

Chapter 2

Quantum Monte Carlo methods

In this chapter we will make a description of the numerical methods that we have been using in order to give a microscopic description of a quantum many body system.

We are interested in giving an accurate description of a quantum fluid of identical particles interacting by means of a pair potential. The complete description of such a system at zero temperature is given by the Schrödinger equation (SE):

$$H|\Psi\rangle = E|\Psi\rangle \quad (2.1)$$

where the hamiltonian H is given, in general, by

$$H = -\frac{\hbar^2}{2m} \sum_{i=1}^N \nabla_i^2 + \sum_{i=1}^N V_1(\mathbf{r}_i) + \frac{1}{2} \sum_{i=1}^N \sum_{j=1, j \neq i}^N V_2(\mathbf{r}_i - \mathbf{r}_j) \quad (2.2)$$

where V_1 is an external potential corresponding to an externally applied field and V_2 is a pair interaction that describe the inter-particle interactions.

In the following, we will use the following notation. We call \mathbf{R} the whole set of coordinates of the system, i. e., $\mathbf{R} = \{\mathbf{r}_1, \dots, \mathbf{r}_N\}$. With this definition, the operator $\nabla_{\mathbf{R}}^2 = \sum_{i=1}^N \nabla_i^2$ is the laplacian needed for the kinetic term, and finally the potential term will be $V(\mathbf{R}) = \sum_{i=1}^N V_1(\mathbf{r}_i) + \frac{1}{2} \sum_{i=1}^N \sum_{j=1, j \neq i}^N V_2(\mathbf{r}_i - \mathbf{r}_j)$.

2.1 Variational Monte Carlo

Variational Monte Carlo (VMC) [47] is the simplest and fastest Monte Carlo method that can be used to obtain an approximate solution to the many-body problem by using the variational principle.

2.1.1 Variational principle

The variational principle tells us that if we consider a trial wave function Ψ_T the expectation value

$$E[\Psi_T] = \frac{\langle \Psi_T | H | \Psi_T \rangle}{\langle \Psi_T | \Psi_T \rangle} \quad (2.3)$$

is an upper bound to the ground state energy of the Hamiltonian H . This statement can be easily shown by expanding the trial wave function Ψ in the basis of eigenstates of the Hamiltonian

$$|\Psi_T\rangle = \sum_n a_n |\phi_n\rangle \quad (2.4)$$

where the functions $|\phi_n\rangle$ verify

$$H|\phi_n\rangle = E_n|\phi_n\rangle \quad \text{and} \quad \langle \phi_n | \phi_m \rangle = \delta_{n,m} \quad (2.5)$$

We can use the eigenstate expansion (2.4) in the expectation value (2.1) obtaining the following

$$E[\Psi_T] = \frac{(\sum_n a_n^* \langle \phi_n |) H (\sum_m a_m |\phi_m\rangle)}{(\sum_n a_n^* \langle \phi_n |) (\sum_m a_m |\phi_m\rangle)} \quad (2.6)$$

where by using the properties (2.5) we can finally write the energy of the trial wave function as:

$$E[\Psi_T] = \frac{\sum_n |a_n|^2 E_n}{\sum_n |a_n|^2}. \quad (2.7)$$

In the last expression one can easily see that the expectation value of the energy for the trial wave function $|\Psi_T\rangle$ is always greater than the ground state energy of the hamiltonian unless $|\Psi_T\rangle = |\phi_0\rangle$. It is useful to consider trial (or variational) wave functions that depends on one or more parameters $(\lambda_1, \dots, \lambda_n)$ called variational parameters. Those parameters can be optimized to get the lowest energy for a given family of wave functions $|\Psi_T(\lambda_1, \dots, \lambda_n)\rangle$. In the

simplest case of an uniparametric family of variational wave functions $|\Psi_T(\lambda)\rangle$ the energy expectation value will be given by

$$E[\Psi_T(\lambda)] = \frac{\langle \Psi_T(\lambda) | H | \Psi_T(\lambda) \rangle}{\langle \Psi_T(\lambda) | \Psi_T(\lambda) \rangle} \quad (2.8)$$

and we can find the optimal variational energy of the hamiltonian by simply minimising this energy expectation value:

$$\left. \frac{dE[\lambda]}{d\lambda} \right|_{\lambda_{optimal}} = 0 \quad (2.9)$$

2.1.2 Monte Carlo sampling of a variational wave function

The idea behind the variational Monte Carlo method (VMC) is to perform the evaluation of the expectation value in (2.3), that is in general a high dimension integral, by means of a stochastic sampling of a given variational wave function using the Metropolis algorithm.

In position basis the expectation value in (2.3) can be written as

$$E[\Psi_T] = \frac{\int d\mathbf{R} \Psi_T^*(\mathbf{R}) H \Psi_T(\mathbf{R})}{\int d\mathbf{R} \Psi_T^*(\mathbf{R}) \Psi_T(\mathbf{R})}. \quad (2.10)$$

This integral expression can be written in a more convenient way for Monte Carlo sampling if we think that the square modulus of the wave function gives the probability of finding the system in the configuration \mathbf{R} ,

$$\langle E \rangle_{\Psi_T} = \int d\mathbf{R} E_L(\mathbf{R}) P(\mathbf{R}), \quad (2.11)$$

where the following two quantities are defined: the probability distribution, $P(\mathbf{R})$

$$P(\mathbf{R}) = \frac{\Psi_T^*(\mathbf{R}) \Psi_T(\mathbf{R})}{\int d\mathbf{R} \Psi_T^*(\mathbf{R}) \Psi_T(\mathbf{R})}; \quad (2.12)$$

and the so-called local energy, $E_L(\mathbf{R})$

$$E_L(\mathbf{R}) = \frac{H \Psi_T(\mathbf{R})}{\Psi_T(\mathbf{R})}. \quad (2.13)$$

The function $P(\mathbf{R})$ is a well behaved probability distribution that can be sampled using the Metropolis algorithm in order to obtain a sequence of configurations of the system distributed according to it.

Given an ensemble of N_{MC} configurations drawn from $P(\mathbf{R})$ we can simply evaluate the energy expectation value of the hamiltonian as:

$$\langle E \rangle_{\Psi_T} \approx \frac{1}{N_{MC}} \sum_{i=1}^{N_{MC}} E_L(\mathbf{R}_i), \quad (2.14)$$

and, in general, any observable O can be evaluated along the Monte Carlo sampling as:

$$\langle O \rangle_{\Psi_T} \approx \frac{1}{N_{MC}} \sum_{i=1}^{N_{MC}} O(\mathbf{R}_i). \quad (2.15)$$

So, given a trial wave function one can compute any observable of interest simply by using expression (2.15).

2.1.3 Variational Monte Carlo algorithm

At this point we have all the ingredients to give an algorithmic description of the VMC method. Let's explain the steps of the VMC algorithm:

1. Draw an initial configuration of the system of interest, \mathbf{R} .
2. Guess a new configuration as $\mathbf{R}' = \mathbf{R} + \delta\mathbf{R}$, with $\delta\mathbf{R}$ coming from a uniform or gaussian probability distribution function that verifies $p(\mathbf{R}' \rightarrow \mathbf{R}) = p(\mathbf{R} \rightarrow \mathbf{R}')$.
3. Evaluate the transition probability as $Q = \frac{\Psi_T^2(\mathbf{R}')}{\Psi_T^2(\mathbf{R})}$
4. Accept or reject the new configuration using Metropolis algorithm.
5. Compute observables of interest.
6. Repeat 2 - 5 to achieve desired accuracy in the calculation.

2.2 Imaginary time propagation methods

VMC is a fast and simple method to compute properties of a quantum many - body system, but it has a very important limitation: all the expectation values of any observable in VMC is completely determined by the trial wave function. The quality of the results obtained in a VMC simulation is directly related to the quality of the variational wave function, so one can expect that

for situations where the wave function is poorly known VMC method is not an accurate solution of the quantum problem.

To overcome the limitations of the VMC method we can consider a different family of Monte Carlo methods that can solve the Schrödinger equation by transforming it into an integral equation. The evolution of a quantum system is given by the time dependent Schrödinger equation:

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \sum_{i=1}^N \nabla^2 \Psi + \sum_{i=1}^N V_1(\mathbf{r}_i) \Psi + \frac{1}{2} \sum_{i=1}^N \sum_{j=1, j \neq i}^N V_2(\mathbf{r}_i - \mathbf{r}_j) \Psi. \quad (2.16)$$

We are mainly interested in the ground-state properties of the system. This can be done by defining the imaginary time as $\tau = \frac{it}{\hbar}$ and thus considering the imaginary-time dependent Schrödinger equation

$$-\frac{\partial \Psi}{\partial \tau} = -\frac{\hbar^2}{2m} \sum_{i=1}^N \nabla^2 \Psi + \sum_{i=1}^N V_1(\mathbf{r}_i) \Psi + \frac{1}{2} \sum_{i=1}^N \sum_{j=1, j \neq i}^N V_2(\mathbf{r}_i - \mathbf{r}_j) \Psi. \quad (2.17)$$

The imaginary-time dependent Schrödinger equation can be written in operator form as:

$$-\frac{\partial |\Psi(\tau)\rangle}{\partial \tau} = H |\Psi(\tau)\rangle \quad (2.18)$$

whose formal solution is:

$$|\Psi(\tau)\rangle = e^{-H\tau} |\Psi(0)\rangle. \quad (2.19)$$

The wave function at $\tau = 0$ can be expanded in terms of the eigenstates of the hamiltonian

$$|\Psi(0)\rangle = \sum_{i=0}^{\infty} a_i |\phi_i\rangle \quad (2.20)$$

and introduce this eigenstate expansion in (2.19) to obtain

$$|\Psi(\tau)\rangle = \sum_{i=0}^{\infty} a_i e^{-\tau \epsilon_i} |\phi_i\rangle. \quad (2.21)$$

If the eigenvalues of the hamiltonian are ordered as $\epsilon_0 < \epsilon_1 < \epsilon_2 < \dots$ one can see from (2.21) that for $\tau \rightarrow \infty$ all contributions are exponentially vanishing and the slowest decaying term is the corresponding to the ground state of the system. So we can write

$$|\Psi(\tau \rightarrow \infty)\rangle \approx a_0 e^{-\tau E_0} |\phi_0\rangle. \quad (2.22)$$

There are several ways to implement the imaginary time propagation of an initial wave function that correspond to different quantum Monte Carlo methods. We have used two main approaches to solve this problem that we will see in the following two sections.

2.2.1 Diffusion Monte Carlo

The first method that we present to implement the imaginary time propagation is the diffusion Monte Carlo method (DMC) [47, 48]. DMC exploits the analogy between the imaginary-time dependent Schrödinger equation and the diffusion equation to achieve the stationary regime of the problem. The stationary solution is proportional to the ground state of the many body quantum problem.

The starting point is the imaginary time dependent Schrödinger equation with an energy shift $H \rightarrow H - E_T$:

$$-\frac{\partial|\Psi(\tau)\rangle}{\partial\tau} = (H - E_T)|\Psi(\tau)\rangle, \quad (2.23)$$

If we write explicitly the hamiltonian operator in eq. (2.23) we can write the SE as:

$$-\frac{\partial\Psi}{\partial\tau} = -\frac{\hbar^2}{2m}\nabla_{\mathbf{R}}^2\Psi + (V(\mathbf{R}) - E_T)\Psi \quad (2.24)$$

That is a standard diffusion equation with an additional term that can be interpreted as a sink/source of probability.

If we write now the spectral decomposition of the time-dependent wave function in terms of the imaginary time τ we obtain the following expression:

$$\Psi(\mathbf{R}, \tau) = \sum_n a_n \phi_n(\mathbf{R}) e^{-(\epsilon_n - E_T)\tau} \quad (2.25)$$

If we assume that the eigenvalues ϵ_n are ordered as $\epsilon_0 < \epsilon_1 < \dots < \epsilon_n < \dots$ we can infer that the asymptotic behavior of $\Psi(\mathbf{R}, \tau)$ is given by:

- if $E_T > \epsilon_0$ the wave function Ψ diverges.
- if $E_T < \epsilon_0$ the wave function Ψ vanishes.
- if $E_T = \epsilon_0$ the wave function $\Psi \approx c_0 \phi_0$.

The physical interpretation of the method is clear, we must perform an imaginary time evolution until the asymptotic regime is reached, and by a clever choice of the reference energy, E_T , we will find the ground state energy.

There are two practical considerations about the outline of the DMC method as it is presented here. The first one is that the initial many-body wave function $\Psi(\mathbf{R}, 0)$ must have a significant overlap with the ground state wave function $\phi_0(\mathbf{R})$ if we want a_0 being not too small. The second consideration is that this simple version of DMC requires that the ground state wave function must be positive definite as it effectively happens with the many-body ground state wave function for a system of bosons; for fermions the situation is different and some approximations must be done.

After this last considerations, we will explain how the many-body SE can be integrated using Monte Carlo techniques.

Monte Carlo integration of the many-body Schrödinger equation

For the suitable integration of the many-body SE we have to transform the differential equation in an equivalent integral equation, and, this is easily done by considering the Green's function formalism.

The Green's function of the SE can be defined in an operatorial formalism, and then we will find the equivalent coordinate representation and using it, a practical expression for the Green's function.

The independent-basis SE for our problem is given by:

$$\frac{\partial |\Psi\rangle}{\partial \tau} = -(H - E_T)|\Psi\rangle \quad (2.26)$$

that can be formally solved by means of the time evolution operator $U(\tau, 0)$ as follows:

$$|\Psi(\tau)\rangle = U(\tau, 0)|\Psi(0)\rangle \quad (2.27)$$

where $U(\tau, 0)$ is given by:

$$U(\tau, 0) = e^{-(H-E_T)\tau} \quad (2.28)$$

now we can project the solution of the SE given in eq. (2.27) in position basis

$$\langle \mathbf{R} | \Psi(\tau) \rangle = \int d\mathbf{R}' \langle \mathbf{R} | U(\tau, 0) | \mathbf{R}' \rangle \langle \mathbf{R}' | \Psi(0) \rangle \quad (2.29)$$

that can be written as:

$$\Psi(\mathbf{R}, \tau) = \int d\mathbf{R}' \langle \mathbf{R} | U(\tau, 0) | \mathbf{R}' \rangle \Psi(\mathbf{R}', 0). \quad (2.30)$$

Then we finally have written an integral equation, equivalent to the many-body SE and the only problem is to determine the kernel of the integral equation given by $\langle \mathbf{R} | U(\tau, 0) | \mathbf{R}' \rangle$ that we define as:

$$G(\mathbf{R}, \mathbf{R}', \tau) \equiv \langle \mathbf{R} | U(\tau, 0) | \mathbf{R}' \rangle \quad (2.31)$$

that is the Green's function of the SE. This Green's function can be determined by solving the differential equation:

$$-\frac{\partial G}{\partial \tau} = -\frac{\hbar^2}{2m} \nabla_{\mathbf{R}}^2 G + (V(\mathbf{R}) - E_T)G \quad (2.32)$$

with the initial condition:

$$G(\mathbf{R}, \mathbf{R}', 0) = \delta(\mathbf{R} - \mathbf{R}') \quad (2.33)$$

The SE is then written in terms of the Green's function as:

$$\Psi(\mathbf{R}, \tau) = \int d\mathbf{R}' G(\mathbf{R}, \mathbf{R}', \tau) \Psi(\mathbf{R}', 0) \quad (2.34)$$

This is an integral equation that can be solved using Monte Carlo integration. The problem with the previous integral equation is that the Green's function of the problem is not known. However, we can evaluate the imaginary time evolution of the wave function using the following property of the Green's function,

$$\int d\mathbf{R}'' G(\mathbf{R}, \mathbf{R}'', \tau) G(\mathbf{R}'', \mathbf{R}', \tau) = G(\mathbf{R}, \mathbf{R}', 2\tau) \quad (2.35)$$

Then, we can consider the full propagation in imaginary time as successive propagations of time step $\Delta\tau$, and then, we only need to find some short-time approximation for the total Green's function. We can write the following expression for the propagation of the wave function:

$$\Psi(\mathbf{R}, \Delta\tau) = \int d\mathbf{R}' G(\mathbf{R}, \mathbf{R}', \Delta\tau) \Psi(\mathbf{R}', 0) \quad (2.36)$$

or generalizing this expression to an arbitrary step n ,

$$\Psi(\mathbf{R}, n\Delta\tau) = \int d\mathbf{R}' G(\mathbf{R}, \mathbf{R}', \Delta\tau) \Psi(\mathbf{R}', (n-1)\Delta\tau) \quad (2.37)$$

And then, as we have seen before, we only need to find some suitable approximation for the Green's function for small $\Delta\tau$.

Short time Green's function

The differential equation that defines the Green's function is given by:

$$-\frac{\partial G(\mathbf{R}, \mathbf{R}', \tau)}{\partial \tau} = \left[-\frac{\hbar^2}{2m} \nabla_{\mathbf{R}}^2 + (V(\mathbf{R}) - E_T) \right] G(\mathbf{R}, \mathbf{R}', \tau) \quad (2.38)$$

with the boundary condition $G(\mathbf{R}, \mathbf{R}', 0) = \delta(\mathbf{R} - \mathbf{R}')$.

Now the main problem to obtain an expression for the total Green's function comes from the non commutativity of the kinetic and potential terms in the hamiltonian. However, the evaluation of the Green's function corresponding to each of the individual pieces is trivial to do. If we consider the two contributions to the Green's function separately we will have, for the kinetic term:

$$G_K(\mathbf{R}, \mathbf{R}', \tau) = \langle \mathbf{R} | e^{-\frac{\hat{p}^2}{2m}\tau} | \mathbf{R}' \rangle \quad (2.39)$$

That can be easily evaluated in position basis by means of gaussian integration, giving a final kinetic Green's function:

$$G_K(\mathbf{R}, \mathbf{R}', \tau) = \left(\frac{m}{2\pi\hbar^2\tau} \right)^{\frac{dN}{2}} \exp \left[-\frac{m}{\hbar^2} \frac{(\mathbf{R} - \mathbf{R}')^2}{2\tau} \right] \quad (2.40)$$

where d is the dimensionality of the studied system.

For the interaction term we have:

$$G_V(\mathbf{R}, \mathbf{R}', \tau) = \langle \mathbf{R} | e^{-(V-E_T)\tau} | \mathbf{R}' \rangle \quad (2.41)$$

that in position basis is:

$$G_V(\mathbf{R}, \mathbf{R}', \tau) = \exp [-(V(\mathbf{R}) - E_T)\tau] \delta(\mathbf{R} - \mathbf{R}') \quad (2.42)$$

With the propagators G_K and G_V we can build short time approximations to the total Green's function.

The time evolution operator defined in (2.28) can be approximated in different ways. A possible approximation of order $\Delta\tau^2$ is the following:

$$U(\Delta\tau) = e^{-(K+V-E_T)\Delta\tau} \approx e^{-K\Delta\tau} e^{-(V-E_T)\Delta\tau} + O(\Delta\tau^2) \quad (2.43)$$

which gives an approximate Green's function given by:

$$G(\mathbf{R}, \mathbf{R}', \Delta\tau) = \left(\frac{m}{2\pi\hbar^2\Delta\tau} \right)^{\frac{dN}{2}} e^{-(V(\mathbf{R})-E_T)\Delta\tau} \exp \left[-\frac{m}{\hbar^2} \frac{(\mathbf{R} - \mathbf{R}')^2}{2\Delta\tau} \right] + O(\Delta\tau^2) \quad (2.44)$$

that is exact at first order in $\Delta\tau$.

Another possible decomposition of the time evolution operator is the following:

$$U(\Delta\tau) = e^{-(K+V-E_T)\Delta\tau} \approx e^{-(V-E_T)\frac{\Delta\tau}{2}} e^{-K\Delta\tau} e^{-(V-E_T)\frac{\Delta\tau}{2}} + O(\Delta\tau^3) \quad (2.45)$$

which gives an approximate Green's function given by:

$$G(\mathbf{R}, \mathbf{R}', \Delta\tau) = \left(\frac{m}{2\pi\hbar^2\Delta\tau} \right)^{\frac{dN}{2}} e^{-\left(\frac{V(\mathbf{R})+V(\mathbf{R}')}{2} - E_T \right) \Delta\tau} \exp \left[-\frac{m}{\hbar^2} \frac{(\mathbf{R} - \mathbf{R}')^2}{2\Delta\tau} \right] + O(\Delta\tau^3) \quad (2.46)$$

which is exact at second order in $\Delta\tau$.

Importance sampling

In real many body problems with hard-core-like interaction potentials the simple DMC algorithm shows a poor convergence to the ground state solution, with large statistical fluctuations in the mean values of the evaluated observables. However, this can be corrected by means of importance sampling.

In this section we will explain the trick that makes DMC a really powerful method to solve many-body problems: the importance sampling technique. In the previous section we have seen how the imaginary time-dependent Schrödinger equation can be solved by means of Monte Carlo techniques. In this section, we will rewrite it for a different wave function given by:

$$f(\mathbf{R}, \tau) \equiv \Psi_T(\mathbf{R})\Psi(\mathbf{R}, \tau) \quad (2.47)$$

where $\Psi_T(\mathbf{R})$ is a trial (or guiding) wave function that is expected to be a good approximation to the exact ground state wave function of the system and it is intended to guide the random walk process in order to obtain a faster convergence.

We can write the SE for the function $f(\mathbf{R}, \tau)$ from equation (2.24) simply by substituting $\Psi(\mathbf{R}, \tau) = \frac{f(\mathbf{R}, \tau)}{\Psi_T(\mathbf{R})}$. This gives the following differential equation:

$$-\frac{\partial f}{\partial \tau} = -\frac{1}{2}\nabla_{\mathbf{R}}^2 f + \nabla(\mathbf{F}f) + (E_L(\mathbf{R}) - E_T)f \quad (2.48)$$

where we have defined the drift force (or velocity) as:

$$\mathbf{F}(\mathbf{R}) \equiv \nabla_{\mathbf{R}} \log \Psi_T(\mathbf{R}) \quad (2.49)$$

and $E_L(\mathbf{R})$ is the local energy defined in (2.13) that can be written using the definition of the drift force as:

$$E_L(\mathbf{R}) = -\frac{\hbar^2}{2m} \left[\nabla_{\mathbf{R}}^2 \log \Psi_T(\mathbf{R}) + (\mathbf{F}(\mathbf{R}))^2 \right] + V(\mathbf{R}) \quad (2.50)$$

Equation (2.48) can be written in operator notation as:

$$-\frac{\partial f}{\partial \tau} = (K + D + B)f \quad (2.51)$$

where K is the kinetic (or diffusive) term, D is the drift term and B is the termed branching term. As in the non-importance sampling case, we can write the evolution in imaginary time of the new wave function $f(\mathbf{R}, \tau)$ as an evolution operator acting on the initial wave function:

$$|f(\tau)\rangle = U(\tau, 0)|f(0)\rangle = e^{-(K+D+B)\tau}|f(0)\rangle \quad (2.52)$$

In position basis the previous equation is:

$$f(\mathbf{R}, \tau) = \int d\mathbf{R}' \langle \mathbf{R} | e^{-(K+D+B)\tau} | \mathbf{R}' \rangle f(\mathbf{R}', 0) \quad (2.53)$$

The Green's function of each individual term in the new hamiltonian are:

$$\begin{cases} G_K(\mathbf{R}, \mathbf{R}', \tau) = \left(\frac{m}{2\pi\hbar^2\Delta\tau} \right)^{\frac{dN}{2}} \exp \left[-\frac{(\mathbf{R}-\mathbf{R}')^2}{2\tau} \right] \\ G_D(\mathbf{R}, \mathbf{R}', \tau) = \delta(\mathbf{R} - \mathcal{R}(\tau)) \\ G_B(\mathbf{R}, \mathbf{R}', \tau) = e^{-(E_L(\mathbf{R})-E_T)\tau} \delta(\mathbf{R} - \mathbf{R}') \end{cases} \quad (2.54)$$

where $\mathcal{R}(\tau)$ is given by:

$$\frac{d\mathcal{R}(\tau)}{d\tau} = \mathbf{F}(\mathcal{R}(\tau)) \quad (2.55)$$

that is the classical trajectory of the configuration moving at a velocity given by the drift term.

As in the non-importance sampling case we can split the time evolution operator in several ways. A first order decomposition is given by:

$$U(\Delta\tau) = e^{-(K+D+B)\Delta\tau} = e^{-K\Delta\tau} e^{-D\Delta\tau} e^{-B\Delta\tau} + O(\Delta\tau^2) \quad (2.56)$$

which gives the approximate Green's function:

$$\begin{aligned} G(\mathbf{R}, \mathbf{R}', \Delta\tau) &= \left(\frac{m}{2\pi\hbar^2\Delta\tau} \right)^{\frac{dN}{2}} e^{-(E_L(\mathbf{R})-E_T)\Delta\tau} \\ &\exp \left[-\frac{m}{\hbar^2} \frac{(\mathbf{R} - \mathcal{R}'(\Delta\tau))^2}{2\Delta\tau} \right] + O(\Delta\tau^2) \end{aligned} \quad (2.57)$$

where $\mathcal{R}'(\Delta\tau)$ is the solution of (2.55) with the initial condition $\mathcal{R}'(0) = \mathbf{R}'$ solved at first order in $\Delta\tau$, this can be done for example by $\mathcal{R}'(\Delta\tau) = \mathbf{R}' + \mathbf{F}(\mathbf{R}')\Delta\tau$.

A higher order decomposition is given by [49]:

$$U(\Delta\tau) = e^{-B\frac{\Delta\tau}{2}} e^{-D\frac{\Delta\tau}{2}} e^{-K\Delta\tau} e^{-D\frac{\Delta\tau}{2}} e^{-B\frac{\Delta\tau}{2}} + O(\Delta\tau^3) \quad (2.58)$$

which gives the approximate Green's function:

$$G(\mathbf{R}, \mathbf{R}', \Delta\tau) = \left(\frac{m}{2\pi\hbar^2\Delta\tau}\right)^{\frac{dN}{2}} e^{-\left(\frac{E_L(\mathbf{R})+E_L(\mathbf{R}')}{2}-E_T\right)\Delta\tau} \int d\mathbf{R}'' \delta(\mathbf{R} - \mathcal{R}''(\Delta\tau/2)) \exp\left[-\frac{m}{\hbar^2} \frac{(\mathbf{R}'' - \mathcal{R}'(\Delta\tau/2))^2}{2\Delta\tau}\right] + O(\Delta\tau^3) \quad (2.59)$$

where $\mathcal{R}'(\Delta\tau/2)$ and $\mathcal{R}''(\Delta\tau/2)$ are the solutions of (2.55) with initial conditions \mathbf{R}' and \mathbf{R}'' respectively. In this quadratic Green's function one must solve the differential equation 2.55 with a second order algorithm.

Diffusion Monte Carlo algorithm with importance sampling

In the DMC method the probability density function $f(\mathbf{R}, \tau)$ is represented as an ensemble of N_W points in the configuration space called walkers. A walker is defined by the positions of all the particles of the system $\mathbf{R} = \{\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N\}$. In this approximation we can write the function f as:

$$f(\mathbf{R}, \tau) = \mathcal{N} \sum_{i=1}^{N_W} \delta(\mathbf{R} - \mathbf{R}_i(\tau)) \quad (2.60)$$

where \mathcal{N} simply gives the normalization factor.

Once we have defined the function $f(\mathbf{R}, \tau)$ at the present time step we need to describe how the Green's function given in (2.59) acts over it. At this point we decompose the full effect of the Green's function in three different steps.

The first step is a free diffusion. This process describes the isotropic diffusion of a walker through the configuration space and can be easily implemented by

$$\mathbf{R}' = \mathbf{R} + \boldsymbol{\eta}\sqrt{\Delta\tau} \quad (2.61)$$

where $\boldsymbol{\eta}$ is a normalized gaussian random vector drawn from the free (or kinetic) Green's function G_K defined in eq. (2.54) with $\boldsymbol{\eta} = \mathbf{R}' - \mathbf{R}$. This gaussian diffusion must be performed for walkers in the ensemble at time τ .

After the gaussian diffusion process there is the drift step. This step represents the effect of the importance sampling technique in the DMC algorithm. This process tries to guide the imaginary time evolution of the walkers to regions of the configuration space where the wave function is expected to be large. The implementation of this step is as follows, first one needs to evaluate the drift force defined in eq. (2.49) and then use some second order integration method to integrate the differential equation (2.55). In our case we use the second order Runge-Kutta method [49] given by the two following steps:

$$\begin{aligned}\mathbf{R}'' &= \mathbf{R}' + \Delta\tau\mathbf{F}(\mathbf{R}') \\ \mathbf{R}''' &= \mathbf{R}'' + \frac{\Delta\tau}{2}(\mathbf{F}(\mathbf{R}'') + \mathbf{F}(\mathbf{R}'))\end{aligned}\tag{2.62}$$

The last part of the effect of the Green's function over the probability distribution function is the key point of the DMC method, the branching process. Up to this point the two different contributions to the short time Green's function conserves the norm of the function f , but in order to solve exactly the many body Schrödinger equation we have to add a term that is a source/sink of walkers. The branching process duplicates walkers that best mimics the exact ground state distribution or alternatively kills walkers that are far from the desired solution.

The implementation of the branching process can be done by simply making N_{sons} copies of each walker where N_{sons} is given by

$$N_{sons} = \text{int}\left(e^{-(E_L(\mathbf{R})-E_T)\tau} + \chi\right)\tag{2.63}$$

where χ is a uniform random number in the range $[0, 1)$ and $\text{int}()$ is the integer part function.

At this point it is clear that we can adjust the reference energy E_T in order to reduce the fluctuations in the number of walkers and keep the population size in the desired range. Another important issue is that when the number of walkers remains statistically constant the trial energy E_T is an estimator of the ground state energy of the many body system.

At the end of an imaginary time step we will obtain a new probability distribution function given by:

$$f(\mathbf{R}, \tau + \Delta\tau) = \mathcal{N} \sum_{i=1}^{N'_W} \delta(\mathbf{R} - \mathbf{R}_i(\tau + \Delta\tau))\tag{2.64}$$

So, in summary we can write the DMC algorithm as:

1. Generate an initial set of walkers.
2. Evaluate the drift force (2.49) and the local energy (2.50) for each walker.
3. For each walker perform the diffusion, drift and branching processes as explained above.
4. When asymptotic regime is reached repeat 2-3 until statistical accuracy is the desired.

2.2.2 Path integral ground state

In this section we introduce the last Monte Carlo method that we have used along this work. It is the path integral ground state (PIGS), also known as variational path integral [50, 51, 52, 53, 54]. This method has common points with the two methods discussed previously (VMC and DMC). We can describe briefly the PIGS method as a variational Monte Carlo method using an imaginary time propagated trial wave function.

As we have seen previously we can write the imaginary time dependent Schrödinger equation as an equivalent integral equation (2.30), and use that expression for the wave function $\Psi(\mathbf{R}, \tau)$ as a variational wave function in a Monte Carlo calculation. In such a Monte Carlo calculation we can use as the probability distribution function the following expression

$$\Psi(\mathbf{R}, \tau) = \int d\mathbf{R}' G(\mathbf{R}, \mathbf{R}', \tau) \Psi(\mathbf{R}, 0) \quad (2.65)$$

The idea behind the PIGS method is similar to the previously commented in DMC. We can decompose the Green's function in several steps as:

$$G(\mathbf{R}_M, \mathbf{R}_0, \tau) \approx \int d\mathbf{R}_{M-1} \dots d\mathbf{R}_1 \prod_{j=0}^{M-1} G(\mathbf{R}_{j+1}, \mathbf{R}_j, \Delta\tau) \quad (2.66)$$

where $\Delta\tau = \frac{\tau}{M}$. Using the decomposition of the Green's function we can write the ground state wave function as:

$$\Psi_0(\mathbf{R}) = \lim_{M \rightarrow \infty} \int d\mathbf{R}_{M-1} \dots d\mathbf{R}_0 \prod_{j=0}^{M-1} G(\mathbf{R}_{j+1}, \mathbf{R}_j, \Delta\tau) \Psi(\mathbf{R}_0, 0). \quad (2.67)$$

It is obvious that in a computational simulation one must work with a finite M value, so the point is to build a variational wave function with a finite number

of convolution terms, using as initial condition a carefully chosen trial wave function, $\Psi(\mathbf{R}, 0) = \Psi_T(\mathbf{R})$. With these considerations the variational wave function in PIGS can be written as:

$$\Psi_{PIGS}(\mathbf{R}, \tau) = \int d\mathbf{R}_{M-1} \dots d\mathbf{R}_0 \prod_{i=0}^{M-1} G(\mathbf{R}_{j+1}, \mathbf{R}_j, \Delta\tau) \Psi_T(\mathbf{R}_0) \quad (2.68)$$

where $\mathbf{R}_M = \mathbf{R}$. With this last expression for the PIGS wave function we can evaluate the energy of the many body problem as

$$E_{PIGS}(\tau) = \frac{\int d\mathbf{R} \Psi_{PIGS}(\mathbf{R}, \tau) \hat{H} \Psi_{PIGS}(\mathbf{R}, \tau)}{\int d\mathbf{R} \Psi_{PIGS}(\mathbf{R}, \tau) \Psi_{PIGS}(\mathbf{R}, \tau)}. \quad (2.69)$$

The variational principle ensures that this expression is an strict upper bound of the ground state energy of the many body problem. At this stage we can see that the advantage of PIGS over VMC is that within this method we have a systematic process that allows to obtain a variational energy that is in principle as close to the exact ground state function as we need. One only have to increase the number of convolution terms in order to obtain a better variational estimation for the ground state energy. One can compute the energy for increasing values of M and find an asymptotic regime where the bias introduced by considering a finite number of convolution terms is smaller than the statistical uncertainties introduced by the Monte Carlo process.

We have seen how to evaluate the energy of the system in terms of the variational function Ψ_{PIGS} . One can write the expectation value of any other operator as follows

$$\langle \hat{O} \rangle = \frac{\int d\mathbf{R} O(\mathbf{R}) |\Psi_{PIGS}(\mathbf{R}, \tau)|^2}{\int d\mathbf{R} |\Psi_{PIGS}(\mathbf{R}, \tau)|^2}. \quad (2.70)$$

From the previous expression and the explicit form of Ψ_{PIGS} given in (2.68) we can write that expectation value as

$$\langle \hat{O} \rangle = \int d\mathbf{R} O(\mathbf{R}) P(\mathbf{R}), \quad (2.71)$$

where the probability distribution function is given by

$$P(\mathbf{R}_0, \dots, \mathbf{R}_{2M}) = \frac{\Psi_T(\mathbf{R}_0) \prod_{j=0}^{2M-1} G(\mathbf{R}_{j+1}, \mathbf{R}_j, \Delta\tau) \Psi_T(\mathbf{R}_{2M})}{\int d\mathbf{R}_0 \dots d\mathbf{R}_{2M} \Psi_T(\mathbf{R}_0) \prod_{j=0}^{2M-1} G(\mathbf{R}_{j+1}, \mathbf{R}_j, \Delta\tau) \Psi_T(\mathbf{R}_{2M})}. \quad (2.72)$$

An important issue of the PIGS method is the short-time approximation of the Green's function of the system, which is the representation of the time evolution operator in the position basis,

$$G(\mathbf{R}, \mathbf{R}', \Delta\tau) = \langle \mathbf{R} | e^{-\hat{H}\Delta\tau} | \mathbf{R}' \rangle \quad (2.73)$$

where $\hat{H} = \hat{K} + \hat{V}$ is the hamiltonian of the system and \hat{K} and \hat{V} are the kinetic and potential energy operators respectively. The simplest short time approximation to the Green's function is the primitive approximation given by

$$e^{-\hat{H}\tau} = e^{-\hat{K}\Delta\tau} e^{-\hat{V}\Delta\tau} + O(\Delta\tau^2). \quad (2.74)$$

The representation of the kinetic and potential part of the Green's function is shown in the following expressions:

$$\begin{aligned} G_K(\mathbf{R}, \mathbf{R}', \Delta\tau) &= \left(\frac{m}{2\pi\hbar^2\Delta\tau} \right)^{\frac{dN}{2}} e^{-\frac{m}{\hbar^2} \frac{(\mathbf{R}-\mathbf{R}')^2}{2\Delta\tau}} \\ G_V(\mathbf{R}, \mathbf{R}', \Delta\tau) &= e^{-V(\mathbf{R})\Delta\tau} \delta(\mathbf{R} - \mathbf{R}') \end{aligned} \quad (2.75)$$

where d is the dimensionality of the system. Using the primitive approximation we can obtain the Green's function for any imaginary time value τ increasing the number of convolution terms in (2.72). The convergence to the exact result is guaranteed by the Trotter formula:

$$e^{-\tau\hat{H}} = \lim_{M \rightarrow \infty} \left(e^{-\Delta\tau\hat{K}} e^{-\Delta\tau\hat{V}} \right)^M. \quad (2.76)$$

The classical isomorphism

We have seen in the previous section the theoretical basis of the PIGS method. In this section we will show an important issue of the method, the classical isomorphism. The Green's function $G(\mathbf{R}, \mathbf{R}', \tau)$ can be written explicitly in terms of the kinetic and potential contributions given in (2.75) as:

$$G(\mathbf{R}_0, \mathbf{R}_{2M}, \tau) = \left(\frac{m}{2\pi\hbar^2\Delta\tau} \right)^{\frac{dNM}{2}} \int d\mathbf{R}_1, \dots, d\mathbf{R}_{2M-1} \prod_{j=0}^{2M-1} e^{-\frac{m}{\hbar^2} \frac{(\mathbf{R}_{j+1} - \mathbf{R}_j)^2}{2\Delta\tau} - V(\mathbf{R}_j)\Delta\tau} \quad (2.77)$$

where $\mathbf{R}_0 = \mathbf{R}'$, $\mathbf{R}_{2M} = \mathbf{R}$ and $\tau = M\Delta\tau$. The exponent of the kinetic term can be written as:

$$-\frac{m}{\hbar^2} \frac{(\mathbf{R}_{j+1} - \mathbf{R}_j)^2}{2\Delta\tau} = -\frac{m}{2\hbar^2\Delta\tau} \sum_{i=1}^N (\mathbf{r}_{j+1,i} - \mathbf{r}_{j,i})^2 \quad (2.78)$$

while the potential term can be written as:

$$-V(\mathbf{R})\Delta\tau = -\Delta\tau \sum_{i=1}^N \left(V_1(\mathbf{r}_{i,j}) + \frac{1}{2} \sum_{k=1, k \neq i}^N V_2(\mathbf{r}_{i,j} - \mathbf{r}_{k,j}) \right) \quad (2.79)$$

where N is the number of particles of the system. Using the expressions (2.78) and (2.79) one can write explicitly the probability distribution function $P(\mathbf{R}_1, \dots, \mathbf{R}_M)$ from equation (2.72) as

$$\begin{aligned} P(\mathbf{R}_1, \dots, \mathbf{R}_{2M}) &= \frac{1}{\mathcal{Z}} \left(\frac{m}{2\pi\hbar^2\Delta\tau} \right)^{\frac{dNM}{2}} e^{[-\sum_{i=1}^N \frac{m}{2\hbar^2\Delta\tau} \sum_{j=0}^{2M-1} (\mathbf{r}_{i,j+1} - \mathbf{r}_{i,j})^2]} \times \\ &\times e^{[-\Delta\tau \sum_{i=1}^N \sum_{j=0}^{2M-1} (V_1(\mathbf{r}_{i,j}) + \frac{1}{2} \sum_{k=1, k \neq i}^N V_2(\mathbf{r}_{i,j} - \mathbf{r}_{k,j}))]} \times \\ &\times e^{(\log \Psi_T(\mathbf{r}_{1,0}, \dots, \mathbf{r}_{N,0}) + \log \Psi_T(\mathbf{r}_{1,2M}, \dots, \mathbf{r}_{N,2M}))} \end{aligned} \quad (2.80)$$

where \mathcal{Z} is the following normalization integral

$$\begin{aligned} \mathcal{Z} &= \int d\mathbf{R}_0, \dots, d\mathbf{R}_{2M} \left(\frac{m}{2\pi\hbar^2\Delta\tau} \right)^{\frac{dNM}{2}} e^{[-\sum_{i=1}^N \frac{m}{2\hbar^2\Delta\tau} \sum_{j=0}^{2M-1} (\mathbf{r}_{i,j+1} - \mathbf{r}_{i,j})^2]} \times \\ &\times e^{[-\Delta\tau \sum_{i=1}^N \sum_{j=0}^{2M-1} (V_1(\mathbf{r}_{i,j}) + \frac{1}{2} \sum_{k=1, k \neq i}^N V_2(\mathbf{r}_{i,j} - \mathbf{r}_{k,j}))]} \times \\ &\times e^{(\log \Psi_T(\mathbf{r}_{1,0}, \dots, \mathbf{r}_{N,0}) + \log \Psi_T(\mathbf{r}_{1,2M}, \dots, \mathbf{r}_{N,2M}))} \end{aligned} \quad (2.81)$$

This last expression is completely analogous to the canonical partition function of a system of N classical open polymers each of them having $2M+1$ particles (or beads) bounded by harmonic springs (the kinetic energy terms). Each polymer interacts with the rest by means of the potential terms in a special way, there is only interaction between beads corresponding to equal imaginary times.

Basic path integral ground state algorithm

Using the classical isomorphism the PIGS method can be thought as a variational Monte Carlo method applied to a system of N linear polymers that interact between them. Starting from a set of initial configurations given by $\{\mathbf{X}_1, \dots, \mathbf{X}_N\}$ where each \mathbf{X}_i is the set of positions of one of these linear polymers, i. e. $\mathbf{X}_i = \{\mathbf{R}_0^{(i)}, \dots, \mathbf{R}_{2M+1}^{(i)}\}$.

The PIGS algorithm is schematically given by:

1. Draw an initial configuration for each linear polymer $\{\mathbf{X}_1, \dots, \mathbf{X}_N\}$ representing the full imaginary time path of each particle.

2. Guess a new configuration for the system by making $\mathbf{X}'_i = \mathbf{X}_i + \delta\mathbf{X}_i$.
3. Evaluate the transition probability to the new configuration as

$$Q = \frac{P(\mathbf{X}_1, \dots, \mathbf{X}'_i, \dots, \mathbf{X}_N)}{P(\mathbf{X}_1, \dots, \mathbf{X}_i, \dots, \mathbf{X}_N)}. \quad (2.82)$$

4. Accept or reject the new configuration using Metropolis algorithm.
5. Compute observables of interest.
6. Repeat 2 - 5 to achieve the desired accuracy.

This is a basic PIGS algorithm build in complete analogy with the variational Monte Carlo method that can be improved in several ways. The first problem of this simple algorithm is that their efficiency can be not very high due to the presence of the kinetic terms connecting different beads in each polymer. In the following, we will see how to improve the efficiency of the sampling.

Staging algorithm

As we have commented previously, the simple sampling of the path integral can have some efficiency problems due to the presence of the kinetic springs. There are several methods to improve the efficiency of the sampling that can exploit the fact that the kinetic part of the action can be exactly sampled. In this work we have used the staging algorithm [55] with this purpose.

The staging algorithm works by purposing smart collective motions of several beads of each linear polymer. The positions of the new configuration are randomly generated using the kinetic part of the action and then the Metropolis test must only be applied to the potential part improving dramatically the efficiency of the algorithm.

In order to implement the collective motions let's consider the free (or kinetic) part of the action as a product of kinetic contributions involving all the beads of a single chain:

$$\begin{aligned} G_0(\mathbf{x}_0, \mathbf{x}_{2M}, \tau) = & G_0(\mathbf{x}_0, \mathbf{x}_1, \Delta\tau) \times \dots \times \\ & \times G_0(\mathbf{x}_i, \mathbf{x}_{i+1}, \Delta\tau) \times \dots \times G_0(\mathbf{x}_{i+j-1}, \mathbf{x}_{i+j}, \Delta\tau) \times \dots \\ & \times G_0(\mathbf{x}_{2M-1}, \mathbf{x}_{2M}, \Delta\tau) \end{aligned} \quad (2.83)$$

where the \mathbf{x} variable make reference to the d -dimensional coordinates of any of the N chains of the system. We are interested in build a new set of positions

$\{\mathbf{x}_{i+1}, \dots, \mathbf{x}_{i+j-1}\}$ generated randomly according to the free particle action. We can define the function S as:

$$S(\mathbf{x}_i, \mathbf{x}_{i+j}, j\Delta\tau) = \prod_{k=1}^j G_0(\mathbf{x}_{i+k-1}, \mathbf{x}_{i+k}, \Delta\tau) \quad (2.84)$$

and define a new set of coordinates \mathbf{y} that allows us to write S in a decoupled form given by

$$S(\mathbf{x}_i, \mathbf{x}_{i+j}, j\Delta\tau) = G_0(\mathbf{x}_i, \mathbf{x}_{i+j}, j\Delta\tau) \prod_{k=1}^{j-1} G_0^{(k)}(\mathbf{x}_{i+k}, \mathbf{y}_{i+k}, \Delta\tau) \quad (2.85)$$

where the function $G_0^{(k)}$ is defined as

$$G_0^{(k)}(\mathbf{x}_{i+k}, \mathbf{y}_{i+k}, \Delta\tau) = \left(\frac{m_k}{2\pi\hbar^2\Delta\tau} \right)^{\frac{d}{2}} e^{-\frac{m_k}{\hbar^2} \frac{(\mathbf{x}_{i+k} - \mathbf{y}_{i+k})^2}{2\Delta\tau}}. \quad (2.86)$$

As it can be seen from (2.86) the new coordinates imply a redefinition of the mass term $m \rightarrow m_k$. So finally we can write the staging coordinates and the new mass term as:

$$\mathbf{y}_{i+k} = \frac{\mathbf{x}_{i+j} + \mathbf{x}_{i+k-1}(j - (k - 1))}{j - k} \quad (2.87)$$

$$m_k = m \left(\frac{j - (k - 1)}{j - k} \right) \quad (2.88)$$

Using this smart change of variables we can generate collective motions of several beads in a single chain by simply generating gaussian random numbers as:

$$\mathbf{x}'_{i+k} = \mathbf{y}_{i+k} + \eta \sqrt{\frac{\hbar^2\tau}{m_k}} \quad (2.89)$$

where η is a $U(0, 1)$ random number.

Using this method we generate a set of new coordinates using the kinetic action as probability distribution function so we must sample only the potential action in the Metropolis algorithm.

High order approximation to the Green's function

Another aspect that can be improved in the simple PIGS method that we have explained is the approximation to the short time Green's function of the system. In the introduction of the method we have developed all the theory using the so-called primitive approximation that is accurate up to second order in $\Delta\tau$.

$$\langle \mathbf{R} | e^{(T+V)\Delta\tau} | \mathbf{R}' \rangle = \langle \mathbf{R} | e^{\frac{V}{2}\Delta\tau} e^{T\Delta\tau} e^{\frac{V}{2}\Delta\tau} | \mathbf{R}' \rangle \quad (2.90)$$

An obvious improvement is to consider some higher order decomposition for the propagator of the system.

A more accurate form of the Green's function allows for a faster convergence of the method and, as a consequence, a decrease in the required number of beads or a larger time step to achieve the convergence. In this work we have used the following approximation for the short time propagator [56, 57, 58]:

$$\langle \mathbf{R} | e^{(T+V)\Delta\tau} | \mathbf{R}' \rangle = \langle \mathbf{R} | e^{\frac{V}{6}\Delta\tau} e^{\frac{T}{2}\Delta\tau} e^{\frac{2W}{3}\Delta\tau} e^{\frac{T}{2}\Delta\tau} e^{\frac{V}{6}\Delta\tau} | \mathbf{R}' \rangle + O(\Delta\tau^5) \quad (2.91)$$

where

$$W = V + \frac{1}{48}[V, [T, V]] \quad (2.92)$$

Using this high order decomposition for the short time propagator the Green's function can be written as:

$$G(\mathbf{R}, \mathbf{R}', \Delta\tau) = G^{(0)}(\mathbf{R}, \mathbf{R}'', \Delta\tau)G^{(1)}(\mathbf{R}'', \mathbf{R}', \Delta\tau) + O(\Delta\tau^5) \quad (2.93)$$

where the functions $G^{(0)}$ and $G^{(1)}$ are given by:

$$G^{(i)}(\mathbf{R}, \mathbf{R}', \Delta\tau) = G_K(\mathbf{R}, \mathbf{R}', \Delta\tau) \times G_V^{(i)}(\mathbf{R}, \mathbf{R}', \Delta\tau) \quad (2.94)$$

and

$$G_V^{(i)}(\mathbf{R}, \mathbf{R}', \Delta\tau) = \begin{cases} e^{-\frac{2}{3}V(\mathbf{R}')\Delta\tau} & \text{if } i \text{ is even} \\ e^{-\frac{4}{3}V(\mathbf{R}')\Delta\tau - \frac{\hbar^2\Delta\tau^3}{9m} \sum_{j=1}^N |\nabla_j V(\mathbf{R}')|^2} & \text{if } i \text{ is odd} \end{cases} \quad (2.95)$$

This expression for the short time Green's function is a particular case of a more general family of approximations derived from symplectic decompositions of the propagator [57].

Fourth order path integral ground state algorithm with staging

The improved PIGS algorithm that incorporates staging sampling to improve the convergence of the method is the following

1. Draw an initial configuration for each linear polymer $\{\mathbf{X}_1, \dots, \mathbf{X}_N\}$ representing the full imaginary time path of each particle.
2. Guess a new configuration for the system by making use of the staging method.
3. Evaluate the transition probability to the new configuration as

$$Q = \frac{P(\mathbf{X}_1, \dots, \mathbf{X}'_i, \dots, \mathbf{X}_N)}{P(\mathbf{X}_1, \dots, \mathbf{X}_i, \dots, \mathbf{X}_N)}. \quad (2.96)$$

4. Accept or reject the new configuration using Metropolis algorithm.
5. Compute observables of interest.
6. Repeat 2 - 5 to achieve the desired accuracy.

The main difference between the improved and the basic algorithms is that in the improved algorithm the new configurations of the system are proposed using the staging method that, as we have seen, samples exactly the kinetic part of the action and therefore the transition probability involves only the evaluation of potential action.

In addition to the given steps it is convenient to accelerate the convergence by performing full chain translations of each chain between several steps of the simulation. This translations are proposed as:

$$\mathbf{X}'_i = \mathbf{X}_i + \delta \mathbf{X}_i \quad (2.97)$$

and then are accepted or rejected using the Metropolis algorithm.

2.3 Evaluating properties

In this section we will show how the observables of interest are evaluated from the Monte Carlo sampling. We are interested in the evaluation of the energy per particle of the system, that allows us to build the equation of state, and also in structural quantities like the pair distribution function and its Fourier transform, the static structure factor. Another important quantity to evaluate is the one-body density matrix that gives information about the Bose-Einstein condensation in the system.

2.3.1 Energy per particle

The energy of a quantum system can be evaluated as the expected value of the many body hamiltonian given by:

$$H = -\frac{\hbar^2}{2m} \sum_{i=1}^N \nabla^2 + \sum_{i=1}^N V_1(\mathbf{r}_i) + \sum_{i<j} V_2(\mathbf{r}_i - \mathbf{r}_j) \quad (2.98)$$

As we have seen the Schrödinger equation is given by:

$$\langle \Psi | H | \Psi \rangle = E \langle \Psi | \Psi \rangle \quad (2.99)$$

so the energy can be evaluated by the following expression

$$E[\Psi] = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} \quad (2.100)$$

that can be put in integral form as:

$$E[\Psi] = \frac{\int d\mathbf{R} \Psi^*(\mathbf{R}) H \Psi(\mathbf{R})}{\int d\mathbf{R} |\Psi(\mathbf{R})|^2} \quad (2.101)$$

and can be expressed in terms of the probability distribution as

$$E[\Psi] = \frac{\int d\mathbf{R} |\Psi(\mathbf{R})|^2 \frac{H\Psi(\mathbf{R})}{\Psi(\mathbf{R})}}{\int d\mathbf{R} |\Psi(\mathbf{R})|^2} = \int d\mathbf{R} P(\mathbf{R}) E_{loc}(\mathbf{R}) \quad (2.102)$$

where $P(\mathbf{R}) = \frac{|\Psi(\mathbf{R})|^2}{\int d\mathbf{R} |\Psi(\mathbf{R})|^2}$ and $E_{loc} = \frac{H\Psi(\mathbf{R})}{\Psi(\mathbf{R})}$.

The hamiltonian acting on the wave function can be split in the kinetic and potential terms, the potential term can be simply written as:

$$\frac{V\Psi(\mathbf{R})}{\Psi(\mathbf{R})} = \sum_{i=1}^N V_1(\mathbf{r}_i) + \sum_{i<j} V_2(\mathbf{r}_i - \mathbf{r}_j) \quad (2.103)$$

and the kinetic term:

$$\frac{K\Psi(\mathbf{R})}{\Psi(\mathbf{R})} = -\frac{\hbar^2}{2m} \frac{\nabla_{\mathbf{R}}^2 \Psi(\mathbf{R})}{\Psi(\mathbf{R})}. \quad (2.104)$$

It is convenient to write the acting of the laplacian on the wave function as:

$$\frac{\nabla_{\mathbf{R}}^2 \Psi(\mathbf{R})}{\Psi(\mathbf{R})} = \nabla_{\mathbf{R}}^2 \log \Psi(\mathbf{R}) + (\nabla_{\mathbf{R}} \log \Psi(\mathbf{R}))^2 \quad (2.105)$$

Variational Monte Carlo

In a variational Monte Carlo sampling we have no access to the exact wave function of the system so, in general, we can evaluate the energy substituting the exact wave function by the trial wave function $\Psi_T(\mathbf{R})$, is we do this change the second term in (2.105) can be identified as the drift force and the total local energy can be written as:

$$E_{loc}(\mathbf{R}) = -\frac{\hbar^2}{2m} (\nabla_{\mathbf{R}}^2 \log \Psi_T(\mathbf{R}) + F(\mathbf{R})^2) + V(\mathbf{R}) \quad (2.106)$$

In a VMC simulation this quantity is obviously an approximation to the exact ground state energy of the system.

Diffusion Monte Carlo

In a DMC simulation we sample the product of the exact wave function of the system times the trial (or guiding) wave function so the energy of the system can be written as:

$$E = \frac{\int d\mathbf{R} \Psi(\mathbf{R}) \Psi_T(\mathbf{R}) E_{loc}(\mathbf{R})}{\int \Psi_T(\mathbf{R}) \Psi(\mathbf{R})} = \frac{\int d\mathbf{R} \Psi(\mathbf{R}) \Psi_T(\mathbf{R}) \frac{H\Psi_T(\mathbf{R})}{\Psi_T(\mathbf{R})}}{\int \Psi_T(\mathbf{R}) \Psi(\mathbf{R})} \quad (2.107)$$

so finally we can write

$$E = \frac{\int d\mathbf{R} \Psi(\mathbf{R}) H \Psi_T(\mathbf{R})}{\int \Psi_T(\mathbf{R}) \Psi(\mathbf{R})} \quad (2.108)$$

thanks to the hermiticity the hamiltonian can act on the left or on the right and considering that $H|\Psi\rangle = E_0|\Psi\rangle$ we can write

$$E = E_0 \frac{\int d\mathbf{R} \Psi(\mathbf{R}) \Psi_T(\mathbf{R})}{\int \Psi_T(\mathbf{R}) \Psi(\mathbf{R})} = E_0 \quad (2.109)$$

So in a DMC simulation we also have to evaluate the expectation value of the local energy function.

Path integral ground state

In a PIGS simulation the evaluation of the energy can be done in several ways. In this work, we have chosen the mixed estimator as in the case of DMC. In PIGS the physical observables must be evaluated at the mid-point of the chain

but in the case of the energy, as we are evaluating the expected value of the hamiltonian it can act on the extreme points ($\mathbf{R}_0, \mathbf{R}_M$) given that

$$[H, e^{-H\tau}] = 0 \quad (2.110)$$

So the mixed estimator of the energy on a PIGS simulation is given by:

$$E = \sum_{i=1}^N \frac{H\Psi_T(\mathbf{R}_0)}{\Psi_T(\mathbf{R}_0)} = \sum_{i=1}^N E_{loc}(\mathbf{R}_0) \quad (2.111)$$

2.3.2 Pair distribution function

Another observable of interest in the study of quantum gases is the so called pair distribution function that is given by the following expression:

$$g(\mathbf{r}_1, \mathbf{r}_2) = \frac{N(N-1)}{n^2} \frac{\int |\Psi(\mathbf{R})|^2 d\mathbf{r}_3 \cdots d\mathbf{r}_N}{\int |\Psi(\mathbf{R})|^2 d\mathbf{r}_1 \cdots d\mathbf{r}_N}. \quad (2.112)$$

In an homogeneous system the pair distribution function depends only in the relative position $\mathbf{r}_1 - \mathbf{r}_2$. The equation (2.112) can be written in the following form by defining $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$

$$g(\mathbf{r}) = \frac{N(N-1)}{n^2 L^d} \frac{\int \delta(\mathbf{r}_1 - \mathbf{r}_2 - \mathbf{r}) |\Psi(\mathbf{R})|^2 d\mathbf{R}}{\int |\Psi(\mathbf{R})|^2 d\mathbf{R}}. \quad (2.113)$$

where L is the size of the simulation box and d is the dimensionality of the system. This last expression is written in a more suitable form for a Monte Carlo evaluation.

In order to have more statistic and reduce the variance of the estimator it is common to sum over all possible pairs of particles in the system, if we do so the final expression that we will evaluate in our Monte Carlo simulations is

$$g(\mathbf{r}) = \frac{2}{nN} \frac{\int \sum_{i < j} \delta(\mathbf{r}_{ij} - \mathbf{r}) |\Psi(\mathbf{R})|^2 d\mathbf{R}}{\int |\Psi(\mathbf{R})|^2 d\mathbf{R}}. \quad (2.114)$$

where $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$.

The evaluation of the pair distribution function in the Monte Carlo sampling it is simply implemented by making an histogram of the relative distance of each pair of particles of the system.

2.3.3 Static structure factor

A quantity related with the pair distribution function that is very interesting in the study of the macroscopic state of a quantum gas is the static structure factor, that is also accessible experimentally.

The static structure factor is related with the Fourier transform of the pair distribution function

$$S(\mathbf{k}) = 1 + n \int d\mathbf{r} e^{-i\mathbf{q}\cdot\mathbf{r}} (g(\mathbf{r}) - 1). \quad (2.115)$$

Despite of its apparent simplicity, this expression is not the best way to evaluate the static structure factor in a Monte Carlo calculation. Instead of using (2.115) it is better to use the alternative definition of $S(\mathbf{k})$ that states that it is given by the correlation of the momentum distribution between \mathbf{k} and $-\mathbf{k}$

$$NS(\mathbf{k}) = \langle \rho_{-\mathbf{k}} \rho_{\mathbf{k}} \rangle - |\langle \rho_{\mathbf{k}} \rangle|^2 \quad (2.116)$$

Using the property $\rho_{-\mathbf{k}} = \rho_{\mathbf{k}}^*$ we can write (2.116) as

$$NS(\mathbf{k}) = \langle |\rho_{\mathbf{k}}|^2 \rangle - |\langle \rho_{\mathbf{k}} \rangle|^2 \quad (2.117)$$

The density distribution in a Monte Carlo calculation is given by

$$n(\mathbf{r}) = \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i) \quad (2.118)$$

that can be expressed in the momentum space as:

$$\rho_{\mathbf{k}} = \int e^{i\mathbf{k}\cdot\mathbf{r}} n(\mathbf{r}) = \sum_{i=1}^N e^{i\mathbf{k}\cdot\mathbf{r}_i} = \sum_{i=1}^N \cos \mathbf{k} \cdot \mathbf{r}_i + i \sum_{i=1}^N \sin \mathbf{k} \cdot \mathbf{r}_i \quad (2.119)$$

Using the definition of $\rho_{\mathbf{k}}$ we can write finally the expression for the evaluation of the static structure factor as:

$$\begin{aligned} NS(\mathbf{k}) = & \left\langle \left(\sum_{i=1}^N \cos \mathbf{k} \cdot \mathbf{r}_i \right)^2 + \left(\sum_{i=1}^N \sin \mathbf{k} \cdot \mathbf{r}_i \right)^2 \right\rangle \\ & - \left| \left\langle \sum_{i=1}^N \cos \mathbf{k} \cdot \mathbf{r}_i \right\rangle \right|^2 - \left| \left\langle \sum_{i=1}^N \sin \mathbf{k} \cdot \mathbf{r}_i \right\rangle \right|^2 \end{aligned} \quad (2.120)$$

In an homogeneous system the last two terms vanish.

The last consideration concerns the values of \mathbf{k} in an homogeneous system, as we simulate the system in a finite simulation cell we must choose values of \mathbf{k} that are compatible with the size of the box:

$$k_i = \frac{2\pi}{L_i} n_i \quad (2.121)$$

where $n_i = 1, 2, \dots$ and L_i are the length of the box in the direction i .

2.3.4 One body density matrix

The last quantity that we are interested in is the one body density matrix that gives us information about the Bose - Einstein condensation in the system. In an homogeneous system the one body density matrix $\rho(\mathbf{r})$ is given by:

$$\rho(\mathbf{r} - \mathbf{r}') = N \frac{\int \cdots \int \Psi^*(\mathbf{r}, \mathbf{r}_2, \cdots, \mathbf{r}_N) \Psi(\mathbf{r}', \mathbf{r}_2, \cdots, \mathbf{r}_N) d\mathbf{r}_2 \cdots d\mathbf{r}_N}{\int \cdots \int |\Psi(\mathbf{r}, \cdots, \mathbf{r}_N)|^2 d\mathbf{r}_1 \cdots d\mathbf{r}_N} \quad (2.122)$$

In VMC the wave function that we are sampling is the $\Psi_T(\mathbf{R})$ so the previous expression can be written as:

$$\rho(\mathbf{r} - \mathbf{r}') = N \frac{\int \cdots \int \frac{\Psi_T^*(\mathbf{r}, \mathbf{r}_2, \cdots, \mathbf{r}_N)}{\Psi_T^*(\mathbf{r}', \mathbf{r}_2, \cdots, \mathbf{r}_N)} |\Psi_T(\mathbf{r}', \mathbf{r}_2, \cdots, \mathbf{r}_N)|^2 d\mathbf{r}_2 \cdots d\mathbf{r}_N}{\int \cdots \int |\Psi_T(\mathbf{r}, \cdots, \mathbf{r}_N)|^2 d\mathbf{r}_1 \cdots d\mathbf{r}_N} \quad (2.123)$$

where $P(\mathbf{R}) = \frac{|\Psi(\mathbf{R})|^2}{\int |\Psi(\mathbf{R})|^2 d\mathbf{R}}$.

On the other hand in the DMC method we are sampling the mixed function $f(\mathbf{R}) = \Psi_T(\mathbf{R})\Psi(\mathbf{R})$ so the expression (2.122) is

$$\rho(\mathbf{r} - \mathbf{r}') = N \frac{\int \cdots \int \Psi_T^*(\mathbf{r}, \mathbf{r}_2, \cdots, \mathbf{r}_N) \Psi(\mathbf{r}', \mathbf{r}_2, \cdots, \mathbf{r}_N) d\mathbf{r}_2 \cdots d\mathbf{r}_N}{\int \cdots \int |f(\mathbf{r}, \cdots, \mathbf{r}_N)|^2 d\mathbf{r}_1 \cdots d\mathbf{r}_N} \quad (2.124)$$

that can be written again as:

$$\rho(\mathbf{r} - \mathbf{r}') = N \frac{\int \cdots \int \frac{\Psi_T^*(\mathbf{r}, \mathbf{r}_2, \cdots, \mathbf{r}_N)}{\Psi_T^*(\mathbf{r}', \mathbf{r}_2, \cdots, \mathbf{r}_N)} f(\mathbf{r}', \mathbf{r}_2, \cdots, \mathbf{r}_N) d\mathbf{r}_2 \cdots d\mathbf{r}_N}{\int \cdots \int f(\mathbf{r}, \cdots, \mathbf{r}_N) d\mathbf{r}_1 \cdots d\mathbf{r}_N} \quad (2.125)$$

From the asymptotic behavior of the one body density matrix the condensate fraction of the system can be extracted as:

$$\lim_{|\mathbf{r} - \mathbf{r}'| \rightarrow \infty} \frac{\rho(\mathbf{r} - \mathbf{r}')}{n} = \frac{N_0}{N} \quad (2.126)$$

where N_0 is the number of particles on the condensate.

2.4 Trial wave functions

A key ingredient of the zero temperature quantum Monte Carlo methods is the trial wave function of the system. The trial function allows us to introduce all the a priori information about the physics of the system to improve the convergence and accuracy of the Monte Carlo sampling.

It is usual in the study of quantum bosonic fluids to consider the wave function as:

$$\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N) = \exp(U_1 + U_2 + U_3 + \dots + U_N) \quad (2.127)$$

where the different functions U_i are terms involving correlations of i particles,

$$\begin{aligned} U_1 &= \sum_{j=1}^N u_1(\mathbf{r}_j) \\ U_2 &= \sum_{i<j} u_2(\mathbf{r}_i, \mathbf{r}_j) \\ U_3 &= \sum_{i<j<k} u_3(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k) \end{aligned} \quad (2.128)$$

A common approximation is to consider a wave function containing only terms involving two body correlations, which implies $U_i = 0 \quad \forall i > 2$, such a wave function is called Jastrow wave function and can be written as:

$$\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N) = \exp\left(\sum_{i<j} u_2(\mathbf{r}_i, \mathbf{r}_j)\right) \quad (2.129)$$

where $u_2(\mathbf{r}_i, \mathbf{r}_j) = u_2(\mathbf{r}_i - \mathbf{r}_j)$ for an homogeneous system like a gas or a liquid. The two body correlation function $\exp(u_2(\mathbf{r}_i - \mathbf{r}_j))$ it is chosen to reproduce the exact behaviour of the two body problem at low distances in order to avoid the possible singularities of the local energy at short distances caused by interactions that are strongly repulsive at short distances. For a non homogeneous system like a crystalline solid we have to consider in general a one body term in addition to the two body Jastrow term in order to help the Monte Carlo sampling to find the ground state configuration of the system.