

Variational Monte-Carlo Simulations of Atomic Systems

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<https://github.com/lastis/FYS4411>

Abstract

This is where the abstract goes. Write something smart here.

I. INTRODUCTION

To evaluate the results of the numerical methods, we investigated the possibility of finding a closed-form solution of the ground-state energy using the Variational Principle.

II. METHODS

A. Definitions

The Helium atom consists of two electrons orbiting a nucleus, where the distance between electron 1 and the nucleus, and electron 2 and the nucleus are labeled as $r_1 = \sqrt{x_1^2 + y_1^2 + z_1^2}$ and $r_2 = \sqrt{x_2^2 + y_2^2 + z_2^2}$.

The total potential energy of the system is modelled as

$$V(r_1, r_2) = -\frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}}$$

where the interaction between each electron and the nucleus is given by the two first terms. The mutual electron-electron repulsion is given by the last. The distance between the electrons is $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$.

The Hamiltonian of the system is thusly,

$$\hat{H} = -\frac{\nabla_1^2}{2} - \frac{\nabla_2^2}{2} - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}}$$

C. Variational Monte Carlo (VMC)

The integrals to be solved in the variational method, does not scale well with traditional integral methods when increasing the number of particles and dimensions and using more complex wave functions.

Therefore, we introduce the brute-force Monte Carlo method to solve the integrals.

The radii $\{r_1, r_2, r_{12}\}$ are scaled, and are dimensionless. The Laplace operator of a function f in three dimensions, $\nabla^2 f$, can be represented as

$$\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right) f + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) f + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} f$$

in spherical coordinates, and as

$$\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) f$$

in cartesian coordinates.

B. The Variational Principle

The Variation Principle states that if we have a Hamiltonian \hat{H} and a trial wavefunction ψ_T , an upper bound for the ground state energy is given by equation (1).

The principle is that the given integral is a value of the energy of a given wave function and when the wave function is varied, the according values of the energy is the output. If we then record the lowest energy, the ground state, we also have the wave function of the ground state.

C.1 VMC Algorithm

- Initialization.
 - Set a fixed number of MC steps.
 - Choose initial position \mathbf{R} and variational parameters α .
 - Calculate $|\psi_T(\mathbf{R})|^2$
- Set energy and variance and start the MC calculation.
 - Find the trial position $\mathbf{R}' = \mathbf{R} + \delta \times r$, where $r \in [0, 1]$ is randomly selected.

- Use the Metropolis algorithm to determine if the move $w = \frac{P(\mathbf{R}')}{P(\mathbf{R})}$ is accepted or rejected.
- Given that the move is accepted, set $\mathbf{R} = \mathbf{R}'$.
- Update averages.

- Compute final averages.

D. The Metropolis Algorithm

The Metropolis algorithm samples a normalized probability distribution by a stochastic process. In other words, it is a method for simulating random walks, which we can use to do brute-force Monte Carlo computations.

Define $P_i^{(n)}$ as the probability for finding the system in state i at some step n .

- Sample a possible new state j with a probability $T_{i \rightarrow j}$.
- With probability $A_{i \rightarrow j}$, accept j as a new state. Set it as the new sample. The move is rejected with probability $1 - A_{i \rightarrow j}$. set i as the sample again.

E. Importance Sampling

A random walker is the most efficient way to sample where the wave function is large. To increase this we can implement importance sampling where the walk in space is effected by the trial wave function.

The results are based on the Fokker-Planck equation and the Langevin equation. This makes the step look similar to a diffusion process where the new position is given by,

$$y = x + DF(x)\delta t + \xi\sqrt{\Delta t}.$$

ξ is a gaussian random variable and Δt is a chosen timestep. For atomic units D is $1/2$ and Δt is a variable for the simulation. In our plots $\Delta t = 0.01$.

An important part of this result is that the walker is effected by $F(x)$ which contains the trial wavefunction. This has been named the quantum force.

$$\mathbf{F} = 2\frac{1}{\Psi_T}\nabla\Psi_T.$$

This also has the result of changing the random number check in the Metropolis algorithm from : $q(y, x) = |\Psi_T(y)|^2/|\Psi_T(x)|^2$ to:

$$q(y, x) = \frac{G(x, y, \Delta t)|\Psi_T(y)|^2}{G(y, x, \Delta t)|\Psi_T(x)|^2}.$$

Where G is the Green function given by,

$$G(y, x, \Delta t) = \frac{1}{(4\pi D\Delta t)^{3N/2}} \cdot \exp\left(-(y - x - D\Delta t F(x))^2/4D\Delta t\right).$$

F. Statistical Analysis

The MC calculation are a set of computational *experiments*, with statistical errors. In the experiments we are interested in the mean value of the ground energies and the density distribution. The individual samples are not as interesting to us and we would rather like to look in the variance of the mean value.

The variance of the mean value is closely connected with the correlation in the individual samples. This can be shown mathematically, but the result is this:

$$\sigma^2(m) = \frac{1}{n^2} \sum_{i,j=1}^n \text{Cov}(x_i, x_j)$$

Both our random walker and walking with importance sampling gives correlated samples. In our case, blocking is the technique of finding out how many steps the walker has to go to be as uncorrelated as possible with it's first step. If we then plot the variance in mean as a function of block size we will see that the variance reaches a plateau.

This plateau means that increasing the sample length will no longer change the variance in the mean significantly. This makes us able to more easily calculate variance in the mean because we know how short block sizes we can use. This is used to make the standard deviation interval around our densities.

F.1 Blocking Implementation

- Compute MC calculation, store samples in array.
- Loop over a set of block sizes n_b .
- For each n_b , calculate the mean of the block and store these values in a new array.
- Take the mean and variance of this array.
- Store results.

G. The Trial Wavefunctions for Helium

To conclude if the computational methods are implemented correctly, we should check that the results are reasonable. We do this by finding a mathematical approximation of the closed form expression.

Given the trial wavefunction $\psi_T(\mathbf{R}, \alpha)$, we define a new quantity

$$E_L = \frac{1}{\psi_T} \hat{\mathbf{H}} \psi_T$$

where α is a set of variational parameters. E_{L1} is called the local energy

G..1 The first trial wavefunction

We first model the variational solution with a trial function of one variation parameter α . It has the form

$$\psi_{T1}(\mathbf{r}_1, \mathbf{r}_2) = \exp(-\alpha(r_1 + r_2))$$

The only part of the operator \hat{H} that affects the wavefunction are the Laplace operators.

Since ψ_{T1} is only spatially dependent on r_1 and r_2 , the Laplaces of ψ_{T1} reduces to

$$\nabla_i^2 \psi_{T1} = \left(\frac{\partial^2}{\partial r_i^2} + \frac{2}{r_i} \frac{\partial}{\partial r_i} \right) \psi_{T1} = \left(\alpha^2 - \alpha \frac{2}{r_i} \right) \psi_{T1}$$

for $i = 1, 2$, since

$$\begin{aligned} \frac{\partial}{\partial r_i} e^{-\alpha(r_1+r_2)} &= -\alpha e^{-\alpha(r_1+r_2)} \\ \frac{\partial^2}{\partial r_i^2} e^{-\alpha(r_1+r_2)} &= \alpha^2 e^{-\alpha(r_1+r_2)} \end{aligned}$$

This gives us the following trial energy

$$\begin{aligned} E_{L1} &= \frac{1}{\psi_{T1}} \left(-\alpha^2 + \alpha \left(\frac{1}{r_1} + \frac{1}{r_1} \right) - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}} \right) \psi_{T1} \\ &= (\alpha - 2) \left(\frac{1}{r_1} + \frac{1}{r_2} \right) + \frac{1}{r_{12}} - \alpha^2 \end{aligned}$$

The 2 in the $\alpha - 2$ term is the number of protons, Z.

G..2 The second trial wavefunction

To approximate the closed-form solution even better, we assume another trial wavefunction based on ψ_{T1} , namely

$$\psi_{T2}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_{12}) = \exp(-\alpha(r_1 + r_2)) \exp\left(\frac{r_{12}}{2(1 + \beta r_{12})}\right)$$

The second part is dependent on the distance between the electrons, and is called the correlation part, which accounts for the effect between the electrons.

One can then in the same way as for ψ_{T1} calculate the local energy. The correlations part will give us some trouble when we try to calculate the Laplacian. This is due to the distance between \mathbf{r}_1 and \mathbf{r}_2 , since this quantity is dependent on the angles φ and θ . It has the form

$$\begin{aligned} E_{L2} &= E_{L1} + \frac{1}{2(1 + \beta r_{12})^2} \left(\frac{\alpha(r_1 + r_2)}{r_{12}} \left(1 - \frac{\mathbf{r}_1^T \mathbf{r}_2}{r_1 r_2} \right) \right. \\ &\quad \left. - \frac{1}{2(1 + \beta r_{12})^2} - \frac{2}{r_{12}} + \frac{2\beta}{1 + \beta r_{12}} \right) \end{aligned}$$

H. The Trial Wavefunction for Beryllium

We can use a trial wavefunction on the same form as for Hydrogen and Helium

$$\begin{aligned} \psi_T(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4) &= Det(\phi_1(\mathbf{r}_1), \phi_2(\mathbf{r}_2), \phi_3(\mathbf{r}_3), \phi_4(\mathbf{r}_4)) \\ &\quad \cdot \prod_{i < j}^4 \exp\left(\frac{r_{ij}}{2(1 + \beta r_{ij})}\right) \end{aligned}$$

where we approximate the Slater determinant Det as

$$\begin{aligned} \psi_T(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4) &\propto (\phi_{1s}(\mathbf{r}_1)\phi_{2s}(\mathbf{r}_2) - \phi_{1s}(\mathbf{r}_2)\phi_{2s}(\mathbf{r}_1)) \\ &\quad \cdot (\phi_{1s}(\mathbf{r}_3)\phi_{2s}(\mathbf{r}_4) - \phi_{1s}(\mathbf{r}_4)\phi_{2s}(\mathbf{r}_3)) \end{aligned}$$

where the hydrogenic wavefunctions for the two spin orbitals are given by

$$\phi_{1s}(\mathbf{r}_i) = e^{-\alpha r_i}$$

and

$$\phi_{2s}(\mathbf{r}_i) = (1 - \alpha r_i/2) e^{-\alpha r_i/2}$$

I. Onebody Density and Charge Density

The one-body density is computed from the form

$$\rho(\mathbf{R}) = |\psi(\mathbf{R})|^2$$

This is implemented as NOTE: ... in our program.

J. Implementation

The methods described above are implemented in an object oriented C++ program which is simple to use, and does not have any dependencies.

Most of the code is contained in the class VMC-Solver.cpp and VMCsolver.h. These were created to contain the full system and parameters for a single run.

To start a simulation one must instantiate the solver and initialize the system, either by file and/or manually. After this the integration can be run and all data will be contained in the solver object. The last step is to collect data from the solver.

All plot data are generated by individual programs using the mentioned solver. Plots are generated using python.

K. Trial Wavefunctions

The trial wavefunction of Beryllium can be written as a product of a Slater determinant part and a correlation part on the form

$$\psi_T(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4) = \psi_D \psi_C \quad (2)$$

where the Slater determinant is

$$\begin{aligned} \psi_D &= Det(\phi_1(\mathbf{r}_1), \phi_2(\mathbf{r}_2), \phi_3(\mathbf{r}_3), \phi_4(\mathbf{r}_4)) \\ &= (\phi_{1s}^1 \phi_{2s}^2 - \phi_{1s}^2 \phi_{2s}^1) (\phi_{1s}^3 \phi_{2s}^4 - \phi_{1s}^4 \phi_{2s}^3) \end{aligned} \quad (3)$$

and the correlation part is

$$\psi_C = \prod_{i < j}^4 g_{ij} = \prod_{i < j}^4 \exp\left(\frac{\alpha r_{ij}}{1 + \beta r_{ij}}\right) \quad (4)$$

Here $\phi_i(\mathbf{r}_i)$ are the hydrogen-like wavefunctions. They are given by the 1s and 2s orbital parts

$$\begin{aligned}\phi_{1s}^i &= e^{-\alpha r_i} \\ \phi_{2s}^i &= (1 - \alpha r_i/2) e^{-\alpha r_i/2}\end{aligned}$$

which are dependent on the cartesian positions $\mathbf{r}_i = (x_i, y_i, z_i)$. The relative distance between two particles is

$$r_{ij} = |\mathbf{r}_j - \mathbf{r}_i| = \sqrt{(x_j - x_i)^2 + (y_j - y_i)^2 + (z_j - z_i)^2}$$

and obviously $r_{ij} = r_{ji}$.

We want to determine the local energy E_L to approximate the ground state energy of the atom. The general expression for the local energy is

$$E_L = \frac{1}{\psi_T(\mathbf{R})} \hat{\mathbf{H}} \psi_T(\mathbf{R})$$

and the Hamiltonian can generally be described as a sum of the contributions to the potential energy by the electron-electron repulsion and the nucleus-electron interaction, as well as the kinetic energy. This gives us a Hamiltonian for N particles on the form

$$\begin{aligned}\hat{\mathbf{H}} &= \hat{\mathbf{K}} + \hat{\mathbf{V}} \\ &= \sum_i (\hat{k}_i + \hat{v}_i) + \sum_{i < j} \hat{v}_{ij} \\ &= - \sum_{i=1}^N \left[\frac{\hat{\nabla}_i^2}{2} + \frac{Z}{r_i} \right] + \sum_{i=1}^{N-1} \sum_{j=i+1}^N \frac{1}{r_{ij}}\end{aligned}$$

Where Z is the atomic number.

From this expression, it's clear that $\hat{\mathbf{K}}$ is the only operator that changes the trial wavefunction when we calculate the local energy. Therefore, we must calculate the following quantities

$$\frac{1}{\psi_T} \hat{k}_i \psi_T = -\frac{1}{2} \frac{\hat{\nabla}_i^2 \psi_T}{\psi_T}$$

For Beryllium, the trial wavefunction is a product of the Slater determinant part and the correlation part, namely $\psi_T = \psi_D \psi_C$.

The product rule of differentiation gives us

$$\frac{\hat{\nabla}^2 \psi_T}{\psi_T} = \frac{\hat{\nabla}^2 \psi_D}{\psi_D} + 2 \frac{\hat{\nabla} \psi_D}{\psi_D} \cdot \frac{\hat{\nabla} \psi_C}{\psi_C} + \frac{\hat{\nabla}^2 \psi_C}{\psi_C}$$

L. Efficient Computation of the Slater Determinant

For larger atoms, the evaluation of the gradient and the Laplacian of the Slater determinant becomes increasingly numerically demanding to compute. Computing these quantities with brute force, leads to $N \cdot d$ operations to find the determinant and thus multiplying this with our $O(N^3)$ operations. In the following, we derive a method that deals with this issue, and achieves a lower number of operations.

We can approximate the Slater determinant as

$$\Phi(\mathbf{r}_1, \dots, \mathbf{r}_N) \propto \det \uparrow \cdot \det \downarrow$$

where the spin determinants are the determinants which only depend on spin up and spin down respectively. The determinants are 2×2 for Beryllium and 5×5 for Neon. This is true only if $\hat{\mathbf{H}}$ is spin independent.

Then, $\det \hat{D} = |\hat{D}| = |\hat{D}|_{\uparrow} \cdot |\hat{D}|_{\downarrow}$, where the Slater matrices are dependent on the positions of the electrons. Each time we update the positions and differentiate the Slater determinant, the Slater matrix is changed, but by calculating the determinant from scratch each time, we will certainly do unnecessary computations.

This is solved by the following algorithm, that instead of calculating the determinant, updates the *inverse* of the Slater matrix suitably.

We first express (i, j) elements of the inverse of \hat{D} as

$$d_{ij}^{-1} = \frac{C_{ji}}{|\hat{D}|}$$

where C_{ji} is the transposed cofactor-matrix element of \hat{D} .

This motivates the ratio

$$R \equiv \frac{|\hat{D}(\mathbf{r}^{new})|_{\uparrow}}{|\hat{D}(\mathbf{r}^{old})|_{\uparrow}} = \frac{\sum_{j=1}^N d_{ij}^{new} C_{ij}^{new}}{\sum_{j=1}^N d_{ij}^{old} C_{ij}^{old}}$$

Every time we move particle i , the i -th row of \hat{D} changes, and we have to update the inverse. However, the i -th row of \hat{C} is independent¹ of the i -th row of \hat{D} , which means that we must have

$$\hat{C}_{ij}^{new} = \hat{C}_{ij}^{old} = (d_{ji}^{-1})^{old} \cdot |\hat{D}| \text{ for } j = 1, \dots, N$$

and using

$$\sum_{k=1}^N d_{ik} d_{kj}^{-1} = \delta_{ij}$$

The result is

$$R = \sum_{j=1}^N d_{ij}^{new} (d_{ji}^{-1})^{old} = \sum_{j=1}^N \phi_j(\mathbf{r}_i^{new}) d_{ji}^{-1}(\mathbf{r}_i^{old})$$

The algorithm for updating the inverse of the matrix when a new position is accepted is then

We can then calculate the gradient and laplacian as

$$\begin{aligned}\frac{\hat{\nabla}_k |\hat{D}|}{|\hat{D}|} &= \sum_{j=1}^N \nabla_k \phi_j(\mathbf{r}_i^{new}) d_{ji}^{-1}(\mathbf{r}_i^{old}) \\ \frac{\hat{\nabla}_k^2 |\hat{D}|}{|\hat{D}|} &= \sum_{j=1}^N \nabla_k^2 \phi_j(\mathbf{r}_i^{new}) d_{ji}^{-1}(\mathbf{r}_i^{old})\end{aligned}$$

REMEMBER TO SAY SOMETHING ABOUT NUMBER OF OPERATIONS.

¹Since the cofactor-matrix elements c_{ij} is defined by removing i -th row and j -th column from a matrix \hat{A} , and then taking the determinant of the remaining matrix.

Algorithm 1 Inverse of Slater Matrix

```

1: procedure UPDATE COLUMNS  $j \neq i$ 
2:   for each column  $i \neq j$  do
3:      $S_j = \sum_{l=1}^N d_{il}(\mathbf{r}^{new}) d_{lj}^{-1}(\mathbf{r}^{old})$ 
4:      $(d_{kj}^{-1})^{new} = (d_{kj}^{-1})^{old} - \frac{S_j}{R} (d_{ki}^{-1})^{old}$ 
5: procedure UPDATE COLUMN  $i$ 
6:    $(d_{ki}^{-1})^{new} = \frac{1}{R} (d_{ki}^{-1})^{old}$ 

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III. RESULTS

Appendix A: Mathematical Derivations

1. The wavefunction of Beryllium

We start by finding the first and second derivative of the determinant part, which are only dependent on the radii of the particles. This means that the gradient can be written

$$\hat{\nabla} f = \hat{\mathbf{r}} \frac{\partial f}{\partial r} \quad \text{and} \quad \hat{\nabla}^2 f = \frac{\partial^2 f}{\partial r^2} + \frac{2}{r} \frac{\partial f}{\partial r}$$

where $\mathbf{r} = r\hat{\mathbf{r}}$.

We define the functions

$$f_i \equiv -\frac{\alpha \mathbf{r}_i}{2}$$

$$g_i \equiv \exp(f_i)$$

$$F_{ij} \equiv \phi_{1s}(\mathbf{r}_i) \phi_{2s}(\mathbf{r}_j) - \phi_{1s}(\mathbf{r}_j) \phi_{2s}(\mathbf{r}_i)$$

and use them to simplify derivatives of the Hydrogen-like wavefunctions in the following way

$$\begin{aligned}
\phi_{1s}^i &= g_i^2 \\
\frac{\partial \phi_{1s}^i}{\partial r_i} &= -\alpha g_i^2 \\
\frac{\partial^2 \phi_{1s}^i}{\partial r_i^2} &= \alpha^2 g_i^2 \\
\phi_{2s}^i &= g_i(1 + f_i) \\
\frac{\partial \phi_{2s}^i}{\partial r_i} &= -\alpha g_i(1 + f_i/2) \\
\frac{\partial^2 \phi_{2s}^i}{\partial r_i^2} &= \frac{3\alpha^2}{4} g_i(1 + f_i/3) \\
\phi_{2p_k}^i &= \alpha k_i g_i \text{ for } k_i = x_i, y_i, z_i \\
\frac{\partial \phi_{2p_k}^i}{\partial r_i} &= \left(\frac{1}{r_i} - \frac{\alpha}{2} \right) \alpha k_i g_i \\
\frac{\partial^2 \phi_{2p_k}^i}{\partial r_i^2} &= \left(\left[\frac{1}{r_i} - \frac{\alpha}{2} \right]^2 - \frac{1}{r_i} \right) \alpha k_i g_i
\end{aligned}$$

and then the terms required to calculate the Slater determi-

nant

$$\begin{aligned}
F_{ij} &= g_i^2(1 + f_j)g_j - g_j^2(1 + f_i)g_i \\
\frac{\partial F_{ij}}{\partial r_i} &= -\alpha g_i g_j (g_i(1 + f_j) - g_j(1 + f_i/2)) \\
\frac{\partial^2 F_{ij}}{\partial r_i^2} &= \alpha^2 g_i g_j (g_i(1 + f_j) - \frac{3}{4} g_j(1 + f_i/3)) \\
\frac{\partial F_{ij}}{\partial r_j} &= \alpha g_i g_j (g_j(1 + f_i) - g_i(1 + f_j/2)) \\
\frac{\partial^2 F_{ij}}{\partial r_j^2} &= -\alpha^2 g_i g_j (g_j(1 + f_i) - \frac{3}{4} g_i(1 + f_j/3))
\end{aligned}$$

The determinant part is

$$\psi_D = F_{12} F_{34}$$

where the first is only affected by differentiation with respect to particle 1 or 2, and opposite for the second part

$$\begin{aligned}
\frac{\hat{\nabla}_1 \psi_D}{\psi_D} &= \frac{\hat{\nabla}_1 F_{12}}{F_{12}} & \frac{\hat{\nabla}_2 \psi_D}{\psi_D} &= \frac{\hat{\nabla}_2 F_{12}}{F_{12}} \\
\frac{\hat{\nabla}_3 \psi_D}{\psi_D} &= \frac{\hat{\nabla}_3 F_{34}}{F_{34}} & \frac{\hat{\nabla}_4 \psi_D}{\psi_D} &= \frac{\hat{\nabla}_4 F_{34}}{F_{34}}
\end{aligned}$$

The result is two different quantities

$$\frac{\hat{\nabla}_k \psi_D}{\psi_D} = \begin{cases} \frac{\hat{\nabla}_i F_{ij}}{F_{ij}} &= -\alpha \frac{\mathbf{r}_i}{r_i} \frac{(g_i(1+f_j) - g_j(1+f_i/2))}{g_i(1+f_j) - g_j(1+f_i)}, \text{ if } k = i = j - 1 \\ \frac{\hat{\nabla}_j F_{ij}}{F_{ij}} &= -\alpha \frac{\mathbf{r}_j}{r_j} \frac{(g_i(1+f_j/2) - g_j(1+f_i))}{g_i(1+f_j) - g_j(1+f_i)}, \text{ if } k = j = i + 1 \end{cases}$$

one for particles 1 and 3, and one for 2 and 4, where $i \in 1, 3$ and $j \in 2, 4$.

For the second derivative part, we have

$$\frac{\hat{\nabla}_k^2 \psi_D}{\psi_D} = \begin{cases} \frac{\hat{\nabla}_i^2 F_{ij}}{F_{ij}} &= \frac{\alpha^2 (g_i(1+f_j) - \frac{3}{4} g_j(1+f_i/3)) - \frac{2\alpha}{r} (g_i(1+f_j) - g_j(1+f_i))}{g_i(1+f_j) - g_j(1+f_i)} \\ \frac{\hat{\nabla}_j^2 F_{ij}}{F_{ij}} &= \frac{\alpha^2 (\frac{3}{4} g_i(1+f_j/3) - g_j(1+f_i)) - \frac{2\alpha}{r} (g_i(1+f_j/2) - g_j(1+f_i))}{g_i(1+f_j) - g_j(1+f_i)} \end{cases}$$

with the same conditions as above. Now we move on to the calculation of the correlation parts, given by the function in (4).

First off, we define

$$f_{ij} \equiv \frac{a r_{ij}}{1 + \beta r_{ij}}$$

with the corresponding derivatives (with respect to r_{ij})

$$\begin{aligned}
f'_{ij} &= \frac{a}{(1 + \beta r_{ij})^2} \\
f''_{ij} &= \frac{-2a\beta}{(1 + \beta r_{ij})^3}
\end{aligned}$$

The gradient of the wavefunction, divided by the wavefunction, for particle k in the x -direction is then

$$\left[\frac{\hat{\nabla}_k \psi_C}{\psi_C} \right]_x = \frac{1}{\psi_C} \frac{\partial \psi_C}{\partial x_k}$$

If we look at the first derivative in the x -direction, we see that the parts of the wavefunction that is not dependent on k , will remain unaffected by the differentiation. When we split the expression for $i < k$ and $k > i$, we get that

$$\begin{aligned}
\frac{\partial \psi_C}{\partial x_k} &= \prod_{i,j \neq k} g_{ij} \frac{\partial}{\partial x_k} \left[\prod_{i < k} g_{ik} \cdot \prod_{i > k} g_{ki} \right] \\
&= \prod_{i,j \neq k} g_{ij} \left[\prod_{i > k} g_{ki} \frac{\partial}{\partial x_k} \prod_{i < k} g_{ik} + \prod_{i < k} g_{ik} \frac{\partial}{\partial x_k} \prod_{i > k} g_{ki} \right] \\
&= \prod_{i,j \neq k} g_{ij} \left[\prod_{i > k} g_{ki} \sum_{i < k} \frac{\partial g_{ik}}{\partial x_k} \prod_{p \neq i} g_{pi} + \prod_{i < k} g_{ik} \sum_{i > k} \frac{\partial g_{ki}}{\partial x_k} \prod_{q \neq i} g_{iq} \right] \\
&= \prod_{i < j} g_{ij} \left[\frac{1}{\prod_{i < k} g_{ik}} \sum_{i < k} \frac{\partial g_{ik}}{\partial x_k} \prod_{p \neq i} g_{pi} + \frac{1}{\prod_{i > k} g_{ki}} \sum_{i > k} \frac{\partial g_{ki}}{\partial x_k} \prod_{p \neq i} g_{pi} \right] \\
&= \psi_C \left[\sum_{i < k} \frac{1}{g_{ik}} \frac{\partial g_{ik}}{\partial x_k} + \sum_{i > k} \frac{1}{g_{ki}} \frac{\partial g_{ki}}{\partial x_k} \right] \quad (5)
\end{aligned}$$

Here we factorized the wavefunction outside the expression, and noticed that the only part that doesn't cancel is the ik -th and ki -th in the sums.

Dividing by the wavefunction, we get

$$\begin{aligned}
\left[\frac{\hat{\nabla}_k \psi_C}{\psi_C} \right]_x &= \sum_{i=1}^{k-1} \frac{1}{g_{ik}} \frac{\partial g_{ik}}{\partial x_k} + \sum_{i=k+1}^N \frac{1}{g_{ki}} \frac{\partial g_{ki}}{\partial x_k} \\
&= \sum_{i=1}^{k-1} \frac{\partial f_{ik}}{\partial x_k} - \sum_{i=k+1}^N \frac{\partial f_{ki}}{\partial x_i} \\
&= \sum_{i=1}^{k-1} \frac{x_k - x_i}{r_{ik}} \frac{\partial f_{ik}}{\partial r_{ik}} - \sum_{i=k+1}^N \frac{x_i - x_k}{r_{ki}} \frac{\partial f_{ki}}{\partial r_{ki}}
\end{aligned}$$

since g_{ij} is an exponential function, so $\partial g_{ij}/\partial x_i = g_{ij} \partial f_{ij}/\partial x_i$. We also used the fact that $\partial g_{ij}/\partial x_i = -\partial g_{ij}/\partial x_j$ to differentiate with respect to the second index in both of the sums. Finally, we have used the chain rule to attain an expression that is dependent on the distance between the two particles

$$\frac{\partial f_{ij}}{\partial x_j} = \frac{\partial f_{ij}}{\partial r_{ij}} \frac{\partial r_{ij}}{\partial x_j} = \frac{x_j - x_i}{r_{ij}} \frac{\partial f_{ij}}{\partial r_{ij}}$$

Thus

$$\begin{aligned}
\frac{\hat{\nabla}_k \psi_C}{\psi_C} &= \sum_{i=1}^{k-1} \frac{\mathbf{r}_{ik}}{r_{ik}} \frac{\partial f_{ik}}{\partial r_{ik}} - \sum_{i=k+1}^N \frac{\mathbf{r}_{ki}}{r_{ki}} \frac{\partial f_{ki}}{\partial r_{ki}} \\
&= \sum_{i=1}^{k-1} \frac{\mathbf{r}_{ik}}{r_{ik}} \frac{a}{(1 + \beta r_{ik})^2} - \sum_{i=k+1}^N \frac{\mathbf{r}_{ki}}{r_{ki}} \frac{a}{(1 + \beta r_{ki})^2} \\
&= \sum_{i \neq k} \frac{\mathbf{r}_{ik}}{r_{ik}} \frac{a}{(1 + \beta r_{ik})^2}
\end{aligned}$$

From (5), we can gather that the double derivative part is

described by

$$\begin{aligned}
\left[\frac{\hat{\nabla}^2 \psi_C}{\psi_C} \right]_x &= \frac{1}{\psi_C} \frac{\partial}{\partial x_k} \left(\psi_C \left[\sum_{i < k} \frac{\partial f_{ik}}{\partial x_k} + \sum_{i > k} \frac{\partial f_{ki}}{\partial x_k} \right] \right) \\
&= \left[\sum_{i < k} \frac{\partial^2 f_{ik}}{\partial x_k^2} + \sum_{i > k} \frac{\partial^2 f_{ki}}{\partial x_k^2} \right] + \frac{1}{\psi_C} \frac{\partial \psi_C}{\partial x_k} \left[\sum_{i < k} \frac{\partial f_{ik}}{\partial x_k} + \sum_{i > k} \frac{\partial f_{ki}}{\partial x_k} \right] \\
&= \sum_{i \neq k} \frac{\partial^2 f_{ik}}{\partial x_k^2} + \left[\sum_{i=1}^{k-1} \frac{\partial f_{ik}}{\partial x_k} - \sum_{i=k+1}^N \frac{\partial f_{ki}}{\partial x_i} \right]^2 \\
&= \sum_{i \neq k} \frac{\partial}{\partial x_k} \left(\frac{\partial f_{ik}}{\partial r_{ik}} \frac{\partial r_{ik}}{\partial x_k} \right) + \left[\sum_{i \neq k} \frac{\partial r_{ik}}{\partial x_k} \frac{\partial f_{ik}}{\partial r_{ik}} \right]^2 \\
&= \sum_{i \neq k} \left[\frac{\partial r_{ik}}{\partial x_k} \frac{\partial}{\partial x_k} \frac{\partial f_{ik}}{\partial r_{ik}} + \frac{\partial f_{ik}}{\partial r_{ik}} \frac{\partial^2 r_{ik}}{\partial x_k^2} \right] + \left[\sum_{i \neq k} \frac{\partial r_{ik}}{\partial x_k} f'_{ik} \right]^2 \\
\left[\frac{\hat{\nabla}^2 \psi_C}{\psi_C} \right]_x &= \sum_{i \neq k} \left[\left(\frac{\partial r_{ik}}{\partial x_k} \right)^2 f''_{ik} + f'_{ik} \frac{r_{ik}^2 - (x_k - x_i)^2}{r_{ik}^3} \right] \\
&\quad + \sum_{j \neq k} \left[\frac{\partial r_{ik}}{\partial x_k} f'_{ik} \left(\frac{\partial r_{ik}}{\partial x_k} f'_{ik} + \sum_{j \neq k, i} \frac{\partial r_{jk}}{\partial x_k} f'_{jk} \right) \right] \\
\left[\frac{\hat{\nabla}^2 \psi_C}{\psi_C} \right]_x &= \sum_{i \neq k} \left[\left(\frac{\partial r_{ik}}{\partial x_k} \right)^2 f''_{ik} + f'_{ik} \frac{r_{ik}^2 - (x_k - x_i)^2}{r_{ik}^3} \right] \\
&\quad + \sum_{j \neq k} \left[\left(\frac{\partial r_{ik}}{\partial x_k} f'_{ik} \right)^2 + \sum_{j \neq k, i} \frac{\partial r_{ik}}{\partial x_k} f'_{ik} \frac{\partial r_{jk}}{\partial x_k} f'_{jk} \right] \\
\left[\frac{\hat{\nabla}^2 \psi_C}{\psi_C} \right]_x &= \sum_{i \neq k} \left[\left(\frac{x_k - x_i}{r_{ik}} \right)^2 f''_{ik} + f'_{ik} \frac{r_{ik}^2 - (x_k - x_i)^2}{r_{ik}^3} \right] \\
&\quad + \sum_{j \neq k} \left[\left(\frac{x_k - x_i}{r_{ik}} f'_{ik} \right)^2 + \sum_{j \neq k, i} \frac{(x_k - x_i)(x_k - x_j)}{r_{ik} r_{jk}} f'_{ik} f'_{jk} \right] \\
\left[\frac{\hat{\nabla}^2 \psi_C}{\psi_C} \right]_x &= \sum_{i \neq k} \left[\left(\frac{x_k - x_i}{r_{ik}} \right)^2 f''_{ik} + f'_{ik} \frac{r_{ik}^2 - (x_k - x_i)^2}{r_{ik}^3} \right] \\
&\quad + \sum_{i, j \neq k} \frac{(x_k - x_i)(x_k - x_j)}{r_{ik} r_{jk}} f'_{ik} f'_{jk}
\end{aligned}$$

If we now sum up for all dimensions, we get

$$\begin{aligned}
\frac{\hat{\nabla}^2 \psi_C}{\psi_C} &= \sum_{i \neq k} \left[\frac{r_{ik}^2}{r_{ik}^2} f''_{ik} + f'_{ik} \frac{3r_{ik}^2 - r_{ik}^2}{r_{ik}^3} \right] + \sum_{i, j \neq k} \frac{(\mathbf{r}_k - \mathbf{r}_i)(\mathbf{r}_k - \mathbf{r}_j)}{r_{ik} r_{jk}} f'_{ik} f'_{jk} \\
&= \sum_{i \neq k} \left[f''_{ik} + \frac{2}{r_{ik}} f'_{ik} \right] + \sum_{i, j \neq k} \frac{(\mathbf{r}_k - \mathbf{r}_i)(\mathbf{r}_k - \mathbf{r}_j)}{r_{ik} r_{jk}} f'_{ik} f'_{jk}
\end{aligned}$$