UiO : University of Oslo

Computational Physics: Project 3

Variational Monte Carlo project

Jannes Klee

Anja Bielefeld

December 5, 2014

Contents

1 Introduction

In this report we will be using natural units:

$$\hbar = c = e = m_e = 1$$
$$\Rightarrow [E] = \text{a.u.},$$

where $\hbar$ is the Planck constants divided by 2π, c is the speed of light, e is the elemantary charge and m_e is the electron mass. The unit of enegry than becomes atomic units, denoted as a.u.

2 The physical problem

Quantum dots are nanoscopic crystals usually from semiconducting materials being of a size to exhibit quantum mechanical properties. In this report we will look at systems of electrons confined in a harmonic oscillator, which acts like a trap. These systems can be considered as quantum dots. In order to study any system like that, we have to look at the Hamiltonian, which consists of two parts:

$$\hat{H} = \hat{H}_0 + \hat{H}_1, \tag{1}$$

where $\hat{H}_0$ describes the standard harmonic oscillator and $\hat{H}_1$ the repulsive term between the charged particles (in this case electrons). We can than write

$$\hat{H} = \sum_{i=1}^{N} \left(-\frac{1}{2}\nabla_i^2 + \frac{1}{2}\omega^2 r_i^2 \right) + \sum_{i<j} \frac{1}{r_{ij}} \tag{2}$$

The quantity N denotes the number of charged particles, ω is the oscillator frequency, r_i is the position of particle i given by $r_i = \sqrt{r_{ix}^2 + r_{iy}^2}$ and the distance between two particles is referred to as $r_{ij} = \sqrt{\mathbf{r_1} - \mathbf{r_2}}$.
From quantum mechanics we know, that the wave function corresponding to this Hamiltonian for one electron in two dimensions (x, y) is

$$\phi_{n_x,n_y}(x,y) = AH_{n_x}(\sqrt{\omega}x)H_{n_y}(\sqrt{\omega}y)\exp\left[-\frac{\omega}{2}(x^2+y^2)\right]. \tag{3}$$

In this equation the Hermite polynomials $H_{n_x}(\sqrt{\omega}x)$ appear as well as the constant A, which is there because of the normalization.
To get the energy E, we have to consider the Eigenvalue equation

$$\hat{H}\phi_\lambda = E\phi_\lambda, \tag{4}$$

which leads to the energy

$$E_{n_x,n_y} = \omega(n_x + n_y + 1) \tag{5}$$

Looking at the lowest energy state we have $E_{(1)} = \omega$.
Advancing now to the case of two electrons who do not repell each other we have two independent Hamiltonians, one for each electron, and as a result two independent eigenvalue problems as in euqation 4. This leads to the same energy as before, but this time the energy must be taken into account twice. So we get:

$$E_{(2)} = E_{(1)} + E_{(1)} = 2E_{(1)}. \tag{6}$$

The corresponding wave function is then given by

$$\Phi(\mathbf{r_1}, \mathbf{r_2}) = C\exp\left[-\frac{\omega}{2}(r_1^2 + r_2^2)\right]. \tag{7}$$

As in equation 3 C is the normalization constant.
Since the particles we are considering are fermions, we must regard the spin as well. The overall spin must be zero, because according to the Pauli principle two fermions cannot have the same quantum numbers. The electrons we are looking at are having exactly the same energy of $E = \omega$, so their only way of obeying the princple is to have different spins. There are two possible states:

$$|\uparrow\downarrow> \text{ and } |\downarrow\uparrow> \tag{8}$$

Hence one of the electrons has spin 1/2 and the other one has spin -1/2. Despite this they are indistinguishable, so both states are possible.
Regarding the wave function there we will now make an Ansatz for simplifying the wave function ψ:

$$\psi(\mathbf{r_1}, \sigma_\mathbf{1}, \mathbf{r_2}, \sigma_\mathbf{2}) = R(\mathbf{r_1}, \mathbf{r_2})X(\sigma_\mathbf{1}, \sigma_\mathbf{2}) \tag{9}$$

with

$$R(\mathbf{r_1}, \mathbf{r_2}) = \varphi_{n_{x_1} n_{y_1}}(x_1, y_1)\varphi_{n_{x_2} n_{y_2}}(x_2, y_2) \tag{10}$$

In this Ansatz $R(\mathbf{r_1}, \mathbf{r_2})$ is the part of the wave function depending on the positions and $X(\sigma_\mathbf{1}, \sigma_\mathbf{2})$ is the spin-depending part, the matrices $\sigma_\mathbf{1}$ and $\sigma_\mathbf{2}$ are the spin matrices for particle 1 and 2.
According to this Ansatz we can focus on the position-based part of the wave function for the following analysis.

2.1 Many-body problems

Furthermore we are going to focus on many-body problem by considering up to six electrons. In this case, the wave function can be written as

$$\Psi(\mathbf{r_1}, \mathbf{r_2}, \cdots, \mathbf{r_6}) = \det(\phi_1(\mathbf{r_1}), \phi_2(\mathbf{r_2}), \cdots, \phi_6(\mathbf{r_6}) \prod_{i<j}^{6} \exp\left[\frac{a r_{ij}}{(1+\beta r_{ij}}\right], \tag{11}$$

where again the $\phi_i(r_i)$ refer to single particle wave functions as in equation 3.
The determinant is also known to be called Slater determinant. Although it is the determinant of a 6×6-matrix, it can be expressed in terms of 3×3-determinants according to Cramer's rule, because two belonging wave function with antiparallel spin are identical.

$$\begin{vmatrix} \phi_1(r_1) & \phi_1(r_2) & \cdots & \phi_1(r_6) \\ \phi_2(r_1) & \ddots & & \vdots \\ \vdots & & \ddots & \vdots \\ \phi_6(r_1) & \cdots & \cdots & \phi_6(r_6) \end{vmatrix} = \begin{vmatrix} \phi_1(r_1) & \phi_1(r_2) & \phi_1(r_3) \\ \phi_3(r_1) & \phi_3(r_2) & \phi_3(r_3) \\ \phi_5(r_1) & \phi_5(r_2) & \phi_5(r_3) \end{vmatrix} \cdot \begin{vmatrix} \phi_2(r_4) & \phi_2(r_5) & \phi_2(r_6) \\ \phi_4(r_4) & \phi_4(r_5) & \phi_4(r_6) \\ \phi_6(r_4) & \phi_6(r_5) & \phi_6(r_6) \end{vmatrix} \tag{12}$$

3 The method

As presented in the previous section the eigenvalue problem of two electrons in a harmonic oscillator without any interaction terms can be easily solved. Looking at electrons in a quantum dot this calculation gains complexity. This is why we introduce the Variational Monte Carlo Method for estimating the electron states.

3.1 Variational Monte Carlo method

In the Variational principle, we take the eigenvalue problem form equation 4 and expand the wave function as following:

$$\varphi_0 = \sum_{\lambda=0}^{\infty} c_{0\lambda}\psi_\lambda, \tag{13}$$

where $c_{0\lambda}$ are coefficients.
In quantum mechanics the energy is the expectation value

$$E = \frac{\langle\psi_0|\hat{H}|\psi_0\rangle}{\langle\psi_0|\psi_0\rangle} \tag{14}$$

So when we apple the expansion to this, we get:

$$\frac{\langle\varphi_0|\hat{H}|\varphi_0\rangle}{\langle\varphi_0|\varphi_0\rangle} \tag{15}$$

$$= \frac{\sum_{\alpha,\beta} c^*_{0\alpha}c_{0\beta}\int d\tau\psi^*_\alpha(\tau)\hat{H}\psi_\beta(\tau)}{\sum_{\alpha,\beta} c^*_{0\alpha}c_{0\beta}\int d\tau\psi^*_\alpha(\tau)\psi_\beta(\tau)} \tag{16}$$

$$= \frac{\sum_\alpha E_\alpha|c_{0\alpha}|^2}{\sum_\alpha |c_{0\alpha}|^2}, \tag{17}$$

because by construction $\langle\psi_\alpha|\psi_\beta\rangle = \delta_{\alpha\beta}$ for eigenfunctions ψ_α, ψ_{beta}.
We have to consider two cases now:

- If the expansion φ_0 is not the eigenfunction ψ_0 we get the an energy

$$E_0 \leqslant \frac{\langle\varphi_0|\hat{H}|\varphi_0\rangle}{\langle\varphi_0|\varphi_0\rangle}. \tag{18}$$

- If the expansion φ_0 is exact the eigenfunction ψ_0 we get the exact energy

$$E_0 = \frac{\langle\varphi_0|\hat{H}|\varphi_0\rangle}{\langle\varphi_0|\varphi_0\rangle}. \tag{19}$$

In the second case the variance of the energy

$$\mathrm{var}(E) = \langle H^2\rangle - \langle H\rangle^2 = 0. \tag{20}$$

As the expansion wave function φ_0 we use a trial wave function we will call $\psi_T(\mathbf{r_1}, \mathbf{r_2}, \alpha, /beta)$, with α and β being the variational parameters. In this report the trial wave function for two electrons has the form:

$$\psi_T(\mathbf{r_1}, \mathbf{r_2}) = C\exp\left[-\frac{\omega}{2}(r_1^2 + r_2^2)\right]\exp\left[\frac{a_{12}r_{12}}{(1+\beta r_{12})}\right] \tag{21}$$

with

$$a_{12} = \begin{cases} 1, & \text{for } \uparrow\downarrow \\ 1/3, & \text{for } \uparrow\uparrow, \downarrow\downarrow \end{cases} \tag{22}$$

And

$$r_{12} = \sqrt{\mathbf{r_1} - \mathbf{r_2}} \tag{23}$$

Then we will compute the expectation value $E(\alpha)$ and find its minimum or alternatively the minimum of its variance $\mathrm{var}(E(\alpha))$...

3.2 Monte Carlo methods

The basis of the method explained above are the Monte Carlo methods, which can be referred to as statistical simulation methods. The central building block of these methods is the propability distribution function (PDF), which is used to describe and characterize the physical problem. This does not restrict the method to statistical problems, but by displaying the desired solution in terms of PDF's, non-stochastic problems can be handled as well. During a Monte-Carlo simulation, random numbers must be generated covering an interval uniformly. Using these numbers, many random samples are taken from the PDF. In order to get the desired result the average of all samples is computed. According to this, the precision of the simulation rises with the amount of samples. The error has to be estimated to get an impression of the simulation's precision.
On the contrary of statistical random number-based methods in standard mathematical modelling, the problem would be distretized and solved by a numerical approach.

3.2.1 Pseudo-random number generation

As a main ingredient, random numbers play as important role in Monte-Carlo simulations and therefore have to be 'as random as possible'. The generation of truely random numbers is not practically not possible, this is why the random numbers we work with are pseudo-random, generated by an algorithm fullfilling the criteria of

- generating equally distributed numbers in a given interval (usually [0,1])
- repeating random number sequences seldom
- being fast
- generating insignificantly correlated numbers

I this report, we use random number generators explained in Press et al. (1999), that are called `ran0` and `ran1`.
Furthermore, we generate random gaussian distributed random numbers using `gaussian`

3.3 Metropolis algorithm

The difficult part of Monte-Carlo simulations is the selection rule for random states. One must find a method when to reject and when to accept the generated state. Precision and efficiency strongly depend on this rule. Supposing we have a distribution such as the one shown in figure 1 and we have already picked an initial random variable at r_i. Since we are performing the simulation on many samples, we now have to pick a new random number keeping in mind, that there are two cases, which must be avoided:

- Choosing repeatedly numbers very close to the initial value such as r_j in figure 1. We would then 'get stuck' around the interval of r_i and therefore loose the overview of the function we are evalutating.
- Jumping numbers far away from the initial value, where the distribution is negligable, for example to r_k in figure 1.

Preventing the simulation in creating biased averages and being unprecise is possible by using the Metropolis algorithm, which is a Markov process, satisfying both ergodicity and detailed balance.
Markov chains are referred to as random walks with selected propability to make a move, which is independent of the previous step. An example of this movement is the Brownian random walk shown in figure 2, where a particle moves in the x-y-plane with step length 1 preforming hundred steps. The propability of moving is the same for every direction. Using Markov processes, we can generate new random states and reach the most likely state (equilibrium) after a certain time.

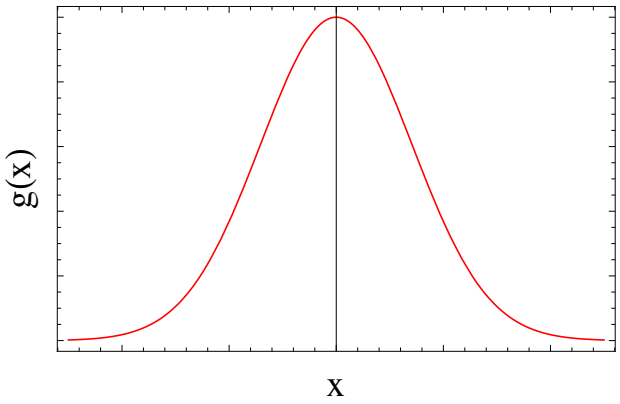

Figure 1: Gaussian distribution showing problems in selection of random states

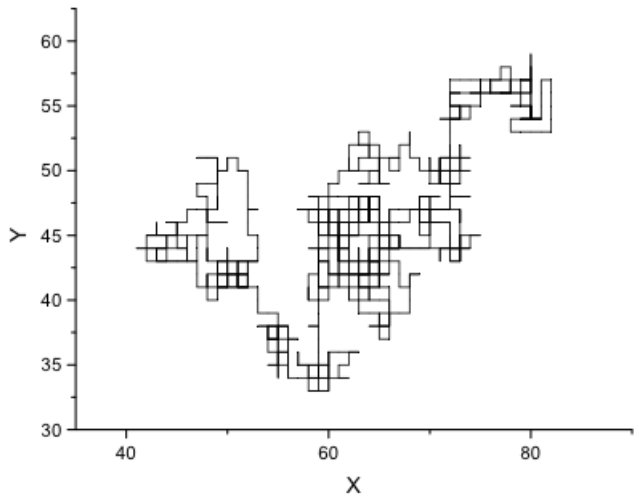

Figure 2: Brownian random walk of 100 steps in x-y-plane and step length 1

3.3.1 Importance sampling

There are lots of examples in science, where biasing is disturbing and should be avoided. One of them are the require unbiased uncorrelated random numbers in section 3.2.1. In Monte-carlo methods, biasing can be tool to increase the simulation's efficiency by preforming a Metropolis walk biased by the trial wave function. Since our problem is somewhat simular to a diffusion process in one dimension for one particle, we may use an approach based on the Fokker-Planck and the Langevin equation.
The 'old' and 'new' positions in space can be caluclated by

$$r_{old} = \eta \tag{24}$$
$$r_{new} = r_{old} + \eta + \delta t D F_{old}, \tag{25}$$

where η denotes a gaussian distributed random variable, δt refers to the time step, D is the diffusion constant, which is in our case set to $D = 0.5$ and F_{old} is the quantum force at position r_{old}. Note, that η are different random numbers.
The term responsible for biasing the walk in space x is the quantum force, which leads the walk to regions with large trial wave function. In a brute force Metropolis algorithm, the propability of moving would be the same for all directions. The quantum force is

$$\mathbf{F} = 2\frac{1}{\psi_T}\nabla\psi_T \tag{26}$$

In order to include this biasing in the Metropolis algorithm, we will replace

$$q(r_{old}, r_{new}) = \frac{|\psi_T(r_{new})|^2}{|\psi_T(r_{old})|^2} \tag{27}$$

by

$$q(r_{old}, r_{new}) = \frac{G(r_{old}, r_{new}, \delta t)|\psi_T(r_{new})|^2}{G(r_{new}, r_{old}, \delta t)|\psi_T(r_{old})|^2}, \tag{28}$$

where the quantity G refers to the Greensfunction

$$G(y, x, \delta t) = \frac{1}{(4\pi D\delta t)^{3N/2}} \exp\left[-(y - x - D\delta t F(x))^2 \frac{1}{4D\delta t}\right] \tag{29}$$

3.4 Closed form solutions

The quantum force (eq. 26) and the kinetic energy part are till now calculated with a brute force derivation. A disadvantage of this method is that the wavefunction has to be evaluated multiple times at different positions $r+h$, $r-h$ respectively. In order to optimize this step one can implement the analytical expressions. These are derived in Høgberget (2013). The quantum force can thereby be expressed by

referenzierung auf funktion

$$\mathbf{F_i} = 2\left(\frac{\nabla_i|\mathbf{S}\uparrow|}{|\mathbf{S}\uparrow|} + \frac{\nabla_i J}{J}\right). \tag{30}$$

The first part of the right side denotes the gradient of the Slater determinant, the second one the gradient of the Jastrow factor. It has to be payed attention that this is the expression for only one particle with index i moved with spin up. Considering a spin down particle the $|\mathbf{S}\uparrow|$ becomes $|\mathbf{S}\downarrow|$. Further the kinetic part of the local energy arises as a result of

$$\frac{\nabla_i^2\Psi_T}{\Psi_T} = \frac{\nabla_i^2|\mathbf{S}\uparrow|}{|\mathbf{S}\uparrow|} + \frac{\nabla_i^2 J}{J} + 2\left(\frac{\nabla_i|\mathbf{S}\uparrow|}{|\mathbf{S}\uparrow|}\cdot\frac{\nabla_i J}{J}\right), \tag{31}$$

again assuming a spin up particle.
The missing expressions can be obtained by deriving the trial wavefunction **??** . This is also done in

referenz zu allgemeiner trial wave-function

Høgberget (2013) and reveals

$$\frac{\nabla_i J}{J} = \sum_{k \neq i=1}^{N} \frac{a_{ik}}{r_{ik}} \frac{\mathbf{r_i} - \mathbf{r_k}}{(1 + \beta r_{ik})^2} \tag{32}$$

for the gradient and

$$\frac{\nabla_i^2 J}{J} = \left| \frac{\nabla_i J}{J} \right| - \sum_{k \neq i=1}^{N} a_{ik} \frac{\beta r_{ik} - 1}{r_{ik} (1 + \beta r_{ik})^3} \tag{33}$$

for the laplacian of the jastrow factor. The variables and constants are the already known ones of equation **??** . The derivations of the Slater determinants can be calculated to

referenz zu trialwavefunction für viele teilchen

$$\frac{\nabla_i |\mathbf{S}|}{|\mathbf{S}|} = \sum_k \left(\nabla_i \phi_k(\mathbf{r}_i) \right) \left(\mathbf{S}_{ki}^{-1} \right) \tag{34}$$

for the gradient and

$$\frac{\nabla_i^2 |\mathbf{S}|}{|\mathbf{S}|} = \sum_k^{N/2} \left(\nabla_i^2 \phi_k(\mathbf{r}_i) \right) \left(\mathbf{S}_{ki}^{-1} \right) \tag{35}$$

for the laplacian. For the first part on the right side of eqs. 34 and 35 exists analytical expressions which can be determined by applying the operands on the single particle equation **??**. These can also be found in tabulated form in Høgberget (2013, app. D). The last term $\mathbf{S}_{ki}^{-1}$ is the transpose of the inverse Slater matrix.

referenziere single particle function

The closed form solutions are fully implemented in the code and can be found at Github on the branch `closed_form`. Unfortunately there were still unresolved problems which yielded to non-correct energies in the solutions (details in the evaluation).

4 Results and discussion

We will now first take a look at the case of two electrons in a potential with different oscillator energies. In order to do so, we preform a Variational Monte Carlo simluation and use the Metropolis algorithm explained in section 3.3 to find the energy of the ground state. Therefore we use numerical derivation. We will later introduce analytical calculations based on closed-form expressions as well (section 4.3). Besides, we put emphasis on the correlations introduced by the Jastro factor by computing the kinetic and potential energy of the ground state for different osciallator frequencies.
In addition we introduce importance sampling and analyse the dependency of the results to the time step δt.

4.1 Two electron case

Since it is the easiest case, we first look at two electrons in a quantum dot interacting with each other. According to **?** the corresponding energy is at $E = 3$ a.u. (atomic units).
Concerning the simulation we start by considering a wide range of $\alpha \in [0.7, 1.3]$ and $\beta \in [0.2, 0.6]$ first and preform a more precise simulation afterwards. The goal is to find the variational parameters α and β, where the energy is at its minimum. After the first simulation we notice, that the minimum must be somewhere around $\alpha \in [0.9, 1.1]$ and $\beta \in [0.35, 0.45]$. This is why we preform a somulation with these boundaries and use 3 000 000 Metropolis cycles to get an accurate result. In figure 3 the energy is plotted depending on both variational parameters α and β. The 3D-plot results in a bended plane ressembling to a valley. For increasing α the corresponding β at minimal energy is decreasing. The minimum energy calculated is

$$E = 3.0003 \text{ a.u.} \tag{36}$$

at

$$\alpha = 0.9867, \tag{37}$$
$$\beta = 0.4033. \tag{38}$$

As mentioned before we were expecting the energy to be at $E = 3$ a.u., so the calculated value matches the expected one very well.
To get a better understanding of the influence the parameters have on the calculated energy figure 4 shows the energy's α-dependency for different β. Consistent with figure 3 this figure shows, that the β is shifted depending on α and that α has a larger influence on the energy. The errors plotted in figure 4 are almost invisible, since they are very small compared to the energy fluctuations at varying α and β. There are not many cases, where the error is significantly high, so we consider our results to be of sufficient accuracy.

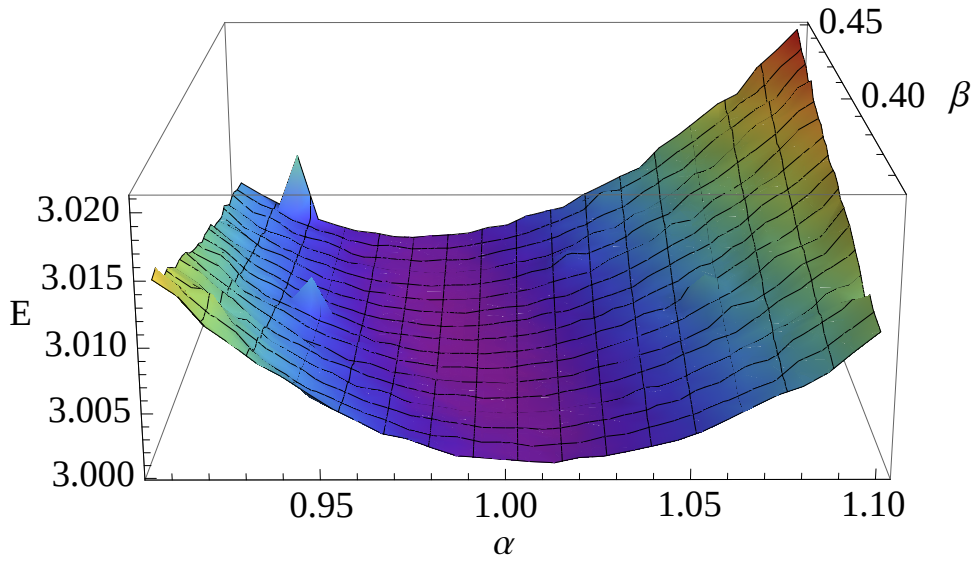

Figure 3: Plot of α- and β-dependencies of the ground state energy for two interacting electrons at the ground state.

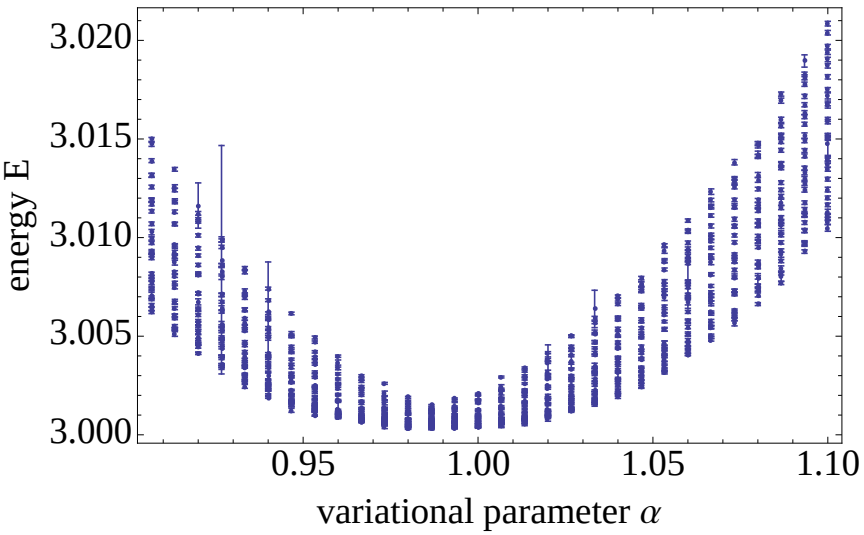

Figure 4: Plot of α-dependency of the ground state energy for two interacting electrons at the ground state.

5 Conclusion

References

Hjorth-Jensen, M. (2014). Computational physics, lecture notes fall 2014. University of Oslo.

Høgberget, J. (2013). Quantum monte-carlo studies of generalized many-body systems. Master's thesis, Universitetet i Oslo.

Press, W., Flannery, B., Teukolsky, S., and Vetterling, W. (1999). *Numerical Recipes in C++: The Art of Scientific Computing*. Cambridge University Press.