

Chapter 5

Quantum Monte Carlo

This chapter is devoted to the study of quantum 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

$$\hat{H} = \hat{T} + \hat{V}; \quad (5.1)$$

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

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

$$\hat{V} = V(\mathbf{R}). \quad (5.3)$$

In these equations \hbar is the Plank's constant divided by 2π , m the particles mass, N the number of particles and the vector $\mathbf{R} \equiv (\mathbf{r}_1, \dots, \mathbf{r}_N)$ 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 $V(\mathbf{R})$ is determined by inter-particle interactions, in which case it can be written as the sum of pair contributions $V(\mathbf{R}) = \sum_{i<j} v(\mathbf{r}_i - \mathbf{r}_j)$, where $v(\mathbf{r})$ is the inter-particle potential; it can also be due to an external field, call it $v_{\text{ext}}(\mathbf{r})$, in which case it is just the sum of single particle contributions $V(\mathbf{R}) = \sum_i v_{\text{ext}}(\mathbf{r}_i)$.

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 $\exp(-\beta\hat{H})$, where $\beta = 1/k_B T$, with k_B the Boltzmann's constant. The expectation value of an observable operator \hat{O} is:

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

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

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

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

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

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

$$Z(N, T, V) = \int \rho(\mathbf{R}, \mathbf{R}, \beta) d\mathbf{R}. \quad (5.7)$$

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

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

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

$$\rho(\mathbf{R}_1, \mathbf{R}_3, \beta_1 + \beta_2) = \int \rho(\mathbf{R}_1, \mathbf{R}_2, \beta_1) \rho(\mathbf{R}_2, \mathbf{R}_3, \beta_2) d\mathbf{R}_2. \quad (5.9)$$

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:

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

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

$$\rho(\mathbf{R}_1, \mathbf{R}_{M+1}, \beta) = \int \cdots \int d\mathbf{R}_2 d\mathbf{R}_3 \cdots d\mathbf{R}_M \rho(\mathbf{R}_1, \mathbf{R}_2, \tau) \rho(\mathbf{R}_2, \mathbf{R}_3, \tau) \cdots \rho(\mathbf{R}_M, \mathbf{R}_{M+1}, \tau). \quad (5.11)$$

Eq. (5.11) is not useful as it is since the density matrices $\rho(\mathbf{R}_j, \mathbf{R}_{j+1}, \tau)$ 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 $\rho(\mathbf{R}_j, \mathbf{R}_{j+1}, \tau)$ 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*):

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

(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:

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

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:

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

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):

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

For later convenience we introduce the following definition:

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

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:

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

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:

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

The Trotter formula guarantees that in the limit $M \rightarrow \infty$ 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 $\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_M$.

Time-slice: the j -th term of a system configuration, indicated with \mathbf{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: $\{\mathbf{r}_1^i, \mathbf{r}_2^i, \dots, \mathbf{r}_j^i, \dots, \mathbf{r}_M^i\}$.

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

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

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

For distinguishable particles $\mathbf{R}_{M+1} \equiv \mathbf{R}_1$. Note that eq. (5.19) represents the partition function of a classical system of polymers. Every polymer is a necklace 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:

$$i\hbar\frac{\partial}{\partial t}\phi(\mathbf{R}, t) = \hat{H}\phi(\mathbf{R}, t). \quad (5.20)$$

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

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

It is the solution of the Schrödinger equation with the initial condition $\phi(\mathbf{R}, 0) = \delta(\mathbf{R} - \mathbf{R}')$. 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:

$$\phi(\mathbf{R}, t) = \int G(\mathbf{R}, \mathbf{R}', t)\phi(\mathbf{R}', 0)d\mathbf{R}'. \quad (5.22)$$

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:

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2}. \quad (5.23)$$

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

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

We introduce twice the completeness relation $\int |p\rangle \langle p| dp = \mathbf{I}$, where $|p\rangle$ are the eigenstates of the momentum operator:

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

Here we have used the expression of the momentum eigenstates in coordinate space $\langle x|p\rangle = \frac{1}{\sqrt{2\pi\hbar}} \exp(ipx/\hbar)$, and their orthogonality $\langle p|p'\rangle = \delta(p-p')$. 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 $f(x) = \exp(-x^2/(4a^2))$ is again a Gaussian function:

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

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

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

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:

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

where \mathbf{P} is one of the $N!$ permutations of the particle labels; this means that $\mathbf{P}\mathbf{R} = (\mathbf{r}^{p(1)}, \mathbf{r}^{p(2)}, \dots, \mathbf{r}^{p(N)})$, where $p(i)$, with $i = 1, 2, \dots, N$, 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:

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

with the new boundary condition $\mathbf{R}_{M+1} = \mathbf{P}\mathbf{R}_1$. As a consequence of symmetrization the necklaces constituting the polymers are not closed on themselves. The last bead of the i -th world line, \mathbf{r}_M^i , is connected to the first bead of the $p(i)$ -th world-line, $\mathbf{r}_1^{p(i)}$.

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*:

$$\pi(X) P(X, X') = \pi(X') P(X', X), \quad (5.30)$$

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:

$$A(X, X') = \min(1, \chi(X, X')), \quad (5.31)$$

where

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

If, for example, we choose to displace one bead, say \mathbf{r}_j^i , to another point, call it $\mathbf{r}_j^{i'}$, 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

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

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 world-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:

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

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 :

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

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*):

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

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).

5.2 Diffusion Monte Carlo

Diffusion Monte Carlo (DMC) is a tool to study the ground-state properties of quantum systems. This means that using DMC one can simulate many-body systems at zero temperature. When applied to bosons, DMC provides the exact result for the ground-state energy and for other diagonal properties. By introducing some approximation, one can also treat fermionic systems. One approximation which has proven to be reliable is the so-called *fixed-node approximation*. Similarly, one can extend DMC to study excited states.

DMC is based on the solution of the time-dependent Schrödinger equation written in imaginary time:

$$-\frac{\partial}{\partial \beta} \phi(\mathbf{R}, \beta) = \hat{H} \phi(\mathbf{R}, \beta), \quad (5.36)$$

where $\beta = it/\hbar$. The formal solution of eq. (5.36) is:

$$\phi(\mathbf{R}, \beta) = \exp(-\beta \hat{H}) \phi(\mathbf{R}, 0). \quad (5.37)$$

Let us expand $\phi(\mathbf{R}, \beta)$ on the basis of the eigenstates $\phi_n(\mathbf{R}, \beta)$:

$$\phi(\mathbf{R}, \beta) = \sum_{n=0}^{\infty} c_n \phi_n(\mathbf{R}, \beta) = \sum_{n=0}^{\infty} c_n \phi_n(\mathbf{R}) \exp(-E_n \beta). \quad (5.38)$$

The states ϕ_n are the solution of the time independent Schrödinger equation $\hat{H}\phi_n = E_n\phi_n$ with eigenvalues E_n . We order them in such a way that E_n monotonically increases with the quantum number n . In the long time limit $\beta \rightarrow \infty$ eq. (5.38) reduces to:

$$\phi(\mathbf{R}, \beta) \approx c_0\phi_0(\mathbf{R}) \exp(-E_0\beta). \quad (5.39)$$

In other words, the contribution of the ground state dominates the sum in eq. (5.38). States with $n \neq 0$ decay exponentially faster. In the following we will see that by introducing an energy shift we can obtain a normalized wave function.

In the case of Bose systems at zero temperature one can assume, without loss of generality, that $\phi_0(\mathbf{R})$ is real and positive definite¹. Fermi systems and excited states of bosons will be addressed in subsection 5.2.2.

Let us introduce the Green's function of eq. (5.36):

$$\rho(\mathbf{R}, \mathbf{R}', \beta) = \left\langle \mathbf{R} \left| \exp\left(-\beta\hat{H}\right) \right| \mathbf{R}' \right\rangle. \quad (5.40)$$

Notice that $\rho(\mathbf{R}, \mathbf{R}', \beta)$ is equal to the thermal density matrix (5.6). The Green's function permits to write the eq. (5.36) in the integral form:

$$\phi(\mathbf{R}, \beta) = \int \rho(\mathbf{R}, \mathbf{R}', \beta)\phi(\mathbf{R}', 0)d\mathbf{R}'. \quad (5.41)$$

This integral equation may be interpreted as a diffusion process guided by $\rho(\mathbf{R}, \mathbf{R}', \beta)$ from the initial state $\phi(\mathbf{R}', 0)$ to the final state $\phi(\mathbf{R}, \beta)$ at time β .

The evolution during the long time interval β can be generated repeating a large number of short time-steps τ . In the limit $\tau \rightarrow 0$, one can make use of the *primitive approximation* (see section 5.1):

$$\rho(\mathbf{R}_1, \mathbf{R}_3, \tau) \approx \left(\frac{m}{2\pi\hbar^2\tau}\right)^{dN/2} \exp\left[-\frac{(\mathbf{R}_1 - \mathbf{R}_2)^2}{2\hbar^2\tau/m}\right] \exp[-\tau V(\mathbf{R}_2)] \delta(\mathbf{R}_2 - \mathbf{R}_3). \quad (5.42)$$

In a DMC simulation, one treats $\phi(\mathbf{R}, \beta)$ as the density distribution of a large ensemble of equivalent copies of the many-body system, usually called *walkers*. The simulation starts with an arbitrary initial distribution. The population of walkers diffuses according to the Green's function (5.42). The first term corresponds to a free-particle diffusion, which can be implemented by adding to \mathbf{R}_1 a vector whose components are sampled from a gaussian distribution. The second term in eq. (5.42), instead, does not cause displacement of particles. It only determines a change in the probability density. This effect, usually called *branching*, can be implemented by allowing variations in the number of walkers. We have to assign to each walker a number of descendant n_d proportional to the weight $\exp[-\tau(V(\mathbf{R}_2) - E)]$. Notice that we have included the energy shift E , which serves to normalize the density distribution. One could simply set n_d to be equal to the integer number which is closest to w . However, this discretization of the weight w would result in a considerable loss of information. A much more efficient procedure is obtained by calculating n_d according to the following rule:

$$n_d = \text{int}(w + \eta), \quad (5.43)$$

¹If a magnetic field is present the wave function must have an imaginary part also.

where η is a uniform random variable in the range $[0, 1]$, and the function $\text{int}()$ takes the integer part of the argument. In this way one makes use of the full information contained in the signal w . If $n_d > 1$, one has to create $n_d - 1$ identical copies of the walker and include them in the total population. If $n_d = 0$, one has to erase the current walker from the population. The parameter E acts as a normalization factor. It must be adjusted during the simulation in order to maintain the total number of walkers close to an average value, call it n_{ave} . This is an algorithm parameter which has to be optimized. For small values of n_{ave} one has systematic deviations from the exact results. On the other hand, large values of n_{ave} result in computationally demanding simulations.

If we generate a long random walk performing sequentially the two types of update that we have described, the asymptotic distribution $\phi(\mathbf{R}, \beta \rightarrow \infty)$ converges to the exact ground state $\phi_0(\mathbf{R})$.

5.2.1 Importance Sampling

The algorithm described in the previous subsection is extremely inefficient for large particle numbers, especially if the inter-particle interaction is not smooth. The efficiency can be enormously enhanced by using the *importance sampling* technique. To implement this method one has to design a *trial wave function*, call it ϕ_{T} , that approximately describes the exact ground-state ϕ_0 . For example, in the case of homogeneous liquid or gases an accurate approximation of the ground-state is given by the *Jastrow wave function*:

$$\phi_{\text{J}}(\mathbf{R}) = \prod_{i < j} f_2(|\mathbf{r}_i - \mathbf{r}_j|), \quad (5.44)$$

where the function $f_2(r)$ describes the direct correlation between particles i and j . In dilute systems, like ultracold gases, it can be set equal to the solution of the two-body problem for the relative motion of the pair.

One then solves the modified Schrödinger equation (in imaginary time) for the product $f(\mathbf{R}, \beta) = \phi_{\text{T}}(\mathbf{R})\phi(\mathbf{R}, \beta)$:

$$-\frac{\partial}{\partial \beta} f(\mathbf{R}, \beta) = -\frac{\hbar^2}{2m} \Delta f(\mathbf{R}, \beta) + \frac{\hbar^2}{2m} \nabla (\mathbf{F} f(\mathbf{R}, \beta)) + (E_{\text{loc}}(\mathbf{R}) - E) f(\mathbf{R}, \beta), \quad (5.45)$$

where $\mathbf{F} = \frac{2\nabla \phi_{\text{T}}(\mathbf{R})}{\phi_{\text{T}}(\mathbf{R})}$ is called *pseudo force* and the *local energy* $E_{\text{loc}}(\mathbf{R})$ is defined by:

$$E_{\text{loc}}(\mathbf{R}) = \frac{\hat{H} \phi_{\text{T}}(\mathbf{R})}{\phi_{\text{T}}(\mathbf{R})}. \quad (5.46)$$

The function $f(\mathbf{R}, \beta)$ is interpreted as density distribution of the population of walkers. In the long time limit it converges to the product $\phi_{\text{T}}(\mathbf{R})\phi_0(\mathbf{R})$. It is easy to see that the average of the local energy (5.46) is equal to the ground-state energy. Instead, for observable operators that do not commute with the Hamiltonian, one obtains the *mixed estimator* $\langle \phi_0 | \hat{O} | \phi_{\text{T}} \rangle / \langle \phi_0 | \phi_{\text{T}} \rangle$.²

²For diagonal operators, one can implement exact estimators using the *forward walking* technique (see references).

The diffusion process that solves eq. (5.45) is similar to the one described above. The free-particle diffusion must be implemented in the same way. Between this free-particle diffusion and the branching term, one must introduce an additional update which consists in a drift of particle coordinates guided by the pseudo-force \mathbf{F} :

$$\mathbf{R}_2 = \mathbf{R}_1 + \frac{\hbar^2 \tau}{2m} \mathbf{F}(\mathbf{R}_1). \quad (5.47)$$

This drift guides the walkers in regions with high probability. The branching term has to be implemented similarly to what described before, but substituting the local energy $E_{\text{loc}}(\mathbf{R})$ to the bare potential $V(\mathbf{R})$. In fact, with an accurate choice of the trial wave function ϕ_{T} , the local energy has small fluctuations. This permits to stabilize the populations of walkers, which, if no importance sampling was implemented, would instead oscillate widely rendering the simulation unfeasible.

5.2.2 Fixed Node Diffusion Monte Carlo

The conclusion that the DMC algorithm samples, after long times, a density distribution proportional to the exact ground state ϕ_0 , is based on the hypothesis that ϕ_0 and ψ_{T} are not orthogonal. If, instead, they are orthogonal, the asymptotic distribution is proportional to the lowest excited state ϕ_1 not orthogonal to ψ_{T} . This property is often used to simulate excited states of bosons or the ground state of fermions, which can be considered as the first fully antisymmetric eigenstate of the Hamiltonian. Having to deal with non-positive definite wave functions introduces the well known *sign problem*. Several procedures exist to circumvent this pathology. Here we describe the *fixed-node* approximation. This approximation consists in forcing the ground state of the Fermi system ϕ_{F} to have the same nodal structure as the trial wave function. It is evident that, if ϕ_{F} and ψ_{T} change sign together, the probability distribution is always positive. It can be proven that the fixed-node constraint provides an upper bound to the ground-state energy of fermions. In particular, if the nodes of ψ_{T} were exact, the FNDMC would provide the exact ground-state energy. In a DMC simulation, the nodal constraint on ϕ_{F} corresponds to forcing the walkers not to cross the nodal surface.

Just to show an example, we describe now one type of antisymmetric trial wave function which has proven to capture the essential properties of several Fermi systems in the homogeneous normal phase. This is the so-called *Jastrow-Slater* wave function. If we consider a spin-polarized system (all fermions have the same spin-projection) in a box of size L with periodic boundary conditions, the Jastrow-Slater wave function ϕ_{JS} is the product of a Jastrow factor (5.44) and a Slater determinant of plane waves:

$$\phi_{\text{JS}}(\mathbf{R}) = \phi_{\text{J}}(\mathbf{R}) \text{Det}_{\alpha,n} [\exp(i\mathbf{k}_{\alpha} \cdot \mathbf{r}_n)], \quad (5.48)$$

where the index $n = 1, \dots, N$ labels particles and \mathbf{k}_{α} are the wave vectors compatible with periodic boundary conditions.

Techniques to go beyond the fixed-node approximation exist, but they have not proven to be robust. The sign problem has to be considered still unsolved.

5.2.3 Useful references

- J. Boronat, in *Microscopic approaches to quantum liquids in confined geometries*, chapter 2, ed. by E. Krotscheck and J. Navarro, World Scientific (2002).
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- I. Kosztin, B. Faber and K. Schulten, *Introduction to the Diffusion Monte Carlo Method*, arXiv:physics/9702023.
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Chapter 6

Electronic structure of molecules and atoms

6.1 Introduction

In this chapter we will discuss the arguably most important quantum many body problem – the electronic structure problem – relevant for almost all properties of matter relevant in our daily life. With $O(10^{23})$ atoms in a typical piece of matter, the exponential scaling of the Hilbert space dimension with the number of particles is a nightmare. In this chapter we will discuss first the exact solution by exact diagonalization of simplified effective models, and then approximate methods that reduce the problem to a polynomial one, typically scaling like $O(N^4)$ and even $O(N)$ in modern codes that aim for a sparse matrix structure. These methods map the problem to a single-particle problem and work only as long as correlations between electrons are weak.

This enormous reduction in complexity is however paid for by a crude approximation of electron correlation effects. This is acceptable for normal metals, band insulators and semi-conductors but fails in materials with strong electron correlations, such as almost all transition metal compounds.

6.2 The electronic structure problem

For many atoms (with the notable exception of Hydrogen and Helium which are so light that quantum effects are important in daily life), the nuclei of atoms are so much heavier than the electrons that we can view them as classical particles and can consider them as stationary for the purpose of calculating the properties of the electrons. Using this Born-Oppenheimer approximation the Hamiltonian operator for the electrons becomes

$$H = \sum_{i=1}^N \left(-\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}_i) \right) + e^2 \sum_{i < j} \frac{1}{|\vec{r}_i - \vec{r}_j|} \quad (6.1)$$

where the potential of the M atomic nuclei with charges Z_i at the locations \vec{R}_i is given by

$$V(\vec{r}) = -e^2 \sum_{i=1}^M \frac{Z_i}{|\vec{R}_i - \vec{r}|}. \quad (6.2)$$

The Car-Parinello method for molecular dynamics, which we will discuss later, moves the nuclei classically according to electronic forces that are calculated quantum mechanically.

Using a basis set of L orbital wave functions $\{f_i\}$, the matrix elements of the Hamilton operator (6.1) are

$$t_{ij} = \int d^3\vec{r} f_i^*(\vec{r}) \left(\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) \right) f_j(\vec{r}) \quad (6.3)$$

$$V_{ijkl} = e^2 \int d^3\vec{r} \int d^3\vec{r}' f_i^*(\vec{r}) f_j(\vec{r}) \frac{1}{|\vec{r} - \vec{r}'|} f_k^*(\vec{r}') f_l(\vec{r}') \quad (6.4)$$

and the Hamilton operator can be written in second quantized notation as

$$H = \sum_{ij\sigma} t_{ij} a_{i\sigma}^\dagger a_{j\sigma} + \frac{1}{2} \sum_{ijkl\sigma\sigma'} V_{ijkl} a_{i\sigma}^\dagger a_{k\sigma'}^\dagger a_{l\sigma'} a_{j\sigma}. \quad (6.5)$$

6.3 Basis functions

Before attempting to solve the many body problem we will discuss basis sets for single particle wave functions.

6.3.1 The electron gas

For the free electron gas with Hamilton operator

$$H = - \sum_{i=1}^N \frac{\hbar^2}{2m} \nabla^2 + e^2 \sum_{i<j} v_{ee}(\vec{r}_i, \vec{r}_j) \quad (6.6)$$

$$v_{ee}(\vec{r}, \vec{r}') = \frac{1}{|\vec{r} - \vec{r}'|} \quad (6.7)$$

the ideal choice for basis functions are plane waves

$$\psi_{\vec{k}}(\vec{r}) = \exp(-i\vec{k}\vec{r}). \quad (6.8)$$

Such plane wave basis functions are also commonly used for band structure calculations of periodic crystals.

At low temperatures the electron gas forms a Wigner crystal. Then a better choice of basis functions are eigenfunctions of harmonic oscillators centered around the classical equilibrium positions.

6.3.2 Atoms and molecules

Which functions should be used as basis functions for atoms and molecules? We can let ourselves be guided by the exact solution of the Hydrogen atom and use the so-called **Slater-Type-Orbitals** (STO):

$$f_{inlm}(r, \theta, \phi) \propto r^{n-1} e^{-\zeta_i r} Y_{lm}(\theta, \phi). \quad (6.9)$$

These wave functions have the correct asymptotic radial dependence and the correct angular dependence. The values ζ_i are optimized so that the eigenstates of isolated atoms are reproduced as accurately as possible.

The main disadvantage of the STOs becomes apparent when trying to evaluate the matrix elements in equation (6.4) for basis functions centered around two different nuclei at position \vec{R}_A and \vec{R}_B . There we have to evaluate integrals containing terms like

$$\frac{1}{|\vec{r} - \vec{r}'|} e^{-\zeta_i |\vec{r} - \vec{R}_A|} e^{-\zeta_j |\vec{r} - \vec{R}_B|} \quad (6.10)$$

which cannot be solved in any closed form.

The **Gauss-Type-Orbitals** (GTO)

$$f_{ilmn}(\vec{r}) \propto x^l y^m z^n e^{-\zeta_i r^2} \quad (6.11)$$

simplify the evaluation of matrix elements, as Gaussian functions can be integrated easily and the product of Gaussian functions centered at two different nuclei is again a single Gaussian function:

$$e^{-\zeta_i |\vec{r} - \vec{R}_A|^2} e^{-\zeta_j |\vec{r} - \vec{R}_B|^2} = K e^{-\zeta |\vec{r} - \vec{R}|^2} \quad (6.12)$$

with

$$K = e^{-\frac{\zeta_i \zeta_j}{\zeta_i + \zeta_j} |\vec{R}_A - \vec{R}_B|^2} \quad (6.13)$$

$$\zeta = \zeta_i + \zeta_j \quad (6.14)$$

$$\vec{R} = \frac{\zeta_i \vec{R}_A + \zeta_j \vec{R}_B}{\zeta_i + \zeta_j} \quad (6.15)$$

Also the term $\frac{1}{|\vec{r} - \vec{r}'|}$ can be rewritten as an integral over a Gaussian function

$$\frac{1}{|\vec{r} - \vec{r}'|} = \frac{2}{\sqrt{\pi}} \int_0^\infty dt e^{-t^2 (\vec{r} - \vec{r}')^2}. \quad (6.16)$$

and thus all the integrals (6.4) reduce to purely Gaussian integrals which can be performed analytically.

As there are $O(L^4)$ integrals of the type (6.4), quantum chemistry calculations typically scale as $O(N^4)$. Modern methods can be used to reduce the effort to an approximately $O(N)$ method, since the overlap of basis functions at large distances becomes negligibly small.

Independent of whether one chooses STOs or GTOs, extra care must be taken to account for the non-orthogonality of these basis functions.