Chapter 5

Quantum Monte Carlo

This chapter is devoted to the study of quatum many body systems using Monte Carlo techniques. We analyze two of the methods that belong to the large family of the quantum Monte Carlo techniques, namely the Path-Integral Monte Carlo (PIMC) and the Diffusion Monte Carlo (DMC, also named Green's function Monte Carlo). In the first section we start by introducing PIMC.

5.1 Path Integrals in Quantum Statistical Mechanics

In this section we introduce the path-integral description of the properties of quantum many-body systems. We show that path integrals permit to calculate the static properties of systems of Bosons at thermal equilibrium by means of Monte Carlo methods.

We consider a many-particle system described by the non-relativistic Hamiltonian

$$\hat{H} = \hat{T} + \hat{V}; \tag{5.1}$$

in coordinate representation the kinetic operator $\hat{T}$ and the potential operator $\hat{V}$ are defined as:

$$\hat{T} = -\frac{\hbar^2}{2m}\sum_{i=1}^{N}\Delta_i, \text{ and} \tag{5.2}$$

$$\hat{V} = V(\boldsymbol{R}). \tag{5.3}$$

In these equations $\hbar$ is the Plank's constant divided by 2π, m the particles mass, N the number of particles and the vector $\boldsymbol{R} \equiv (\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N)$ describes their positions. We consider here systems in d dimensions, with fixed number of particles, temperature T, contained in a volume V.
In most case, the potential $V(\boldsymbol{R})$ is determined by inter-particle interactions, in which case it can be written as the sum of pair contributions $V(\boldsymbol{R}) = \sum_{i<j} v(\boldsymbol{r}_i - \boldsymbol{r}_j)$, where $v(\boldsymbol{r})$ is the inter-particle potential; it can also be due to an external field, call it $v_{\text{ext}}(\boldsymbol{r})$, in which case it is just the sum of single particle contributions $V(\boldsymbol{R}) = \sum_i v_{\text{ex}}(\boldsymbol{r}_i)$.

We first assume that particles, although being identical, are distinguishable. Therefore, they obey Boltzmann statistics. In section 5.1.3 we will describe the treatment of identical particles obeying Bose statistics.

All the static properties of a quantum many-body system in thermal equilibrium are obtainable from the thermal density matrix $\exp\left(-\beta\hat{H}\right)$, where $\beta = 1/k_B T$, with k_B the Boltzmann's constant. The expectation value of an observable operator $\hat{O}$ is:

$$\langle\hat{O}\rangle = \mathrm{Tr}\left(\hat{O}\exp\left(-\beta\hat{H}\right)\right)/Z, \tag{5.4}$$

where the partition function Z is the trace of the density matrix:

$$Z = \mathrm{Tr}\left(\exp\left(-\beta\hat{H}\right)\right). \tag{5.5}$$

In the following we will find convenient to use the density matrix in coordinate representation. We denote its matrix elements as:

$$\rho\left(\boldsymbol{R}, \boldsymbol{R}', \beta\right) \equiv \left\langle \boldsymbol{R}\left|\exp\left(-\beta\hat{H}\right)\right|\boldsymbol{R}'\right\rangle. \tag{5.6}$$

The partition function is the integral of the diagonal matrix elements over all possible configurations:

$$Z\left(N, T, V\right) = \int \rho\left(\boldsymbol{R}, \boldsymbol{R}, \beta\right) \mathrm{d}\boldsymbol{R}. \tag{5.7}$$

The product of two density matrices is again a density matrix:

$$\exp\left(-\left(\beta_1 + \beta_2\right)\hat{H}\right) = \exp\left(-\beta_1\hat{H}\right)\exp\left(-\beta_2\hat{H}\right). \tag{5.8}$$

This property, often referred to as 'product property', written in coordinate representation gives a convolution integral:

$$\rho\left(\boldsymbol{R}_1, \boldsymbol{R}_3, \beta_1 + \beta_2\right) = \int \rho\left(\boldsymbol{R}_1, \boldsymbol{R}_2, \beta_1\right)\rho\left(\boldsymbol{R}_2, \boldsymbol{R}_3, \beta_2\right)\mathrm{d}\boldsymbol{R}_2. \tag{5.9}$$

If we apply the product property M times we obtain the density matrix at the inverse temperature β as the product of M density matrices at the inverse temperature $\tau = \beta/M$. In operator form:

$$\exp\left(-\beta\hat{H}\right) = \left(\exp\left(-\tau\hat{H}\right)\right)^M. \tag{5.10}$$

We call *time step* the quantity τ. Eq. (5.10) written in coordinate representation becomes:

$$\rho\left(\boldsymbol{R}_1, \boldsymbol{R}_{M+1}, \beta\right) = \int\cdots\int \mathrm{d}\boldsymbol{R}_2\mathrm{d}\boldsymbol{R}_3\cdots\mathrm{d}\boldsymbol{R}_M \\ \rho\left(\boldsymbol{R}_1, \boldsymbol{R}_2, \tau\right)\rho\left(\boldsymbol{R}_2, \boldsymbol{R}_3, \tau\right)\cdots\rho\left(\boldsymbol{R}_M, \boldsymbol{R}_{M+1}, \tau\right). \tag{5.11}$$

Eq. (5.11) is not useful as it is since the density matrices $\rho(\boldsymbol{R}_j, \boldsymbol{R}_{j+1}, \tau)$ are, in general, unknown quantities. We note, however, that if M is a large number, then the time-step τ, which corresponds to the high temperature MT, is small. If in eq. (5.11) we replace the exact density matrix $\rho(\boldsymbol{R}_j, \boldsymbol{R}_{j+1}, \tau)$ with a 'short time' or 'high temperature' approximation we obtain a multidimensional integral of known functions. Furthermore, in coordinate representation the density matrix is positive definite. It is known that many-variable integrals of positive functions can be calculated efficiently by means of Monte Carlo methods.

The simplest expression for the 'high temperature' density matrix is the so called *primitive approximation*. It consists in neglecting all terms beyond the one which is linear in τ in the left-hand side exponent of the following operator identity (*Baker-Campbell-Hausdorff relation*):

$$\exp\left(-\tau\left(\hat{T}+\hat{V}\right)+\frac{\tau^2}{2}\left[\hat{T},\hat{V}\right]+\cdots\right)=\exp\left(-\tau\hat{T}\right)\exp\left(-\tau\hat{V}\right). \tag{5.12}$$

(In this equation dots indicate terms which contain powers of τ higher than the second.) One obtains the following approximate expression for the density matrix operator:

$$\exp\left(-\tau\hat{H}\right)\cong\exp\left(-\tau\hat{T}\right)\exp\left(-\tau\hat{V}\right). \tag{5.13}$$

It is easy to write the matrix elements of the kinetic density matrix $\exp\left(-\tau\hat{T}\right)$ and the potential density matrix $\exp\left(-\tau\hat{V}\right)$ in coordinate representation. The latter is diagonal:

$$\left\langle \boldsymbol{R}_i\left|\exp\left(-\tau\hat{V}\right)\right|\boldsymbol{R}_{i+1}\right\rangle=\exp\left(-\tau V\left(\boldsymbol{R}_1\right)\right)\delta\left(\boldsymbol{R}_1,\boldsymbol{R}_2\right), \tag{5.14}$$

given that we consider potentials that are diagonal in coordinate space. The former, in free space, is a gaussian propagator (see section 5.1.2):

$$\left\langle \boldsymbol{R}_i\left|\exp\left(-\tau\hat{T}\right)\right|\boldsymbol{R}_{i+1}\right\rangle=\left(2\pi\hbar^2\tau/m\right)^{-dN/2}\exp\left[-\frac{\left(\boldsymbol{R}_i-\boldsymbol{R}_{i+1}\right)^2}{2\hbar^2\tau/m}\right]. \tag{5.15}$$

For later convenience we introduce the following definition:

$$\rho^{\text{free}}\left(\boldsymbol{R},\boldsymbol{R}',\tau\right)\equiv\left(2\pi\hbar^2\tau/m\right)^{-dN/2}\exp\left[-\frac{\left(\boldsymbol{R}-\boldsymbol{R}'\right)^2}{2\hbar^2\tau/m}\right]. \tag{5.16}$$

In the limit of large Trotter number M equation (5.10) remains exact if we use the primitive approximation eq. (5.12) in its right hand side. This is guaranteed by the Trotter formula:

$$\exp\left(-\beta\left(\hat{T}+\hat{V}\right)\right)=\lim_{M\to+\infty}\left[\exp\left(-\tau\hat{T}\right)\exp\left(-\tau\hat{V}\right)\right]^M, \tag{5.17}$$

which holds for any pairs of operators bounded from below. The kinetic operator $\hat{T}$ and the potential operators $\hat{V}$ of interest to us satisfy this requirement. To make the consequence of the Trotter formula explicit in coordinate representation we substitute the

matrix elements of the kinetic and the potential density matrices eqs. (5.15) and (5.14) in the path-integral formula (5.11). We arrive at the following $dN(M-1)$-dimensional integral:

$$\rho\left(\boldsymbol{R}_1, \boldsymbol{R}_{M+1}, \beta\right) \cong \int \cdots \int \prod_{j=2}^{M} \mathrm{d}\boldsymbol{R}_j \prod_{j=1}^{M} \left\{\rho^{\mathrm{free}}\left(\boldsymbol{R}_j, \boldsymbol{R}_{j+1}, \tau\right) \exp\left[-\tau V\left(\boldsymbol{R}_j\right)\right]\right\}. \quad (5.18)$$

The Trotter formula guarantees that in the limit $M \to \infty$ this is an exact equation. If M is a large, but finite, number the integral (5.18) can be computed using the Monte Carlo procedure. One big issue is the determination of the lowest value of M for which the systematic error due to M being finite is smaller than the unavoidable statistical error associated to the Monte Carlo evaluation.

At this point it is useful to introduce some definitions we will employ extensively in the next lectures.

Many-particle path: also called '*system configuration*', it is the set of the dNM coordinates $\boldsymbol{R}_1, \boldsymbol{R}_2, \ldots, \boldsymbol{R}_M$.

Time-slice: the $j-$th term of a system configuration, indicated with $\boldsymbol{R}_j$, contains the dN coordinates of the N particles at imaginary time $(j-1)\tau$ and will be called '*time-slice*'.

World line: the '*world line*' i is the set of coordinates describing the path of the particle i in imaginary time: $\left\{\boldsymbol{r}_1^i, \boldsymbol{r}_2^i, \ldots, \boldsymbol{r}_j^i, \ldots, \boldsymbol{r}_M^i\right\}$.

Bead: we call '*beads*' the M components of a world line.

The trace of the density matrix (5.18) gives the partition function:

$$Z\left(N, V, T\right) = \int \rho\left(\boldsymbol{R}_1, \boldsymbol{R}_1, \beta\right) \mathrm{d}\boldsymbol{R}_1 = \int \cdots \int \prod_{j=1}^{M} \mathrm{d}\boldsymbol{R}_j \prod_{j=1}^{M} \left\{\rho^{\mathrm{free}}\left(\boldsymbol{R}_j, \boldsymbol{R}_{j+1}, \tau\right) \exp\left[-\tau V\left(\boldsymbol{R}_j\right)\right]\right\}. \quad (5.19)$$

For distinguishable particles $\boldsymbol{R}_{M+1} \equiv \boldsymbol{R}_1$. Note that eq. (5.19) represents the partition function of a classical system of polymers. Every polymer is a necklake of beads interacting as if they were connected by ideal springs. This harmonic interaction is due to the kinetic density matrix. In the primitive approximation beads with the same imaginary time index j, i.e., belonging to the same time-slice, interact with the inter-particle potential $v(r)$. With higher order approximations one generally introduces effective interparticle interactions. This is the famous mapping of quantum to classical systems introduced by Feynman to describe the properties of superfluid helium. Each quantum particle has been substituted by a classical polymer. The size of polymers is of order $\lambda_T = \sqrt{2\pi\hbar^2\beta/m}$, the de Broglie thermal wave-length, and represents the indetermination on the position of the corresponding quantum particle. In the section 5.1.3 we will see how the indistinguishability of identical particles modifies the 'polymer' description of the quantum many body system.

5.1.1 Analogy inverse temperature – imaginary time

In the previous sections we have shown that the partition function of a quantum system can be decomposed using path-integrals. It is interesting to notice that a path-integral can be regarded as a time-evolution in *imaginary time*. To understand this, let us consider the time-dependent Schrödinger equation:

$$i\hbar\frac{\partial}{\partial t}\phi(\boldsymbol{R},\tau)=\hat{H}\phi(\boldsymbol{R},\tau). \tag{5.20}$$

The Green's function of eq. (5.20) is:

$$G(\boldsymbol{R},\boldsymbol{R}',t)=\left\langle \boldsymbol{R}\left|\exp\left(-it/\hbar\hat{H}\right)\right|\boldsymbol{R}'\right\rangle. \tag{5.21}$$

It is the solution of the Schrödinger equation with the initial condition $\phi\left(\boldsymbol{R},0\right)=\delta\left(\boldsymbol{R}-\boldsymbol{R}'\right)$. It governs the time-evolution of the wave function. In fact, using the Green's function one can write the differential equation (5.20) in the integral form:

$$\phi(\boldsymbol{R},t)=\int G(\boldsymbol{R},\boldsymbol{R}',t)\phi(\boldsymbol{R}',0)\mathrm{d}\boldsymbol{R}'. \tag{5.22}$$

Now, we can notice that eq. (5.21) is analogous to the thermal density matrix (5.6) once one substitutes $\beta\rightarrow it/\hbar$ in eq. (5.6).

5.1.2 Free-particle density matrix

Let us consider a free particle in 1D. The Hamiltonian describing this system is:

$$\hat{H}=-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2}. \tag{5.23}$$

It is easy to determine the thermal density matrix corresponding to this Hamiltonian. We start from the definition:

$$\rho\left(x,x',\beta\right)=\left\langle x\left|\exp\left(-\beta\hat{H}\right)\right|x'\right\rangle; \tag{5.24}$$

We introduce twice the completeness relation $\int\left|p\right\rangle\left\langle p\right|\mathrm{d}p=\boldsymbol{I}$, where $\left|p\right\rangle$ are the eigenstates of the momentum operator:

$$\begin{aligned}\rho\left(x,x',\beta\right)=\int\mathrm{d}p\int\mathrm{d}p'\left\langle x|p\right\rangle\left\langle p\left|\exp\left(-\beta\hat{H}\right)\right|p'\right\rangle\left\langle p'|x'\right\rangle=\\ \frac{1}{2\pi}\int\mathrm{d}p/\hbar\exp\left(i\left(x-x'\right)p/\hbar\right)\exp\left(-\frac{\beta}{2m}p^2\right).\end{aligned} \tag{5.25}$$

Here we have used the expression of the momentum eigenstates is coordinate space $\left\langle x|p\right\rangle=\frac{1}{\sqrt{2\pi\hbar}}\exp\left(ixp/\hbar\right)$, and their orthogonality $\left\langle p|p'\right\rangle=\delta\left(p-p'\right)$. In the last integral in eq. (5.25) we recognize the inverse-Fourier transform of a Gaussian function. The

Fourier transform $F(k)$ of the function $f(x) = \exp\left(-x^2/(4a^2)\right)$ is again a Gaussian function:

$$F(k) = \sqrt{2a}\exp\left(ak^2\right). \tag{5.26}$$

Using this result in eq. (5.25) we obtain that the free-particle density matrix is a Gaussian propagator:

$$\rho\left(x, x', \beta\right) = \sqrt{\frac{m}{2\pi\beta\hbar^2}}\exp\left(-\frac{m}{2\beta\hbar^2}\left(x - x'\right)^2\right). \tag{5.27}$$

5.1.3 Bose symmetry

The expression (5.19) for the partition function is not symmetrical under particle exchange, so it holds for distinguishable particles only. The correct expression for identical particles obeying Bose (Fermi) statistics should be symmetrical (anti-symmetrical) under particle exchange. A convenient way to symmetrize the density matrix (5.18) is to sum over all possible permutations of the particle labels in one of the two arguments:

$$\rho_{\text{Bose}}\left(\boldsymbol{R}_1, \boldsymbol{R}_2, \beta\right) = \frac{1}{N!}\sum_P \rho\left(\boldsymbol{R}_1, \mathbf{P}\boldsymbol{R}_2, \beta\right), \tag{5.28}$$

where $\mathbf{P}$ is one of the $N!$ permutations of the particle labels; this means that $\mathbf{P}\boldsymbol{R} = \left(\boldsymbol{r}^{p(1)}, \boldsymbol{r}^{p(2)}, \ldots, \boldsymbol{r}^{p(N)}\right)$, where $p(i)$, with $i = 1, 2, \ldots, N$, is the particle label in permutation with the i-th particle. If we trace the symmetrized density matrix eq. (5.28) we obtain the partition function for identical Bose particles:

$$Z_{\text{Bose}}\left(N, V, T\right) = \frac{1}{N!}\sum_P \int \cdots \int \prod_{j=1}^{M} \mathrm{d}\boldsymbol{R}_j \prod_{j=1}^{M}\left\{\rho^{\text{free}}\left(\boldsymbol{R}_j, \boldsymbol{R}_{j+1}, \tau\right)\exp\left[-\tau V\left(\boldsymbol{R}_j\right)\right]\right\}, \tag{5.29}$$

with the new boundary condition $\boldsymbol{R}_{M+1} = \mathbf{P}\boldsymbol{R}_1$. As a consequence of symmetrization the necklaces constituting the polymers are not closed on themselves. The last bead of the i-th world line, $\boldsymbol{r}_M^i$, is connected to the first bead of the $p(i)$-th world-line, $\boldsymbol{r}_1^{p(i)}$.
At low temperatures, where the thermal wave-length λ_T is comparable to the average inter-particle distance, large permutations cycles form. These are responsible for macroscopic quantum phenomena such as superfluidity and Bose-Einstein condensation.
An exact evaluation of the $N!$ addends summed in eq.(5.29) becomes soon unfeasible by increasing N. Fortunately, all terms are positive definite, then we can still arrange a Monte Carlo procedure for the evaluation of eq. (5.29). If we considered Fermi particles, an additional '+' or '−' sign would appear in front of each term, the former for even permutations, the latter for odd permutations. A Monte Carlo evaluation of the Fermi partition function would lead to an exponentially small signal to noise ratio going to small T and large N. As a consequence of this *sign problem* the path-integral calculation becomes unfeasible unless one introduces some systematic approximations.

5.1.4 Path sampling methods

In this section we describe the Monte Carlo procedure to sample path-integrals.
One has to set a random walk through configuration space. Let $P(X, X')$ be the probability to jump from configuration X to X'. One can prove that if the transition matrix $P(X, X')$ satisfies the *detailed balance condition*:

$$\pi(X) P(X, X') = \pi(X') P(X', X), \tag{5.30}$$

then the random walk samples points with probability $\pi(X)$.
One very flexible algorithm that satisfies eq. (5.30) is the famous *Metropolis algorithm*. This algorithm is divided in two steps. The first is the proposal of a transition from point X to X' with an arbitrary probability $T(X, X')$. The second consists in an acceptance/rejection stage. The proposal is accepted with the probability defined by:

$$A(X, X') = \min(1, \chi(X, X')), \tag{5.31}$$

where

$$\chi(X, X') = \frac{\pi(X') T(X', X)}{\pi(X) T(X, X')}. \tag{5.32}$$

If, for example, we choose to displace one bead, say $\boldsymbol{r}_j^i$, to another point, call it $\boldsymbol{r}_j^{i\prime}$, that we sample uniformly from a sphere with center in the old position, then one has that $T(X', X) = T(X, X')$ by symmetry and that the probability to accept the move is determined by

$$\chi(X, X') = \frac{\exp\left[-\frac{\left(\boldsymbol{r}_{j-1}^i - \boldsymbol{r}_j^{i\prime}\right)^2 + \left(\boldsymbol{r}_j^{i\prime} - \boldsymbol{r}_{j+1}^i\right)^2}{2\hbar^2\tau/m}\right]}{\exp\left[-\frac{\left(\boldsymbol{r}_{j-1}^i - \boldsymbol{r}_j^i\right)^2 + \left(\boldsymbol{r}_j^i - \boldsymbol{r}_{j+1}^i\right)^2}{2\hbar^2\tau/m}\right]} \exp\left[-\tau\left(V\left(\boldsymbol{R}_j'\right) - V\left(\boldsymbol{R}_j\right)\right)\right]. \tag{5.33}$$

This type of 'single bead' move becomes extremely inefficient when the number of time-slices M increases (*critical slowing down*), so one faces ergodicity problems. To increase efficiency one can implement a direct sampling of the kinetic-energy part of the probability distribution for one bead or for a larger piece of a word-line. There are several algorithms that permit drawing a free-particle path (see references). With this type of move rejections are only determined by inter-particle interactions and/or external potentials.

5.1.5 Calculating properties

The expectation value of any operator $\hat{O}$ associated to a physical observable can be written as a path integral in the following form:

$$\bar{O} \equiv \langle O(X) \rangle \equiv \frac{1}{N!} \sum_P \int O(X) \pi(X, \mathbf{P}) \, \mathrm{d}X. \tag{5.34}$$

The energy per particle E/N of a quantum many body system is the expectation value of the Hamiltonian operator $\hat{H}$ divided by the number of particles N. According to

its thermodynamic definition we can also obtain E/N through a β-derivative of the partition function Z:

$$\frac{E\left(N,V,\beta\right)}{N}=-\frac{1}{NZ}\frac{\partial Z\left(N,V,\beta\right)}{\partial\beta}.$$

If we apply this derivative to the symmetrized partition function defined in eq. (5.29) we obtain the following estimator for the energy per particle (called *thermodynamic estimator*):

$$\frac{E_{\mathrm{th}}}{N}=\left\langle \frac{d}{2\tau}-\frac{m}{2(\hbar\tau)^{2}MN}\sum_{j=1}^{M}\left(\boldsymbol{R}_{j}-\boldsymbol{R}_{j+1}\right)^{2}+\frac{1}{MN}\sum_{j=1}^{M}V\left(\boldsymbol{R}_{j}\right)\right\rangle . \tag{5.35}$$

5.1.6 Useful references

- *A statistical approach to Quantum Mechanics*, by M. Creutz and B. Freedman, Annals of Physics 132 (1981) 427.
- A Java demonstration of Path integral Monte Carlo by A. Santamaria can be found at *http://fisteo12.ific.uv.es/∼santamar/qapplet/metro.html*. Note that the parameters of the quartic potential can be adjusted interactively.
- D. M. Ceperley, Review of Modern Physics **67**, 279 (1995).