions to this method is featured in the following section.

5.2 Extensions

This approximation method can be extended and improved upon in several ways. A few simple extensions would be to add more Slater determinants to the expansion, adapt the code for a varying number of particles and states and to adjust the implementation so it could handle systems in three-dimensions. Another extension, which is of great interest, would be to use this method to calculate excited states of systems. This could be done by finding states through this method with the added demand that they be orthogonal to the approximated ground state.

An aspect of this method which has not been thoroughly investigated in this thesis is the effect of the choice of the values in expression 56 (how the amplitudes are decreased as steps in the expansion are added). Different values for these numbers would results in different curves in a figure similar to figure 7 (if the variances were also calculated). The starting values would be the same and the different calculations would converge towards the same end, however at different rates. A possibility would be to do the same calculation for a particular interaction strength several times with these numbers varying. This would yield different values when interpolating the curves which could give an indication of the most likely ground state energy.

Another possibility concerning the interpolation technique would be to use the calculated ground state to evaluate the expectation values of other observables than the energy. These could then be interpolated with respect to the energy variance. This has been done in ref. [5] where for the nucleus of ^{56}Ni the

expectation value of occupation numbers and quadrupole moment has been calculated and interpolated. In this example a Monte-Carlo method was used and both the ground state and a few excited states were calculated.

The distribution of states within the calculated ground state could be further analysed which due to the large standard deviation was assumed to consist in part by an excited state. This could be further investigated by calculating the expectation value of the cube of the Hamiltonian. Through this the skewness of the ground state could be evaluated, though this would be more computationally expensive to calculate than the standard deviation.

Should this method be used to do calculations on larger systems, its efficiency would have to be improved as this was not considered in the current implementation. One way of increasing the speed of the calculations would be to alter the optimisation method used. The currently used method, the gradient descent method with a fixed step length, is not terribly effective. A simple change would be to use a varying step length in this method, which could be done in several ways. This could decrease the number of times energy would have to be evaluated, though it would increase the number of gradients that has to be calculated. Using this approach could speed the calculations up considerably as a majority of the time in this implementation is spent taking steps in the direction of the gradient. The use of an analytical gradient would further improve this speed. Another positive of using a varying step length is that local minima could be avoided.

References

- [1] C. David Sherril, *An Introduction to Configuration Theory*, 1995
- [2] J.J. Sakurai and Jim J. Napolitano, *Modern Quantum Mechanics*, 2014
- [3] Willem H. Dickhoff and Dimitri Van Neck, *Many-Body Theory Exposed!*, 2005
- [4] Yutaka Utsuno, Noritaka Shimizu, Takaharu Otsuka and Takashi Abe. Efficient computation of Hamiltonian matrix elements between non-orthogonal Slater determinants. *Computer Physics Communications*, 184(2013):102-108, 2012
- [5] Noritaka Shimizu, Yutaka Utsuno, Takahiro Mizusaki, Takaharu Otsuka, Takashi Abe and Michio Honma. Novel extrapolation method in the Monte Carlo shell model. *Physical Review C*, 82, 061305(R), 2010
- [6] Lloyd N. Trefethen and David Bau, III, *Numerical Linear Algebra*, 1997
- [7] Lars-Christer Böiers, *Mathematical Methods of Optimization*, 2010
- [8] Andreas Wacker, Gunnar Ohlen, and Stephanie Reimann, *Compendium Quantum Mechanics FYSN17/FMFN01*, 2013
- [9] The on-line encyclopedia of integer sequences, <https://oeis.org/>
- [10] Gillis Carlsson, *Derivation of Hartee-Fock equations from a variational approach*, 2017

A Gram-Schmidt Orthogonalization

The stable Gram-Schmidt method is used to orthonormalise the columns in the $N_s \times N_p$ matrix D . The j th column in the resulting matrix Q (referred to as q_j) is calculated as [6]:

$$\begin{aligned}v_j^{(1)} &= D_j \\v_j^{(2)} &= v_j^{(1)} - q_1 q_1^* v_j^{(1)} \\v_j^{(3)} &= v_j^{(2)} - q_2 q_2^* v_j^{(2)} \\&\vdots \\v_j &= v_j^{(j)} = v_j^{(j-1)} - q_{j-1} q_{j-1}^* v_j^{(j-1)} \\q_j &= \frac{v_j}{\|v_j\|_2}\end{aligned}\tag{97}$$

B Method of gradient descent

The method of gradient descent is an optimisation method which finds the minimum of function f by utilising the following principle through iteration [7]:

$$\begin{aligned}d &= -\nabla f(x_k) \\x_{k+1} &= x_k + \lambda d\end{aligned}\tag{98}$$

where d is the calculated gradient of function f and λ is a chosen number. This principle is utilized until:

$$f(x_{k+1}) > f(x_k)\tag{99}$$