

Variational Monte Carlo for a 2D semiconductor Quantum Dot

Jacopo Cocomello, Antonio Anna Mele, Luca Zuanazzi

June 2020

Introduction

A quantum dot is in general a device that displays the behavior of a zero dimensional system, i.e. it presents spectra that are similar to those, for instance, of an atom as opposed to that of a wire, a sheet or a bulk system. Two-dimensional quantum dots are a special class of such devices that are normally obtained by etching a so-called quantum well, an interface between two differently doped semiconductor layers (such as, for instance, GaAs and $\text{Al}_x\text{Ga}_{1-x}\text{As}$). At the interface a potential well is formed, such that the effective transverse confinement energy $\hbar\omega_\perp \gg E$, where E are the typical energy scales in the longitudinal direction. In this regime a 2D quantum dot containing N electrons can be described by an effective Hamiltonian of the form

$$H = \sum_{i=1}^N \left(-\frac{\hbar^2}{2m_e m^*} \nabla_i^2 + \frac{1}{2} m_e m^* \omega^2 r_i^2 \right) + \frac{e^2}{\epsilon} \sum_{i < j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \quad (1)$$

with $\mathbf{r}_i = (x_i, y_i)$, m^* is the electron effective mass and ϵ is an effective dielectric constant partly accounting for the reduced dimensionality effects. We will set $m^* = 0.067$ and $\epsilon = 12.4$. Throughout the whole exercise we will use effective atomic units, corresponding to set $\hbar = 4\pi\epsilon_0 = m_e m^* = e^2/\epsilon = 1$. Lengths and energies are then expressed respectively in effective Bohr radii and effective Hartrees

$$a_0^* = \frac{4\pi\epsilon_0 \hbar^2 \epsilon}{m_e m^* e^2} \simeq 9.794 \text{ nm} \quad E_h^* = \frac{\hbar^2}{m_e m^* a_0^{*2}} \simeq 11.86 \text{ meV} \quad (2)$$

Our goal is to find an estimate of the ground state solution for the Schrödinger equation corresponding to the Hamiltonian (1) for a set of small N by means of the Variational Monte Carlo (VMC) method. The general form of the variational wave function can be assumed to be a product of a mean field solution and a Jastrow correction

$$\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N) = \phi_{MF}(\mathbf{r}_1, \dots, \mathbf{r}_N) \left[\prod_{i < j} f_{ij}(r_{ij}) \right] \quad (3)$$

with $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$.

Jastrow function

The Jastrow function has the form

$$f_{ij}(r) = \exp \left(\frac{a_{ij} r}{1 + b_{ij} r} \right) \quad (4)$$

where the coefficients a_{ij} are determined by the cusp condition, which for our system reads

$$\lim_{r \rightarrow 0} \frac{H f_{\uparrow\downarrow}(r)}{f_{\uparrow\downarrow}(r)} < \infty \quad \lim_{r \rightarrow 0} \frac{H r f_{\uparrow\uparrow}(r)}{r f_{\uparrow\uparrow}(r)} < \infty \quad (5)$$

Clearly, only the part of the Hamiltonian depending on r_{ij} enters in the limit. For the case where electrons i and j have antiparallel spins, we obtain

$$\frac{H f_{\uparrow\downarrow}(r)}{f_{\uparrow\downarrow}(r)} = -\frac{1}{2f_{\uparrow\downarrow}(r)} \nabla^2 f_{\uparrow\downarrow}(r) + \frac{1}{r} \quad (6)$$

We recall the Laplacian in polar coordinates has the form

$$\nabla^2 = \frac{1}{r} \frac{\partial}{\partial r} r \frac{\partial}{\partial r} + \frac{1}{r^2} \frac{\partial^2}{\partial \theta^2} \quad (7)$$

Keeping only the leading terms for small r we have

$$\frac{Hf_{\uparrow\downarrow}(r)}{f_{\uparrow\downarrow}(r)} = -\frac{a_{\uparrow\downarrow} - a_{\uparrow\downarrow}(4b_{\uparrow\downarrow} - a_{\uparrow\downarrow})r + \mathcal{O}(r^2)}{2r} + \frac{1}{r} = \frac{2 - a_{\uparrow\downarrow}}{2r} + \frac{a_{\uparrow\downarrow}(4b_{\uparrow\downarrow} - a_{\uparrow\downarrow})}{2} + \mathcal{O}(r) \quad (8)$$

which is finite in the limit $r \rightarrow 0$ if we set $a_{\uparrow\downarrow} = 2$. For the case where electrons i and j have parallel spins, we instead have

$$\begin{aligned} \frac{Hrf_{\uparrow\uparrow}(r)}{rf_{\uparrow\uparrow}(r)} &= -\frac{1}{2rf_{\uparrow\uparrow}(r)}\nabla^2 rf_{\uparrow\uparrow}(r) + \frac{1}{r} \\ &= -\frac{1}{2r^2} + \frac{2 - 3a_{\uparrow\uparrow}}{2r} + \frac{a_{\uparrow\uparrow}(8b_{\uparrow\uparrow} - a_{\uparrow\uparrow})}{2} + \mathcal{O}(r) \end{aligned} \quad (9)$$

Here we cannot avoid the divergence for $r \rightarrow 0$ but we can take care of the Coulomb term setting $a_{\uparrow\uparrow} = 2/3$.

Single particle wave function

With the aim to construct the mean field wave function we focus on the non-interacting problem

$$-\frac{1}{2}\nabla^2\varphi_\alpha(\mathbf{r}) + \frac{1}{2}\omega^2 r^2\varphi_\alpha(\mathbf{r}) = \lambda_\alpha\varphi_\alpha(\mathbf{r}) \quad (10)$$

Such equation can be solved in two different ways; the easiest is realizing that the problem consists in two independent harmonic oscillators, one along x and the other along y . We can then separate variables and write

$$\varphi_\alpha(\mathbf{r}) = \varphi_{n_x, n_y}(x, y) = \psi_{n_x}(x)\psi_{n_y}(y) \quad \lambda_\alpha = \omega(n_x + n_y + 1) \quad (11)$$

with

$$\psi_n(x) = \frac{1}{\sqrt{2^n n!}} \left(\frac{\omega}{\pi}\right)^{\frac{1}{4}} H_n(\sqrt{\omega}x) \exp\left(-\frac{\omega x^2}{2}\right) \quad n = 0, 1, 2, \dots \quad (12)$$

The other way exploits the rotational symmetry along the z axis expressing the stationary states in terms of eigenstates of the total energy and the z component of the angular momentum. This time we use polar coordinates and separate spatial and angular part as follow

$$\varphi_\alpha(\mathbf{r}) = \varphi_{n,m}(r, \theta) = R_{n,m}(r) \frac{e^{im\theta}}{\sqrt{2\pi}} \quad m = 0, \pm 1, \pm 2, \dots \quad (13)$$

m being the projection along z of the angular momentum. The total angular momentum quantum number is $l = |m|$. The spatial part is the solution of

$$\left(-\frac{1}{2}\frac{d^2}{dr^2} - \frac{1}{2r}\frac{d}{dr} + \frac{m^2}{2r^2} + \frac{1}{2}\omega^2 r^2\right) R_{n,m}(r) = \lambda_{n,m} R_{n,m}(r) \quad (14)$$

To simplify the notation we change variable $t = \sqrt{\omega}x$. The previous equation can then be rewritten as

$$R''(t) + \frac{1}{t}R'(t) + \left(\frac{2\lambda}{\omega} - \frac{m^2}{t^2} - t^2\right) R(t) = 0 \quad (15)$$

In the limits of $t \rightarrow 0$ and $t \rightarrow \infty$ one can easily obtain the asymptotic behaviours

$$R(t \rightarrow 0) \rightarrow t^l \quad R(t \rightarrow \infty) \rightarrow e^{-t^2/2} \quad (16)$$

We exploit the long range behaviour setting $R(t) = P(t)e^{-t^2/2}$, equation (15) then becomes

$$P''(t) + \left(\frac{1}{t} - 2t\right) P'(t) + \left(\frac{2\lambda}{\omega} - \frac{m^2}{t^2} - 2\right) P(t) = 0 \quad (17)$$

Now we expand P in power series exploiting the short range behaviour, namely $P(t) = t^l \sum_{k=0}^{\infty} c_k t^k$. Inserting this expression we have

$$\sum_{k=0}^{\infty} c_k \left[k(k+2l)t^{k+l-2} + 2\left(\frac{\lambda}{\omega} - k - l - 1\right) t^{k+m} \right] = 0 \quad (18)$$

For this to be identically zero every coefficient must vanish. The coefficient of t^{l-1} is $c_1(1+2l)$ and is zero only if c_1 is zero itself. For the other powers we can change index, $k \rightarrow k+2$ in the first part of the sum, and obtain the following recurrence relation

$$c_{k+2}(k+2)(k+2+2l) + 2c_k \left(\frac{\lambda}{\omega} - k - l - 1\right) = 0 \quad (19)$$

Hence, all the coefficients with an odd k are zero while the ones with k even can all be obtained from c_0 , which is determined by the normalization condition. One may see that, in order to have the correct long range asymptotic behaviour, the series must stop at some k . This means that there must exist a k for which

$$\lambda = \omega(k+l+1) \quad k = 0, 2, 4, \dots \quad (20)$$

where k must be an even integer because we recall that only the even coefficients have survived. Thus we can write

$$\lambda = \omega(2n+l+1) \quad n = 0, 1, 2, \dots \quad (21)$$

We now look for a relation between the first $|n_x, n_y\rangle$ and $|n, m\rangle$ states. The ground state has $\lambda = \omega$ and reads

$$\varphi_{0,0}(x, y) = \varphi_{0,0}(r, \theta) = \sqrt{\frac{\omega}{\pi}} \exp\left(-\frac{\omega r^2}{2}\right) \quad (22)$$

The first excited state has $\lambda = 2\omega$ and is two-fold degenerate. The Cartesian and polar representations read

$$\begin{aligned} \varphi_{1,0}(x, y) &= \omega \sqrt{\frac{2}{\pi}} x e^{-\omega r^2/2} & \varphi_{0,1}(r, \theta) &= \frac{\omega}{\sqrt{\pi}} r e^{-\omega r^2/2} e^{i\theta} \\ \varphi_{0,1}(x, y) &= \omega \sqrt{\frac{2}{\pi}} y e^{-\omega r^2/2} & \varphi_{0,-1}(r, \theta) &= \frac{\omega}{\sqrt{\pi}} r e^{-\omega r^2/2} e^{-i\theta} \end{aligned}$$

Their relation is easily determined

$$\begin{pmatrix} |n_x = 1, n_y = 0\rangle \\ |n_x = 0, n_y = 1\rangle \end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \\ -i & i \end{pmatrix} \begin{pmatrix} |n = 0, m = 1\rangle \\ |n = 0, m = -1\rangle \end{pmatrix} \quad (23)$$

The next excited states correspond to $\lambda = 3\omega$ and are three-fold degenerate, namely

$$\begin{aligned} \varphi_{1,1}(x, y) &= 2\omega \sqrt{\frac{\omega}{\pi}} x y e^{-\omega r^2/2} & \varphi_{1,0}(r, \theta) &= \sqrt{\frac{\omega}{\pi}} (\omega r^2 - 1) e^{-\omega r^2/2} \\ \varphi_{2,0}(x, y) &= \sqrt{\frac{\omega}{2\pi}} (2\omega x^2 - 1) e^{-\omega r^2/2} & \varphi_{0,2}(r, \theta) &= \omega \sqrt{\frac{\omega}{2\pi}} r^2 e^{-\omega r^2/2} e^{2i\theta} \\ \varphi_{0,2}(x, y) &= \sqrt{\frac{\omega}{2\pi}} (2\omega y^2 - 1) e^{-\omega r^2/2} & \varphi_{0,-2}(r, \theta) &= \omega \sqrt{\frac{\omega}{2\pi}} r^2 e^{-\omega r^2/2} e^{-2i\theta} \end{aligned}$$

Their relation is given by

$$\begin{pmatrix} |n_x = 1, n_y = 1\rangle \\ |n_x = 2, n_y = 0\rangle \\ |n_x = 0, n_y = 2\rangle \end{pmatrix} = \frac{1}{2} \begin{pmatrix} 0 & -i\sqrt{2} & i\sqrt{2} \\ 1 & 1 & \sqrt{2} \\ -1 & -1 & \sqrt{2} \end{pmatrix} \begin{pmatrix} |n = 1, m = 0\rangle \\ |n = 0, m = 2\rangle \\ |n = 0, m = -2\rangle \end{pmatrix} \quad (24)$$

Lastly, we construct an orthonormal set of real orbitals in polar coordinates

$$\varphi_{1s} = \varphi_{0,0}(r, \theta) = \sqrt{\frac{\omega}{\pi}} e^{-\omega r^2/2} \quad \lambda_{1s} = \omega \quad (25)$$

$$\varphi_{1p_x} = \sqrt{2} \operatorname{Re}(\varphi_{0,1}(r, \theta)) = \omega \sqrt{\frac{2}{\pi}} r \cos(\theta) e^{-\omega r^2/2} \quad \lambda_{1p_x} = 2\omega \quad (26)$$

$$\varphi_{1p_y} = \sqrt{2} \operatorname{Im}(\varphi_{0,1}(r, \theta)) = \omega \sqrt{\frac{2}{\pi}} r \sin(\theta) e^{-\omega r^2/2} \quad \lambda_{1p_y} = 2\omega \quad (27)$$

$$\varphi_{2s} = \varphi_{1,0}(r, \theta) = \sqrt{\frac{\omega}{\pi}} (\omega r^2 - 1) e^{-\omega r^2/2} \quad \lambda_{2s} = 3\omega \quad (28)$$

$$\varphi_{1d_x} = \sqrt{2} \operatorname{Re}(\varphi_{0,2}(r, \theta)) = \omega \sqrt{\frac{\omega}{\pi}} r^2 \cos(2\theta) e^{-\omega r^2/2} \quad \lambda_{1d_x} = 3\omega \quad (29)$$

$$\varphi_{1d_y} = \sqrt{2} \operatorname{Im}(\varphi_{0,2}(r, \theta)) = \omega \sqrt{\frac{\omega}{\pi}} r^2 \sin(2\theta) e^{-\omega r^2/2} \quad \lambda_{1d_y} = 3\omega \quad (30)$$

Notice that $\varphi_{1p_x} = \varphi_{1,0}(x, y)$ and $\varphi_{1p_y} = \varphi_{0,1}(x, y)$.

Mean field wave function

Since the Hamiltonian (1) acts only on the spatial part and thus commutes with any spin operator, we can consider electrons' spins as constants that we assign at the beginning of the simulation and never change, making electrons with different spin distinguishable. The antisymmetry of the mean field wave function must then come only from an exchange of two electrons with same spin. Therefore, assuming the first N_\uparrow electrons to have spin $+1/2$ we can generally build ϕ_{MF} as a product of two Slater determinants

$$\phi_{MF}(\mathbf{r}_1, \dots, \mathbf{r}_N) = \det [\varphi_\alpha(\mathbf{r}_{\beta_\uparrow})] \det [\varphi_\alpha(\mathbf{r}_{\beta_\downarrow})] \quad (31)$$

with $\beta_\uparrow = 1, \dots, N_\uparrow$ and $\beta_\downarrow = N_\uparrow + 1, \dots, N$. We now explicitly analyze each case of N electrons we will deal with.

$N = 2$

The smallest number of electrons we can consider is $N = 2$. In order to place both electrons in the ground state we must assign them opposite spins. Obviously it doesn't matter which one has spin up or down, with the notation of (31) where the up-spin electrons are listed first we have $N_\uparrow = 1$. The mean field wave function is then

$$\phi_{MF}(\mathbf{r}_1, \mathbf{r}_2) = \det [\varphi_{1s}(\mathbf{r}_1)] \det [\varphi_{1s}(\mathbf{r}_2)] = \varphi_{1s}(\mathbf{r}_1) \varphi_{1s}(\mathbf{r}_2) \quad (32)$$

$N = 3$

Again we place two electrons with opposite spin in the single particle ground state φ_{1s} but then we have two energetically equivalent possible states for the third electron; φ_{1p_x} or φ_{1p_y} .

In order to preserve the rotational symmetry in the xy plane we have to average between the two possibilities. Assuming the third electron to have spin down we have $N_{\uparrow} = 1$ and the mean field wave function turns out to be

$$\begin{aligned}\phi_{MF}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) &= \det [\varphi_{1s}(\mathbf{r}_1)] \left(\det [\varphi_{1s}(\mathbf{r}_2)\varphi_{1p_x}(\mathbf{r}_3)] + \det [\varphi_{1s}(\mathbf{r}_2)\varphi_{1p_y}(\mathbf{r}_3)] \right) \\ &= \varphi_{1s}(\mathbf{r}_1) \left[\varphi_{1s}(\mathbf{r}_2)\varphi_{1p_x}(\mathbf{r}_3) - \varphi_{1s}(\mathbf{r}_3)\varphi_{1p_x}(\mathbf{r}_2) + \varphi_{1s}(\mathbf{r}_2)\varphi_{1p_y}(\mathbf{r}_3) - \varphi_{1s}(\mathbf{r}_3)\varphi_{1p_y}(\mathbf{r}_2) \right]\end{aligned}\quad (33)$$

Note that, to preserve the normalization, we should have divided by $\sqrt{2}$ but, as we will see later, the normalization of the wave function is not relevant in the calculations.

$N = 5$

As always we place two electrons in the φ_{1s} state. Then we can put two electrons in the φ_{1p_x} and one in the φ_{1p_y} or vice versa. As in the case with $N = 3$, we have to average between the two possibilities. Assuming to have $N_{\uparrow} = 3$ the mean field wave function can be written as

$$\phi_{MF}(\mathbf{r}_1, \dots, \mathbf{r}_5) = \det [\varphi_{1s}(\mathbf{r}_1)\varphi_{1p_x}(\mathbf{r}_2)\varphi_{1p_y}(\mathbf{r}_3)] \left(\det [\varphi_{1s}(\mathbf{r}_4)\varphi_{1p_x}(\mathbf{r}_5)] + \det [\varphi_{1s}(\mathbf{r}_4)\varphi_{1p_y}(\mathbf{r}_5)] \right) \quad (34)$$

$N = 6$

This time simply all the first three energy levels are fully occupied, hence $N_{\uparrow} = 3$ and the mean field wave function reads

$$\phi_{MF}(\mathbf{r}_1, \dots, \mathbf{r}_6) = \det [\varphi_{1s}(\mathbf{r}_1)\varphi_{1p_x}(\mathbf{r}_2)\varphi_{1p_y}(\mathbf{r}_3)] \det [\varphi_{1s}(\mathbf{r}_4)\varphi_{1p_x}(\mathbf{r}_5)\varphi_{1p_y}(\mathbf{r}_6)] \quad (35)$$

Local energy calculation

Given the form of the wave function as in (3) we need to calculate its gradient and Laplacian to obtain the local kinetic energy in both the usual way and as Jackson-Feenberg formulation. Letting $\mathbf{R} = \mathbf{r}_1, \dots, \mathbf{r}_N$, the gradient with respect to \mathbf{R} of the wave function reads

$$\begin{aligned}\nabla \Psi(\mathbf{R}) &= \nabla (\phi_{MF}(\mathbf{R}) J(\mathbf{R})) \\ &= J(\mathbf{R}) \nabla \phi_{MF}(\mathbf{R}) + \phi_{MF}(\mathbf{R}) \nabla J(\mathbf{R})\end{aligned}\quad (36)$$

where $J(\mathbf{R})$ is the product of Jastrow functions. The Laplacian is

$$\begin{aligned}\nabla^2 \Psi(\mathbf{R}) &= \nabla \cdot \nabla (\phi_{MF}(\mathbf{R}) J(\mathbf{R})) \\ &= J(\mathbf{R}) \nabla^2 \phi_{MF}(\mathbf{R}) + \phi_{MF}(\mathbf{R}) \nabla^2 J(\mathbf{R}) + 2 \nabla \phi_{MF}(\mathbf{R}) \cdot \nabla J(\mathbf{R}).\end{aligned}\quad (37)$$

Focusing on the Jastrow part we calculate its gradient and its Laplacian. Considering the gradient of only one particle (say the k -th)

$$\begin{aligned}\nabla_k J(\mathbf{R}) &= \nabla_k \left[\prod_{i < j}^N f(r_{ij}) \right] = \nabla_k \left(\exp \sum_{i < j}^N \frac{a_{ij} r_{ij}}{1 + b_{ij} r_{ij}} \right) = J(\mathbf{R}) \nabla_k \left(\sum_{i < j}^N \frac{a_{ij} r_{ij}}{1 + b_{ij} r_{ij}} \right) \\ &= J(\mathbf{R}) \sum_{i < j}^N \nabla_k U_{ij} = J(\mathbf{R}) \sum_{k < j}^N \nabla_k U_{kj} + J(\mathbf{R}) \sum_{i < k}^N \nabla_k U_{ik} \\ &= J(\mathbf{R}) \sum_{k < j}^N U'_{kj} \frac{\mathbf{r}_{kj}}{r_{kj}} - J(\mathbf{R}) \sum_{i < k}^N U'_{ik} \frac{\mathbf{r}_{ik}}{r_{ik}} = J(\mathbf{R}) \sum_{j \neq k}^N U'_{kj} \frac{\mathbf{r}_{kj}}{r_{kj}} \\ &= J(\mathbf{R}) \sum_{j \neq k}^N \frac{a_{kj}(\mathbf{r}_k - \mathbf{r}_j)}{r_{kj}(1 + b_{kj} r_{kj})^2}\end{aligned}\quad (38)$$

where

$$U_{ij} = \frac{a_{ij}r_{ij}}{1 + b_{ij}r_{ij}}, \quad U'_{ij} = \frac{a_{ij}}{(1 + b_{ij}r_{ij})^2}. \quad (39)$$

The Laplacian is obtained by applying the divergence to the gradient, hence

$$\begin{aligned} \nabla_k^2 J(\mathbf{R}) &= \nabla_k J(\mathbf{R}) \cdot \sum_{j \neq k}^N \frac{a_{kj}(\mathbf{r}_k - \mathbf{r}_j)}{r_{kj}(1 + b_{kj}r_{kj})^2} + J(\mathbf{R}) \nabla_k \cdot \sum_{j \neq k}^N \frac{a_{kj}(\mathbf{r}_k - \mathbf{r}_j)}{r_{kj}(1 + b_{kj}r_{kj})^2} \\ &= J(\mathbf{R}) \sum_{l \neq k}^N \frac{a_{kl}(\mathbf{r}_k - \mathbf{r}_l)}{r_{kl}(1 + b_{kl}r_{kl})^2} \cdot \sum_{j \neq k}^N \frac{a_{kj}(\mathbf{r}_k - \mathbf{r}_j)}{r_{kj}(1 + b_{kj}r_{kj})^2} + J(\mathbf{R}) \sum_{j \neq k}^N \frac{a_{kj}(1 - b_{kj}r_{kj})}{r_{kj}(1 + b_{kj}r_{kj})^3} \\ &= J(\mathbf{R}) \left[\frac{\nabla_k J(\mathbf{R})}{J(\mathbf{R})} \cdot \frac{\nabla_k J(\mathbf{R})}{J(\mathbf{R})} + \sum_{j \neq k}^N \frac{a_{kj}(1 - b_{kj}r_{kj})}{r_{kj}(1 + b_{kj}r_{kj})^3} \right] \end{aligned} \quad (40)$$

We can notice that both in gradient and in Laplacian of J we are left with a multiplying $J(\mathbf{R})$ factor in the final result. We can get rid of this factor if we focus on the quantities $(\nabla J(\mathbf{R}))/J(\mathbf{R})$ and $(\nabla^2 J(\mathbf{R}))/J(\mathbf{R})$ instead of the gradient and the Laplacian alone. This can be generalized to the total wave function $\Psi(\mathbf{R})$ as it is shown later in equation (58).

This notation is particularly useful to evaluate gradient and Laplacian of the mean field part.

The mean field part of the total wave function is written as the product of two Slater determinants (see equation (31)). The gradient of the mean field part is then the sum the two terms

$$\nabla \phi_{MF}(\mathbf{R}) = \nabla (\det [\varphi_\alpha(\mathbf{r}_{\beta_\uparrow})]) \det [\varphi_\alpha(\mathbf{r}_{\beta_\downarrow})] + \det [\varphi_\alpha(\mathbf{r}_{\beta_\uparrow})] \nabla (\det [\varphi_\alpha(\mathbf{r}_{\beta_\downarrow})]). \quad (41)$$

We can calculate instead the logarithmic derivative and thus obtain

$$\frac{\nabla \phi_{MF}(\mathbf{r}_1, \dots, \mathbf{r}_N)}{\phi_{MF}(\mathbf{r}_1, \dots, \mathbf{r}_N)} = \frac{\nabla \det [\varphi_\alpha(\mathbf{r}_{\beta_\uparrow})]}{\det [\varphi_\alpha(\mathbf{r}_{\beta_\uparrow})]} + \frac{\nabla \det [\varphi_\alpha(\mathbf{r}_{\beta_\downarrow})]}{\det [\varphi_\alpha(\mathbf{r}_{\beta_\downarrow})]} \quad (42)$$

We will pay our attention on the calculation of $\nabla_k \ln(\det [\varphi_\alpha(\mathbf{r}_\beta)])$.

Let's first work in general with a matrix A and look for the derivative with respect to the i -th component of the $2N$ dimensional vector \mathbf{R} , i.e. $\partial_i \ln[\det(A)]$. The logarithmic derivative can be written as

$$\partial_i \ln[\det(A)] = \frac{\partial_i \det(A)}{\det(A)}, \quad (43)$$

and if we introduce Jacobi's formula

$$\partial_i \det(A) = \det(A) \text{Tr}[A^{-1} \partial_i A] \quad (44)$$

we have

$$\partial_i \ln[\det(A)] = \text{Tr}[A^{-1} \partial_i A] \quad (45)$$

If we identify $A_{\alpha\beta} = \varphi_\alpha(\mathbf{r}_\beta)$ we can clearly see that $\partial_i A_{\alpha\beta} = 0$ unless ∂_i is the derivative with respect to one of the components of \mathbf{r}_β . The trace then becomes just one matrix element of the product $A^{-1} \partial_i A$, namely

$$\nabla_k \ln[\det(A)] = \sum_{\alpha} A_{k\alpha}^{-1} \nabla_k A_{\alpha k} \quad (46)$$

Hence:

$$\frac{\nabla_k \phi_{MF}(\mathbf{r}_1, \dots, \mathbf{r}_N)}{\phi_{MF}(\mathbf{r}_1, \dots, \mathbf{r}_N)} = \frac{\nabla_k \det [\varphi_\alpha(\mathbf{r}_{\beta_\uparrow})]}{\det [\varphi_\alpha(\mathbf{r}_{\beta_\uparrow})]} + \frac{\nabla_k \det [\varphi_\alpha(\mathbf{r}_{\beta_\downarrow})]}{\det [\varphi_\alpha(\mathbf{r}_{\beta_\downarrow})]} = \quad (47)$$

$$= \sum_{\alpha} (SL(\varphi(\mathbf{r}_{\uparrow})))_{k\alpha}^{-1} \nabla_k (SL(\varphi(\mathbf{r}_{\uparrow}))_{\alpha k} + \sum_{\alpha} (SL(\varphi(\mathbf{r}_{\downarrow})))_{k\alpha}^{-1} \nabla_k (SL(\varphi(\mathbf{r}_{\downarrow}))_{\alpha k} \quad (48)$$

where SL means Slater matrix. It must be pointed out that if $k = 0, \dots, 2N_\uparrow$ only the first sum will survive in the last equation, if $k = 2(N_\uparrow + 1), \dots, 2N$ only the second sum will survive. The Laplacian of the mean field part is

$$\begin{aligned}\nabla^2 \phi_{MF}(\mathbf{R}) &= \nabla^2 (\det [\varphi_\alpha(\mathbf{r}_{\beta_\uparrow})]) \det [\varphi_\alpha(\mathbf{r}_{\beta_\downarrow})] + \det [\varphi_\alpha(\mathbf{r}_{\beta_\uparrow})] \nabla^2 (\det [\varphi_\alpha(\mathbf{r}_{\beta_\downarrow})]) + \\ &\quad + 2\nabla(\det [\varphi_\alpha(\mathbf{r}_{\beta_\uparrow})]) \cdot \nabla (\det [\varphi_\alpha(\mathbf{r}_{\beta_\downarrow})]) = \\ &= \nabla^2 (\det [\varphi_\alpha(\mathbf{r}_{\beta_\uparrow})]) \det [\varphi_\alpha(\mathbf{r}_{\beta_\downarrow})] + \det [\varphi_\alpha(\mathbf{r}_{\beta_\uparrow})] \nabla^2 (\det [\varphi_\alpha(\mathbf{r}_{\beta_\downarrow})])\end{aligned}\quad (49)$$

Hence:

$$\frac{\nabla^2 \phi_{MF}(\mathbf{R})}{\phi_{MF}(\mathbf{R})} = \frac{\nabla^2 (\det [\varphi_\alpha(\mathbf{r}_{\beta_\uparrow})])}{\det [\varphi_\alpha(\mathbf{r}_{\beta_\uparrow})]} + \frac{\nabla^2 (\det [\varphi_\alpha(\mathbf{r}_{\beta_\downarrow})])}{\det [\varphi_\alpha(\mathbf{r}_{\beta_\downarrow})]}\quad (50)$$

The Laplacian of the determinant can be calculated with the following expressions, where A is the Slater matrix:

$$\frac{\nabla^2 \det(A)}{\det(A)} = \frac{\sum_{i=0}^{2N} \partial_i^2 \det(A)}{\det(A)} = \sum_{i=0}^{2N} \text{Tr}[A^{-1} \partial_i^2 A]\quad (51)$$

Proof.

$$\begin{aligned}\partial_i^2 \det(A) &= \partial_i (\det(A) \text{Tr}[A^{-1} \partial_i A]) = \partial_i \det(A) \text{Tr}[A^{-1} \partial_i A] + \det(A) \partial_i \text{Tr}[A^{-1} \partial_i A] \\ &= \det(A) (\text{Tr}[A^{-1} \partial_i A])^2 + \det(A) \text{Tr}[\partial_i A^{-1} \partial_i A] + \det(A) \text{Tr}[A^{-1} \partial_i^2 A]\end{aligned}\quad (52)$$

We use the following fact:

$$\partial_i A^{-1} = -A^{-1} \partial_i A A^{-1}\quad (53)$$

Therefore:

$$\begin{aligned}\partial_i^2 \det(A) &= \det(A) (\text{Tr}[A^{-1} \partial_i A])^2 - \det(A) \text{Tr}[A^{-1} \partial_i A A^{-1} \partial_i A] + \det(A) \text{Tr}[A^{-1} \partial_i^2 A] \\ &= \det(A) (\text{Tr}[A^{-1} \partial_i A])^2 - \det(A) \text{Tr}[(A^{-1} \partial_i A)^2] + \det(A) \text{Tr}[A^{-1} \partial_i^2 A]\end{aligned}\quad (54)$$

$$= \det(A) \text{Tr}[A^{-1} \partial_i^2 A]\quad (55)$$

where in the last identity we have have used:

$$(\text{Tr}[A^{-1} \partial_i A])^2 = \text{Tr}[(A^{-1} \partial_i A)^2]\quad (56)$$

which can be easily shown if we use the definition of matrix trace and if we observe that $\partial_i A_{\alpha\beta} = 0$ unless ∂_i is the derivative with respect to one of the components of \mathbf{r}_β . ■

This calculation can be avoided if we assume that the mean field wave function is an eigenstate of the non interacting Hamiltonian. Thus this is used only in the calculations needed to check the results for non-interacting case. Indeed we have

$$\left(-\frac{1}{2} \sum_{k=0}^N \nabla_k^2 + \frac{1}{2} \omega^2 \sum_{k=0}^N r_k^2 \right) \phi_{MF}(\mathbf{R}) = E_0 \phi_{MF}(\mathbf{R})\quad (57)$$

hence the local energy of the interacting case turns out to be

$$\begin{aligned}\frac{H\Psi(\mathbf{R})}{\Psi(\mathbf{R})} &= \frac{1}{\Psi(\mathbf{R})} \left(-\frac{1}{2} \nabla^2 + \frac{1}{2} \omega^2 \sum_{k=0}^N r_k^2 + \sum_{i<j} \frac{1}{r_{ij}} \right) \Psi(\mathbf{R}) \\ &= -\frac{1}{2} \left(\frac{\nabla^2 \phi_{MF}(\mathbf{R})}{\phi_{MF}(\mathbf{R})} + \frac{\nabla^2 J(\mathbf{R})}{J(\mathbf{R})} + 2 \frac{\nabla \phi_{MF}(\mathbf{R})}{\phi_{MF}(\mathbf{R})} \cdot \frac{\nabla J(\mathbf{R})}{J(\mathbf{R})} \right) + \frac{1}{2} \omega^2 \sum_{k=0}^N r_k^2 + \sum_{i<j} \frac{1}{r_{ij}} \\ &= -\frac{1}{2} \left(\frac{\nabla^2 J(\mathbf{R})}{J(\mathbf{R})} + 2 \frac{\nabla \phi_{MF}(\mathbf{R})}{\phi_{MF}(\mathbf{R})} \cdot \frac{\nabla J(\mathbf{R})}{J(\mathbf{R})} \right) + E_0 + \sum_{i<j} \frac{1}{r_{ij}}\end{aligned}\quad (58)$$

In the following we will sketch the procedure to calculate the logarithmic gradient and Laplacian of the Jastrow part of the wave function $J(\mathbf{R})$.

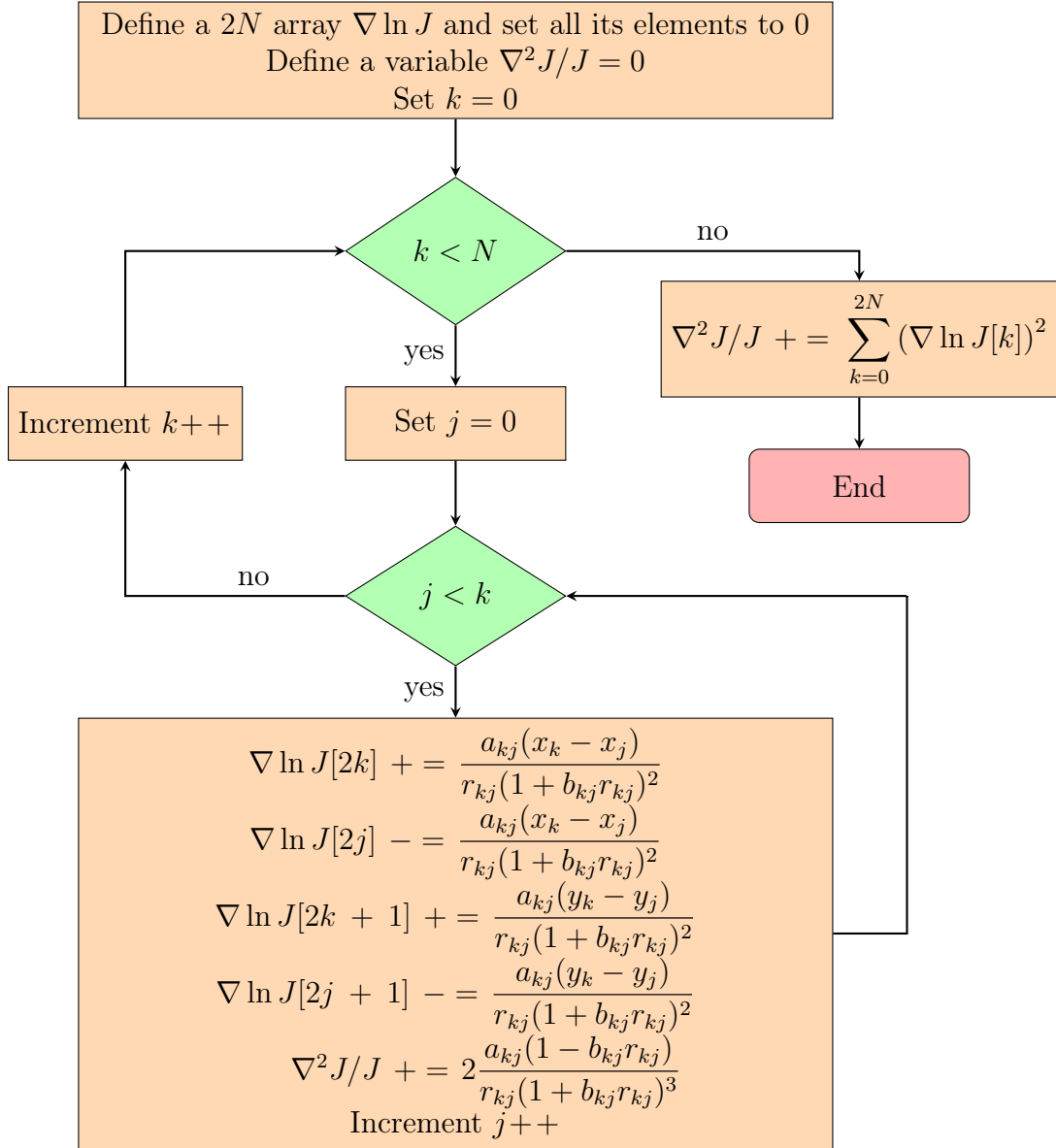


Figure 1: Flowchart of the calculation of the logarithmic gradient and Laplacian of $J(\mathbf{R})$.

The shorthanded local kinetic energy will be :

$$\begin{aligned}
T_A &= -\hbar^2/2m \int \Psi_T \nabla^2 \Psi_T dR = -\hbar^2/2m \int \Psi_T \nabla^2 \Psi_T dR = \\
&= -\hbar^2/2m \int \Psi_T J(\mathbf{R}) \nabla^2 \phi_{MF}(\mathbf{R}) dR - \hbar^2/2m \int \Psi_T \phi_{MF}(\mathbf{R}) \nabla^2 J(\mathbf{R}) dR + \\
&\quad - 2\hbar^2/2m \int \Psi_T \nabla \phi_{MF}(\mathbf{R}) \cdot \nabla J(\mathbf{R}) dR \\
&= -\hbar^2/2m \left(\int \phi_{MF}(\mathbf{R}) J^2(\mathbf{R}) \nabla^2 \phi_{MF}(\mathbf{R}) dR + \int \phi_{MF}^2(\mathbf{R}) J(\mathbf{R}) \nabla^2 J(\mathbf{R}) dR + \right. \\
&\quad \left. + 2 \int \phi_{MF}(\mathbf{R}) J(\mathbf{R}) \nabla \phi_{MF}(\mathbf{R}) \cdot \nabla J(\mathbf{R}) dR \right)
\end{aligned} \tag{59}$$

We can write the local kinetic energy also in the following way:

$$\begin{aligned}
T_B &= -\hbar^2/4m \left[\int \Psi_T \nabla^2 \Psi_T dR - \int \nabla \Psi_T \nabla \Psi_T dR \right] = \\
&= -\hbar^2/4m \int \Psi_T J(\mathbf{R}) \nabla^2 \phi_{MF}(\mathbf{R}) dR - \hbar^2/4m \int \Psi_T \phi_{MF}(\mathbf{R}) \nabla^2 J(\mathbf{R}) dR + \\
&\quad - 2\hbar^2/4m \int \Psi_T \nabla \phi_{MF}(\mathbf{R}) \cdot \nabla J(\mathbf{R}) dR - \hbar^2/4m \int \nabla(\phi_{MF}(\mathbf{R}) J(\mathbf{R})) \cdot \nabla(\phi_{MF}(\mathbf{R}) J(\mathbf{R})) dR \\
&= -\hbar^2/4m \left(\int \phi_{MF}(\mathbf{R}) J^2(\mathbf{R}) \nabla^2 \phi_{MF}(\mathbf{R}) dR + \int \phi_{MF}^2(\mathbf{R}) J(\mathbf{R}) \nabla^2 J(\mathbf{R}) dR + \right. \\
&\quad + 2 \int \phi_{MF}(\mathbf{R}) J(\mathbf{R}) \nabla \phi_{MF}(\mathbf{R}) \cdot \nabla J(\mathbf{R}) dR + \int J^2(\mathbf{R}) \nabla \phi_{MF}(\mathbf{R}) \cdot \nabla \phi_{MF}(\mathbf{R}) dR \quad (60) \\
&\quad \left. + 2 \int J(\mathbf{R}) \phi_{MF}(\mathbf{R}) \nabla \phi_{MF}(\mathbf{R}) \cdot \nabla J(\mathbf{R}) dR + \int \phi_{MF}^2(\mathbf{R}) \nabla J(\mathbf{R}) \cdot \nabla J(\mathbf{R}) dR \right)
\end{aligned}$$

Previous formulas for local kinetic energy can easily be computed using before mentioned results for $\nabla J(\mathbf{R})$, $\nabla^2 J(\mathbf{R})$, $\nabla \phi_{MF}(\mathbf{R})$, $\nabla^2 \phi_{MF}(\mathbf{R})$.

T_A and T_B are analytically identical, hence the difference of these two kinetic energy values could be used to evaluate the numerical error in computation.

To sum up, in the interacting case, in order to evaluate the local kinetic energy: for computing $\nabla J(\mathbf{R})$ and $\nabla^2 J(\mathbf{R})$, we can use the algorithm described before in the flowchart; in order to compute $\nabla^2 \phi_{MF}(\mathbf{R})$, we use the trick described previously of the knowledge of the non interacting case energies; and in order to compute $\nabla \phi_{MF}(\mathbf{R})$, we use formula (48).

Non interacting case

In this section we show a possible way to test a MC algorithm for the non-interacting case of the problem we want to analyse, since in this situation we know the analytical solution.

We want to build a Monte Carlo algorithm which is able to calculate the expectation energy of the non interacting system of N electrons which is described by the Hamiltonian

$$\hat{H}_0 = \sum_{i=1}^N \left(-\frac{1}{2} \nabla_i^2 + \frac{1}{2} \omega^2 r_i^2 \right). \quad (61)$$

We expect that the value of energy we obtain in this case will be compatible with the single particle spectrum we discussed previously.

The ground-state solution to the eigenvalue problem

$$\hat{H}_0 \Psi(\mathbf{r}_1, \dots, \mathbf{r}_N) = E_0 \Psi(\mathbf{r}_1, \dots, \mathbf{r}_N), \quad (62)$$

is one of the wave functions we already described in the section relative to mean field wave function. The eigenvalue is

$$E_0 = g_1 \lambda_{1s} + g_2 \lambda_{1p},$$

where g_1 and g_2 are the number of electrons in one of the states which has energy λ_{1s} or λ_{1p} respectively. As we already stated before the single particle spectrum is given by $\lambda_{n,l} = \omega(2n + l + 1)$, which means that $\lambda_{1s} = \omega$ and $\lambda_{1p} = 2\omega$. The multi-particle non interacting system will have ground-state energy which depends on the number of electrons in the way that is shown in Table 1.

We checked all cases but the $N = 4$ and each time we found perfect correspondence between numerical and analytical results.

In order to compute the local energy, in this case, we used formulas (48) and (51).

N	2	3	4	5	6
E_0	2ω	4ω	6ω	8ω	10ω

Table 1: Ground-state energies for non-interacting system with N electrons.

Metropolis algorithm

In this section we show how to estimate with a Monte Carlo simulation the expectation value of the total energy, which can be written as

$$E = \frac{\int \Psi^2(\mathbf{R}) E_L(\mathbf{R}) d^{2N} R}{\int \Psi^2(\mathbf{R}) d^{2N} R} \quad E_L(\mathbf{R}) = \frac{H\Psi(\mathbf{R})}{\Psi(\mathbf{R})} \quad (63)$$

We use the Metropolis algorithm to generate random samples of \mathbf{R} distributed as the square modulus of the normalized wave function. From a sequence of n samples we use the central limit theorem to estimate the total energy with

$$E = \langle E_L \rangle \pm \sqrt{\frac{1}{n-1} \langle (E_L - \langle E_L \rangle)^2 \rangle} \quad (64)$$

We indicate the τ -th generated sample with $\mathbf{R}(\tau)$, $\tau = 1, \dots, n$. To obtain the next sample we calculate the proposal

$$\mathbf{P} = \mathbf{R}(\tau) + \Delta(\eta_1 - 0.5) \quad (65)$$

where Δ is a fixed parameter while η_1 is a random number uniformly distributed in the interval $[0, 1)$. Then we generate another random number η_2 to decide whether to accept the proposal or not

$$\mathbf{R}(\tau + 1) = \begin{cases} \mathbf{P} & \text{if } \frac{\Psi^2(\mathbf{P})}{\Psi^2(\mathbf{R}(\tau))} > \eta_2 \\ \mathbf{R}(\tau) & \text{otherwise} \end{cases} \quad (66)$$

This procedure is repeated $2N$ times, in each of which \mathbf{P} is obtained adding Δ to a different component of \mathbf{R} . In principle, the final result is independent of the initial configuration $\mathbf{R}(\tau = 0)$ however, since in practice we perform a finite simulation, it's better to start from a plausible configuration. We displace the N electrons equally spaced on a circumference centered in the origin. The radius of such circumference is obtained minimizing the potential energy, namely

$$V(r) = \frac{N}{2} \omega^2 r^2 + \frac{N}{4r} \sum_{k=1}^{N-1} \frac{1}{\sin\left(\frac{k\pi}{N}\right)} \quad (67)$$

hence

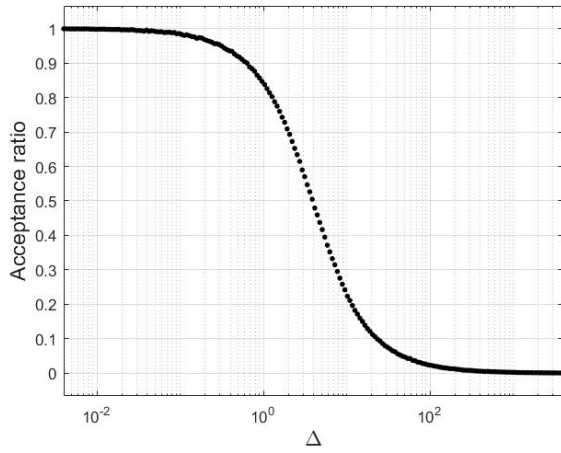
$$\frac{dV}{dr} = 0 \quad \Rightarrow \quad r = \left(\frac{1}{4\omega^2} \sum_{k=1}^{N-1} \frac{1}{\sin\left(\frac{k\pi}{N}\right)} \right)^{\frac{1}{3}} \quad (68)$$

Moreover, we discard the first 1000 generated samples of \mathbf{R} before starting computing the local energy. In this way the system reaches a random plausible initial configuration, therefore the final result is not affected by our arbitrary choices.

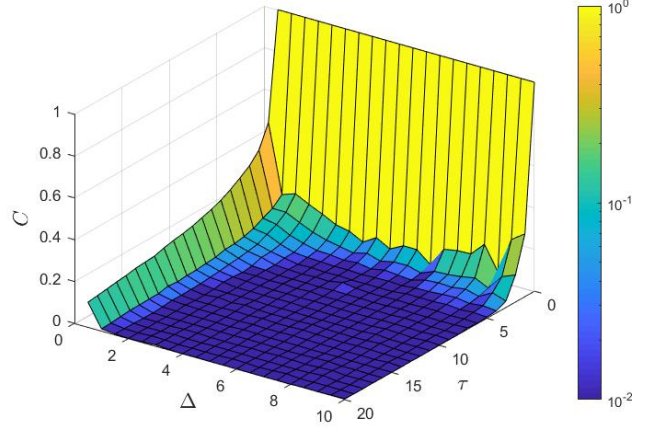
The value of the parameter Δ is typically chosen as the one that minimizes the autocorrelation of the samples and leads to an acceptance ratio of proposals of about 50%. We recall the definition of autocorrelation $C(\tau)$ for our variable of interest $E_L(\tau) = E_L(\mathbf{R}(\tau))$

$$C(\tau) = \frac{\langle E_L(t) E_L(t + \tau) \rangle - \langle E_L \rangle^2}{\langle E_L^2 \rangle - \langle E_L \rangle^2} \quad (69)$$

In Figure 2 we plot the autocorrelation and acceptance ratio for different values of Δ .



(a) Acceptance ratio.

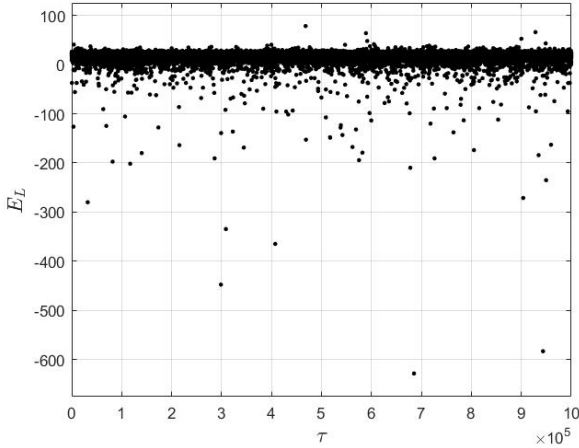


(b) Autocorrelation.

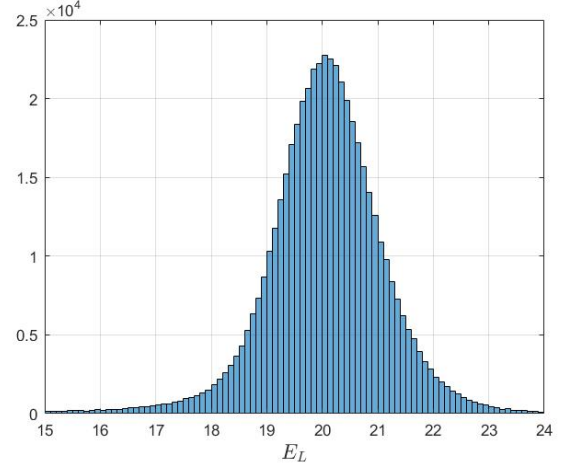
Figure 2: Acceptance ratio and acutocorrelation obtained with different Δ for the case of $N = 6$. We've set $\omega = 1$ and $b_{\uparrow\uparrow} = b_{\uparrow\downarrow} = 2$.

In this situation a good choice is $\Delta = 4$, for which the acceptance ratio is about 50% and the correlation at $C(\tau = 1) \simeq 0.042$ is already smaller than the typical threshold value e^{-1} .

In Figure 3 we show the behaviour of the local energy during a simulation for the case of $N = 6$, setting $\omega = 1$ and $b_{\uparrow\uparrow} = b_{\uparrow\downarrow} = 2$, with $n = 10^6$ samples.



(a) Evolution of E_L as a function of τ .



(b) Histogram of E_L during the simulation.

Figure 3: Local energy during a simulation for $N = 6$. We've set $\omega = 1$ and $b_{\uparrow\uparrow} = b_{\uparrow\downarrow} = 2$.

The final estimate of the total energy is

$$E = (20.628 \pm 0.003) E_h^* \quad (70)$$

Minimization of the energy functional

We are now ready to perform a minimization of the total energy varying the parameters $b_{\uparrow\uparrow}$ and $b_{\uparrow\downarrow}$. To do so, we will use the method of steepest descent, which requires the knowledge of

the gradient of the function to minimize

$$\nabla E = \left(\frac{\partial E}{\partial b_{\uparrow\downarrow}}, \frac{\partial E}{\partial b_{\uparrow\uparrow}} \right) \quad (71)$$

There is an efficient way to compute derivatives of the total energy, for example

$$\frac{\partial E}{\partial b_{\uparrow\downarrow}} \simeq \frac{E(b_{\uparrow\downarrow} + db, b_{\uparrow\uparrow}) - E(b_{\uparrow\downarrow}, b_{\uparrow\uparrow})}{db} \quad (72)$$

Using a so called *reweighting* method we can avoid doing another entire simulation to compute $E(b_{\uparrow\downarrow} + db, b_{\uparrow\uparrow})$. To simplify the notation we define $\mathbf{b} = (b_{\uparrow\downarrow}, b_{\uparrow\uparrow})$. Let \mathbf{b}' be a set of parameters infinitesimally close to \mathbf{b} , in our case it stands for $(b_{\uparrow\downarrow} + db, b_{\uparrow\uparrow})$. With this notation the total energy reads

$$E(\mathbf{b}') = \frac{\int \Psi^2(\mathbf{R}, \mathbf{b}') E_L(\mathbf{R}, \mathbf{b}') d^{2N} R}{\int \Psi^2(\mathbf{R}, \mathbf{b}') d^{2N} R} \quad (73)$$

Now we define a weight function

$$W(\mathbf{R}, \mathbf{b}', \mathbf{b}) = \frac{\Psi^2(\mathbf{R}, \mathbf{b}')}{\Psi^2(\mathbf{R}, \mathbf{b})} = \exp \left[2 \sum_{i < j} \left(U_{ij}(\mathbf{b}') - U_{ij}(\mathbf{b}) \right) \right] \quad (74)$$

and rewrite (73) as follows

$$E(\mathbf{b}') = \frac{\int \Psi^2(\mathbf{R}, \mathbf{b}) W(\mathbf{R}, \mathbf{b}', \mathbf{b}) E_L(\mathbf{R}, \mathbf{b}') d^{2N} R}{\int \Psi^2(\mathbf{R}, \mathbf{b}) W(\mathbf{R}, \mathbf{b}', \mathbf{b}) d^{2N} R} \quad (75)$$

One can see that now $E(\mathbf{b}')$ is expressed in terms of averages that can be computed only from samples distributed as $\Psi^2(\mathbf{R}, \mathbf{b})$. Therefore, with one simulation we can calculate both $E(\mathbf{b}) = \langle E_L(\mathbf{b}) \rangle$ and $E(\mathbf{b}')$ through a weighted mean

$$E(\mathbf{b}') = \frac{\langle W(\mathbf{b}', \mathbf{b}) E_L(\mathbf{b}') \rangle}{\langle W(\mathbf{b}', \mathbf{b}) \rangle} \quad (76)$$

Obviously, the reasoning is the same for $\mathbf{b}' = (b_{\uparrow\downarrow} + db, b_{\uparrow\uparrow})$ or $\mathbf{b}' = (b_{\uparrow\downarrow}, b_{\uparrow\uparrow} + db)$. A practical technicality must be remarked: the value of db is limited by the precision of the simulation, dictated by the parameter n . Indeed, having $E(\mathbf{b}) = \langle E_L \rangle \pm \sigma$ then $E(\mathbf{b}')$ must differ by at least σ in order to have a meaningful value for the derivatives of the energy functional.

In case of $N = 2$ there is dependence of the local energy only on the parameter $b_{\uparrow\downarrow}$. After the minimization is then easy to analyse closer such dependence, see Figure 4.

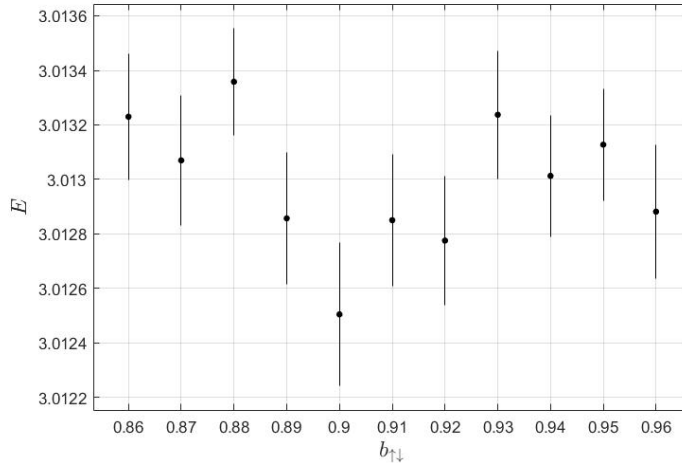


Figure 4: Total energy of $N = 2$ electrons obtained for $\omega = 1$ and different values of $b_{\uparrow\downarrow}$ close to the minimum. We've set $n = 10^7$.

With a similar analysis we can estimate the ground state energy for all the other number N of electrons. The results are summarized in the following Table 2

N	$b_{\uparrow\downarrow}$	$b_{\uparrow\uparrow}$	E
2	0.90	/	3.0125 ± 0.0003
3	0.95	0.50	6.3834 ± 0.0004
5	1.10	0.46	15.0084 ± 0.0007
6	0.83	0.43	19.676 ± 0.001

Table 2: Minima found of the total energy with the corresponding Jastrow parameters.

Special case of $N = 4$ electrons

For $N = 4$ electrons we must consider three different cases:

- $L = 0$ $S = 1$: We have three \uparrow and one \downarrow electrons. In the $1s$ orbital we have one \uparrow and one \downarrow electron, in $1p_x$, as in $1p_y$, we have one \uparrow .

$$\phi_{MF}(\mathbf{r}_1, \dots, \mathbf{r}_4) = \det [\varphi_{1s}(\mathbf{r}_1)\varphi_{1p_x}(\mathbf{r}_2)\varphi_{1p_y}(\mathbf{r}_3)] \varphi_{1s}(\mathbf{r}_4) \quad (77)$$

- $L = 2$ $S = 0$: We have two \uparrow and two \downarrow electrons. In the $1s$ orbital we have one \uparrow and one \downarrow electron. We have two possibilities for the remaining 2 electrons. We can have \uparrow and \downarrow both in $1p_x$ or both in $1p_y$.

$$\begin{aligned} \phi_{MF}(\mathbf{r}_1, \dots, \mathbf{r}_4) = & \det [\varphi_{1s}(\mathbf{r}_1)\varphi_{1p_x}(\mathbf{r}_2)] \det [\varphi_{1s}(\mathbf{r}_3)\varphi_{1p_x}(\mathbf{r}_4)] + \\ & + \det [\varphi_{1s}(\mathbf{r}_1)\varphi_{1p_y}(\mathbf{r}_2)] \det [\varphi_{1s}(\mathbf{r}_3)\varphi_{1p_y}(\mathbf{r}_4)] \end{aligned} \quad (78)$$

- $L = 0$ $S = 0$: We have two \uparrow and two \downarrow electrons. In the $1s$ orbital we have one \uparrow and one \downarrow electron. We have two possibilities for the remaining 2 electrons. We can have \uparrow in $1p_x$ and \downarrow in $1p_y$ or \uparrow in $1p_y$ and \downarrow in $1p_x$.

$$\begin{aligned} \phi_{MF}(\mathbf{r}_1, \dots, \mathbf{r}_4) = & \det [\varphi_{1s}(\mathbf{r}_1)\varphi_{1p_x}(\mathbf{r}_2)] \det [\varphi_{1s}(\mathbf{r}_3)\varphi_{1p_y}(\mathbf{r}_4)] + \\ & + \det [\varphi_{1s}(\mathbf{r}_1)\varphi_{1p_y}(\mathbf{r}_2)] \det [\varphi_{1s}(\mathbf{r}_3)\varphi_{1p_x}(\mathbf{r}_4)] \end{aligned} \quad (79)$$

We must figure out which out of the states listed before has the lowest energy. Only that one, after a variational Monte Carlo procedure, will lead to an estimate of the true ground state energy. We know that the Coulomb repulsion of the electrons accounts for a positive contribution to the total energy and decreases with the relative distances between the particles. The ground state should then guarantee a low probability of electrons coming close to each other.

In order to have so, the spatial part of the wavefunction should be antisymmetric; indeed for an antisymmetric spatial wavefunction it is impossible for two particles to be in the same position. Furthermore, since the wavefunction must be a well behaved function, being 0 at zero distance implies to be close to 0 at small distance. Therefore it is less likely that two electrons come near each other with an antisymmetric wavefunction than it is with a symmetric wavefunction. Imposing an antisymmetric spatial wavefunction, in order to have the total wavefunction antisymmetric, we must force the spin part to be symmetric. Therefore, between the states listed before, the one we expect to be the ground state is the $L = 0$ $S = 1$ state.

With the techniques described in the previous sections, we minimize the energy functional corresponding to the three states with $N = 4$, verifying that the ground state is the one with $L = 0$ and $S = 1$; see Table 3.

L	S	$b_{\uparrow\downarrow}$	$b_{\uparrow\uparrow}$	E
0	1	0.80	0.34	10.06 ± 0.01
2	0	0.81	0.80	10.53 ± 0.01
0	0	0.93	0.79	10.40 ± 0.01

Table 3: Total energy and minima b_{ij} values for $N = 4$ electrons and $\omega = 1$.