FYS4411 - Computational Physics II: Quantum Mechanical Systems

Project 2 - Variatonal Monte Carlo Studies of Electronic Systems.

Alfred Alocias Mariadason

https://www.github.com/Oo1Insane1oO/FYS4411

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Abstract

I INTRODUCTION

Using the Variational Monte Carlo, this project aims to find and analyze quantities such as the ground state energy and single-particle densities of quantum dots for so-called closed shell systems.

We use the usual approach by estimating expectation value of the ground state energy with the variational principle and minimizing. The algorithm used for the Monte Carlo method is the well known Metropolis algorithm.

The reason for using a Monte Carlo method for minimizing the trial ground state energy is because the expectation value would in general be a multi-dimensional integral depending on the number of particles and number of parameters involved in the total wave function. Such an integral is not adequately solved by traditional methods(i.e Gaussian-quadrature).

The desired result is that the Metropolis algorithm with importance sampling yields a better result both from a computational point of view. That is it finds a good estimate for the ground state energy efficiently without wasting to much time on the configuration space. The wave function only has small values in this large space meaning a homogeneous distribution of calculation points would yield a poor result, a non-homogeneous approach(such as with the Metropolis algorithm) would then, hopefully, gives a better result.

II THEORY

»INSERT DESCRIPTION«

II.A HERMITE POLYNOMIALS

Hermite polynomials $H(x)$ are solutions to the differential equation

$$\frac{\mathrm{d}^2 H}{\mathrm{d}x^2} - 2x\frac{\mathrm{d}H}{\mathrm{d}x} + (\lambda - 1)H = 0 \tag{1}$$

The polynomials fulfill the orthogonality relation

$$\int_{-\infty}^{\infty} \mathrm{e}^{-x^2} H_n^2 \mathrm{d}x = 2^n n! \sqrt{\pi} \tag{2}$$

with the recurrence relation

$$H_{n+1} = 2xH_n - 2nH_{n-1} \tag{3}$$

and standardized relation

$$H_n = (-1)^n \mathrm{e}^{x^2} \frac{\partial^n}{\partial x^n} \mathrm{e}^{-x^2} \tag{4}$$

From equation 4 one can find an expression for the derivative of the Hermite polynomial as

$$\frac{\partial^m H_n}{\partial x^m} = 2^m m! \frac{n!}{(n-m)!} H_{n-m} \tag{5}$$

II.B HARMONIC OSCILLATOR

II.B.1 Cartesian Coordinates

The harmonic oscillator system in 2 dimensions and in natural units is given by the following Hamiltonian

$$\hat{H}_0 = \frac{1}{2}\sum_{i=1}^{N}\left(-\nabla_i^2 + \omega^2 r_i^2\right) \tag{6}$$

The wave functions in this case is then:

$$\phi_{n_x,n_y}(x,y) = AH_{n_x}(\sqrt{\omega}x)H_{n_y}(\sqrt{\omega}y)\exp\left(-\frac{\omega}{2}(x^2+y^2)\right) \tag{7}$$

where H_n is a Hermite polynomial of order n and A is a normalization constant. The quantum numbers n_x and n_y go as $n_x, n_y = 0, 1, 2 \ldots$. While ω is the oscillator frequency.
The energies is

$$E = \hbar\omega\left(n_x + n_y + 1\right) \tag{8}$$

II.C FOURIER TRANSFORMATION

Given an integrable function $f : \mathbb{R} \to \mathbb{C}$ the Fourier transform to variable x is defined to be

$$\tilde{f}(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(x) \mathrm{e}^{ixs} \mathrm{d}x \tag{9}$$

with $x, s \in \mathbb{R}$.
The inverse transformation is given as

$$f(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \tilde{f}(k) \mathrm{e}^{-isx} \mathrm{d}s \tag{10}$$

II.D CONJUGATE GRADIENT METHOD

Suppose we have a linear system defined as

$$A\vec{x} = \vec{b} \tag{11}$$

where A is a nxn real, symmetric and positive definite matrix while $\vec{x}$ and $\vec{b}$ are a non-zero real vectors.
Define now the conjugate directions of two vectors $\vec{x}_i, \vec{x}_j : \mathbb{R} \to \mathbb{R}$ giving the constraint

$$\vec{x}_i^T A \vec{x}_j = \vec{0} \tag{12}$$

This means that in the iterative process of finding $\vec{x}$ we perform searches within the conjugate directions of $\vec{x}$.
Since the conjugate constraint(equation 12) is defined by an inner product within the space A is defined, the two vectors $\vec{x}_i$ and $\vec{x}_j$ are orthogonal. If we now define a span P

$$P = \{\vec{p}_1, \ldots, \vec{p}_n\} \tag{13}$$

consisting of n mutually orthogonal conjugate directions $\vec{p}_i$, we have a basis for $\mathbb{R}^n$. Expanding the solution x_{i+1} to equation 11 in the mentioned basis

$$\vec{x} = \sum_{i=1}^{n} C_i \vec{p}_i \tag{14}$$

the linear system can be rewritten as

$$A\vec{x} = \sum_{i=1}^{n} C_i A \vec{p}_i = \vec{b} \tag{15}$$

Giving the inner product

$$\vec{p}_k^T A \vec{x} = \sum_{i=1}^{n} C_i \vec{p}_k^T A \vec{p}_i \tag{16}$$

and we can define the coefficients C_k as

$$C_k = \frac{\vec{p}_k^T \vec{b}}{\vec{p}_k^T A \vec{p}_k} \tag{17}$$

The problem at hand is then to choose a sequence of n conjugate directions P and compute the coefficients C_k.

II.D.1 Iterative Method

The conjugate gradient method can in a similar manner be used on an iterative basis. We start with an initial guess $\vec{x}_0$ for the solutions and consider the linear system

$$A\vec{x} = \vec{b} - \vec{r} \tag{18}$$

where $A, \vec{x}$ and $\vec{b}$ are defined as before and $\vec{r}$ is a so-called residual.
Let $\vec{r}_k$ be the residual at the k-th step with a negative gradient. Using a similar approach as before we get that the conjugate direction $\vec{p}_{i+1}$ is

$$\vec{p}_{i+1} = \vec{r}_k - \frac{\vec{p}_k^T A \vec{r}_k}{\vec{p}_k^T A \vec{p}_k} \vec{p}_k \tag{19}$$

The iterative process is then to compute the directions and then solve the arising linear system by computing the coefficients as given in equation 17.
The iterative process is then to compute

$$\vec{x}_{k+1} = \vec{x}_k + C_k \vec{p}_{k+1} \tag{20}$$

with

$$C_k = \frac{\vec{p}_k^T \vec{r}_k}{\vec{p}_k^T A \vec{p}_k} \tag{21}$$

The residual $\vec{r}_k$ at the k-th step is defined from equation 18 as

$$\vec{r}_k = \vec{b} - A\vec{x}_k \tag{22}$$

II.E SECOND DERIVATIVE TEST

Given a real valued function $f(\vec{x}) : \mathbb{R}^n \rightarrow \mathbb{R}$ where $\vec{x} \in \mathbb{R}^n$ and f has second partial derivatives which exist and are continuous over its domain, the so-called Hessen matrix elements for f is defined as follows [9]

$$A_{ij} \equiv \frac{\partial^2 f}{\partial x_i \partial x_j} \tag{23}$$

The properties of A can be used to determine critical points of f. The statements are;

- If A is positive definite(all positive eigenvalues) at $\vec{x}$ then f has an isolated local minimum at $\vec{x}$.
- If A is negative definite(all negative eigenvalues) at $\vec{x}$ then f has an isolated local maximum at $\vec{x}$.
- If A is indefinite(both positive and negative eigenvalues) then f has a saddle point at $\vec{x}$.
- If A is positive-semi-definite, the test is inconclusive and $\vec{x}$ might be a local extremal or a saddle point.

II.F PORDUCT OF SUMS

The product of two sums A and B can be written as

$$\begin{aligned}
A \cdot B &= \left(\sum_{n=1}^{N} f_n\right) \cdot \left(\sum_{m=1}^{N} g_m\right) \\
&= \left(\sum_{n=1}^{N}\sum_{m=1}^{N} f_n g_m - \sum_{n=1}^{N} f_n g_n\right) + \sum_{n=1}^{N} f_n g_n \\
&= \sum_{n=1}^{N} f_n \left(\sum_{m=1}^{N} g_m - g_n\right) + \sum_{n=1}^{N} f_n g_n \\
&= \sum_{n=1}^{N} f_n \left(\sum_{m\neq n} g_m\right) + \sum_{n=1}^{N} f_n g_n \\
&= \sum_{n=1}^{N}\sum_{m\neq n} \left(f_n \left(g_m + g_n\right)\right)
\end{aligned} \tag{24}$$

II.G LAPLACE EXPANSION

Given a $n \times n$ matrix $M = [m_{ij}]$ and $i, j \in [1, \ldots, n]$, then the determinant of M is

$$\det(M) = \sum_{j=1}^{n} m_{ij} C_{ij} \tag{25}$$

where C_{ij} is the i, j-element of the so-called cofactor matrix defined as the sub-matrix arising from removing the i-th row and j-th column from M. The cofactor matrix element is given as

$$C_{ij} = (-1)^{i+j} M_{ij} \tag{26}$$

where the indices i and j run from 1 up to $n-1$ [9].

II.H DERIVATIVE OF DETERMINANT

We can express the derivative with respect to t for a square matrix $A(t)$ of size n which has a differentiable map $\mathrm{d}A \in \mathbb{R} \to \mathbb{R}^n$ as

$$\frac{\partial A(t)}{\partial t} = \mathrm{Tr}\left(\mathrm{adj}\left(A(t)\right)\frac{\partial A(t)}{\partial t}\right) \tag{27}$$

where Tr is the trace and adj is the adjugate(transpose of cofactor matrix). This relation is known as Jacobi's formula »REF HERE«.
We can specialize Jacobi's formula to

$$\frac{\partial A(t)}{\partial t} = \det(A)\,\mathrm{Tr}\left(A(t)^{-1}\frac{\partial A(t)}{\partial t}\right) \tag{28}$$

if A is invertible. This relation follows from the definition of the adjugate which gives

$$A\mathrm{adj}\left(A\right) = \det(A)\mathbb{1} \tag{29}$$

and in turn if A is invertible

$$A^{-1} = \frac{1}{\det(A)}\mathrm{adj}\left(A\right) \tag{30}$$

Here $\mathbb{1}$ is the $n \times n$ identity matrix.

II.I METROPOLIS-HASTINGS ALGORITHM

The Metropolis algorithm bases itself on moves (also called transitions) as given in a Markov process(or Markov chain). Define a probability distribution function(PDF) $w_j(t)$ with a transition probability $w(i \to j)$ which for a given time-step yields in the Markov formula

$$w_i(t+\varepsilon) = \sum_j w(j \to i)\,w_j(t) \tag{31}$$

The transition probability is defined with an acceptance probability distribution $A(j \to i)$ and a proposed probability distribution $T(j \to i)$ as

$$w(j \to i) = A(j \to i)\,T(j \to i) \tag{32}$$

The acceptance A is the probability for the move to be accepted and the proposal T is different for each problem.
In order for this transition chain to reach a desired convergence and reversibility we have the well known condition for detailed balance »INSERT REF«. This condition gives us that the probability distribution functions satisfy the following condition

$$w_i T_{i\to j} A_{i\to j} = w_j T_{j\to i} A_{j\to i} \Rightarrow \frac{w_i}{w_j} = \frac{T_{j\to i}A_{j\to i}}{T_{i\to j}A_{i\to j}} \tag{33}$$

We now need to choose an acceptance which fulfills equation 33 and a common choice is the Metropolis condition

$$A_{j\to i} = \min\left(1, \frac{w_i T_{i\to j}}{w_j T_{j\to i}}\right) \tag{34}$$

The Metropolis-Hastings algorithm is thus

(i) Pick initial state i at random.

(ii) Pick proposed state at random in accordance to $T_{j\to i}$.

(iii) Accept state according to $A_{j\to i}$.

(iv) Jump to step (ii) until a specified number of states have been generated.

(v) Save the state i and jump to step (ii).

II.J VARIATIONAL PRINCIPLE

The variational principle states the following restriction on the ground state energy for a given symmetry

$$E_0 \leq \langle E[\Phi_T]\rangle = \int \phi_T^* \hat{H}\phi_T \mathrm{d}\tau = \langle \phi_T|\hat{H}|\phi_T\rangle \tag{35}$$

that is the ground state energy E_0 is bounded by the expectation value of the trial energy.

II.K IMPORTANCE SAMPLING

In order to use the Metropolis algorithm as explained in section II.I, we need to find the proposal probability distribution labeled $T_{j\to i}$. This is what is known as importance sampling.
This section will derive the importance sampling by using the Fokker-Planck equation for one particle

$$\frac{\partial P}{\partial t} = D\frac{\partial}{\partial x}\left(\frac{\partial}{\partial x} - F\right)P(x,t) \tag{36}$$

where F is a drift term and D is a diffusion constant, and the Langevin equation

$$\frac{\partial x(t)}{\partial t} = DF(x(t)) + \eta \tag{37}$$

where η is a Gaussian distributed random variable.

II.K.1 Quantum Force

Since we are working with a isotropic diffusion characterized by a time-dependant probability density our system must obey the summed total Fokker-Planck equation

$$\frac{\partial P}{\partial t} = \sum_i D\frac{\partial}{\partial x_i}\left(\frac{\partial}{\partial x_i} - F_i\right)P(x,t) \tag{38}$$

where F_i is now the i'th component of the drift velocity term(given by an external potential). Since the probability is assumed to be convergent, that is it converges to a stationary probability density the time dependence at this point is zero for all i. We also know that the drift should be of form $F = g(x)\frac{\partial P}{\partial x}$ giving

$$\frac{\partial^2 P}{\partial {x_i}^2} = P\frac{\partial g}{\partial P}\left(\frac{\partial P}{\partial x_i}\right)^2 + Pg\frac{\partial^2 P}{\partial {x_i}^2} + g\left(\frac{\partial P}{\partial x_i}\right)^2 \tag{39}$$

Now we may use the condition for stationary density meaning the left hand side of equation 39 must equal zero giving that $g = 1/P$(only possibility the derivatives cancel). Inserting in $P = \psi_T$ (see »INSERT REF«) we get that the expression for the quantum force is

$$F_i = \frac{2}{\Psi_T}\nabla_i\Psi_T \tag{40}$$

Notice that the quantum force is defined individually for each particle because of the assumption of of stationary probability density.

II.K.2 Solution

Using Eulers method(Euler-Maruyama method»INSERT REF«) on the Langevin equation(equation 37) one obtains the new positions

$$y = x + DF(x)\Delta t + \xi\sqrt{\Delta t} \tag{41}$$

with $D = 1/2$ in natural units due to the kinetic energy term and Δt is a time-step parameter. The random variable ξ is within a Gaussian distribution of variance one and standard deviation zero.
For the differential equation (equation 36) we insert in for the quantum force given in equation 40 and arrive at the following diffusion equation

$$\frac{\partial P}{\partial t} = -D\frac{\partial^2 P}{\partial r^2} \tag{42}$$

This equation is solved by using a Fourier transform in the spatial coordinate r according to equation 9 giving the equation

$$\frac{\partial \tilde{P}(s,t)}{\partial t} = -Ds^2\tilde{P}(s,t) \tag{43}$$

with solution

$$\tilde{P}(s,\Delta t) = \tilde{P}(s,0)\mathrm{e}^{-Ds^2\Delta t} \tag{44}$$

Initially the probability density is centered at $D\Delta tF(x)$, that is the drift term. This can be expressed terms of a Dirac-delta function, meaning

$$P(y,x,0) = \delta(y - D\Delta tF(x)) \tag{45}$$

where y is given in equation 41. Making an inverse transformation as described in equation 10 and solving the subsequent transcendental integral yields in

$$P(y,x,\Delta t) = \frac{1}{\sqrt{4\pi D\Delta t}}\exp\left(-\frac{(y - x - D\Delta tF(x))^2}{4D\Delta t}\right) \tag{46}$$

which gives us the acceptance

$$A_{y\to x} = \min\left(1, \frac{|\psi_T(y)|^2 P(y,x,\Delta t)}{|\psi_T(x)|^2 P(x,y,\Delta t)}\right) \tag{47}$$

II.L VMC

This section will explain and derive the equations involved in the Variational Monte Carlo method. The whole section will assume that we have the following trial wave function, ψ_T

$$\psi_T(\vec{r}_1,\dots,\vec{r}_N) \equiv \det(\phi_1(\vec{r}_1,\alpha),\dots,\phi(\vec{r}_N,\alpha))\prod_{i<j}^{N}\exp\left(\frac{ar_{ij}}{1+\beta r_{ij}}\right) \tag{48}$$

with the $\vec{r}$'s being the position of the electrons and the ϕ's being the wave function to some known system(i.e harmonic oscillator). The position r_{ij} is a relative distance $\left|\vec{r}_i-\vec{r}_j\right|$ while α and β are variational parameters and a is a specific constant dependant of the total spin symmetry of electron i and j as

$$a = \begin{cases} 1, & \text{anti-parallel spin} \\ \frac{1}{3}, & \text{parallel spin} \end{cases} \tag{49}$$

This is also known as a Pade-Jastrow factor.
We also define the total Hamiltonian of the system for the quantum dot case as

$$\hat{H} = \hat{H}_O + \hat{H}_I \tag{50}$$

with $\hat{H}_O$ being the harmonic oscillator defined in equation 6 and $\hat{H}_I$ being the Hamiltonian for the electron interactions(Coulomb interaction) defined as

$$\hat{H}_I = \sum_{i<j}\frac{1}{r_{ij}} \tag{51}$$

Lastly, we work in natural units setting $\hbar = c = 1$, and all the above equations(equations 48, 49, 50 and 51) also assume natural units.

II.L.1 Expectation Value and Local Energy

Given the Hamiltonian equation 50 and a trial wave function $\Psi_T(R,\Lambda)$ and using the variational principle, as given in equation 35 the upper bound for the ground state energy E_0 if $H(r)$ is

$$E[\hat{H}(R,\Lambda)] \leq \left\langle\hat{H}\right\rangle = \frac{\langle\Psi_T|\hat{H}|\Psi_T\rangle}{\langle\Psi_T|\Psi_T\rangle} \tag{52}$$

where $R=(r_1,\dots,r_N)$ is the positions to N particles and $\Lambda=(\lambda,\dots,\lambda_M)$ are the M variational parameters.
Now we can expand the trial wave function $\Psi_T(R,\Lambda)$ in the orthonormal eigenstates of the Hamiltonian $\hat{H}$(which form a complete set)

$$\Psi_T(r) = \sum_i c_i\Psi_i(r) \tag{53}$$

and the upper bound given in equation 52 is

$$E_0 \leq \frac{\sum_{ij} c_i c_j^* \left\langle\Psi_j\right|\hat{H}\left|\Psi_i\right\rangle}{\sum_{ij} c_i c_j^* \left\langle\Psi_j\middle|\Psi_i\right\rangle} = \frac{\sum_n a_n^2 E_n}{\sum_n a_n^2} \tag{54}$$

where the eigenequation for the Hamiltonian $\hat{H}\Psi_n = E_n\Psi_n$ was used. The expression given in equation 52 is the expectation value we evaluate in each variational step that is we choose α according to some minimization algorithm and re-evaluate the expectation value.
In order to introduce the transition probability as given in the Metropolis algorithm(see section II.I) the expectation value, equation 54, needs to be rewritten in terms of a PDF. We can define this as

$$P(R) \equiv \frac{|\Psi_T(R)|^2}{\int|\Psi_T(R)|^2\mathrm{d}R} \tag{55}$$

Now we observe that if we define a quantity

$$E_L(R,\Lambda) \equiv \frac{1}{\Psi_T(R,\Lambda)}\hat{H}\Psi_T(R,\Lambda) \tag{56}$$

which is the so-called local energy. The expectation value given in equation 54 can be rewritten as

$$E[H] = \int P(R)E_L(R,\Lambda)\mathrm{d}R \approx \frac{1}{N}\sum_{i=1}^{N}P(r_i,\Lambda)E_L(r_i,\Lambda) \tag{57}$$

which is of the form given in equation 31 and N is the number of states(or Monte Carlo cycles).

II.L.2 Analytical Expression for Local Energy

We use the Metropolis algorithm to find an estimate for the expectation value to the energy. In this expression we have a so-called local energy defined as

$$E_L = \frac{1}{\psi_T}\hat{H}\psi_T \tag{58}$$

This expression shows up in the integrand as the multiplied function to the PDF which is used in the Metropolis algorithm.

II.L.3 Two Electron Case

We start by finding the local energy in the case with two electrons. The trial wave function is in this case(related to equation 7) using equation 48

$$\psi_T(\vec{r}_1,\vec{r}_2) = A\exp\left(-\frac{\alpha\omega}{2}\left(r_1^2+r_2^2\right)\right)\exp\left(\frac{ar_{12}}{1+\beta r_{12}}\right) \tag{59}$$

Using the definition of the trial wave function, equation 56 and the total Hamiltonian(equation 50) the local energy with equation 56 is

$$E_L = \frac{1}{\psi_T}\left(\hat{H}_O\psi_T + \hat{H}_I\psi_T\right) \tag{60}$$

we solve the first part $\hat{H}_O\psi_T$

$$\hat{H}_O\psi_T = \frac{1}{2}\left(-\nabla_1^2 - \nabla_2^2 + \omega^2\left(r_1^2+r_2^2\right)\right)\psi_T \tag{61}$$

Starting with the Laplacian for electron 1 and solving the second derivative with respect to x_1 we have

$$\frac{\partial^2\psi_T}{\partial {x_1}^2} = A\exp\left(-\frac{\alpha\omega}{2}\left(r_2^2+y_1^2\right)\right)\frac{\partial^2}{\partial {x_1}^2}\left[\exp\left(-\frac{\alpha\omega}{2}x_1^2 + \frac{a}{\beta+\frac{1}{r_{12}}}\right)\right] \tag{62}$$

Starting with the first derivative in the exponential we get

$$\left.\begin{aligned} \frac{\partial}{\partial x_1}\left[-\frac{\alpha\omega}{2}x_1^2\right] &= -\alpha\omega x_1 \\ \frac{\partial}{\partial x_1}\left[\frac{a}{\beta+\frac{1}{r_{12}}}\right] &= \frac{a(x_1-x_2)}{r_{12}(1+\beta r_{12})^2} \end{aligned}\right\} \Rightarrow \frac{\partial\psi_T}{\partial x_1} = \left(-\alpha\omega x_1 + \frac{a(x_1-x_2)}{r_{12}(1+\beta r_{12})^2}\right)\psi_T \tag{63}$$

meaning equation 62 is

$$\begin{aligned} \frac{\partial^2\psi_T}{\partial {x_1}^2} &= A\exp\left(-\frac{\alpha\omega}{2}\left(r_2^2+y_1^2\right)\right)\frac{\partial}{\partial x_1}\left[-\alpha\omega x_1 + \frac{a(x_1-x_2)}{r_{12}(1+\beta r_{12})^2}\right]\exp\left(-\frac{\alpha\omega}{2}x_1^2 + \frac{a}{\beta+\frac{1}{r_{12}}}\right) \\ &= \frac{\partial}{\partial x_1}\left[\left(-\alpha\omega x_1 + \frac{a(x_1-x_2)}{r_{12}(1+\beta r_{12})}\right)\psi_T\right] \end{aligned} \tag{64}$$

Using the product rule for differentiation and starting with the first expression we get that

$$\frac{\partial}{\partial x_1}\left[-\alpha\omega x_1 + \frac{a(x_1-x_2)}{r_{12}(1+\beta r_{12})^2}\right] = -\alpha\omega + \frac{a}{r_{12}(1+\beta r_{12})^2} - \frac{a(x_1-x_2)^2(1+3\beta r_{12})}{r_{12}^3(1+\beta r_{12})^3} \tag{65}$$

giving

$$\begin{aligned} \frac{\partial^2\psi_T}{\partial {x_1}^2} &= \psi_T\frac{\partial}{\partial x_1}\left[-\alpha\omega x_1 + \frac{a(x_1-x_2)}{r_{12}(1+\beta r_{12})^2}\right] + \left(-\alpha\omega x_1 + \frac{a(x_1-x_2)}{r_{12}(1+\beta r_{12})^2}\right)\frac{\partial\psi_T}{\partial x_1} \\ &= \left[-\alpha\omega + \frac{a}{(1+\beta r_{12})^2} - \frac{a(x_1-x_2)^2(1+3\beta r_{12})}{r_{12}^3(1+\beta r_{12})^3} + \left(-\alpha\omega x_1 + \frac{a(x_1-x_2)}{r_{12}(1+\beta r_{12})^2}\right)^2\right]\psi_T \end{aligned} \tag{66}$$

The second derivative with respect to y_1 yields with a similar derivation

$$\frac{\partial^2\psi_T}{\partial {y_1}^2} = \left[-\alpha\omega + \frac{a}{(1+\beta r_{12})^2} - \frac{a(y_1-y_2)^2(1+3\beta r_{12})}{r_{12}^3(1+\beta r_{12})^3} + \left(-\alpha\omega y_1 + \frac{a(y_1-y_2)}{r_{12}(1+\beta r_{12})^2}\right)^2\right]\psi_T \tag{67}$$

The second derivatives with respect to x_2 and y_2, are derived in a similar manner, only we get a change in signs when differentiating r_{12}. This gives

$$\frac{\partial^2\psi_T}{\partial {x_2}^2} = \left[-\alpha\omega + \frac{a}{r_{12}(1+\beta r_{12})^2} - \frac{a(x_1-x_2)^2(1+3\beta r_{12})}{r_{12}^3(1+\beta r_{12})^3} + \left(\alpha\omega x_2 + \frac{a(x_1-x_2)}{r_{12}(1+\beta r_{12})^2}\right)^2\right]\psi_T \tag{68}$$

and

$$\frac{\partial^2\psi_T}{\partial {y_2}^2} = \left[-\alpha\omega + \frac{a}{r_{12}(1+\beta r_{12})^2} - \frac{a(y_1-y_2)^2(1+3\beta r_{12})}{r_{12}^3(1+\beta r_{12})^3} + \left(\alpha\omega y_2 + \frac{a(y_1-y_2)}{r_{12}(1+\beta r_{12})^2}\right)^2\right]\psi_T \tag{69}$$

gathering equations 66, 67, 68 and 69 we get

$$\begin{aligned}(\nabla_1^2+\nabla_2^2)\psi_T &= \frac{\partial^2\psi_T}{\partial {x_1}^2} + \frac{\partial^2\psi_T}{\partial {y_1}^2} + \frac{\partial^2\psi_T}{\partial {x_2}^2} + \frac{\partial^2\psi_T}{\partial {y_2}^2} \\ &= \left[-4\alpha\omega + \frac{4a}{r_{12}(1+\beta r_{12})^2} - \frac{2a(1+3\beta r_{12})}{r_{12}(1+\beta r_{12})^3} + \alpha^2\omega^2\left(r_1^2+r_2^2\right) - \frac{2a\alpha\omega r_{12}}{(1+\beta r_{12})^2} + \frac{2a^2}{(1+\beta r_{12})^4}\right]\psi_T \quad (70) \\ &= \left[\alpha^2\omega^2\left(r_1^2+r_2^2\right) - 4\alpha\omega - \frac{2a\alpha\omega r_{12}}{(1+\beta r_{12})^2} + \frac{2a}{(1+\beta r_{12})^2}\left(\frac{a}{(1+\beta r_{12})^2} + \frac{1}{r_{12}} - \frac{2\beta}{1+\beta r_{12}}\right)\right]\psi_T \quad (71)\end{aligned}$$

and the local energy(equation 60) is finally

$$E_L = \frac{1}{2}\omega^2\left(1-\alpha^2\right)\left(r_1^2+r_2^2\right) + 2\alpha\omega - \frac{a}{(1+\beta r_{12})^2}\left(\frac{a}{(1+\beta r_{12})^2} - \alpha\omega r_{12} + \frac{1}{r_{12}} - \frac{2\beta}{1+\beta r_{12}}\right) + \frac{1}{r_{12}} \tag{72}$$

II.L.4 General Case

For the general case with N electrons(still closed shell) the local energy is defined as in equation 60, but with ψ_T defined as in equation 48. The Laplacian in this case would then be

$$\nabla_N^2 = \sum_{k=1}^{N}\nabla_k^2 = \sum_{k=1}^{N}\left(\frac{\partial^2}{\partial {x_k}^2} + \frac{\partial^2}{\partial {y_k}^2}\right) \tag{73}$$

that is a sum over the single-particle spacial Laplacians.
As mentioned we derive an expression based on the fact that we only move one particle at a time. This means we can rewrite the derivative ratio given in the local energy and arrive at

$$E_L = \frac{1}{2}\sum_{k=1}^{N}\left(\omega^2 r_k^2 - \nabla_k^2\phi_j(r_k)\psi_{jk}^{-1}(\vec{r})\right)\sum_{i<j}\frac{1}{r_{ij}} \tag{74}$$

See section II.M for a more clear derivation for the above expression. We now need the derivative to the single particle wave functions. Start by defining a new function $g(\vec{r},\beta)$ as the Jastrow-factor

$$g(\vec{r},\beta) \equiv \prod_{i<j}\exp\left(\frac{a}{\beta + \frac{1}{r_{ij}}}\right) \tag{75}$$

and apply equation 73 to the single particle wave function BLAAARGGG

$$\begin{aligned}\nabla_N^2\psi_T^2 &= \sum_{k=1}^{N}\nabla_k^2\left[\det(\Phi(\vec{r},\alpha))g(\vec{r},\beta)\right] \\ &= \sum_{k=1}^{N}\left(2\left(\frac{\partial\det(\Phi(\vec{r},\alpha))}{\partial x_k}\frac{\partial g(\vec{r},\beta)}{\partial x_k} + \frac{\partial\det(\Phi(\vec{r},\alpha))}{\partial y_k}\frac{\partial g(\vec{r},\beta)}{\partial y_k}\right) + \det(\Phi(\vec{r},\alpha))\nabla_k^2 g(\vec{r},\beta) + g(\vec{r},\beta)\nabla_k^2\det(\Phi(\vec{r},\alpha))\right)\end{aligned} \tag{76}$$

We have used a short-hand notation $\det(\Phi)$ defined as

$$\det(\Phi(\vec{r},\alpha)) \equiv \det(\phi_1(r_1),\dots,\phi_N(r_N)) \tag{77}$$

and used the product rule for differentiation.
Starting by solving $\nabla_k^2\det(\Phi(\vec{r},\alpha))$ with the Laplace expansion given in section II.G. The Laplace expansion simplifies the expression due to the fact that the cofactors are independant of the k-th particle. This gives us

$$\begin{aligned}\nabla_k^2\det(\Phi(\vec{r},\alpha)) &= \nabla_k^2\sum_{i=1}^{N}C_{ij}\Phi_{ij} \\ &= \nabla_k\cdot\left(C_{kj}\nabla_k\Phi_{kj}\right) \\ &= C_{kj}\nabla_k^2\Phi_{kj}\end{aligned} \tag{78}$$

The single particle wave function is

$$\Phi_{kj} = \phi_{n_{x_j} n_{y_j}}(r_k, \alpha) = H_{n_{x_j}}\left(\sqrt{\omega} x_k\right) H_{n_{y_j}}\left(\sqrt{\omega} y_k\right) \exp\left(-\frac{\alpha\omega}{2}\left(x_k^2 + y_k^2\right)\right) \tag{79}$$

The expression to be solved for the k-th particle is thus

$$\begin{aligned}\nabla_k^2 \Phi_{kj} &= H_{n_{y_j}}\left(\sqrt{\omega} y_k\right) \exp\left(-\frac{\alpha\omega}{2} y_k^2\right) \frac{\partial^2}{\partial {x_k}^2}\left(H_{n_{x_j}}\left(\sqrt{\omega} x_k\right) \exp\left(-\frac{\alpha\omega}{2} x_k^2\right)\right) \\ &+ H_{n_{x_j}}\left(\sqrt{\omega} x_k\right) \exp\left(-\frac{\alpha\omega}{2} x_k^2\right) \frac{\partial^2}{\partial {y_k}^2}\left(H_{n_{y_j}}\left(\sqrt{\omega} y_k\right) \exp\left(-\frac{\alpha\omega}{2} y_k^2\right)\right)\end{aligned} \tag{80}$$

Solving the differential for x_k and similarly y_k by substituting $s = \sqrt{\omega} x_k = \sqrt{\omega} y_k$ and labeling $n_x, n_y \to n$ and defining

$$\begin{aligned} e(x_k) &\equiv \exp\left(-\frac{\alpha\omega}{2} x_k^2\right) \\ e(y_k) &\equiv \exp\left(-\frac{\alpha\omega}{2} y_k^2\right)\end{aligned} \tag{81}$$

Using the product rule for differentiation and equation 5 for the derivative of the Hermite polynomials with the recursion relation given in equation 3 for $H_n(s)$ gives

$$\begin{aligned}\omega \frac{\partial^2}{\partial s^2}\left(H_n(s) e(s)\right)) &= \omega\left(\frac{\partial^2 H_n}{\partial x^2} - 2\alpha s \frac{\partial H_n}{\partial x} + \alpha\left(\alpha s^2 - 1\right) H_n(s)\right) e(s) \\ &= \omega\left(8n(n-1)H_{n-2}(s) - 4n\alpha s H_{n-1}(s) + \alpha(\alpha s^2 - 1)(2sH_{n-1}(s) - 2(n-1)H_{n-2})\right) e(s) \\ &= \omega\left[2(n-1)\left(4n - \alpha\left(\alpha s^2 - 1\right)\right) H_{n-2}(s) + 2\alpha s\left(\alpha s^2 - 1 - 2n\right) H_{n-1}(s)\right] e(s) \\ &= \omega\left[2(n-1)\left(4n - \alpha\left(\alpha s^2 - 1\right)\right) H_{n-2}(s) + \alpha\left(\alpha s^2 - 1 - 2n\right)(H_n(s) + 2(n-1)H_{n-2}(s))\right] e(s) \\ &= \omega\left[2n(n-1)(2-\alpha)\frac{H_{n-2}}{H_n} + \alpha\left(\alpha s^2 - 1 - 2n\right)\right] H_n(s) e(s)\end{aligned} \tag{82}$$

We have in the latter step used equation 3 to find H_{n-1}.
Defining

$$\Theta_{n_{x_k} n_{y_k}}(x_k, y_k, \alpha) \equiv 2\omega(2-\alpha)\left[n_{x_k}\left(n_{x_k} - 1\right)\frac{H_{n_{x_k}-2}}{H_{n_{x_k}}} + n_{y_k}\left(n_{y_k} - 1\right)\frac{H_{n_{y_k}-2}}{H_{n_{y_k}}}\right] + \alpha\omega\left(\alpha\omega r_k^2 - 2\left(n_{x_k} + n_{y_k} + 1\right)\right) \tag{83}$$

gives

$$\nabla_k^2 \Phi_{kj} = \Theta_{n_{x_k} n_{y_k}}(x_k, y_k, \alpha) \Phi_{kj}(r_k, \alpha) \tag{84}$$

such that

$$\sum_{k=1}^{N} C_{kj} \nabla_k^2 \Phi_{kj} = \det(\Phi(\vec{r}, \alpha)) \sum_{k=1}^{N} \Theta_{n_{x_k} n_{y_k}}(x_k, y_k, \alpha) \tag{85}$$

The Laplacian for g is derived as follows

$$\begin{aligned}\nabla_k^2 g(\vec{r}, \beta) &= \nabla_k^2 \prod_{i<j} \exp\left(\frac{a}{\beta + \frac{1}{r_{ij}}}\right) \\ &= \nabla_k\left(g(\vec{r}, \beta) \sum_{j\neq k} \nabla_k\left(\frac{a}{\beta + \frac{1}{r_{kj}}}\right)\right) \\ &= \nabla_k\left(g(\vec{r}, \beta) \sum_{j\neq k}\left(\frac{a}{\left(1 + \beta r_{kj}\right)^2}\left(x_k - x_j, y_k - y_j\right)\right)\right) \\ &= g(\vec{r}, \beta)\left(\left(\sum_{j\neq k} \frac{a(x_k - x_j)}{r_{kj}\left(1 + \beta r_{kj}\right)^2}\right)^2 + \left(\sum_{j\neq k} \frac{a(y_k - y_j)}{r_{kj}\left(1 + \beta r_{kj}\right)^2}\right)^2 + \sum_{j\neq k}\left(\frac{a}{r_{kj}\left(1 + \beta r_{kj}\right)^2}\left(1 - \frac{2}{1 + \frac{1}{\beta r_{kj}}}\right)\right)\right)\end{aligned} \tag{86}$$

We have just reused the results from equations 63 and 67 in the differentiation above.
We define a new function

$$Q(r_k, \beta) \equiv \left(\left(\sum_{j\neq k} \frac{a(x_k - x_j)}{r_{kj}\left(1 + \beta r_{kj}\right)^2}\right)^2 + \left(\sum_{j\neq k} \frac{a(y_k - y_j)}{r_{kj}\left(1 + \beta r_{kj}\right)^2}\right)^2 + \sum_{j\neq k}\left(\frac{a}{r_{kj}\left(1 + \beta r_{kj}\right)^2}\left(1 - \frac{2}{1 + \frac{1}{\beta r_{kj}}}\right)\right)\right) \tag{87}$$

and insert this into equation 86 yielding

$$\nabla_k^2 g(\vec{r},\beta) = g(\vec{r},\beta) Q(r_k,\beta) \tag{88}$$

For the cross-term in equation 76 we need the single derivatives. Starting with $\det(\Phi(\vec{r},\alpha))$ and using a similar approach as in equation 85 with equation 82 gives

$$\begin{aligned}
\frac{\partial \Phi_{kj}}{\partial x_k} &= \sqrt{\omega}\left(2n\frac{H_{n-1}}{H_n} - \alpha s\right) H_n(s) e(s) \\
&= \Phi_{kj}\sqrt{\omega}\left(2n_{x_k}\frac{H_{n_{x_k}-1}}{H_{n_{x_k}}} - \alpha\sqrt{\omega}x_k\right) \\
&= \Phi_{kj}\left(\frac{n_{x_k}}{x_k} + \frac{n_{x_k}(n_{x_k}-1)}{x_k}\frac{H_{n_{x_k}-2}}{H_{n_{x_k}}} - \alpha\omega x_k\right)
\end{aligned} \tag{89}$$

For $g(\vec{r},\beta)$ we have with equation 86

$$\begin{aligned}
\frac{\partial}{\partial x_k} g(\vec{r},\alpha) &= \frac{\partial}{\partial x_k}\left(\prod_{i<j}\exp\left(\frac{a}{\beta + \frac{1}{r_{ij}}}\right)\right) \\
&= g(\vec{r},\beta)\sum_{j\neq k}\frac{\partial}{\partial x_k}\left(\frac{a}{\beta+\frac{1}{r_{kj}}}\right) \\
&= g(\vec{r},\beta)\sum_{j\neq k}\frac{a\left(x_k - x_j\right)}{r_{kj}\left(1+\beta r_{kj}\right)^2}
\end{aligned} \tag{90}$$

For the derivative with respect to y_k the derivation is exactly as given in equations 89 and 90 above. Defining

$$\begin{aligned}
\Upsilon_{n_{x_k}n_{y_k}}(x_k,y_k,\alpha) \equiv \sum_{j\neq k}\frac{a}{r_{kj}\left(1+\beta r_{kj}\right)^2}\Bigg[&\left(\frac{n_{x_k}}{x_k} + \frac{n_{x_k}(n_{x_k}-1)}{x_k}\frac{H_{n_{x_k}-2}}{H_{n_{x_k}}} - \alpha\omega x_k\right)\left(x_k - x_j\right) \\
&+\left(\frac{n_{y_k}}{y_k} + \frac{n_{y_k}(n_{y_k}-1)}{y_k}\frac{H_{n_{y_k}-2}}{H_{n_{y_k}}} - \alpha\omega y_k\right)\left(y_k - y_j\right)\Bigg]
\end{aligned} \tag{91}$$

gives the final expression for the Laplacian for our wavefunction

$$\nabla_N^2 \Psi_T = \sum_{k=1}^{N}\left(\Upsilon_{n_{x_k}n_{y_k}}(x_k,y_k,\alpha) + \Theta_{n_{x_k}n_{y_k}}(x_k,y_k,\alpha) + Q(r_k,\beta)\right)\Psi_T \tag{92}$$

and the local energy is thus

$$E_L = \frac{1}{2}\sum_{k=1}^{N}\left(\omega^2 r_k - \Upsilon_{n_{x_k}n_{y_k}}(x_k,y_k,\alpha) - \Theta_{n_{x_k}n_{y_k}}(x_k,y_k,\alpha) - Q(r_k,\beta)\right) + \sum_{i<j}^{N}\frac{1}{r_{ij}} \tag{93}$$

with

$$\begin{aligned}
\Theta_{n_{x_k}n_{y_k}}(x_k,y_k,\alpha) &\equiv 2\omega(2-\alpha)\left[n_{x_k}\left(n_{x_k}-1\right)\frac{H_{n_{x_k}-2}}{H_{n_{x_k}}} + n_{y_k}\left(n_{y_k}-1\right)\frac{H_{n_{y_k}-2}}{H_{n_{y_k}}}\right] + \alpha\omega\left(\alpha\omega r_k^2 - 2\left(n_{x_k}+n_{y_k}+1\right)\right) \\
Q(r_k,\beta) &\equiv \left(\left(\sum_{j\neq k}\frac{a(x_k-x_j)}{r_{kj}\left(1+\beta r_{kj}\right)^2}\right)^2 + \left(\sum_{j\neq k}\frac{a(y_k-y_j)}{r_{kj}\left(1+\beta r_{kj}\right)^2}\right)^2 + \sum_{j\neq k}\left(\frac{a}{r_{kj}\left(1+\beta r_{kj}\right)^2}\left(1-\frac{2}{1+\frac{1}{\beta r_{kj}}}\right)\right)\right) \\
\Upsilon_{n_{x_k}n_{y_k}}(x_k,y_k,\alpha) &\equiv \sum_{j\neq k}\frac{a}{r_{kj}\left(1+\beta r_{kj}\right)^2}\Bigg[\left(\frac{n_{x_k}}{x_k} + \frac{n_{x_k}(n_{x_k}-1)}{x_k}\frac{H_{n_{x_k}-2}}{H_{n_{x_k}}} - \alpha\omega x_k\right)\left(x_k-x_j\right) \\
&\qquad + \left(\frac{n_{y_k}}{y_k} + \frac{n_{y_k}(n_{y_k}-1)}{y_k}\frac{H_{n_{y_k}-2}}{H_{n_{y_k}}} - \alpha\omega y_k\right)\left(y_k-y_j\right)\Bigg]
\end{aligned} \tag{94}$$

exactly as given in equations 83, 87 and 91.

II.L.5 Analytic Expression for Hessen Matrix

The Hessen matrix is needed in order to minimize with the conjugate gradient method as described in section II.D. The Hessen matrix in the case where we minimize the local energy with respect to α and β is(using equation 23)

$$A = \begin{pmatrix} \frac{\partial^2 \langle E_L\rangle}{\partial\alpha^2} & \frac{\partial^2 \langle E_L\rangle}{\partial\alpha\partial\beta} \\ \frac{\partial^2 \langle E_L\rangle}{\partial\beta\partial\alpha} & \frac{\partial^2 \langle E_L\rangle}{\partial\beta^2} \end{pmatrix} \tag{95}$$

We solve the derivatives generally for a variatonal parameters c_n. The first derivative is thus

$$\begin{aligned}
\frac{\partial \langle E_L\rangle}{\partial c_n} &= \frac{\partial}{\partial c_n}\left(\int \frac{\psi_T^2 E_L}{\int \psi_T^2 \mathrm{d}\tau}\right) \\
&= \int \left(\frac{\int \psi_T^2 \mathrm{d}\tau \left(2\psi_T E_L \frac{\partial \psi_T}{\partial c_n} + \psi_T^2 \frac{\partial E_L}{\partial c_n}\right) - 2\psi_T^2 E_L \int \psi_T \frac{\partial \psi_T}{\partial c_n}\mathrm{d}\tau}{\left(\int \psi_T^2 \mathrm{d}\tau\right)^2}\right)\mathrm{d}\tau \\
&= 2\left\langle \frac{E_L}{\psi_T}\frac{\partial \psi_T}{\partial c_n}\right\rangle - 2\langle E_L\rangle \left\langle \frac{1}{\psi_T}\frac{\partial\psi_T}{\partial c_n}\right\rangle
\end{aligned} \tag{96}$$

In the last step the hermiticity of the Hamiltonian was used. We have also used the fact that the trial wave function ψ_T is a real function.
The second derivative elements is then

$$\begin{aligned}
\frac{\partial^2 \langle E_L\rangle}{\partial c_n \partial c_m} &= 2\left(\frac{\partial}{\partial c_m}\left(\left\langle \frac{E_L}{\psi_T}\frac{\partial\psi_T}{\partial c_n}\right\rangle\right) - \langle E_L\rangle \frac{\partial}{\partial c_m}\left(\left\langle \frac{1}{\psi_T}\frac{\partial\psi_T}{\partial c_n}\right\rangle\right) - \left\langle \frac{1}{\psi_T}\frac{\partial\psi_T}{\partial c_n}\right\rangle \frac{\partial\langle E_L\rangle}{\partial c_m}\right) \\
&= 2\left(\frac{\partial}{\partial c_m}\left\langle \frac{E_L}{\psi_T}\frac{\partial\psi_T}{\partial c_n}\right\rangle\right) - \langle E_L\rangle \frac{\partial}{\partial c_m}\left(\left\langle \frac{1}{\psi_T}\frac{\partial\psi_T}{\partial c_n}\right\rangle\right) \\
&\quad - 4\left\langle \frac{1}{\psi_T}\frac{\partial\psi_T}{\partial c_n}\right\rangle \left(\left\langle \frac{E_L}{\psi_T}\frac{\partial\psi_T}{\partial c_m}\right\rangle - \langle E_L\rangle \left\langle \frac{1}{\psi_T}\frac{\partial\psi_T}{\partial c_m}\right\rangle\right) \\
&= 2\left(\left\langle \frac{E_L}{\psi_T^2}\frac{\partial\psi_T}{\partial c_n}\frac{\partial\psi_T}{\partial c_m}\right\rangle + \left\langle \frac{1}{\psi_T}\frac{\partial E_L}{\partial c_m}\frac{\partial\psi_T}{\partial c_n}\right\rangle + \left\langle \frac{E_L}{\psi_T}\frac{\partial^2\psi_T}{\partial c_n\partial c_m}\right\rangle - 2\left\langle \frac{E_L}{\psi_T}\frac{\partial\psi_T}{\partial c_n}\right\rangle\left\langle \frac{1}{\psi_T}\frac{\partial\psi_T}{\partial c_m}\right\rangle\right) \\
&\quad - 2\langle E_L\rangle \left(\left\langle \frac{1}{\psi_T^2}\frac{\partial\psi_T}{\partial c_n}\frac{\partial\psi_T}{\partial c_m}\right\rangle + \left\langle \frac{1}{\psi_T}\frac{\partial^2\psi_T}{\partial c_n\partial c_m}\right\rangle - 2\left\langle \frac{1}{\psi_T}\frac{\partial\psi_T}{\partial c_n}\right\rangle\left\langle \frac{1}{\psi_T}\frac{\partial\psi_T}{\partial c_m}\right\rangle\right) \\
&\quad - 4\left(\left\langle \frac{1}{\psi_T}\frac{\partial\psi_T}{\partial c_n}\right\rangle\left\langle \frac{E_L}{\psi_T}\frac{\partial\psi_T}{\partial c_m}\right\rangle - \langle E_L\rangle \left\langle \frac{1}{\psi_T}\frac{\partial\psi_T}{\partial c_n}\right\rangle\left\langle \frac{1}{\psi_T}\frac{\partial\psi_T}{\partial c_m}\right\rangle\right) \\
&= 2\left(\left\langle \frac{E_L}{\psi_T}\frac{\partial^2\psi_T}{\partial c_n\partial c_m}\right\rangle - \langle E_L\rangle \left\langle \frac{1}{\psi_T}\frac{\partial^2\psi_T}{\partial c_n\partial c_m}\right\rangle + \left\langle \frac{E_L}{\psi_T^2}\frac{\partial\psi_T}{\partial c_n}\frac{\partial\psi_T}{\partial c_m}\right\rangle - \langle E_L\rangle \left\langle \frac{1}{\psi_T^2}\frac{\partial\psi_T}{\partial c_n}\frac{\partial\psi_T}{\partial c_m}\right\rangle\right) \\
&\quad + \langle E_L\rangle \left\langle \frac{1}{\psi_T}\frac{\partial\psi_T}{\partial c_n}\right\rangle\left\langle \frac{1}{\psi}\frac{\partial\psi_T}{\partial c_m}\right\rangle - 2\left(\left\langle \frac{E_L}{\psi_T}\frac{\partial\psi_T}{\partial c_n}\right\rangle\left\langle \frac{1}{\psi_T}\frac{\partial\psi_T}{\partial c_m}\right\rangle + \left\langle \frac{E_L}{\psi_T}\frac{\partial\psi_T}{\partial c_m}\right\rangle\left\langle \frac{1}{\psi_T}\frac{\partial\psi_T}{\partial c_n}\right\rangle\right) \\
&\quad + 2\left\langle \frac{1}{\psi_T}\frac{\partial\psi_T}{\partial c_n}\frac{\partial E_L}{\partial c_m}\right\rangle
\end{aligned} \tag{97}$$

For the derivative of the wavefunction, we find the elements individually by using Jacobi's formula as described in section II.H. We see that we need to first find the derivative to the individual elements in Φ. These are simply

$$\begin{aligned}
\frac{\partial \Phi_{ij}}{\partial\alpha} &= \frac{\partial}{\partial\alpha}\left(H_{n_{x_j}} H_{n_{y_j}} \exp\left(-\frac{\alpha\omega}{2} r_i^2\right)\right) \\
&= -\frac{\omega}{2} r_i^2 \Phi_{ij}
\end{aligned} \tag{98}$$

Using Jacobi's formula the first derivative with respect to α of ψ_T is

$$\begin{aligned}
\frac{\partial\psi_T}{\partial\alpha} &= g(\vec{r},\beta)\frac{\partial}{\partial\alpha}(\det(\Phi)) \\
&= g(\vec{r},\beta)\,\mathrm{Tr}\left(\mathrm{adj}(\Phi)\frac{\partial\Phi}{\partial\alpha}\right) \\
&= -g(\vec{r},\beta)\frac{\omega}{2}\mathrm{Tr}(\mathrm{adj}(\Phi)\Phi\cdot R) \\
&= -g(\vec{r},\beta)\det(\Phi(\vec{r},\alpha))\frac{\omega}{2}\mathrm{Tr}(\mathbb{1}\cdot R) \\
&= -\psi_T\frac{\omega}{2}\sum_{i=1}^{N} r_i^2
\end{aligned} \tag{99}$$

where we have use equation 29 and defined the elements of R as

$$R_i \equiv r_i^2 \tag{100}$$

The second derivative with respect to α is with the first derivative just

$$\begin{aligned}\frac{\partial^2\psi_T}{\partial\alpha^2} &= \frac{\partial}{\partial\alpha}\left(-\psi_T\frac{\omega}{2}\sum_{i=1}^N r_i^2\right)\\ &= -\frac{\omega}{2}\sum_{i=1}^N r_i^2\frac{\partial\psi_T}{\partial\alpha}\\ &= \left(\frac{\omega}{2}\sum_{i=1}^N r_i^2\right)^2\psi_T\end{aligned} \tag{101}$$

The derivative with respect to β follows a similar approach as in section II.L.4 giving

$$\begin{aligned}\frac{\partial\psi_T}{\partial\beta} &= \det(\Phi(\vec{r},\alpha))\frac{\partial}{\partial\beta}\left(\prod_{i<j}\exp\left(\frac{a}{\beta+\frac{1}{r_{ij}}}\right)\right)\\ &= \det(\Phi(\vec{r},\alpha))g(\vec{r},\beta)\frac{\partial}{\partial\beta}\left(\sum_{i<j}\frac{a}{\beta+\frac{1}{r_{ij}}}\right)\\ &= -\psi_T\sum_{i\neq j}\frac{a}{\left(\beta+\frac{1}{r_{ij}}\right)^2}\end{aligned} \tag{102}$$

The second derivative is thus

$$\begin{aligned}\frac{\partial^2\psi_T}{\partial\beta^2} &= \frac{\partial}{\partial\beta}\left(-\psi_T\sum_{i\neq j}\frac{a}{\left(\beta+\frac{1}{r_{ij}}\right)^2}\right)\\ &= \left(\left(\sum_{i\neq j}\frac{a}{\left(\beta+\frac{1}{r_{ij}}\right)^2}\right)^2+\sum_{i\neq j}\frac{2a}{\left(\beta+\frac{1}{r_{ij}}\right)^3}\right)\psi_T\end{aligned} \tag{103}$$

where we simply used the product rule for differentiation.
The mixed second derivative is found with equations 99 and 102 giving

$$\begin{aligned}\frac{\partial^2\psi_T}{\partial\alpha\beta} &= \frac{\partial}{\partial\beta}\left(-\psi_T\frac{\omega}{2}\sum_{i=1}^N r_i^2\right)\\ &= \psi_T\frac{\omega}{2}\sum_{i=1}^N r_i^2\sum_{i\neq j}\frac{1}{\left(\beta+\frac{1}{r_{ij}}\right)^2}\end{aligned} \tag{104}$$

The final expression for the elements in the Hessen matrix is thus

$$\begin{aligned}\frac{\partial^2\langle E_L\rangle}{\partial\alpha^2} &= \omega^2\left(\left\langle E_L R^2\right\rangle-\langle E_L\rangle\left\langle R^2\right\rangle+\langle E_L\rangle\langle R\rangle^2-\langle E_L R\rangle\langle R\rangle\right)-\omega\left\langle R\frac{\partial E_L}{\partial\alpha}\right\rangle\\ \frac{\partial^2\langle E_L\rangle}{\partial\beta^2} &= 4\left(\left\langle E_L B_2^2\right\rangle-\langle E_L\rangle\left\langle B_2^2\right\rangle\right)+\langle E_L\rangle\langle B_2\rangle^2-\langle E_L B_2\rangle\langle B_2\rangle-2\left\langle B_2\frac{\partial E_L}{\partial\beta}\right\rangle\\ \frac{\partial^2\langle E_L\rangle}{\partial\alpha\partial\beta} &= \omega\left(2\left(\langle E_L R B_2\rangle-\langle E_L\rangle\langle R B_2\rangle\right)+\frac{1}{2}\langle E_L\rangle\langle R\rangle\langle B_2\rangle-\langle E_L R\rangle\langle B_2\rangle-\langle E_L B_2\rangle\langle R\rangle-\left\langle R\frac{\partial E_L}{\partial\beta}\right\rangle\right)\end{aligned} \tag{105}$$

where

$$\begin{aligned}R &\equiv \sum_{i=1}^N r_i^2 & \frac{\partial\psi_T}{\partial\alpha} &= -\frac{\omega}{2}R\psi_T & \frac{\partial^2\psi_T}{\partial\alpha^2} &= \frac{\omega^2}{4}R^2\psi_T & \frac{\partial^2\psi_T}{\partial\alpha\partial\beta} &= \frac{\omega}{2}RB_2\psi_T\\ B_n &\equiv \sum_{i\neq j}\frac{a}{\left(\beta+\frac{1}{r_{ij}}\right)^n} & \frac{\partial\psi_T}{\partial\beta} &= -B_2\psi_T & \frac{\partial^2\psi_T}{\partial\beta^2} &= \left(B_2^2+2B_3\right)\psi_T\end{aligned} \tag{106}$$

II.M Optimization

In the method described in section II.L the heavy load in terms of calculation lies within the calculation of the determinant ratio given in equations 47 and 40. This section will derive an expression for these ratios in terms of computation time. We will in the whole section assume we only move one particle at a time in the Monte Carlo cycle.

II.M.1 Determinant Ratio

In the Metropolis algorithm we calculate a ratio of determinants in the Metropolis test. Starting by defining a Slater determinant Matrix D with entries defined as

$$D_{ij} \equiv \phi_j(r_i) \tag{107}$$

where the ϕ's are defined as in section II.L.
In terms of cofactors C_{ij} we have

$$\det(D) = \sum_{j=1}^{N} D_{ij} C_{ji} \tag{108}$$

If we now take into light the mentioned assumption about moving only one particle at a time the determinant given in equation 107 only gets a change of one row.
Defining the ratio as

$$R \equiv \frac{\det(D\,(x^{\text{new}}))}{\det(D\,(x^{\text{old}}))} \tag{109}$$

Using the fact that when moving the particle at position r_i the cofactors remain unchanged and inserting in equation 108 into equation 109 we have

$$R = \frac{\sum_{j=1}^{N} D_{ij}(r^{\text{new}}) C_{ji}(r^{\text{old}})}{\sum_{j=1}^{N} D_{ij}(r^{\text{old}}) C_{ij}(r^{\text{old}})} \tag{110}$$

Since the Slater is square(closed shell), we have the following ratio »INSERT REF«

$$\det(D) = \frac{D^{\dagger}}{D} \tag{111}$$

inserting this into equation 110 we get

$$R = \frac{\sum_{j=1}^{N} D_{ij}(r^{\text{new}}) D_{ji}^{-1}(r^{\text{old}})|D|}{\sum_{j=1}^{N} D_{ij}(r^{\text{old}}) D_{ji}^{-1}(r^{\text{old}})|D|} \tag{112}$$

Since D is ivertible »INSERT REF« we have

$$\sum_{k=1}^{N} D_{ik} D_{kj}^{-1} = \delta_{ij} \tag{113}$$

meaning the denominator in equation 112 is equal to 1 and the ratio is finally(with equation 107 inserted)

$$R = \sum_{j=1}^{N} \phi_j(r_i^{\text{new}}) \phi_{ji}^{-1}(r^{\text{old}}) \tag{114}$$

We can follow a similar approach to find the ratio given in equation 40 for the quantum force. The expression is simply

$$\frac{\nabla_i |D(r_i)|}{|D(r_i)|} = \sum_{j=1}^{N} \nabla_i \phi_j(r_i^{\text{new}}) \phi_{ji}^{-1}(r^{\text{old}}) \tag{115}$$

And a similarly for the Laplacian

$$\frac{\nabla_i^2 |D(r_i)|}{|D(r_i)|} = \sum_{j=1}^{N} \nabla_i^2 \phi_j(r_i^{\text{new}}) \phi_{ji}^{-1}(r^{\text{old}}) \tag{116}$$

II.M.2 Inverse of Matrix

In section II.M.1 we derived a formula for calculating the ratio of determinants by the inverse of the old determinant when only one row is changed. This section gives a formula for updating the inverse of a matrix in that case. The formula is

$$D_{kj}^{-1}\left(r^{\text{new}}\right) = \begin{cases} D_{kj}^{-1}\left(r^{\text{old}}\right) - \dfrac{D_{ik}^{-1}\left(r^{\text{old}}\right)}{R} \displaystyle\sum_{l=1}^{N} D_{il}\left(r^{\text{new}}\right) D_{lj}^{-1}\left(r^{\text{old}}\right), & j \neq i \\ \dfrac{D_{ik}^{-1}\left(r^{\text{old}}\right)}{R} \displaystyle\sum_{l=1}^{N} D_{il}\left(r^{\text{old}}\right) D_{lj}^{-1}\left(r^{\text{old}}\right), & j = i \end{cases} \tag{117}$$

as described by Sherman and Morris [3, 8].

II.M.3 Derivative Ratios

In the calculation of the local energy and quantum force we need to calculate the ratio between the derivatives of the trial wave function and the wave function it self. In this section we will derive a formula for these ratios based on the mentioned fact that we move only one particle at a time.
We start with the first derivative and define the one body part to be ψ_ϕ and the correlation term(Jastrow) to be ψ_J meaning $\psi_T = \psi_\phi \psi_J$. This gives the ratio

$$\frac{\nabla \psi_T}{\psi_T} = \frac{\nabla \psi_\phi}{\psi_\phi} + \frac{\nabla \psi_J}{\psi_J} \tag{118}$$

and for the second derivative we have

$$\frac{\nabla^2 \psi_T}{\psi_T} = \frac{\nabla^2 \psi_\phi}{\psi_\phi} + \frac{\nabla^2 \psi_J}{\psi_J} + 2\frac{\nabla \psi_\phi}{\psi_\phi} \cdot \frac{\nabla \psi_J}{\psi_J} \tag{119}$$

For one-body part ψ_ϕ we know that the expression is just a determinant(from equation 48). Using equations 115 and 116 the expressions for the derivative ratios is

$$\begin{aligned} \frac{\nabla \psi_\phi}{\psi_\phi} &= \sum_{j=1}^{N} \nabla_i \phi_j(r_i) \psi_{\phi,ji}^{-1}(\vec{r}) \\ \frac{\nabla^2 \psi_T}{\psi_T} &= \sum_{j=1}^{N} \nabla_i^2 \phi_j(r_i) \psi_{\phi,ji}^{-1}(\vec{r}) \end{aligned} \tag{120}$$

For the correlation factor ψ_J we have an exponential form(see equation 48). The first derivative ratio is thus

$$\left[\frac{\nabla \psi_J}{\psi_J}\right]_x = \sum_{i=1}^{k-1} \frac{x_i - x_k}{r_{ik}} \frac{\partial f_{ik}}{\partial r_{ik}} - \sum_{i=k+1}^{N} \frac{x_k - x_i}{r_{ki}} \frac{\partial f_{ki}}{\partial r_{ki}} \tag{121}$$

due to the fact that the Jastrow-factor factor g is only dependant of the relative distance r_{ij} and is of exponential form and only the $N-1$ terms differentiated survive.
For the second derivative ratio we have similarly

$$\left[\frac{\nabla^2 \psi_J}{\psi_J}\right]_x = \sum_{i,j \neq k} \frac{(\vec{r}_k - \vec{r}_i)(\vec{r}_k - \vec{r}_j)}{r_{ki} r_{kj}} \frac{\partial f_{ki}}{\partial r_{ki}} \frac{\partial f_{kj}}{\partial r_{kj}} + \sum_{j \neq k} \left(\frac{\partial^2 f_{kj}}{\partial {r_{kj}}^2} + \frac{2}{r_{kj}} \frac{\partial f_{kj}}{\partial r_{kj}} \right) \tag{122}$$

The factor f_{ij} is just the function appearing in the exponent of the Jastrow factor.

II.N STATISTICAL ANALYSIS

Since Monte Carlo simulations can be considered to be computer experiments the resulting data can be analysed with the same statistical theory as one would with experimental data. This section will give a brief overview of some of the statistical concepts and explain the method of Blocking(for estimating the standard deviation).

II.N.1 STANDARD DEVIATION, VARIANCE AND COVARIANCE

Given a PDF $P(x)$ the mean value, variance and covariance is

$$\bar{x}_n \equiv \frac{1}{n} \sum_{k=1}^{n} x_k \tag{123}$$

$$\mathrm{var}(x) \equiv \frac{1}{n} \sum_{k=1}^{n} (x_k - \bar{x}_n)^2 \tag{124}$$

$$\mathrm{cov}(x) \equiv \frac{1}{n} \sum_{kl} (x_k - \bar{x}_n)(x_l - \bar{x}_n) \tag{125}$$

for a finite size sample.

II.N.2 Central Limit Theorem

The central limit theorem states that given a PDF P_{X_n} for a sample X_n the mean value can be expressed as

$$\lim_{n\to\infty} p_{\bar{X}_n}(x) = \sqrt{\frac{n}{2\pi\sigma(X)^2}} \exp\left(-\frac{n(x-\bar{X}_n)^2}{2\sigma(X)^2}\right) \tag{126}$$

where $\sigma^2(X)$ is the variance of the sample.

II.N.3 Statistical Error

The error in a sample is just the spread of the mean, i.e the variance of said sample. Set a finite size sample X_n the error would be

$$\sigma_X^2 = \mathrm{var}\left(\bar{X}_n\right) = \frac{1}{n^2}\sum_{ij}\mathrm{cov}\left(X_i, X_j\right) \tag{127}$$

Using the central limit theorem we can approximate the real mean as

$$\langle x_i \rangle \approx \frac{1}{n}\sum_{k=1}^{n} x_k = \bar{x} \tag{128}$$

which gives the approximative covariance

$$\mathrm{cov}\left(X_i, X_j\right) \approx \left\langle (x_i - \bar{x})(x_j - \bar{x}) \right\rangle = \frac{1}{n}\mathrm{cov}(x) \tag{129}$$

and the error is thus

$$\sigma_X^2 = \frac{1}{n}\mathrm{cov}(x) \tag{130}$$

We can split this equation in part giving

$$\begin{aligned}\sigma_X^2 &= \frac{1}{n}\mathrm{var}(x) + \frac{1}{n}\left(\mathrm{cov}(x) - \mathrm{var}(x)\right) \\ &= \frac{1}{n^2}\sum_{k=1}^{n}(x_k - \bar{x}_n) + \frac{2}{n^2}\sum_{k<l}(x_k - \bar{x}_n)(x_l - \bar{x}_n)\end{aligned} \tag{131}$$

II.N.4 Autocorrelation Function

Writing the second term in our error given in equation 131 (the so-called correlation term) as a partial sums gives

$$f_d = \frac{1}{n-d}\sum_{k=1}^{n-d}(x_k - \bar{x}_n)(x_{k+d} - \bar{x}_n) \tag{132}$$

which this we can define the autocorrelation function k_d as

$$k_d \equiv \frac{f_d}{\mathrm{var}(x)} \tag{133}$$

The sample error is now

$$\sigma^2 = \frac{\tau}{n}\mathrm{var}(x) \tag{134}$$

with τ defined as the autocorrelation time

$$\tau \equiv 1 + 2\sum_{d=1}^{n-1} k_d \tag{135}$$

The method of blocking estimates the standard deviation given in

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VII References

[1] David J. Griffiths Chapters 2, 4 and 7, *Introduction to Quantum Mechanics Second Edition*, Pearson, 2005, ISBN 0-13-111892-7.

[2] Morten Hjort-Jensen, *Computational Physics: Hartree-Fock methods and introduction to Many-Body Theory.* https://www.github.com/CompPhysics/ComputationalPhysics2/blob/gh-pages/doc/pub/basicMB/pdf, 2017

[3] Morten Hjort-Jensen, *Computational Physics: Variational Monte Carlo methods.*
https://www.github.com/CompPhysics/ComputationalPhysics2/blob/gh-pages/doc/pub/vmc/pdf, 2017

[4] M. Taut, *Two Electrons in an External Oscillator Potential; Particular analytic solutions of a Coulomb Correlation Problem*, Physical Review A 48, 3561, 1993.

[5] Negele and Orland, *Quantum Many-Particle Systems*, Addison-Wesley.

[6] Fetter and Walecka, *Quantum Theory of Many-Particle Systems*, Mcgraw-Hill, 1971.

[7] Dickhoss and Van Neck, *Many-Body Theory Exposed*, World Scientific, 2006

[8] Jack Sherman and Winifred J. Morrison, *Adjustment of an Inverse Matrix Corresponding to a Change in One Element of a Given Matrix.*
Annals of Mathematical Statistics 21, 1950. doi: http://dx.doi.org/10.1214/aoms/1177729893.

[9] David C. Lay Chapter 3, *Linear Algebra and Its Applications*, Pearson, 2011, ISBN 978-0321835144.