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Auxiliary Field Quantum Monte Carlo method for the electronic ground state problem: application to H_2 molecule

Thesis submitted for the degree of

"Magister Philosophiæ"

CANDIDATE

Pier Luigi Silvestrelli

SUPERVISORS

Prof. Stefano Baroni

Prof. Roberto Car

October 1990

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Introduction

A reliable solution of the electronic structure problem, i.e. the quantum many-body problem of interacting electrons is a very important goal in several areas of science. For instance, accurate calculations of molecular properties such as binding energies, bond lengths, charge distributions and potential energy surfaces are essential in *Quantum Chemistry* for both basic scientific understanding and technological applications.

In *Condensed Matter Physics* a suitable treatment of many-body effects is a crucial achievement especially for studying the new high-temperature superconductors[1] and other strongly correlated systems such as Mott-Hubbard insulators[2] and heavy fermion metals[3].

In order to achieve this result one must accurately compute particle correlation, a very hard task when realistic and truly interesting systems are considered. For a many-electron system the *correlation energy* is defined as the difference between the Hartree-Fock energy, that is the energy obtained when each electron is considered as moving in the average field of the remaining $(N-1)$ electrons with Pauli principle taken into account, and the exact non-relativistic energy. We must point out that the correlation energy contribution is usually very small. For example in molecular systems it is typically of the order of 1%. Therefore if one is only interested in the total molecular energy, then correlation represents a slight correction. However it has an important effect on the calculation of properties like molecular binding energies which are often characterized by an energy scale of only a fraction of the correlation energy; for instance the O-H bond strength in water is about 50% of the molecular correlation energy. In these cases if correlation is not

taken into account wrong results may be obtained even for qualitative predictions.

In the recent years computer power greatly increased and, therefore, this opened the possibility to attack the problem by numerical calculation. In this context various techniques are applied.

The *exact techniques* (full Configuration Interaction[4], Many-Body Perturbation theory[5]...) aim at evaluating the exact ground state of a given hamiltonian $\hat{H}$. In practice, however, these methods are only applicable to systems with a small number of electrons since the number of degrees of freedom of a real many body wave function grows exponentially with the size of the system and the number of electrons.

Obviously a lot of *approximate techniques* exist. We can mention the variational procedures like Hartree, Hartree-Fock[6], and Jastrow[7], the Random Phase Approximation[8] in many-body perturbation theory, and naturally the Local Density Approximation (LDA)[9], which is a very convenient and popular approximation of the well known Density Functional Theory[10,11].

Unfortunately all these approximations are difficult to control and to improve systematically: for example the variational techniques are too much dependent on (and consequently their results largely prejudiced by) the choice of the form of the variational wave function, since only a small number of parameters can practically be varied in order to minimize the ground state estimated energy.

Current approximation methods have costs ranging from the third power to the 7^{th} power of the number of electrons and, therefore, they are still rather cumbersome. For instance the Hartree-Fock method, which is pursued heavily by quantum chemists, is already expensive enough even though it completely neglects correlation.

The Density Functional methods are largely used by condensed matter physi-

cists and are distinguished from the Quantum Chemistry methods by their applicability to large systems (hundreds of electrons with present computing capabilities). However the Density Functional approach is, in practice, implemented by assuming that the exchange-correlation energy density depends locally on the electron density (LDA), and, even though the incorrect character of this assumption is evident, no genuine and really efficient improvement has been developed till now in the DFT framework.

Another group of methods, the *stochastic techniques*, simulate quantum systems and calculate their ground state properties by using classical statistical methods: these techniques are generally called Quantum Monte Carlo methods[12–19]. They are of both the *variational* type in which the Monte Carlo method is used to numerically evaluate expectation values obtained from a given (generally optimized) trial wave function ψ_T, and of the *exact* type in which the Schrödinger equation is solved. In these latter approaches various procedures are used to stochastically sample the exact wave function of the physical system, subject only to statistical errors. Properties of interest are in effect "measured" as the system evolves under the Schrödinger equation. When a stationary state is obtained, averages of the measured quantities provide the desired expectation values.

Monte Carlo algorithms are very promising because they treat correlation effects, either approximately or exactly at a numerical cost having a size dependence similar to that of single-particle approaches (like Hartree or Hartree-Fock). However the proper inclusion of the Pauli principle is a major difficulty in the exact QMC methods. This is basically because the many-body wave function is usually described by a statistically evolving ensemble of configurations (specified by the coordinates of each particle). The Pauli principle, which enforces a spatially nonlocal relation between configurations which differ by the interchange of a pair of

fermionic particles, is thus difficult to implement in the simple local algorithms used to evolve the ensemble.

A particular Quantum Monte Carlo method is performed by introducing auxiliary fields and was successfully used by Scalapino et al.[27,28] to investigate finite temperature properties in the Hubbard model. It was recently suggested as an alternative method of approaching the ground state electronic problem by Sugyiama and Koonin[20]. In this technique, which was pursued by Sorella et al. [21,22] and we use in our thesis, the *Hubbard-Stratonovich Transformation* [23,24](HST) is applied.

The ground state ψ_0 of the hamiltonian $\hat{H}$ is obtained by filtering out from an initial trial wave function ψ_T its ground state component by applying to ψ_T the imaginary time propagator $e^{-\beta\hat{H}}$ for large enough time β.

In fact if $\hat{H}\psi_i = E_i\psi_i$ the exponential decay of the amplitude of higher energy states in the imaginary time evolution:

$$\lim_{\beta\to\infty} e^{-\beta\hat{H}}\psi_T = \lim_{\beta\to\infty} \sum_i e^{-\beta E_i}\psi_i \langle\psi_i|\psi_T\rangle = e^{-\beta E_0}\psi_0 \langle\psi_0|\psi_T\rangle \propto \psi_0$$

leaves only the lowest state ψ_0 in the infinite β limit, provided that $\langle\psi_0|\psi_T\rangle \neq 0$.

The HST of the propagator $e^{-t\hat{H}}$ introduces an *auxiliary field* σ to reduce the exponential of a *two-body* operator to a functional integral over an infinite set of exponentials of *one-body* operators. In fact the imaginary time evolution $e^{-t\hat{H}}$ is convenient for numerical treatment when the hamiltonian contains only one-body operators and no interaction term.

In practice HST transforms the many-body problem in a functional integral over the variables σ, since the two particle interaction term in $\hat{H}$ is replaced by one particle interactions with a set of random time-varying auxiliary fields; integration over a Gaussian distribution of these fields restores the physical interaction.

After a suitable discretization the functional integral can be evaluated numerically by statistical methods (Monte Carlo, Langevin Dynamics, Hybrid Molecular

Dynamics-Monte Carlo techniques,...). Therefore this approach is especially suitable for lattice models. In fact, until now, the auxiliary field formulation has been used extensively to study electron correlations in the Hubbard model[25-30].

In comparison with other Quantum Monte Carlo techniques, this new method could be attractive for condensed matter physics applications essentially (see Chap. 1 for details) because (i) it allows an easier application of the widely used one-body techniques, (ii) antisymmetrization for electrons can be enforced exactly and (iii) the famous "fermion sign problem", which is one of the main difficulty in fermionic many-body calculations, could become less troublesome.

In this thesis, for the first time, the Auxiliary Field Quantum Monte Carlo (AFQMC) method is applied to continuous, physically realistic systems, in particular to the Hydrogen molecule H_2. Here the "fermion sign problem" is not important since the exact ground state wave function is nodeless in coordinate space, nevertheless the generalization from a simple and schematic Hubbard model to a molecular system with a continuous Coulomb potential r^{-1} is, in itself, a non trivial task and even a fundamental step towards a large application of this technique to more interesting and complex physical systems.

In particular we show that application of the AFQMC technique to an ultrasimplified (low energy cutoff) H_2 molecule, where comparison with exact diagonalization results is possible, can be successfully performed. In preliminary applications to a realistic H_2 molecule a new difficulty was found, probably related to the short wavelength fluctuations of the auxiliary fields. At the moment this problem does not seem an insuperable obstacle, provided that an improved version of our algorithm is developed, but we must stress that a satisfactory solution of this difficulty appears to be crucial for any subsequent application of this method to continuous systems.

The outline of this thesis is the following:

In Chap. 1 some of the most popular QMC methods, Variational Monte Carlo (VMC), Green's Function Monte Carlo (GFMC) and Diffusion Monte Carlo (DMC) are reviewed. Then the HST formalism is presented in general terms, with the introduction of auxiliary fields and some arguments are advanced about the potential advantages of the AFQMC method in comparison with other stochastic approaches.

In Chap. 2 this technique is specifically developed in a way suitable to our particular problem with a continuous repulsive potential which determines electron-electron correlation.

Chap. 3 contains a brief discussion about the methods one can adopt in order to perform the functional integral by efficiently sampling the auxiliary fields.

In Chap. 4 we give a concise but exhaustive enough description of many numerical tests performed, together with all technical improvements and tricks we have developed in order to make the method really efficient and practically applicable. Finally the serious fluctuation problem is illustrated and briefly discussed.

Chapter 1

Stochastic methods for the fermionic ground state problem.

1.1 Variational Monte Carlo

The variational method has proved to be a very useful way of computing ground state properties of many-body systems. Conceptually it is quite simple. The variational principle tells us that, for any many-body function $\psi_T(\mathbf{R})$ (here $\mathbf{R} = \{\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N\}$ refers to the coordinates of the N particles), the variational energy E_T defined as:

$$E_T = \frac{\int d\mathbf{R}\psi_T(\mathbf{R})\hat{H}\psi_T(\mathbf{R})}{\int d\mathbf{R}|\psi_T(\mathbf{R})|^2} \tag{1.1.1}$$

will be a minimum when ψ_T is the ground state solution of the Schrödinger equation $\hat{H}\psi_0 = E_0\psi_0$. The variational method then consists of constructing a family of functions $\psi_T(\mathbf{R}, \mathrm{a})$ and optimizing the parameters a so that the energy (1.1.1) is minimized for $\mathrm{a} = \mathrm{a}_0$. The variational energy is a rigorous upper bound to the ground state energy and, if the family of functions was chosen well, then $\psi_T(\mathbf{R}, \mathrm{a}_0)$ will be a good approximation to the ground state wave function.

For example for Fermi liquids the following form for the trial wave function is widely used. It was introduced by Jastrow et al.[7,31,32] who generalize an expression originally developed by Bijl as a good trial function for a Bose liquid

at zero temperature:

$$\psi_T(\mathbf{R}) = \psi_D(\mathbf{R}) \prod_{\alpha\neq\beta} f(|\mathbf{r}_\alpha - \mathbf{r}_\beta|) = \psi_D(\mathbf{R}) e^{-\frac{1}{2}\sum_{\alpha\neq\beta} J(|\mathbf{r}_\alpha - \mathbf{r}_\beta|)} \tag{1.1.2}$$

where $\psi_D(\mathbf{R})$, the ideal Fermi gas wave function, i.e. a determinant of plane waves, is multiplied by a product of two particle correlation functions $f(|\mathbf{r}_\alpha - \mathbf{r}_\beta|)$. We note that the square of the term $e^{-\frac{1}{2}\sum_{\alpha\neq\beta} J(|\mathbf{r}_\alpha - \mathbf{r}_\beta|)}$ is completely equivalent to the Boltzmann distribution of a classical system with $J(r)$ replaced by particle-particle interaction potential over $K_B T$. However, in contrast to the classical situation, now the "potential" $J(r)$ is varied to minimize the energy in (1.1.1). In practice $J(r)$ is chosen to have some functional form with several free parameters which are then varied.

Optimization of a Jastrow wave function (1.1.2) by variational methods often produces a good approximation for ground state wave functions. In practice the main task is to evaluate multidimensional integrals to get expectation values and, in particular, to calculate the variational energy (1.1.1).

The Monte Carlo algorithm [33], which was invented to calculate properties of classical statistical systems, is an extremely powerful way to compute multi-dimensional integrals. In particular, for quantum systems, an algorithm which produces configurations with a probability proportional to the square of the wave function, is required. Then any measurable quantity can be written as an average over such configurations. Let us suppose $\hat{O}$ is an operator and we wish to compute its expectation value defined as

$$\left\langle \hat{O} \right\rangle = \frac{\int d\mathbf{R} \psi_T(\mathbf{R}) \hat{O} \psi_T(\mathbf{R})}{\int d\mathbf{R} |\psi_T(\mathbf{R})|^2}. \tag{1.1.3}$$

Let $\mathbf{R}_i$ be a set of points drawn from the probability distribution:

$$p(\mathbf{R}) = \frac{|\psi_T(\mathbf{R})|^2}{\int d\mathbf{R} |\psi_T(\mathbf{R})|^2} \tag{1.1.4}$$

where the integral in the denominator serves here merely to normalize $p(\mathbf{R})$. Then, for any function $f(\mathbf{R})$, the central limit theorem[34] of probability gives that:

$$\lim_{M\to\infty} \frac{1}{M} \sum_{i=1}^{M} f(\mathbf{R}_i) = \frac{\int d\mathbf{R} f(\mathbf{R}) |\psi_T(\mathbf{R})|^2}{\int d\mathbf{R} |\psi_T(\mathbf{R})|^2} \tag{1.1.5}$$

and in particular:

$$\lim_{M\to\infty} \frac{1}{M} \sum_{i=1}^{M} \psi_T^{-1}(\mathbf{R}_i) O(\mathbf{R}_i) \psi_T(\mathbf{R}_i) = \left\langle \hat{O} \right\rangle . \tag{1.1.6}$$

If $\hat{O} = \hat{H}$ then

$$\left\langle \hat{H} \right\rangle = \lim_{M\to\infty} \frac{1}{M} \sum_{i=1}^{M} E_L(\mathbf{R}_i) \tag{1.1.7}$$

where we have introduced the so-called "local energy": $E_L(\mathbf{R}_i) \equiv \hat{H}\psi_T/\psi_T$. We observe that a good approximate trial function, containing whatever information is known about the exact wave function, yields averages with low statistical uncertainties. In fact if ψ_T is a good approximation to ψ_0, then $E_L(\mathbf{R}) \to E_0$, that is it becomes nearly independent of $\mathbf{R}$.

The Monte Carlo algorithm is a biased random walk in configuration space; as usually carried out each particle is moved one after another to a new position. That move is either accepted or rejected depending on the magnitude of the trial function at the *new* position $\mathbf{R}'$ compared with the *old* position $\mathbf{R}$: if $|\psi_T(\mathbf{R}')|^2 \geq |\psi_T(\mathbf{R})|^2$ the new point $\mathbf{R}'$ is accepted. Otherwise it is accepted with a probability q given by:

$$q = \frac{|\psi_T(\mathbf{R}')|^2}{|\psi_T(\mathbf{R})|^2}. \tag{1.1.8}$$

In general the VMC algorithm[13,35,36] is very simple to program and test, and follows very closely a Monte Carlo simulation of a classical system.

1.2 Diffusion and Green's Function Monte Carlo

The exact Quantum Monte Carlo approach basically aims at evaluating ground state properties by performing the imaginary time propagation $e^{-\beta\hat{H}}\psi_T$. This can be obtained in different ways.

The *Diffusion Monte Carlo* (DMC)[17–19] method uses the time-dependent Schrödinger equation:

$$i\frac{\partial\psi}{\partial t} = \left[-\frac{1}{2}\nabla^2 + V(\mathbf{R})\right]\psi = \hat{H}\psi \tag{1.2.1}$$

where a.u. are used and $V(\mathbf{R})$ is the potential energy of the system. Eq. (1.2.1) can be represented in imaginary time ($\tau \equiv it$):

$$-\frac{\partial\psi}{\partial\tau} = \left[-D\nabla^2 + V(\mathbf{R}) - E_T\right]\psi \tag{1.2.2}$$

with $D = 1/2$ and a constant energy offset, E_T, was introduced for convenience to alter the zero of energy without affecting the properties calculated from the solution of the Schrödinger equation.

Eq. (1.2.2) has real solutions of the form:

$$\psi(\mathbf{R},\tau) = \sum_\alpha \phi_\alpha(\mathbf{R})e^{-(E_\alpha - E_T)\tau}. \tag{1.2.3}$$

So, for positive real τ, the decaying exponential causes the states with the larger eigenvalues to decay away, leaving only the state with the smallest eigenvalue, after long τ (see also Introduction).

To implement *importance sampling*[15], an essential technique used to improve the statistical accuracy of the simulation, the exact wave function is multiplied by a trial wave function ϕ_T to obtain a new function f:

$$f(\mathbf{R},\tau) \equiv \phi_T(\mathbf{R})\psi(\mathbf{R},\tau). \tag{1.2.4}$$

Substituting f/ϕ_T for ψ in eq. (1.2.2), we obtain the following Fokker-Planck equation for $f(\mathbf{R},\tau)$:

$$-\frac{\partial f}{\partial \tau} = -D\nabla^2 f + (E_L(\mathbf{R}) - E_T) f + D\nabla\left[f\mathbf{F}_Q(\mathbf{R})\right] \tag{1.2.5}$$

where $E_L(\mathbf{R}) \equiv \hat{H}\phi_T/\phi_T$ is the local energy obtained from the trial function, and

$$\mathbf{F}_Q(\mathbf{R}) \equiv \nabla \ln |\phi_T(\mathbf{R})|^2 = \frac{2\nabla\phi_T(\mathbf{R})}{\phi_T(\mathbf{R})} \tag{1.2.6}$$

plays the role of a "quantum force".

The terms on the R.H.S of eq. (1.2.5) may be identified as a *diffusion* term, a *source/sink* term and an *advection* term, respectively. As usual, the Monte Carlo simulation of the Fokker-Planck eq. (1.2.5) is carried out by representing the "density" f by particles that take random steps to simulate the diffusion, take directed steps to simulate the advection (the quantum force pushes the particles toward regions of higher importance, that is higher ϕ_T), and are multiplied or eliminated to model sources and sinks.

The asymptotic solution to eq. (1.2.5) is:

$$f(\mathbf{R},\tau) = \phi_T(\mathbf{R})\psi_0(\mathbf{R},\tau)\, e^{-(E_0 - E_T)\tau}. \tag{1.2.7}$$

Then the ground state energy may be calculated[18] by using, at large imaginary times, the average value of the local energy:

$$\left\langle \hat{H} \right\rangle \equiv E_0 = \lim_{\beta\to\infty} \frac{\int d\mathbf{R} f(\mathbf{R},\beta)\, E_L(\mathbf{R})}{\int d\mathbf{R} f(\mathbf{R},\beta)} = \lim_{M\to\infty} \frac{1}{M}\sum_{i=1}^{M} E_L(\mathbf{R}_i) \tag{1.2.8}$$

where M is the number of points $\mathbf{R}_i$ distributed according to $f(\mathbf{R},\beta)$. Again statistical accuracy is greatly improved if a good trial wave function is chosen.

For a generic operator $\hat{O}$, which does not commute with $\hat{H}$, we can obtain its expectation value by considering the approximate estimate[16]:

$$\left\langle \hat{O} \right\rangle = \frac{2}{M}\left[\sum_{i=1}^{M} O(\mathbf{R}_i)\right]_f - \frac{1}{M}\left[\sum_{i=1}^{M} O(\mathbf{R}_i)\right]_{\phi_T^2} + o(\varepsilon^2) \tag{1.2.9}$$

where $|_f$ means: "points $\mathbf{R}_i$ distributed according to function f", and $\varepsilon \propto \psi_0 - \phi_T$.

As far as the *Green's Function Monte Carlo* (GFMC)[15,16,37] method is concerned, one considers the time-independent Schrödinger equation:

$$\left[-\frac{1}{2}\nabla^2 + V(\mathbf{R})\right]\psi(\mathbf{R}) = E\psi(\mathbf{R}). \tag{1.2.10}$$

This may be rewritten in its integral form:

$$\psi(\mathbf{R}) = E\int \mathrm{d}\mathbf{R}' G(\mathbf{R},\mathbf{R}')\,\psi(\mathbf{R}') \tag{1.2.11}$$

where $G(\mathbf{R},\mathbf{R}')$, the Green's function, satisfies the equation:

$$\left[-\frac{1}{2}\nabla^2 + V(\mathbf{R})\right] G(\mathbf{R},\mathbf{R}') = \delta(\mathbf{R}-\mathbf{R}') \tag{1.2.12}$$

and the boundary conditions of the problem.

Let a succession of functions be defined for some initial $\psi^{(0)}(\mathbf{R})$ by:

$$\psi^{(n+1)}(\mathbf{R}) = E\int \mathrm{d}\mathbf{R}' G(\mathbf{R},\mathbf{R}')\,\psi^{(n)}(\mathbf{R}'). \tag{1.2.13}$$

When the spectrum of the hamiltonian is discrete near the ground state $\psi_0(\mathbf{R})$ of the Schrödinger equation, then $\psi_0(\mathbf{R})$ is the limiting value of $\psi^{(n)}(\mathbf{R})$ for large n. It is possible to devise a Monte Carlo method (in the general sense of a random sampling algorithm) which produces populations drawn in turn from the successive $\psi^{(n)}$. In practice, in eq. (1.2.13), the exact eigenvalue of the ground state is substituted by a trial eigenvalue E_T and the main technical problem lies in constructing a method[16] for efficiently sampling $G(\mathbf{R},\mathbf{R}')$, which, in general, does not exhibit an analytic expression. In this case too, some importance sampling technique has to be introduced to get low statistical errors.

1.3 The Auxiliary field method: general description

In the following we introduce a functional integral formulation for interacting fermions. We describe a formalism to calculate ground state properties of a many-body system by using a classical statistical method.

Let us consider the generic hamiltonian $\hat{H} = \hat{K} + \hat{V}_2$, where $\hat{K}$ is a *one-body* operator (generally consisting of kinetic and external potential terms), and $\hat{V}_2$ is a *two-body* interaction term due to electron-electron correlation. We can write $\hat{H}$ in second quantization (for the sake of clearness we use the coordinate representation with basis functions given by delta functions, but, obviously, the procedure holds for a generic representation):

$$\hat{H} = \sum_{i,j} K_{ij} c_i^\dagger c_j + \frac{1}{2} \sum_{i,j} V_{2ij} c_i^\dagger c_j^\dagger c_j c_i \tag{1.3.1}$$

where $V_{2ij} = V_2(|\mathbf{r}_i - \mathbf{r}_j|)$, and $c_i^\dagger$, c_i are the creation and annihilation operators of a particle at position i (for the moment we omit to explicitly write spin indices).

As we are only interested in *ground state* properties, in place of considering the thermodynamic partition function $Z = \mathrm{Tr}\left(e^{-\beta\hat{H}}\right)$, where β indicates the inverse temperature, we consider a *pseudo partition function*[20,38]:

$$Q = \langle \psi_T | \, e^{-\beta\hat{H}} \, | \psi_T \rangle \tag{1.3.2}$$

where ψ_T is a trial wave function and β can be thought of as an imaginary time.

We have already seen (see Introduction) that, if ψ_0 , the ground state of $\hat{H}$, has a non vanishing overlap with the trial wave function ψ_T, the imaginary time propagator $e^{-\beta\hat{H}}$, for $\beta \to \infty$, projects from ψ_T its component along ψ_0; therefore Q behaves asymptotically as the *true* partition function Z:

$$\lim_{\beta\to\infty} Q = |\, \langle \psi_0 | \psi_T \rangle \,|^2 e^{-\beta E_0}. \tag{1.3.3}$$

Then, in terms of Q, the ground state energy is given by

$$E_0 = \lim_{\beta\to\infty}\left(-\frac{1}{\beta}\ln Q\right). \tag{1.3.4}$$

More general expressions for other ground state expectation values can be obtained by differentiating eq. (1.3.4) with respect to appropriate external fields coupled to the quantity of interest. In fact, by using the Hellman-Feynmann theorem, we can calculate the ground state expectation values of a general operator $\hat{O}$, $\langle\psi_0|\,\hat{O}\,|\psi_0\rangle$, by differentiating, with respect to λ, the ground state energy of the corresponding perturbed hamiltonian $\hat{H}+\lambda\hat{O}$:

$$\langle\psi_0|\,\hat{O}\,|\psi_0\rangle = \left.\frac{\partial}{\partial\lambda}\right|_{\lambda=0} E_0(\lambda) = \lim_{\beta\to\infty}\left(-\frac{1}{\beta}\left.\frac{\partial}{\partial\lambda}\right|_{\lambda=0}\ln Q\right). \tag{1.3.5}$$

Hence, in this scheme, the pseudo partition function Q can be considered as the "generator" of all the ground state correlation functions. However, a direct evaluation of Q is actually a difficult task, since $\hat{H}$ contains two-body contributions and ψ_T is a many-body wave function. Now we show that, by using a suitable transformation and introducing auxiliary fields σ, Q can be rewritten as:

$$Q = \frac{1}{C}\int \mathrm{d}\sigma G(\sigma)\,\langle\psi_T|\,\hat{U}(\sigma)\,|\psi_T\rangle \tag{1.3.6}$$

where $G(\sigma)$ is a Gaussian weight and $\hat{U}(\sigma)$ is a one-body, auxiliary field dependent, operator. For each auxiliary field configuration σ propagation $\hat{U}(\sigma)\psi_T$ may be easily performed because $\hat{U}$ does not contain two-body terms. Therefore, in principle, Q can be explicitly computed together with all ground state expectation values, via eq. (1.3.5).

We start by splitting the total imaginary time propagator into a product of P short time propagators and applying the Trotter approximation [39] to each of them:

$$e^{-\beta\hat{H}} = \left(e^{-\Delta\tau\hat{H}}\right)^P = \left(e^{-\frac{\Delta\tau}{2}\hat{K}\mathrm{in}}e^{-\Delta\tau\hat{V}}e^{-\frac{\Delta\tau}{2}\hat{K}\mathrm{in}}\right)^P + o(\Delta\tau^3) \tag{1.3.7}$$

with $\Delta\tau = \frac{\beta}{P}$ and, usually, Trotter decomposition separates the kinetic term $\hat{K}$in, from $\hat{V} = \hat{H} - \hat{K}$in, the remaining component consisting of external and electron-electron potentials. The short time propagator $e^{-\frac{\Delta\tau}{2}\hat{K}\text{in}}e^{-\Delta\tau\hat{V}}e^{-\frac{\Delta\tau}{2}\hat{K}\text{in}}$ is clearly hermitian and positive definite.

Then we can rewrite the approximated short time propagator of the hamiltonian $\hat{H}$ as an *exact* short time propagator of an *equivalent* hamiltonian $\tilde{H}$:

$$e^{-\Delta\tau\tilde{H}} = e^{-\frac{\Delta\tau}{2}\hat{K}\text{in}}e^{-\Delta\tau\hat{V}}e^{-\frac{\Delta\tau}{2}\hat{K}\text{in}} \tag{1.3.8}$$

with $\tilde{H} = \hat{H} + o(\Delta\tau^2)$.

In conclusion all the calculations obtained by using the Trotter approximation give exact ground state properties of the effective hamiltonian $\tilde{H}$ which differ at most by $o(\Delta\tau^2)$ from the desired ground state properties of the true hamiltonian $\hat{H}$.

As we have already said, the evaluation of the propagation performed by operator (1.3.8) is numerically tractable when $\hat{H}$ contains *only one-body* operators. Therefore we can introduce the *Hubbard Stratonovich Transformation* (HST) which exactly aims to reducing the exponential of a two-body operator (e.g. the term involving V_{2ij} in eq. (1.3.1)) to a functional integral, over an auxiliary field, where only exponentials of one-body operators are present.

First of all we can rewrite hamiltonian (1.3.1) by anticommuting the creation and annihilation operators in the normal-ordered two-body interaction:

$$\hat{H} = \sum_{i,j} K_{ij}c_i^\dagger c_j + \frac{1}{2}\sum_{i,j} V_{2ij}\hat{\rho}_i\hat{\rho}_j - \frac{1}{2}\sum_i V_{2ii}\hat{\rho}_i \tag{1.3.9}$$

where $\hat{\rho}_i$ is the fermion density operator and the last term is an unphysical self-interaction contribution which can be temporarily grouped with the one-body term

K and which will be removed later: $K'_{ij} = K_{ij} - \frac{1}{2}V_{2ij}\delta_{ij}$,

$$\hat{H} = \sum_{i,j} K'_{ij} c_i^\dagger c_j + \frac{1}{2}\sum_{i,j} V_{2ij}\hat{\rho}_i\hat{\rho}_j. \tag{1.3.10}$$

Now we apply HST to the exponential of a two body operator which is present in Trotter decomposition (1.3.8) when we perform imaginary time propagation $e^{-\frac{\Delta\tau}{2}\sum_{i,j} V_{2ij}\hat{\rho}_i\hat{\rho}_j}$ (see Appendix A):

$$\begin{aligned} e^{-\frac{\Delta\tau}{2}\sum_{i,j} V_{2ij}\hat{\rho}_i\hat{\rho}_j} &= e^{\frac{\Delta\tau}{2}\sum_{i,j} W_{ij}\hat{\rho}_i\hat{\rho}_j} = \\ &= \left(\det\Delta\tau W_{ij}^{-1}\right)^{\frac{1}{2}} \int \prod_i \frac{\mathrm{d}\tilde{\sigma}_i}{\sqrt{2\pi}} e^{-\frac{\Delta\tau}{2}\sum_{i,j} W_{ij}^{-1}\tilde{\sigma}_i\tilde{\sigma}_j} e^{\Delta\tau\sum_i \tilde{\sigma}_i\hat{\rho}_i} \end{aligned} \tag{1.3.11}$$

where $W_{ij} \equiv -V_{2ij}$ and, for reason of simplicity, we have assumed that V_{2ij} is a definite negative matrix and therefore W_{ij} a positive definite one. In fact (see Appendix A) the previous transformation can be directly applied only for *negative definite* two-body operators contained in the hamiltonian $\hat{H}$. While this property is certainly not true in general (for example electron-electron electrostatic interaction is repulsive), nevertheless HST can always be performed for quite general two-body fermionic operators (see the following chapter) by using suitable techniques with opportune modifications.

Eq. (1.3.11) introduces σ variables as auxiliary fields with dimensions of potentials. In order to avoid using the inverse matrix W_{ij}^{-1} it's possible to change integration variables, by defining:

$$\sigma_i = \sum_j W_{ij}^{-1}\tilde{\sigma}_j \tag{1.3.12}$$

Therefore σ assume the dimensions of densities and eq. (1.3.11) becomes:

$$e^{\frac{\Delta\tau}{2}\sum_{i,j} W_{ij}\hat{\rho}_i\hat{\rho}_j} = \left(\det\Delta\tau W_{ij}\right)^{\frac{1}{2}} \int \prod_i \frac{\mathrm{d}\sigma_i}{\sqrt{2\pi}} e^{-\frac{\Delta\tau}{2}\sum_{i,j} W_{ij}\sigma_i\sigma_j} e^{\Delta\tau\sum_{i,j} W_{ij}\sigma_i\hat{\rho}_j}. \tag{1.3.13}$$

Obviously we have to perform the transformation (1.3.13) at each time step of the imaginary time propagation (1.3.7). Therefore we introduce a time index l in σ variables and we are able to write:

$$e^{\frac{\beta}{2}\sum_{i,j} W_{ij}\hat{\rho}_i\hat{\rho}_j} = \frac{1}{C}\int \prod_{l=1}^{P}\prod_i \mathrm{d}\sigma_i(l) e^{-\frac{\Delta\tau}{2}\sum_{l=1}^{P}\sum_{i,j} W_{ij}\sigma_i(l)\sigma_j(l)} e^{\Delta\tau\sum_{l=1}^{P}\sum_{i,j} W_{ij}\sigma_i(l)\hat{\rho}_j} \tag{1.3.14}$$

where C is a normalization constant given by

$$\frac{1}{C} = \prod_{l=1}^{P} \frac{(\det \Delta\tau W_{ij})^{\frac{1}{2}}}{(2\pi)^{\frac{N_a}{2}}}. \tag{1.3.15}$$

Now if we consider again the complete hamiltonian $\hat{H} = \hat{K}\mathrm{in} + \hat{V}$, with

$$\hat{K}\mathrm{in} = \sum_{i,j} K\mathrm{in}_{ij} c_i^\dagger c_j \tag{1.3.16}$$

$$\begin{aligned}\hat{V} &= \sum_i V_i^{\mathrm{ext}}\hat{\rho}_i + \frac{1}{2}\sum_{i,j} V_{2ij}\hat{\rho}_i\hat{\rho}_j - \sum_i V_{2ii}\hat{\rho}_i = \\ &= \sum_i \left(V_i^{\mathrm{ext}} - \frac{1}{2}V_{2ii}\right)\hat{\rho}_i - \sum_{i,j} W_{ij}\hat{\rho}_i\hat{\rho}_j\end{aligned} \tag{1.3.17}$$

where $V^{\mathrm{ext}}(\mathbf{r})$ is a generic external potential, then we can rewrite the propagation (1.3.7) by using the previous HST relations:

$$\begin{aligned}e^{-\beta\hat{H}} &\simeq \left(e^{-\frac{\Delta\tau}{2}\hat{K}\mathrm{in}} e^{-\Delta\tau\hat{V}} e^{-\frac{\Delta\tau}{2}\hat{K}\mathrm{in}}\right)^P = \\ &= \frac{1}{C}\int \prod_{l=1}^{P}\prod_i \mathrm{d}\sigma_i(l) e^{-\frac{\Delta\tau}{2}\sum_{l=1}^{P}\sum_{i,j} W_{ij}\sigma_i(l)\sigma_j(l)} \times \\ &\times \prod_{l=1}^{P}\left\{ e^{-\frac{\Delta\tau}{2}\hat{K}\mathrm{in}} e^{-\Delta\tau\left(\sum_i V_i^{\mathrm{ext}}\hat{\rho}_i - \sum_{i,j} W_{ij}\sigma_i(l)\hat{\rho}_j\right)} e^{-\frac{\Delta\tau}{2}\hat{K}\mathrm{in}}\right\}.\end{aligned} \tag{1.3.18}$$

Thus, the evolution operator is the functional integral, over auxiliary fields σ, of the evolution operator for a *one-body time dependent* hamiltonian, whose non-kinetic

contribution is given by

$$\hat{V}_1(l) = \sum_i V_i^{\text{ext}} \hat{\rho}_i - \sum_{i,j} W_{ij} \sigma_i(l) \hat{\rho}_j \tag{1.3.19}$$

and weighted by a Gaussian factor. In the last relation we omitted the *self-energy* term $-\frac{1}{2}\sum_i V_{2ii}\hat{\rho}_i$, since it acts as a constant potential in the one-body propagation and (see the following section) this does not affect the computed estimators of ground state properties.

The main advantages of (AFQMC) method over other stochastic techniques (for example DMC or GFMC) are the following:

1)– Two-body interaction terms are replaced with random auxiliary fields which act as external potentials on the particles, therefore the interacting problem is replaced by a sum over an ensemble of non-interacting systems in a set of random time-varying external fields and one can easily apply all typical *one-body* techniques (for instance local and non-local pseudopotentials) in a natural way.

2)– The *antisymmetric* property of the fermion wave function is preserved at any time of field evolution. In fact a Slater determinant trial wave function evolves into another Slater determinant for each auxiliary field configuration sampled.

3)– GFMC or DMC methods accurately describe boson systems but for fermions a difficulty arises. In fact, if, for instance, we consider a DMC approach, the wave function $\psi_t = e^{-t\hat{H}}\psi_T$ can be obtained as a solution of the imaginary time Schrödinger equation which is viewed as a diffusion equation with "branching" and the many-body wave function is described by a statistically evolving set of configurations, each of which is specified by the coordinates of the particles. The weight chosen for the statistical sampling is directly related with the many-body wave function ψ_t itself (see Section 1.2).

The lowest energy solution of the diffusion equation on the space of configura-

tions of the system is nodeless (it's the boson ground state), but, when fermionic systems are to be studying, the antisymmetry of the fermion wave function determines regions of ψ_t with positive and negative sign: each part with definite sign ψ_t^+ and ψ_t^- of the propagated wave function $\psi_t = \psi_t^+ - \psi_t^-$ has a non vanishing component on the more stable boson ground state, so the calculation becomes unstable because, through the imaginary time propagation, each part of the wave functions ψ_t^+ and ψ_t^- is attracted by the bosonic ground state, until the fermionic component becomes undetectable from a numerical point of view.

This instability, the well known *fermion sign problem*, prevented an extensive application of either GFMC or DMC to fermion systems, although the "fixed node approximation" [17,18] allows upper bounds on fermion ground state energies to be determined.

In the AFQMC approach observables are calculated as averages over the set of auxiliary field configurations. The difficulty here is that the quantity to be averaged is not always positive (the statistical weight may be not positive definite).

In practice the *fermion sign problem* reappears since, as $\beta \rightarrow \infty$, the number of positive terms can nearly equal the number of negative terms and the difference, which is the quantity we are interested in, becomes very small compared to the total number of terms. Nevertheless in this situation the fermion sign problem seems to be less dramatic than in GFMC or DMC approaches.

In fact one can show (this aspect was extensively studied by Sorella et al.[21,22,29] and, recently, by Fahy and Hamann[30]), by theoretic arguments and numerical evidence, that, in many non trivial cases, the AFQMC method is stable for arbitrary large imaginary time and that fermion sign problem can often be circumvented with negligible error in the calculated physical quantities.

Finally the AFQMC method is exact apart from statistical errors we can, in

principle, reduce as small as we like, but we expect it requires computer resources which don't grow exponentially like, for example, in a full Configuration Interaction approach. In fact, in the AFQMC procedure, in practice only the calculation of determinants depends on the number of electrons. Therefore a cost increasing with the 3^{rd} power (or less) of the number of electrons (see Chap. 2) has to be foreseen.

Therefore this method seems to be promising and opens new possibilities for the simulation of interacting fermions.

1.4 Ground state properties calculation

In the previous section we used HST to rewrite the pseudo partition function Q as a multidimensional integral over classical auxiliary fields:

$$Q = \langle \psi_T | \, e^{-\beta \hat{H}} \, | \psi_T \rangle = \frac{1}{C} \int \mathrm{d}\sigma \cdot G \cdot \langle \psi_T | \, \hat{U}(\sigma) \, | \psi_T \rangle \tag{1.4.1}$$

where, in a concise expression, we have used G to denote the gaussian weighting factor

$$G = e^{-\frac{\Delta\tau}{2} \sum_l \sum_{i,j} W_{ij} \sigma_i(l) \sigma_j(l)}$$

and $\hat{U}(\sigma)$ denotes the one-body propagator:

$$\hat{U}(\sigma) = \prod_{l=1}^{P} \hat{U}\left[\sigma(l)\right] =$$

$$= \prod_{l=1}^{P} \left\{ -\frac{\Delta\tau}{2} \hat{K}\mathrm{in} \, e^{-\Delta\tau \left(\sum_i V_i^{\mathrm{ext}} \hat{\rho}_i - \sum_{i,j} W_{ij} \sigma_i(l) \hat{\rho}_j \right)} - \frac{\Delta\tau}{2} \hat{K}\mathrm{in} \right\}.$$

At this point the quantum problem would be solved if an exact numerical evaluation of the multidimensional integral (1.4.1) were possible. Unfortunately this is not the case because the functional Q contains a prohibitively large number of variables. Nevertheless we can use a statistical approach by interpreting the functional Q as a *classical* partition function of the variables σ, and apply a statistical method for evaluating Q and related physical quantities. In fact we can write:

$$Q = \frac{1}{C} \int \mathrm{d}\sigma e^{-V(\sigma)/K_B T} \tag{1.4.2}$$

by considering Q as a classical partition function of the variables σ, that "interact", at an *effective temperature* $K_B T = 1$, through a potential:

$$V(\sigma) = -\ln G - \ln \langle \psi_T | \, \hat{U}(\sigma) \, | \psi_T \rangle + \text{const.} =$$

$$= \frac{\Delta\tau}{2} \sum_l \sum_{i,j} W_{ij}\sigma_i(l)\sigma_j(l) - \ln \langle\psi_T|\,\hat{U}(\sigma)\,|\psi_T\rangle + \text{const.} \qquad (1.4.3)$$

Here we assume that the term $\langle\psi_T|\,\hat{U}(\sigma)\,|\psi_T\rangle$ is always positive.This is in general not true (it's the practical manifestation of the *fermion sign problem* - see previous section) because the propagated many-body wave function $\hat{U}(\sigma)\psi_T$ can have a negative overlap with the initial trial wave function.

Now, in order to obtain the ground state expectation value of a given operator $\hat{O}$, we have to compute a well defined classical average, by using eq. (1.3.5):

$$\langle\psi_0|\,\hat{O}\,|\psi_0\rangle = \lim_{\beta\to\infty}\left(-\frac{1}{\beta}\frac{\partial}{\partial\lambda}|_{\lambda=0}\ln Q\right) = Q^{-1}\frac{1}{C}\int \mathrm{d}\sigma E_{\hat{O}}(\sigma)e^{-V(\sigma)} \qquad (1.4.4)$$

with the *estimator* $E_{\hat{O}}(\sigma)$ given by:

$$E_{\hat{O}}(\sigma) = \lim_{\beta\to\infty}\left(-\frac{1}{\beta}\frac{\partial}{\partial\lambda}|_{\lambda=0}\ln\langle\psi_T|\,\hat{U}^{\lambda}(\sigma)\,|\psi_T\rangle\right) \qquad (1.4.5)$$

where the λ-modified propagator $\hat{U}^{\lambda}(\sigma)$ is obtained by adding to the hamiltonian (in practice we add it to the kinetic term) a perturbation $\lambda\hat{O}$. Then $E_{\hat{O}}(\sigma)$ can be calculated, by performing the differentiation with respect to the external perturbation in eq. (1.4.5), as an imaginary time average of independent measurements computed at a fixed imaginary time t:

$$E_{\hat{O}}(\sigma) = \frac{\Delta\tau}{\beta}\frac{\sum_{l=1}^{P} w_l\,\langle\psi_T|\,\hat{U}_\sigma(P,l)\,\hat{O}\hat{U}_\sigma(l,0)\,|\psi_T\rangle}{\langle\psi_T|\,\hat{U}(\sigma)\,|\psi_T\rangle} =$$

$$= \frac{1}{P}\frac{\sum_{l=1}^{P} w_l\,\langle\psi_T|\,\hat{U}_\sigma(P,l)\,\hat{O}\hat{U}_\sigma(l,0)\,|\psi_T\rangle}{\langle\psi_T|\,\hat{U}_\sigma(P,0)\,|\psi_T\rangle} \longrightarrow \frac{1}{\beta}\int_0^{\beta}\mathrm{d}t E^t_{\hat{O}}(\sigma) \qquad (1.4.6)$$

where last relation holds in the limit $\Delta\tau \to 0$, and

$$E^t_{\hat{O}}(\sigma) = \frac{\langle\psi_T|\,\hat{U}_\sigma(\beta,t)\,\hat{O}\hat{U}_\sigma(t,0)\,|\psi_T\rangle}{\langle\psi_T|\,\hat{U}_\sigma(\beta,0)\,|\psi_T\rangle} \qquad (1.4.7)$$

with

$$\hat{U}_\sigma(l,0) = \prod_{l'=0}^{l}\hat{U}\left[\sigma(l')\right]$$

$$\hat{U}_\sigma(P,l) = \prod_{l'=0}^{P-l-1} \hat{U}\left[\sigma(P-l')\right]. \tag{1.4.8}$$

$\hat{U}_\sigma(0,0) = \hat{U}_\sigma(P,P) = \hat{I}$, and the weights w_l are $= \frac{1}{2}$ for $l = 0$, or $l = P$, and $= 1$ otherwise. In practice when one evaluates the estimator with the imaginary time average (1.4.6), the contributions coming from imaginary time measurement close to the initial $t = 0$ and the final $t = \beta$ imaginary time produce a slow convergence of the physical quantities with respect to the inverse temperature. In fact such measurements are too close to the trial wave function and give contribution which vanishes as β^{-1}. In order to improve systematically such convergence in β, we can consider an average over an interval which is far apart from the initial $t = 0$ and final time $t = \beta$, instead of averaging over all the imaginary time slices. Therefore we can use ($n > 2$):

$$E_{\hat{O}}(\sigma) = \frac{1}{\beta\left(1-\frac{2}{n}\right)} \int_{\frac{\beta}{n}}^{\beta\left(1-\frac{1}{n}\right)} \mathrm{d}t E^t_{\hat{O}}(\sigma). \tag{1.4.9}$$

This kind of estimator can be formally obtained by taking the logarithmic derivative of the partition function $Q_{\lambda_T} = \langle\psi_T|^{-\beta\hat{H}_{\lambda_T}}|\psi_T\rangle$:

$$\frac{\partial}{\partial\lambda}|_{\lambda=0}\left(-\frac{1}{\beta\left(1-\frac{2}{n}\right)}\ln\langle\psi_T|^{-\beta\hat{H}_{\lambda_T}}|\psi_T\rangle\right) \tag{1.4.10}$$

where $\hat{H}_{\lambda_T} = \hat{H} + \lambda_T\hat{O}$, and now λ_T acts as a time-dependent perturbation:

$$\lambda_T = \begin{cases} \lambda, & \text{if } \frac{\beta}{n} \le t \le \beta\left(1-\frac{1}{n}\right); \\ 0, & \text{otherwise.} \end{cases}$$

This gives, for $\beta \to \infty$, the correct ground state expectation value with an exponential convergence in β. A good value for n may be $n = 4$.

Then the expectation value of the operator $\hat{O}$ is obtained by evaluating the multidimensional integral (1.4.4) with a statistical method:

$$\left\langle\hat{O}\right\rangle \equiv \langle\psi_0|\hat{O}|\psi_0\rangle = \frac{\int \mathrm{d}\sigma E_{\hat{O}}(\sigma)e^{-V(\sigma)}}{\int \mathrm{d}\sigma e^{-V(\sigma)}} \tag{1.4.11}$$

To this end some *importance sampling* scheme must be used, by generation σ configurations according to the probability function $e^{-V(\sigma)}$. For this purpose one can use either a Monte Carlo algorithm or a Molecular Dynamics strategy: one simply consider the system with σ degrees of freedom in the fictitious classical potential $V(\sigma)$. The variables σ are taken as functions of a formal continuous time variable s (the *fictitious* time). In this way the statistical evaluation of classical expectation values of estimators, depending on the variables σ, can be expressed as a *temporal* average:

$$\left\langle \hat{O} \right\rangle = \frac{\int \mathrm{d}\sigma E_{\hat{O}}(\sigma) e^{-V(\sigma)}}{\int \mathrm{d}\sigma e^{-V(\sigma)}} = \lim_{s\to\infty} \frac{1}{(s-s_0)} \int_{s_0}^{s} \mathrm{d}s' E_{\hat{O}}\left[\sigma(s')\right] \tag{1.4.12}$$

where s_0 is the time needed to reach equilibrium for the Molecular Dynamics eqs., or the Monte Carlo scheme. For infinite fictitious time s eq. (1.4.12) would lead to zero statistical error. Actually this is not feasible and one has always to consider statistical errors.

A naive estimation would give:

$$\Delta\hat{O} \simeq \frac{\left(\left\langle \hat{O}^2 \right\rangle - \left\langle \hat{O} \right\rangle^2\right)^{\frac{1}{2}}}{\sqrt{N_c}} \tag{1.4.13}$$

where N_c is the number of sampled configurations.

However this is not exact since, usually, strong correlation exists between successive configurations. In order to correct for this one could measure the average interval N_i between statistically independent configurations and this should correct (1.4.13) in the form:

$$\Delta\hat{O} \simeq \frac{\left(\left\langle \hat{O}^2 \right\rangle - \left\langle \hat{O} \right\rangle^2\right)^{\frac{1}{2}}}{\sqrt{N_c/N_i}} \tag{1.4.14}$$

The underlying hypothesis is that, at equilibrium, $E_{\hat{O}}(\sigma)$ is gaussianly distributed. Since this is not always the case it's practically convenient to measure statistical

error by dividing the measure into segments of sufficiently length and comparing the averages obtained in these intervals. If the segments are long compared to the correlation time of the simulation, then the *sub-averages* are roughly gaussianly distributed, due to the *central limit theorem*[34]. An estimate of the error using eq. (1.4.13), where N_c now represents the number of sub-averages, is therefore correct and ensures the 68% of probability of finding the exact value of $\left\langle \hat{O} \right\rangle$, within the calculated uncertainty.

1.5 Jastrow Auxiliary Field method

After developing the AFQMC method we can go back to the variational technique where, substantially, a multidimensional integral with, for instance, Jastrow trial wave function has to be evaluated. There have been many approaches to this problem, practically all of them borrowed from the theory of classical fluids: namely cluster expansion, integral equations, Molecular Dynamics and, above all, the Monte Carlo method we described in Section 1.1.

In the following we present a new technique by showing that variational Jastrow estimates of ground state properties may be computed by an Auxiliary Field approach analogous to that we illustrated in Section 1.3 for the exact many-body problem.

First of all let us define a Jastrow operator which is again the exponential of a two-body operator:

$$\hat{U}_J \equiv e^{-\frac{1}{2}\hat{J}} \equiv e^{-\frac{1}{2}\sum_{ij}\sum_{\mu\mu'} J_{ij}\hat{\rho}_{i\mu}\hat{\rho}_{j\mu'}} \tag{1.5.1}$$

such that

$$\psi_J = \hat{U}_J \psi_T \tag{1.5.2}$$

where $J_{ij} = J(|\mathbf{r}_i - \mathbf{r}_j|)$ and ψ_J is the Jastrow many-body wave function. Now, by using Jastrow approximation, the expectation value of a generic operator $\hat{O}$ can be obtained as:

$$\left\langle \hat{O} \right\rangle_J = \frac{\langle \psi_J | \hat{O} | \psi_J \rangle}{\langle \psi_J | \psi_J \rangle}. \tag{1.5.3}$$

According to variational principle, if $\hat{O} \equiv \hat{H}$, then $E_J \equiv \left\langle \hat{H} \right\rangle_J \geq E_0$. By definition (1.5.2) relation (1.5.3) can be rewritten as:

$$\left\langle \hat{O} \right\rangle_J = \frac{\langle \psi_T | e^{-\frac{1}{2}\hat{J}} \hat{O} e^{-\frac{1}{2}\hat{J}} | \psi_T \rangle}{\langle \psi_T | e^{-\hat{J}} | \psi_T \rangle}. \tag{1.5.4}$$

Then it is easy to show that:

$$\left\langle \hat{O} \right\rangle_J = - \left. \frac{\partial}{\partial \lambda} \right|_{\lambda=0} \ln Q_J^\lambda \tag{1.5.5}$$

where the Jastrow "partition function" Q_J^λ is defined as

$$Q_J^\lambda \equiv \langle \psi_T | \, e^{-\frac{\hat{J}}{2}} e^{-\lambda \hat{O}} e^{-\frac{\hat{J}}{2}} \, | \psi_T \rangle \, . \tag{1.5.6}$$

We note that the procedure is formally identical to the scheme previously developed by introducing the pseudo partition function $Q = \langle \psi_T | \, e^{-\beta \hat{H}} \, | \psi_T \rangle$. Here the $\beta \hat{H}$ term is simply substituted by $\hat{J}$.

Now the HST can be performed in order to reduce Jastrow two-body operator to a functional integral, over two auxiliary fields σ_1,σ_2, of one-body field dependent operators. Therefore

$$Q_J^\lambda = \frac{1}{C} \int \mathrm{d}\sigma_1 \mathrm{d}\sigma_2 \cdot G \cdot \langle \psi_T | \, \hat{U}_J(\sigma_1) e^{-\lambda \hat{O}} \hat{U}_J(\sigma_2) \, | \psi_T \rangle \tag{1.5.8}$$

Hence, by applying (1.5.5), we obtain:

$$\left\langle \hat{O} \right\rangle_J = Q_J^{-1} \frac{1}{C} \int \mathrm{d}\sigma e^{-V_J(\sigma)} E_{\hat{O}_J}[\sigma] \tag{1.5.9}$$

where

$$V_J(\sigma) = -\ln G - \ln \langle \psi_T | \, \hat{U}_J(\sigma_1) \hat{U}_J(\sigma_2) \, | \psi_T \rangle \tag{1.5.10}$$

and the Jastrow estimator is given by:

$$E_{\hat{O}_J}[\sigma] = \frac{\langle \psi_T | \, \hat{U}_J(\sigma_1) \hat{O} \hat{U}_J(\sigma_2) \, | \psi_T \rangle}{\langle \psi_T | \, \hat{U}_J(\sigma_1) \hat{U}_J(\sigma_2) \, | \psi_T \rangle} . \tag{1.5.11}$$

Introduction of Jastrow auxiliary fields is a useful technique, not only to perform a variational calculation, but also to reduce computer CPU time required by an exact AFQMC procedure. In fact if the trial many-body wave function ψ_T

is not the usual single Slater determinant obtained by a previous self-consistent Hartree-Fock calculation, but a Jastrow trial wave function ψ_J, which already "contains" a certain amount of particle correlation, we expect a smaller β will be necessary in the imaginary time propagation $e^{-\beta\hat{H}}\psi_J$ in order to attain ground state properties. Hence we can obtain an efficient algorithm by introducing two different kinds of auxiliary fields: one, time dependent, is connected with imaginary time propagation $e^{-\beta\hat{H}}$ performed in the usual Trotter decomposition, and the other is due to the presence of Jastrow propagator $e^{-\hat{J}}$. This procedure can save a relevant amount of computer time since, roughly speaking, we introduce only *two* (Jastrow) propagation step when, generally, *a lot of* imaginary time propagation steps would be necessary to recover the same correlation already present in ψ_J.

Chapter 2

Interacting Electrons.

2.1 The Auxiliary Field method in a realistic physical system

In the following we specify previous general HST relations for a realistic physical system: a *molecule* with positively charged nuclei and electrons interacting with a repulsive Coulomb potential. Our hamiltonian is given by (a.u. are used throughout this thesis):

$$\hat{H} = -\frac{1}{2}\sum_{\alpha=1}^{N}\nabla_{\alpha}^{2} + \sum_{\alpha=1}^{N} V^{\text{ext}}(\mathbf{r}_{\alpha}) + \frac{1}{2}\sum_{\alpha\neq\beta}\frac{1}{|\mathbf{r}_{\alpha}-\mathbf{r}_{\beta}|} + E_{\text{ion}} \tag{2.1.1}$$

with:

$$V^{\text{ext}}(\mathbf{r}_{\alpha}) = -\sum_{I}\frac{Z_I}{|\mathbf{r}_{\alpha}-\mathbf{R}_I|} \tag{2.1.2}$$

$$E_{\text{ion}} = \frac{1}{2}\sum_{I\neq J}\frac{Z_I Z_J}{|\mathbf{R}_I-\mathbf{R}_J|} \tag{2.1.3}$$

and where Greek indices are used for electrons, Latin capital letters for nuclei and Z_I indicates the charge of the I^{th} nucleus.

In order to apply, in practice, the HST formalism we have to "discretize" our problem. For example this may be carried out by introducing a spatial lattice.

In second quantization hamiltonian (2.1.1) becomes:

$$\hat{H} = -\frac{1}{2}\sum_{i,j,\mu,\mu'}\langle i\mu|\nabla^2|j\mu'\rangle\, c_{i\mu}^{\dagger}c_{j\mu'} + \sum_{i,\mu}V^{\text{ext}}(\mathbf{r}_i)\hat{\rho_{i\mu}} + \frac{1}{2}\sum_{i,j,\mu,\mu'}V_{ij}\hat{\rho_{i\mu}}\hat{\rho_{j\mu'}} \tag{2.1.4}$$

where

$$V_{ij} = V\left(|\mathbf{r}_i - \mathbf{r}_j|\right) = \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \tag{2.1.5}$$

and, for simplicity we omitted the useless self-energy contribution (see previous chapter) and the constant ion-ion repulsion term. Now we have explicitly introduced the spin variable $\mu = \uparrow, \downarrow$, and the following relations hold for the fermion density operator $\hat{\rho_{i\mu}} = c^{\dagger}_{i\mu} c_{i\mu}$:

$$\hat{\rho_{i\mu}}^2 = \hat{\rho_{i\mu}} \tag{2.1.6}$$

$$\sum_{i,\mu} \hat{\rho_{i\mu}} = \hat{N}. \tag{2.1.7}$$

Here $\hat{N}$ is the total number of particles operator.

In this case the difficulty is given by the fact that V_{ij} is a positive definite matrix. Therefore when we consider the exponential of two-body term in the Trotter decomposition (1.3.8) we have an expression of the form:

$$e^{\Delta\tau \sum_{i,j} V'_{ij} \hat{\rho_i} \hat{\rho_j}} \tag{2.1.8}$$

where $V'_{ij} = -V_{ij}$. Hence we can't directly apply the HST, since V'_{ij} is a negative definite matrix (see Appendix A). Nevertheless we can solve the problem in the following way. Let's introduce a modified interaction matrix:

$$W_{ij} \equiv \lambda \delta_{ij} - V_{ij}. \tag{2.1.9}$$

Obviously, for λ sufficiently large, W_{ij} is a positive definite matrix. In practice it's convenient to choose λ equal to the maximum eigenvalue of the matrix V_{ij}.

Now if we define the *total density* and *magnetization* operators:

$$\hat{d}_i = \hat{\rho_{i\uparrow}} + \hat{\rho_{i\downarrow}} \tag{2.1.10}$$

$$\hat{m}_i = \hat{\rho_{i\uparrow}} - \hat{\rho_{i\downarrow}} \tag{2.1.11}$$

we can write the two-body term:

$$\frac{1}{2}\sum_{i,j,\mu,\mu'} V_{ij}\rho_{\hat{i}\mu}\rho_{\hat{j}\mu'} = \frac{1}{2}\sum_{i,j} V_{ij}\hat{d}_i\hat{d}_j = \frac{\lambda}{2}\sum_i \hat{d}_i^2 - \frac{1}{2}\sum_{i,j} W_{ij}\hat{d}_i\hat{d}_j. \tag{2.1.12}$$

Then, by using relations (2.1.6, 2.1.7), it's easy to show that:

$$\sum_i \rho_{\hat{i}\uparrow}\rho_{\hat{i}\downarrow} = \frac{1}{2}\left(\hat{N} - \sum_i \hat{m}_i^2\right) \tag{2.1.13}$$

Therefore

$$\sum_i \hat{d}_i^2 = \hat{N} + 2\sum_i \rho_{\hat{i}\uparrow}\rho_{\hat{i}\downarrow} = 2\hat{N} - \sum_i \hat{m}_i^2. \tag{2.1.14}$$

And finally:

$$\frac{1}{2}\sum_{i,j,\mu,\mu'} V_{ij}\rho_{\hat{i}\mu}\rho_{\hat{j}\mu'} = -\frac{1}{2}\sum_{i,j} W_{ij}\hat{d}_i\hat{d}_j - \frac{\lambda}{2}\sum_i \hat{m}_i^2 + \lambda\hat{N}. \tag{2.1.15}$$

In this way:

$$e^{-\frac{\Delta\tau}{2}\sum_{i,j,\mu,\mu'} V_{ij}\rho_{\hat{i}\mu}\rho_{\hat{j}\mu'}} = e^{\frac{\Delta\tau}{2}\left(\sum_{i,j} W_{ij}\hat{d}_i\hat{d}_j + \lambda\sum_i \hat{m}_i^2 - 2\lambda\hat{N}\right)} =$$

$$= e^{\frac{\Delta\tau}{2}\sum_{i,j} W_{ij}\hat{d}_i\hat{d}_j} e^{\frac{\Delta\tau}{2}\lambda\sum_i \hat{m}_i^2} e^{-\Delta\tau\lambda\hat{N}} \tag{2.1.16}$$

In conclusion we have obtained two quadratic contributions $e^{\frac{\Delta\tau}{2}\sum_{i,j} W_{ij}\hat{d}_i\hat{d}_j}$, $e^{\frac{\Delta\tau}{2}\lambda\sum_i \hat{m}_i^2}$ and therefore two distinct Hubbard-Stratonovich transformations are necessary. In practice the presence of spin variables and the strategy used for reducing the negative definite matrix $V'_{ij} = -V_{ij}$ to positive definite forms implied introduction of two different time-dependent auxiliary fields: one, σ^d, coupled with local density and the other, σ^m, with local magnetization. Now we can apply HST:

$$e^{\frac{\Delta\tau}{2}\sum_{i,j} W_{ij}\hat{d}_i\hat{d}_j} = \text{const.}\int\prod_i d\sigma_i^d e^{-\frac{\Delta\tau}{2}\sum_{i,j} W_{ij}\sigma_i'\sigma_j'} e^{\Delta\tau\sum_{i,j} W_{ij}\sigma_i'\hat{d}_j} \tag{2.1.17}$$

$$e^{\lambda\frac{\Delta\tau}{2}\sum_i \hat{m}_i^2} = \text{const.}\int\prod_i d\sigma_i^m e^{-\lambda\frac{\Delta\tau}{2}\sum_i \sigma_i^{m\,2}} e^{\lambda\Delta\tau\sum_i \sigma_i^m\hat{m}_i} \tag{2.1.18}$$

Therefore, on the whole, we obtain:

$$e^{-\frac{\Delta\tau}{2}\sum_{i,j,\mu,\mu'} V_{ij}\hat{\rho_{i\mu}}\hat{\rho_{j\mu'}}} = \int \prod_i \mathrm{d}\sigma_i^m \mathrm{d}\sigma_i^d e^{-\frac{\Delta\tau}{2}\left(\sum_{i,j} W_{ij}\sigma_i^d\sigma_j^d + \lambda\sum_i \sigma_i^{m\,2}\right)} \times$$

$$\times e^{\Delta\tau\left(\sum_{i,j} W_{ij}\sigma_i^d\hat{d}_j + \lambda\sum_i \sigma_i^m\hat{m}_i\right)} e^{-\lambda\Delta\tau\hat{N}} \cdot \text{const.}. \tag{2.1.19}$$

Finally, by considering all time slices in Trotter decomposition, our pseudo partition function becomes:

$$Q = \langle\psi_T|\, e^{-\beta\hat{H}}\,|\psi_T\rangle = \text{const.} \int \mathrm{d}\sigma \cdot G \cdot \langle\psi_T|\,\hat{U}(\sigma)\,|\psi_T\rangle \tag{2.1.20}$$

where the gaussian weighting factor is given by:

$$G = e^{-\frac{\Delta\tau}{2}\sum_{l=1}^{P}\left(\sum_{i,j} W_{ij}\sigma_i^d(l)\sigma_j^d(l) + \lambda\sum_i \sigma_i^{m\,2}(l)\right)} \tag{2.1.21}$$

and the single particle propagator is:

$$\hat{U}(\sigma) = \prod_{l=1}^{P} \hat{U}\left[\sigma(l)\right] =$$

$$= \prod_{l=1}^{P}\left[e^{-\frac{\Delta\tau}{2}\hat{K}\mathrm{in}} e^{-\Delta\tau\left(\sum_i V^{\mathrm{ext}}(\mathbf{r}_i)\hat{d}_i - \sum_{i,j} W_{ij}\sigma_i^d(l)\hat{d}_j - \lambda\sum_i \sigma_i^m(l)\hat{m}_i\right)} e^{-\frac{\Delta\tau}{2}\hat{K}\mathrm{in}}\right]^P \tag{2.1.22}$$

where we have omitted the $e^{-\lambda\Delta\tau\hat{N}}$ term which is inessential in the propagation since, in our calculation, the total number of particles is a fixed quantity. We note that $\hat{U}(\sigma)$ can be written as the product of two propagators $\hat{U}(\sigma) = \hat{U}(\sigma)^{\uparrow} \cdot \hat{U}(\sigma)^{\downarrow}$, each acting on separate spin subspaces. Therefore, since we consider, for the trial many-body wave function, a single Slater determinant made up by $N^{\uparrow}$ spin up and $N^{\downarrow}$ spin down orbitals, $\hat{U}(\sigma)$ acts independently on spin up states $\varphi_{p\uparrow}$ and on spin down states $\varphi_{p\downarrow}$.

Hence we can write:

$$\langle \psi_T | \hat{U}(\sigma) | \psi_T \rangle = \det \langle \varphi_{p\uparrow} | \hat{U}^{\uparrow}(\sigma) | \varphi_{q\uparrow} \rangle \cdot \det \langle \varphi_{p\downarrow} | \hat{U}^{\downarrow}(\sigma) | \varphi_{q\downarrow} \rangle . \qquad (2.1.23)$$

As far as the non-kinetic part contained in the one-body propagator $\hat{U}(\sigma)$ is concerned, we observe that:

$$\langle \mathbf{r}_i | \, e^{-\Delta\tau\left(\sum_j V^{\text{ext}}(\mathbf{r}_j)\hat{d}_j - \sum_{j,k} W_{jk}\sigma_j^d(l)\hat{d}_k - \lambda\sum_j \sigma_j^m(l)\hat{m}_j\right)} | \varphi_{p\uparrow\downarrow} \rangle =$$

$$= e^{-\Delta\tau V_{\uparrow\downarrow}^{\text{eff}}(\mathbf{r}_i,l)} \varphi_{p\uparrow\downarrow}(\mathbf{r}_i). \qquad (2.1.24)$$

In essence HST allows us to use a simple one-body formalism, but with an effective external potential which becomes time-dependent, spin-dependent, and which is a function of σ variables:

$$V_{\uparrow}^{\text{eff}}(\mathbf{r}_i, l) = V^{\text{ext}}(\mathbf{r}_i) - \sum_j W_{ji}\sigma_j^d(l) - \lambda\sigma_i^m(l)$$

$$V_{\downarrow}^{\text{eff}}(\mathbf{r}_i, l) = V^{\text{ext}}(\mathbf{r}_i) - \sum_j W_{ji}\sigma_j^d(l) + \lambda\sigma_i^m(l). \qquad (2.1.25)$$

Finally, in order to apply the kinetic term propagation $e^{-\frac{\Delta\tau}{2}\hat{K}\text{in}}\varphi_{p\uparrow\downarrow}$, it's convenient to evaluate such propagation in reciprocal space (see Chap. 4), where $\hat{K}$in is a diagonal operator, and then to come back to direct space by using the Fast Fourier Transform [40].

2.2 Estimators calculation

The ground state expectation value of an arbitrary operator $\hat{O}$ can be calculated using the fundamental relations (1.4.4 – 1.4.14). Evidently the main task is the calculation of the estimator $E^t_{\hat{O}}(\sigma)$, at a fixed imaginary time t. We start by deriving it for the operator $\hat{O} = c_{i\mu}c^\dagger_{j\mu}$. Eq. (1.4.7) can be easily written as:

$$E^t_{\hat{O}}(\sigma) = \frac{\left\langle c^\dagger_{i\mu}\hat{U}_\sigma(t,\beta)\,\psi_T \middle| c^\dagger_{j\mu}\hat{U}_\sigma(t,0)\,\psi_T \right\rangle}{\left\langle \hat{U}_\sigma(t,\beta)\,\psi_T \middle| \hat{U}_\sigma(t,0)\,\psi_T \right\rangle} \tag{2.2.1}$$

If ψ_T is a N-state single Slater determinant, then eq. (2.2.1) involves the scalar products of two $N+1$-state determinants, due to the presence of the creation operators. Now the scalar product of two Slater determinants is the determinant of the corresponding overlap matrix, that is:

$$E^t_{\hat{O}}(\sigma) = \frac{\det\tilde{A}^\mu(i,j)}{\det A^\mu} \tag{2.2.2}$$

where A^μ is the $N^\mu \times N^\mu$ overlap matrix:

$$A^\mu_{pq} = \langle\varphi_p|\,\hat{U}(\sigma)\,|\varphi_q\rangle = \langle\tilde{\varphi}^<_p(t)|\tilde{\varphi}^>_q(t)\rangle \tag{2.2.3}$$

in which single particle orbitals have the same spin μ and $\tilde{A}^\mu(i,j)$ is the $(N^\mu+1)\times(N^\mu+1)$ matrix defined by

$$\tilde{A}^\mu_{pq} = \begin{pmatrix} \delta_{ij} & \cdots & \tilde{\varphi}^>_q(\mathbf{r}_j) & \cdots \\ \vdots & & & \\ \tilde{\varphi}^<_p(\mathbf{r}_i) & & A^\mu_{pq} & \\ \vdots & & & \end{pmatrix}. \tag{2.2.4}$$

Here we have introduced the *forward* and *backward* propagated wave function for integer times, defined by (see eq. (1.4.8)):

$$\tilde{\varphi}^>_q(t) = \hat{U}_\sigma(t,0)\,\varphi_q = \tilde{\varphi}^>_q(l\cdot\Delta\tau) = \hat{U}_\sigma(l,0)\,\varphi_q \tag{2.2.5}$$

$$\tilde{\varphi}_p^<(t) = \hat{U}_\sigma(t,\beta)\,\varphi_p = \tilde{\varphi}_p^<(l\cdot\Delta\tau) = \hat{U}_\sigma(l,\beta)\,\varphi_p. \tag{2.2.6}$$

At first sight the full calculation of this estimator would seem to be a very expensive task. In fact, by letting the indices i and j assume all possible values corresponding to all possible N_a lattice sites, we obtain N_a^2 matrices of the form (2.2.4). Therefore we should evaluate N_a^2 determinants of order $(N^\mu + 1)$ for each spin value $\mu = \uparrow, \downarrow$. However we can simplify the problem by following Sorella's procedure[29].

In fact, by varying i,j indices, the N_a^2 matrices differ one from another simply by the exchange of one row and one column. Therefore it's convenient to introduce the quantities:

$$B^\mu(i,j) \equiv \sum_{p,q} \tilde{\varphi}_p^>(\mathbf{r}_j)\,(A^\mu)^{-1}_{pq}\,\tilde{\varphi}_q^<(\mathbf{r}_i). \tag{2.2.7}$$

Obviously a determinant remains unchanged if one adds to a column any linear combination of others. Hence we may add to the first column of the matrix $\tilde{A}^\mu$ a linear combination of the other columns in order to make vanishing all the elements of the first column but the one in the *first* row:

$$\det\tilde{A}^\mu = \det\begin{pmatrix} \delta_{ij} - \sum_q b_q\tilde{\varphi}_q^>(\mathbf{r}_j) & \cdots & \tilde{\varphi}_q^>(\mathbf{r}_j) & \cdots \\ \vdots & & & \\ \tilde{\varphi}_p^<(\mathbf{r}_i) - \sum_q b_q A^\mu_{pq} & & A^\mu_{pq} & \\ \vdots & & & \end{pmatrix}. \tag{2.2.8}$$

Now, if we choose:

$$b_q = \sum_{q,q'} (A^\mu)^{-1}_{qq'}\,\tilde{\varphi}_{q'}^<(\mathbf{r}_i) \tag{2.2.9}$$

we obtain the desired result:

$$\tilde{\varphi}_p^<(\mathbf{r}_i) - \sum_q b_q A^\mu_{pq} = 0. \tag{2.2.10}$$

Then, by using definition (2.2.7) and relations (2.2.8 – 2.2.10) we can write:

$$\det\tilde{A}^{\mu} = \det \begin{pmatrix} \delta_{ij} - B^{\mu}(i,j) & \dots & \tilde{\varphi}_q^{>}(\mathbf{r}_j) & \dots \\ \vdots & & & \\ 0 & & A^{\mu}_{pq} & \\ \vdots & & & \end{pmatrix} = \det A^{\mu}\left[\delta_{ij} - B^{\mu}(i,j)\right]. \tag{2.2.11}$$

Therefore the factor $\det A^{\mu}$ cancels out in eq. (2.2.2) and finally we obtain:

$$E^{t}_{c_{i\mu}c^{\dagger}_{j\mu}}(\sigma) \equiv \left\langle c_{i\mu}c^{\dagger}_{j\mu}\right\rangle = \delta_{ij} - B^{\mu}(i,j). \tag{2.2.12}$$

Now the computation of the $N_a \times N_a$ matrices $B^{\uparrow}$ and $B^{\downarrow}$ requires the inversion of two $N^{\mu} \times N^{\mu}$ matrices A^{μ}, amounting ${N^{\uparrow}}^3 + {N^{\downarrow}}^3$ operations, a change of basis $(A^{\mu})^{-1}\tilde{\varphi}^{<}$, that is $\left({N^{\uparrow}}^2 + {N^{\downarrow}}^2\right) N_a$ operations, and remaining $N^{\uparrow} + N^{\downarrow}$ multiplications for each different couple of lattice sites for which the matrices are defined. In total we have $\sum_{\mu}\left({N^{\mu}}^3 + {N^{\mu}}^2 N_a + N^{\mu}N_a^2\right) \simeq N_a^2\left(N^{\uparrow} + N^{\downarrow}\right)$ operations, since , usually, $N_a \gg N^{\mu}$. This is to be compared with the $N_a^2 \sum_{\mu}\left(N^{\mu}+1\right)^3$ operations required by a direct evaluation of $\det\tilde{A}^{\mu}(i,j)$.

Then, obviously:

$$\left\langle c_i^{\dagger}c_j\right\rangle = \delta_{ij} - \left\langle c_j c_i^{\dagger}\right\rangle = B(j,i) \tag{2.2.12}$$

where brackets mean the quantum expectation value calculated over a fixed configuration of σ fields and at a fixed time t, according to definition (2.2.1).

By using standard properties of determinants it's easy to derive (see Appendix B) another useful relation:

$$\left\langle c_i^{\dagger}c_j c_m^{\dagger}c_n\right\rangle = \left\langle c_i^{\dagger}c_j\right\rangle\left\langle c_m^{\dagger}c_n\right\rangle + \left\langle c_i^{\dagger}c_n\right\rangle\left\langle c_j c_m^{\dagger}\right\rangle. \tag{2.2.14}$$

Now, by means of eqq. (2.2.11 – 2.2.14), we can compute all physically interesting ground state estimators, simply by expressing their corresponding operators in terms of c,$c^{\dagger}$. In the following we give explicit formulae for some of them:

a) *particle density*: $\hat{\rho}_{i\mu} = c^{\dagger}_{i\mu} c_{i\mu}$

$$E^{t}_{\hat{\rho}_{i\mu}}(\sigma) = B^{\mu}(i,i) = \sum_{p,q} \tilde{\varphi}^{>}_{p}(\mathbf{r}_i) \left(A^{\mu}\right)^{-1}_{pq} \tilde{\varphi}^{<}_{q}(\mathbf{r}_i). \tag{2.2.15}$$

b) *kinetic energy*: $\hat{K}\mathrm{in} = -\frac{1}{2}\sum_{i,j,\mu} T_{ij} c^{\dagger}_{i\mu} c_{j\mu}$ with $T_{ij} = \langle i|\nabla^2|j\rangle$

$$E^{t}_{\hat{K}\mathrm{in}}(\sigma) = -\frac{1}{2}\sum_{i,j,\mu} T_{ij} B^{\mu}(j,i) = -\frac{1}{2}\sum_{i,j,\mu} T_{ij} \sum_{p,q} \tilde{\varphi}^{>}_{p}(\mathbf{r}_i) \left(A^{\mu}\right)^{-1}_{pq} \tilde{\varphi}^{<}_{q}(\mathbf{r}_j). \tag{2.2.16}$$

c) *external energy*: $\hat{V}^{\mathrm{ext}} = \sum_{i,\mu} V^{\mathrm{ext}}(\mathbf{r}_i) c^{\dagger}_{i\mu} c_{i\mu}$

$$E^{t}_{\hat{V}^{\mathrm{ext}}}(\sigma) = \sum_{i,\mu} V^{\mathrm{ext}}(\mathbf{r}_i) B^{\mu}(i,i) = \sum_{i,\mu} V^{\mathrm{ext}}(\mathbf{r}_i) \sum_{p,q} \tilde{\varphi}^{>}_{p}(\mathbf{r}_i) \left(A^{\mu}\right)^{-1}_{pq} \tilde{\varphi}^{<}_{q}(\mathbf{r}_i). \tag{2.2.17}$$

d) *electron-electron interaction*: $\hat{V}^{\mathrm{ee}} = \frac{1}{2}\sum_{i,j,\mu,\mu'} V_{ij} c^{\dagger}_{i\mu} c^{\dagger}_{j\mu'} c_{j\mu'} c_{i\mu}$

Evidently:

$$\left\langle c^{\dagger}_{i\mu} c^{\dagger}_{j\mu'} c_{j\mu'} c_{i\mu} \right\rangle = \left\langle c^{\dagger}_{i\mu} c_{i\mu} c^{\dagger}_{j\mu'} c_{j\mu'} \right\rangle - \delta_{ij}\delta_{\mu\mu'} \left\langle c^{\dagger}_{i,\mu} c_{j,\mu'} \right\rangle =$$

$$= \left\langle c^{\dagger}_{i,\mu} c_{i,\mu} \right\rangle \left\langle c^{\dagger}_{j,\mu'} c_{j,\mu'} \right\rangle - \left\langle c^{\dagger}_{i,\mu} c_{j,\mu'} \right\rangle \left\langle c^{\dagger}_{j,\mu'} c_{i,\mu} \right\rangle .$$

Hence:

$$E^{t}_{\hat{V}^{\mathrm{ee}}}(\sigma) = \frac{1}{2}\sum_{i,j,\mu,\mu'} V_{ij} B^{\mu}(i,i)\, B^{\mu'}(j,j) - \frac{1}{2}\sum_{i,j,\mu} V_{ij} B^{\mu}(j,i)\, B^{\mu'}(i,j) =$$

$$= \frac{1}{2}\sum_{i,j,\mu,\mu'} V_{ij} \sum_{p,q,p',q'} \left(A^{\mu}\right)^{-1}_{pq} \left(A^{\mu'}\right)^{-1}_{p'q'} \tilde{\varphi}^{<}_{q\mu}(\mathbf{r}_i) \tilde{\varphi}^{>}_{p\mu}(\mathbf{r}_i) \tilde{\varphi}^{<}_{q'\mu'}(\mathbf{r}_j) \tilde{\varphi}^{>}_{p'\mu'}(\mathbf{r}_j) -$$

$$-\frac{1}{2}\sum_{i,j,\mu} V_{ij} \sum_{p,q,p',q'} \left(A^{\mu}\right)^{-1}_{pq} \left(A^{\mu'}\right)^{-1}_{p'q'} \tilde{\varphi}^{<}_{q\mu}(\mathbf{r}_i) \tilde{\varphi}^{>}_{p\mu}(\mathbf{r}_j) \tilde{\varphi}^{<}_{q'\mu'}(\mathbf{r}_j) \tilde{\varphi}^{>}_{p'\mu'}(\mathbf{r}_i) \tag{2.2.18}$$

where, for clarity, we have pointed out the spin component of the orbitals.

Chapter 3

Sampling the auxiliary fields.

3.1 Updating field techniques

In the AFQMC method ground state expectation values can be obtained by calculating functional integrals over auxiliary fields:

$$\left\langle \hat{O} \right\rangle = \frac{1}{Q} \int \mathrm{d}\sigma E_{\hat{O}}(\sigma) e^{-V(\sigma)}. \tag{3.1.1}$$

In order to attain this purpose a lot of strategies are available. Obviously the simplest one is the conventional Monte Carlo method. In this approach the σ fields for all space points (if a spatial discretization is used) and at all imaginary time slices are updated:

$$\sigma^{\mathrm{new}} = \sigma^{\mathrm{old}} + \delta \Delta\sigma \tag{3.1.2}$$

where δ is a uniformly distributed random number between -1 and 1, and $\Delta\sigma$ is a constant factor used to fix the size of the random steps. Then a Metropolis acceptance/rejection test is applied: if $V\left(\sigma^{\mathrm{new}}\right) \leq V\left(\sigma^{\mathrm{old}}\right)$ the new configuration is accepted, otherwise it is accepted with a probability given by $e^{-\left[V(\sigma^{\mathrm{new}})-V(\sigma^{\mathrm{old}})\right]}$. Surely this is not the most efficient way to proceed since all the field variables are updated by completely random movements and, usually, a very small value for $\Delta\sigma$ has to be chosen to obtain a good Metropolis acceptance ratio (between 30 and 70%). Therefore large amounts of computer time are required to correctly sample auxiliary fields.

In Section 1-4 we anticipated that the evaluation of the integrals over σ variables can be performed as a temporal average:

$$\left\langle \hat{O} \right\rangle = \lim_{s \to \infty} \frac{1}{(s - s_0)} \int_{s_0}^{s} \mathrm{d}E_{\hat{O}} \left[\sigma(s')\right]. \tag{3.1.3}$$

In this context σ fields have to be suitably updated in the fictitious time s. An average over all σ can be replaced by an average over a fictitious time evolution in at least two ways.

One can introduce a Gaussian "white noise" function $\eta(s)$ and define the time dependence of σ by the *Langevin* equation:

$$\frac{\mathrm{d}\sigma}{\mathrm{d}s} = -\frac{\partial V(\sigma)}{\partial \sigma} + \eta(s) \tag{3.1.4}$$

with

$$\langle \eta(s)\eta(s') \rangle = 2\delta\left(s - s'\right). \tag{3.1.5}$$

From a physical point of view Langevin equation governs the Brownian motion of particles. The rationale behind this approach[29], first suggested by Parisi[41], is that a Fokker-Planck equation is associated to the stochastic evolution described by (3.1.4, 3.1.5):

$$\frac{\mathrm{d}P(\sigma)}{\mathrm{d}s} = \nabla^2 P + \nabla\left[\nabla V(\sigma)\right] P \tag{3.1.6}$$

where $P(\sigma)$ is the probability that the stochastic trajectory, determined by the Langevin equation, generates a configuration $\{\sigma\}$. In the limit $s \to \infty$ then $P(\sigma) \to e^{-\beta V(\sigma)}$ and one can use this property to sample the Boltzmann factor.

Another approach (see also following Section) is a *microcanonical* method. From a Molecular Dynamical viewpoint $V(\sigma)$ is considered as the potential energy (per unit mass) for a classical dynamics governed by Newton's law, so that:

$$\frac{\mathrm{d}^2\sigma}{\mathrm{d}s^2} = -\frac{\partial V(\sigma)}{\partial \sigma}. \tag{3.1.7}$$

This system conserves total energy and time averages will agree (up to 1/volume effects) with functional averages provided the system is ergodic and the initial conditions are arranged to satisfy the constraint that the kinetic energy should average to 1/2 per degree of freedom.

In practice, in numerical simulations, the continuous dependence on time is replaced by a finite difference approximation, by introducing a fictitious time step Δs. Then, in principle, results have to be extrapolated to $\Delta s \to 0$, since obviously a finite time step introduce errors[42].

A more recent class of simulation techniques, the so-called *Smart Monte Carlo* methods[43-44] promises to be very efficient. In essence one can only approximately integrate the (Langevin or MD) equations of motion taking some discrete sequence of Δs steps. Then this entire trajectory is accepted or rejected by a Metropolis test. It is just this global acceptance/rejection step that makes the algorithm exact. In comparison with a simple MC approach this strategy represents a main improvement since the σ variables are no longer randomly updated, but the force term tends to guide the sampling of the auxiliary fields along the trajectory of the natural motion of the system. On the other hand,due to the presence of Metropolis test, the truncation errors (associated with a finite time step Δs) affecting a pure MD or Langevin procedure disappear. Therefore Δs may be chosen as large as possible while keeping the Monte Carlo acceptance rate satisfactorily high.

In the following section a Hybrid MD technique, we used in our numerical simulations, together with its Smart Monte Carlo improvement, is described in detail.

3.2 The Hybrid MD/MC method

Choosing a method which efficiently samples σ variables is obviously a crucial step. While a definitive answer about the real performances of various existing simulation strategies is still lacking, surely a method which takes into account force-biased updatings, if possible corrected by a Metropolis test, within a Smart Monte Carlo approach, is desirable.

For our calculations we adopted the *Hybrid Molecular Dynamics* approach (HMD)[45], which derives from similar algorithms that are being used in the study of lattice gauge theory[42]. Since Q is interpreted as a classical partition function of the variables σ, with a potential energy $V(\sigma)$ given by

$$V(\sigma) = -\ln G - \ln \langle \psi_T | \hat{U}(\sigma) | \psi_T \rangle + \text{const.} \tag{3.2.1}$$

it is convenient to introduce a momentum variable p conjugate to each auxiliary field variable σ and rewrite the partition function in the form:

$$Z = \text{const.} \int \mathrm{d}p\mathrm{d}\sigma e^{-E_{\text{tot}}(\sigma,p)/K_B T} \tag{3.2.2}$$

where $K_B T = 1$ and $E_{\text{tot}}(\sigma, p)$ is the total classical energy of the auxiliary field σ dynamics:

$$E_{\text{tot}}(\sigma,p) = E_{\text{kin}}(p) + V(\sigma) =$$

$$= \frac{1}{2} \sum_{l=1}^{P} \sum_{i} \left[p_i^{d\,2}(l) + p_i^{m\,2}(l) \right] +$$

$$+ \frac{\Delta\tau}{2} \sum_{l=1}^{P} \left[\sum_{ij} W_{ij} \sigma_i^{d}(l) \sigma_j^{d}(l) + \lambda \sum_{i} \sigma_i^{m\,2}(l) \right] - \ln \langle \psi_T | \hat{U}(\sigma) | \psi_T \rangle + \text{const.} \tag{3.2.3}$$

Since ground state properties are computed by estimators which are functions of σ fields only, the introduction of the p fields has no effect on physical results.

Our task is to obtain a set of configurations of σ and p fields distributed as $e^{-E_{\rm tot}(\sigma,p)}$. Therefore we can adopt a microcanonical approach with the classical dynamics governed by familiar Hamilton's equations:

$$\dot{\sigma} = \frac{\partial E_{\rm tot}\,(\sigma,p)}{\partial p} = p \tag{3.2.4}$$

$$\dot{p} = -\frac{\partial E_{\rm tot}\,(\sigma,p)}{\partial \sigma} = -\frac{\partial V(\sigma)}{\partial \sigma} \tag{3.2.5}$$

where the dots over p and σ signify differentiation with respect to simulation fictitious time s. In practice we consider a *hybrid* scheme (HMD) with two types of updatings. At the beginning and every s_m time units, each p field is replaced by a Gaussian random number distributed as $\exp(-p^2/2)$. Then σ fields and p momenta (till next "randomization") are updated by integrating Hamilton's equations (3.2.4, 3.2.5). This amounts to periodically touching the microcanonical system to a *heat bath.*

If the system is in equilibrium, then the two types of updatings will keep it in equilibrium. If it is out of equilibrium, then the heath bath steps will drive it towards equilibrium, while the integration of Hamilton's equations will be "neutral". Thus the combination of two updating steps will yield the desired distribution.

This method should be efficient enough. In fact, on short time scales the successive increments in σ variables are highly correlated and σ rather quickly moves to "new" values; on larger time scales, any "non-ergodic" tendencies for σ to return too quickly to earlier values will be reduced by the periodic randomization of momenta.

Obviously nonlinear Hamilton's equations must be integrated numerically and this requires the introduction of a finite size, Δs, in fictitious simulation time. The integration may be carried out by the *leap frog* method[46]:

$$p\left(s+\frac{\Delta s}{2}\right)=p\left(s-\frac{\Delta s}{2}\right)-\Delta s\frac{\partial V(\sigma)}{\partial \sigma}|_s \tag{3.2.6}$$

$$\sigma\left(s+\Delta s\right)=\sigma(s)+p\left(s+\frac{\Delta s}{2}\right)\Delta s. \tag{3.2.7}$$

An error of order $(\Delta s)^3$ is introduced at each time step in the integration process. Since we take of order $1/\Delta s$ integration steps between heat bath updates, the total error in measured quantities is of order $(\Delta s)^2$.

As usual Δs parameter has to be chosen by a compromise. In fact making the step size too big leads to systematic errors while making it too small means, for fixed computational effort, that the integral (3.1.3) will be done for too small a time, introducing large statistical errors.

If the Gaussian term is the dominant contribution in potential energy (3.2.1), that is only Gaussian degrees of freedom are important for the system dynamics, an ideal value for the s_m parameter can be determined. In fact one can show[42] that the optimal s_m, which minimizes auxiliary fields autocorrelation functions, is given by $s_m = 1/2\omega_{\min}$, where $\omega_{\min}$ is the minimum frequency present in Gaussian field dynamics.

Now we explicitly derive formulae for the *forces*, $-\partial V(\sigma)/\partial\sigma$, which have to be calculated for integrating the classical equations of motion. Their computation is the most time-consuming phase of the auxiliary field sampling.

As far as the Gaussian part of the potential (3.2.1) is concerned, derivatives may be performed in a straightforward way.

On the contrary, for the remaining part, $-\ln\langle\psi_T|\hat{U}(\sigma)|\psi_T\rangle$, the task is not so trivial.

If we define the force:

$$F_i(l)\equiv-\frac{\partial V(\sigma)}{\partial\sigma_i(l)} \tag{3.2.8}$$

then its non Gaussian part is given by

$$-\frac{\partial}{\partial\sigma_i(l)}\left(-\ln\langle\psi_T|\hat{U}(\sigma)|\psi_T\rangle\right)=$$

$$=\frac{\partial}{\partial\sigma_i(l)}\left(\ln\det\langle\varphi_p^{\uparrow}|\hat{U}^{\uparrow}(\sigma)|\varphi_q^{\uparrow}\rangle+\ln\det\langle\varphi_p^{\downarrow}|\hat{U}^{\downarrow}(\sigma)|\varphi_q^{\downarrow}\rangle\right) \tag{3.2.9}$$

that is the problem of computing the forces is completely decoupled in spin space. The derivative in the last expression affects only the propagator $\hat{U}(\sigma)$ at the time slice l and, in practice, it is performed in the following way. Let us consider the usual overlap matrix $A_{pq}=\langle\varphi_p|\hat{U}(\sigma)|\varphi_q\rangle$. Then determinants appearing in eq. (3.2.9) can be formally written as:

$$\det A=e^{\mathrm{tr}\ln A}. \tag{3.2.10}$$

Therefore:

$$\frac{\partial}{\partial\sigma_i(l)}\ln\det A=\frac{\partial}{\partial\sigma_i(l)}\mathrm{tr}\ln A=\mathrm{tr}\left[\frac{\partial A}{\partial\sigma_i(l)}A^{-1}\right]=\sum_{pq}\left[\frac{\partial A}{\partial\sigma_i(l)}\right]_{pq}A^{-1}_{qp}. \tag{3.2.11}$$

Now the derivative $\partial A/\partial\sigma_i(l)$ can be explicitly calculated by introducing the back and forth propagated orbitals at intermediate times:

$$\varphi_p^{>}(l)=e^{\Delta\tau\hat{K}\mathrm{in}/2}\tilde{\varphi}_p^{>}(l\cdot\Delta\tau) \tag{3.2.12}$$

$$\varphi_q^{<}(l)=e^{-\Delta\tau\hat{K}\mathrm{in}/2}\tilde{\varphi}_q^{<}(l\cdot\Delta\tau) \tag{3.2.13}$$

where this formulation depends on our particular Trotter decomposition (1.6), and $\tilde{\varphi}^{>}$,$\tilde{\varphi}^{<}$ are the back and forth propagated orbitals for integer times, defined in eq. (2.2.5 – 2.2.6). Obviously $\tilde{\varphi}_p^{>}(0)$ and $\tilde{\varphi}_q^{<}(P\Delta\tau)=\tilde{\varphi}_q^{<}(\beta)$ are the one particle orbitals corresponding to the trial Slater determinant ψ_T.

Then we can write (here the two distinct auxiliary fields and the spin variables are restored):

$$\left[\frac{\partial A^{\mu}}{\partial\sigma_i^d(l)}\right]_{pq}=\Delta\tau\sum_j W_{ij}\varphi_{p\mu}^{<}(\mathrm{r}_j,l)\varphi_{q\mu}^{>}(\mathrm{r}_j,l) \tag{3.2.14}$$

$$\left[\frac{\partial A^{\mu}}{\partial \sigma_i^m(l)}\right]_{pq} = \pm\lambda\Delta\tau\varphi^{<}_{p\mu}(\mathbf{r}_i,l)\varphi^{>}_{q\mu}(\mathbf{r}_i,l). \tag{3.2.15}$$

where, in the last equation, sign + refers to spin up ($\mu = \uparrow$) and sign − to spin down ($\mu = \downarrow$).

Finally we give explicit formulae for the forces by considering Gaussian contributions too:

$$F_i^d(l) = -\Delta\tau\sum_j W_{ij}\sigma_j^d(l) + \tag{3.2.16}$$
$$+\Delta\tau\sum_j W_{ij}\left[\sum_{q\uparrow}\varphi^{<A^{-1}}_{q\uparrow}(\mathbf{r}_j,l)\varphi^{>}_{q\uparrow}(\mathbf{r}_j,l) + \sum_{q\downarrow}\varphi^{<A^{-1}}_{q\downarrow}(\mathbf{r}_j,l)\varphi^{>}_{q\downarrow}(\mathbf{r}_j,l)\right]$$

$$F_i^m(l) = -\lambda\Delta\tau\sigma_i^m(l) + \tag{3.2.17}$$
$$+\lambda\Delta\tau\left[\sum_{q\uparrow}\varphi^{<A^{-1}}_{q\uparrow}(\mathbf{r}_i,l)\varphi^{>}_{q\uparrow}(\mathbf{r}_i,l) - \sum_{q\downarrow}\varphi^{<A^{-1}}_{q\downarrow}(\mathbf{r}_i,l)\varphi^{>}_{q\downarrow}(\mathbf{r}_i,l)\right]$$

with

$$\varphi^{<A^{-1}}_{q\mu}(\mathbf{r}_i,l) = \sum_{p\mu}(A^{\mu})^{-1}_{q\mu p\mu}\,\varphi^{<}_{p\mu}(\mathbf{r}_i,l). \tag{3.2.18}$$

As we discussed in previous section, we are not able to numerically integrate the equations of motion exactly, and thus cannot conserve $E_{\mathrm{tot}}(\sigma,p)$ exactly. This problem may be elegantly solved by a slightly modified algorithm: the Hybrid Monte Carlo (HMC) method[30,43].

In practice we incorporate a Metropolis rejection step based on:

$$q = e^{-\left[E_{\mathrm{tot}}(\sigma^{\mathrm{new}},p^{\mathrm{new}}) - E_{\mathrm{tot}}(\sigma^{\mathrm{old}},p^{\mathrm{old}})\right]}. \tag{3.2.19}$$

If $q \geq 1$ we accept $\{\sigma^{\mathrm{new}}\}$ as a new sample distribution, and if $q < 1$ we accept it with probability q. If we reject it, we reuse $\{\sigma^{\mathrm{old}}\}$ as a sample configuration, choose

a new set of random momenta, and integrate again. The above procedure generates a set of configurations which correctly samples the desired distribution[43]. We have considerable latitude in applying it since we can choose both the integration step length Δs and the number of Molecular Dynamics steps n_{MD} between Monte Carlo rejection steps. The effective potential for the classical problem tends to have the form of isolated favorable "valleys" separated by large unfavorable regions, so increasing error in the integration almost always makes $E_{\rm tot}^{\rm new} - E_{\rm tot}^{\rm old}$ more positive, and lowers our acceptance rate. The error increases when either Δs or n_{MD} is increased, while the statistical independence of $\{\sigma^{\rm old}\}$ and $\{\sigma^{\rm new}\}$ increases when the product $n_{MD}\Delta s$ is increased.

In addition this scheme help to overcome another difficulty. If we could integrate the equations of motion exactly, in general σ would be confined to one region of its multidimensional space by the zeros of $\langle \psi_T | \hat{U}(\sigma) | \psi_T \rangle$, since the potential $V(\sigma)$ would have logarithmic infinities at these locations. This would invalidate our sample. However the logarithmic barrier are usually very "thin" on the scale of σ "displacements" and therefore, if a finite, relatively large Δs may be used, our procedure readily makes the (favorable for our sampling) "error" of going through them.

Chapter 4

Technical aspects and results.

As usual, even though theoretical formulation of AFQMC method is well established, to develop a really efficient algorithm, suitable for numerical computation is not a trivial task.

In fact AFQMC was extensively enough applied to the Hubbard model[25–30] but, in that case, various simplifications and variable transformations may be exploited which, unfortunately, do not hold any more when realistic continuous systems are to be considered. Therefore a large amount of numerical tests was necessary in order to achieve a discrete understanding of the technique and to develop a reliable algorithm.

In this Chapter an outline of the main technical aspects, together with description of some solutions to various practical problems, is given. Selected results obtained by the most interesting numerical tests are also presented.

The determination of energies of molecular systems is a problem of general interest in chemistry and physics. We have chosen the Hydrogen molecule to test our algorithm since it is a very simple molecular system, the fermion-sign problem is not present because we have two electrons with opposite spins in the ground state, and accurate theoretical predictions together with high quality experimental measurements about ground state properties (in particular the dissociation energy) are available.

The history of accurate calculations of energies for H_2 begins with the 1933 work of James and Coolidge[47]. Their work represented one of the first success

in solving the Schrödinger equation for molecules. In the 1960's, more accurate results for the Hydrogen molecule were obtained by Kolos and Roothaan[48] and by Kolos and Wolniewicz[49], who established the foundation for future calculations. They implemented a variational approach in which the wave function is expressed in elliptic coordinates, and using a method of Born[50] the hamiltonian is separated into two parts, $\hat{H} = \hat{H}_0 + \hat{H}'$, where $\hat{H}_0$ is the electronic hamiltonian including nuclear repulsion, and $\hat{H}'$ is the hamiltonian for the nuclear motion including coupling between the electrons and the nuclei. The adiabatic approximation is made by neglecting the off-diagonal contributions of $\hat{H}'$. Their calculations have been outlined in detail by Fischer[51]. Improvements by Wolniewicz [52], including a more flexible wave function, a variational-perturbation method to include the off-diagonal contributions to the exact nonrelativistic hamiltonian, and the relativistic and radiative corrections, gave a better dissociation energy. In addition, Bishop and Cheung[53] calculated the energy of H_2 by treating the full four-body problem as a nonadiabatic variational problem.

Recently (August 1990) a very expensive calculation was performed by Traynor et al.[54] by using a massively parallel supercomputer. They obtained the ground state energy of the hydrogen molecule by the Quantum Monte Carlo method of solving the Schrödinger equation, without the use of the Born-Oppenhaimer or any other adiabatic approximation. The wave function sampling was carried out in the full 12-dimensional configuration space of the four particles (two electrons and two protons). Both a DMC and a GFMC algorithm was used. Their result is in close agreement with the best, experimentally determined dissociation energy of McCormack and Eyler[55], $36118.1 \pm 0.2\text{cm}^{-1}$.

4.1 Calculations in Fourier space

The kinetic operator is diagonal in reciprocal space, where, as we have already anticipated, it is convenient to perform kinetic term propagation $e^{-\frac{\Delta\tau}{2}\hat{K}_{\text{in}}}$. Therefore it seems to be natural to expand the one particle wave functions $\varphi_p(\mathbf{r})$, which trial Slater determinant consists of, in plane waves $e^{i\mathbf{kr}}$, which form a complete set of functions. This a well known procedure in Solid State calculations where the periodicity of a Bravais lattice is exploited. In fact if $\varphi_p(\mathbf{r})$ has the periodicity of a Bravais lattice, that is $\varphi_p(\mathbf{r}+\mathbf{R}) = \varphi_p(\mathbf{r})$ for all $\mathbf{r}$ and all $\mathbf{R}$ in the Bravais lattice, then only plane waves with the periodicity of the Bravais lattice can occur in the expansion. Since the set of wave vectors for plane waves with the periodicity of the lattice is just the reciprocal lattice, a function periodic in the direct lattice will have a plane wave expansion of the form:

$$\varphi_p(\mathbf{r}) = \sum_{\mathbf{G}} C_p(\mathbf{G}) e^{i\mathbf{G}\cdot\mathbf{r}} \tag{4.1.1}$$

where the sum is over all reciprocal lattice vectors $\mathbf{G}$. The Fourier coefficients $C_p(\mathbf{G})$ are given by:

$$C_p(\mathbf{G}) = \frac{1}{\Omega}\int \mathrm{d}\mathbf{r}\varphi_p(\mathbf{r}) e^{-i\mathbf{G}\cdot\mathbf{r}}. \tag{4.1.2}$$

where the integral is over any direct lattice primitive cell C, and Ω is the volume of the primitive cell. By a formal point of view this approach means that we are studying a periodically repeated physical system. Nevertheless if an isolated molecule has to be considered, we can, equally well, use this method provided that direct primitive cell is large enough. In practice we choose a cubic box with volume $\Omega = a^3$; then, if a is sufficiently large and the system inside the cell is neutral, we substantially obtain an infinite number of non-interacting copies of the same system and therefore we are able to recover the properties of an isolated molecule.

The number of plane waves involved in expansion (4.1.1) is determined by a kinetic energy cutoff:

$$\frac{1}{2}G^2 \leq E_{\text{cut}}. \tag{4.1.3}$$

Obviously the accuracy of the expansion can be improved simply by increasing the value of the cutoff energy E_{cut} and, consequently, the CPU computer time requested by numerical calculation.

In the AFQMC approach a lot of *convolution* integrals are to be performed. For instance, in order to compute single particle wave function propagation we have to evaluate (see eq. (2.1.25)) a term:

$$V'(\mathbf{r}_i) = \sum_j \sigma_j^d W_{ij} \longrightarrow \int \mathrm{d}\mathbf{r}\sigma(\mathbf{r})W(\mathbf{r},\mathbf{r}_i). \tag{4.1.4}$$

By a numerical point of view it is convenient to calculate (4.1.4) in Fourier space:

$$V'(\mathbf{G}) = \Omega W(G)\sigma^d(\mathbf{G}). \tag{4.1.5}$$

Then $V'(\mathbf{r})$ can be quickly recovered by using the Fast Fourier Transform. In general it is profitable to consider Fourier coefficients of the various quantities as the fundamental variables and to compute ground state properties and σ dynamics forces directly in reciprocal space.

In Appendix C the main expressions for ground state estimators and σ forces are given in terms of Fourier coefficients and these formulae were actually used by our algorithm. Furthermore computational efficiency should be improved by performing the calculations in Fourier space as far as the auxiliary field sampling is concerned[20]. In fact if $\sigma_i = \sigma(\mathbf{r}_i)$ fields were updated by using a spatial mesh, we would obtain rather uncorrelated changes at different mesh points, even though the physical systems is not expected to fluctuate on this scale. Moreover, the integrability of such extremely erratic functions becomes rather questionable.

Therefore it is convenient to update Fourier components $\sigma(\mathbf{G})$ of σ rather than their values at individual spatial mesh points, since this is equivalent to perform "correlated" changes of the field at *all* space points.

4.2 Numerical stability by Gram-Schmidt orthonormalization

By performing single particle wave function propagation, as shown in eqs. (2.2.5 – 2.2.6), a problem about numerical stability appears. In fact, since imaginary time propagation is not unitary, the orthonormality conditions, initially satisfied by the orbitals, are not preserved during such propagation. Therefore, after repeating many times the propagation steps, an orthonormal basis set $\varphi_p(\mathbf{r}), p = 1, \ldots, N$ will no longer remain orthonormal and the algorithm becomes numerically instable. This can be understood since, due to auxiliary fields introduction, the orbitals are independently propagated through an imaginary time one-body propagator $e^{-t\hat{h}_1}$. Thus a direct application of eqs. (2.2.5 – 2.2.6) results in a Slater determinant with a great deal of linear dependence among the wave functions. In this way the numerical information about the fermionic ground state is gradually lost.

In order to have a stable propagation, we can apply *Gram-Schmidt orthonormalization* after every few time slices. In fact the t-time Slater determinant

$$\psi^t = \det\left[\varphi_p^t(\mathbf{r}_i)\right] \tag{4.2.1}$$

can be rewritten in terms of an orthonormal basis set by introducing a transformation:

$$\varphi_p^t = \sum_q U_{pq}\varphi_q' \tag{4.2.2}$$

where the matrix U_{pq} is chosen in such a way that $\langle \varphi_p' | \varphi_q' \rangle = \delta_{pq}$. The matrix U_{pq} is not univocally determined by eq. (4.2.2). A convenient choice is to use the Gram-Schmidt orthonormalization procedure because, in this case, U_{pq} is a

triangular matrix. Now ψ^t can be written as:

$$\psi^t = \det\left[\sum_q U_{pq}\varphi'_q(\mathbf{r}_i)\right] = \det(U)\cdot\det\left[\varphi'_q(\mathbf{r}_i)\right] \tag{4.2.3}$$

where the latter equality simply follows by expanding the determinant of the product of two square matrices: U_{pq} and $\varphi'_q(\mathbf{r}_i)$. Therefore ψ^t can be expressed, up to a constant, by means of orthogonal orbitals. Hence we again have to propagate a Slater determinant, made up by orthogonal orbitals, and one can proceed as usual, until the numerical stability will require another orthonormalization. With such a strategy we can propagate for long time any function without any numerical problem, even though the computation time increases due to the orthonormalization of the orbitals which costs N^2N_a operations.

If the Hydrogen molecule has to be studied, its ground state consists of two electrons with different spins and, actually, Slater determinant are absent. Nevertheless it is still convenient, by a numerical point of view, to normalize frequently enough the propagated wave functions.

4.3 Fourier acceleration

If the real and imaginary parts of the Fourier coefficients $\sigma(\mathbf{G})$ are considered as independent variables, the Gaussian factors, in auxiliary field potential energy $V(\sigma)$ (see eq. $(C.13)$), contribute independent harmonic oscillator terms.

Their oscillation periods set natural time scales which are not greatly modified[30], on the average, by the contributions from the determinants.

It is easy (see Appendix C) to derive the oscillations frequencies and the corresponding periods:

$$\omega^d(G) = \sqrt{\Omega\Delta\tau 8\pi \left(\frac{1}{G^2_{\min}} - \frac{1}{G^2}\right)} \tag{4.3.1}$$

$$\omega^m = \sqrt{\Omega\Delta\tau 8\pi \left(\frac{1}{G^2_{\min}}\right)} \tag{4.3.2}$$

$$T^{d,m}(G) = \frac{2\pi}{\omega^{d,m}(G)}. \tag{4.3.3}$$

We note that σ^m fields oscillate with a constant frequency, while σ^d fields oscillate with G-dependent frequencies. In practice we should limit the size of a single field update, by choosing a small enough value for the parameter Δs - see eq. $(3.2.6 - 3.2.7)$ - in order to maintain stability at short distances, since short-wavelength (large G) structure tends to evolve more quickly than structure at long-wavelengths (small G). In this way the evolution of large scale features is greatly slowed.

This problem can be remedied by introducing *G-dependent masses* in field dynamics. In fact these masses are not fixed by our method and can be chosen according to a criterion of simple technical suitability.

If we define:

$$M^d(G) = \Omega\Delta\tau 8\pi \left(\frac{1}{G^2_{\min}} - \frac{1}{G^2} \right) \tag{4.3.4}$$

$$M^m = \Omega\Delta\tau 8\pi \left(\frac{1}{G^2_{\min}} \right) \tag{4.3.5}$$

then all $\sigma(\mathbf{G})$ auxiliary fields will evolve with the same oscillation frequency:

$$\omega^d(G) = \omega^m = 1 \tag{4.3.6}$$

$$T^{d,m} = 2\pi. \tag{4.3.7}$$

By using this *Fourier acceleration* technique[56,57] we are able to speed up the evolution at long wavelengths without destabilizing the short wavelengths.

4.4 Results and difficulties

In order to save computer resources and to avoid some problems which, as we will discuss in the following, affect our method when high energy cutoffs are used, the most part of our numerical tests were performed by imposing a very small energy cutoff: $G^2/2 \leq E_{\text{cut}} = 0.5$ Ryd's. With this value expansion (4.1.1), for the one-body wave functions, contains only 7 plane waves (corresponding to the (0,0,0) and (1,0,0) shells in reciprocal space), therefore we have a low accuracy and our physical system, the Hydrogen molecule, actually becomes a "toy model". Anyway the main technical features of the method may be fruitfully analyzed, even though quantitative results for ground state properties are meaningless as far as their absolute values are concerned. In addition, in this small cutoff situation, the "exact" (with regard to this cutoff) ground state properties can be quickly obtained by an *exact diagonalization* procedure and this is very useful since we can immediately realize the correctness and precision of our numerical results.

In order to increase correlation energy contribution, which, because of small energy cutoff, would be much smaller than exact H_2 correlation energy, we multiplied electron-electron interaction by a factor 4.

In Fig. 1 a typical AFQMC simulation is shown. The H_2 ground state energy estimator is plotted during its fictitious time evolution. The average value of this estimator, over all fields configurations which are sampled, gives a ground state energy estimate. Hartree-Fock energy (-0.287 a.u.) and exact diagonalization energy (-0.366 a.u.) are also shown: their difference gives the correlation energy contribution. In order to appreciate the convergence of energy estimator average to the exact ground state value, the cumulative average is drawn. With 5000

simulation steps we obtain $E_0 = -0.368 \pm 0.011$ a.u. which correctly estimates the exact value, even though statistical error is large enough due to considerable estimator fluctuations, which are evident in figure.

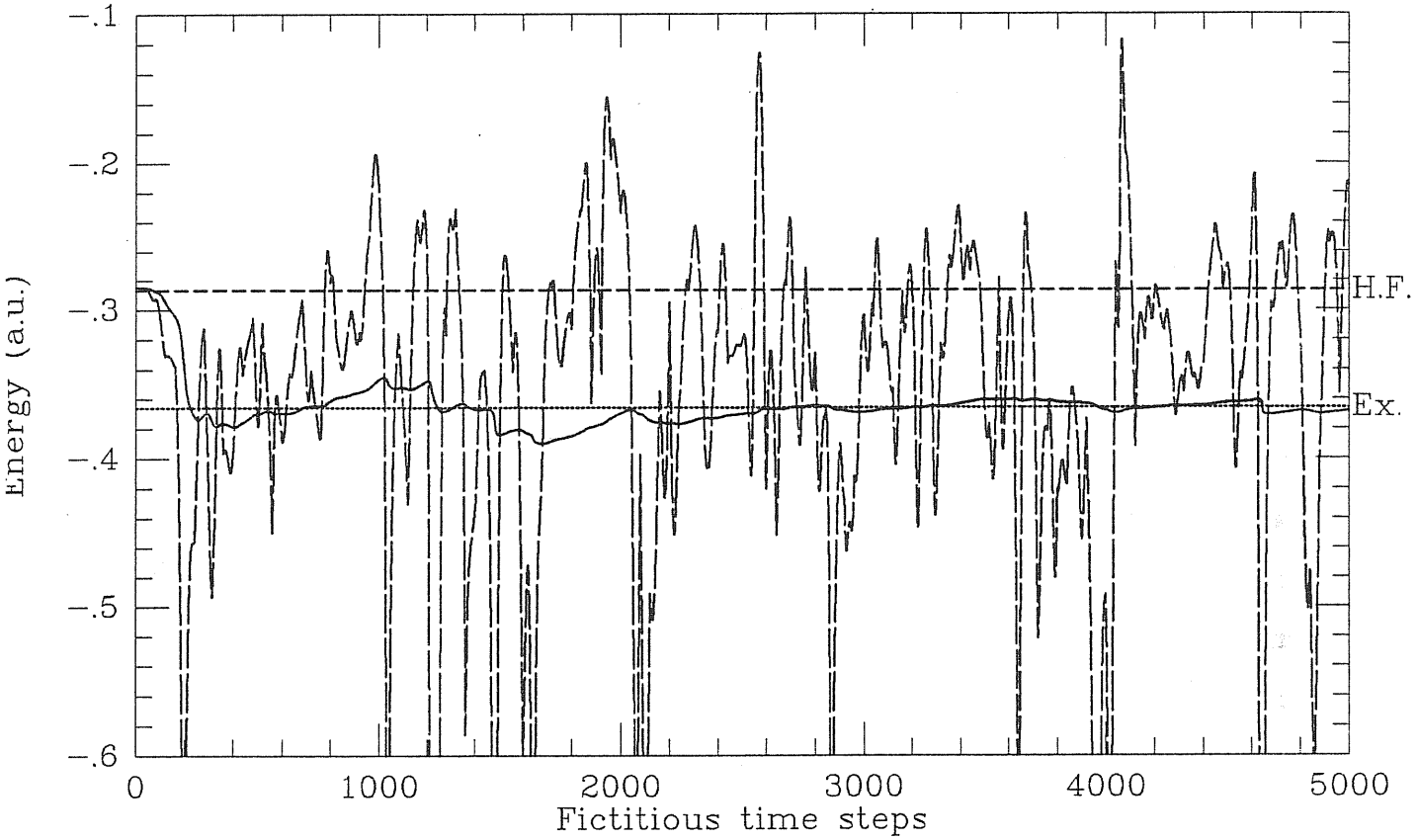

Fig. 1: Fictitious time evolution for H_2 at E_{cut}=0.5 Ryd's in the Hybrid MD scheme. The fluctuating dashed line represents the energy estimator evolution while the continuous line is the cumulative average. As a reference Hartree-Fock and exact results are shown.

In this case σ fields were updated according to a Hybrid MD algorithm (see Chap. 3). The fictitious time step Δs was chosen in such a way to assure a good conserva-

tion in $E_{\rm tot}(\sigma, p)$, the field total energy, during the MD steps between heath-bath updatings: a value $\Delta s = 0.05$ has proven to be suitable if a Fourier acceleration technique (see previous section) is introduced. Heath-bath updatings were performed every 20 MD steps.

As far as the single-particle wave function propagation is concerned, $\Delta\tau$ parameter, which characterizes Trotter decomposition, was chosen by analyzing results obtained by a Local Density algorithm. A $\Delta\tau = 0.03$ value should give rise to a systematic error well smaller then statistical error we can attain even if long simulation runs are performed. Every Trotter time slice propagation single-particle wave functions were normalized. A total number of 64 imaginary time propagation steps, that is $\beta = 1.92$ a.u., has proven to be a long enough propagation, in order to have a good convergence to H_2 ground state.

In our tests Hydrogen nuclei were placed at equilibrium experimental distance for H_2 molecule, $R = 1.401$ a.u.. The trial wave function was the self-consistent solution of a previous Hartree-Fock calculation. The initial configurations of the σ^d, σ^m fields was taken to be the total density and local magnetization respectively, obtained in Hartree-Fock approximation:

$$\sigma^d_{\rm init}(\mathbf{r}, l) = \sigma^d_{\rm init}(\mathbf{r}) = \rho^{\uparrow}(\mathbf{r}) + \rho^{\downarrow}(\mathbf{r}) \tag{4.4.1}$$

$$\sigma^m_{\rm init}(\mathbf{r}, l) = \sigma^m_{\rm init}(\mathbf{r}) = \rho^{\uparrow}(\mathbf{r}) - \rho^{\downarrow}(\mathbf{r}) \tag{4.4.2}$$

for all time slices $l = 1, ..., P$. Simulation of Fig. 1 requires a total of about 500 seconds on a CRAY Y-MP computer. Obviously a better precision, in final result, can be achieved simply by performing longer simulation runs and by considering that statistical error is inversely proportional to the square root of the total number of sampled auxiliary field configurations.

Numerical tests performed by a Hybrid MC algorithm for auxiliary field evolution gave similar results for both ground state energy and its statistical error. In this case a Metropolis acceptance/rejection step is introduced - see Chap. 3 - and Δs parameter has to be chosen in order to get a suitable acceptance rate AR. For instance, by using $\Delta s = 0.1$ we obtain AR= 78%, and, by performing a simulation run with all other parameters equal to those of the previous Hybrid MD calculation, we have an estimate: $E_0 = -0.364 \pm 0.016$ a.u..

A different group of numerical tests was done by using the Variational Jastrow Auxiliary Field method - see section 1.5. For the Jastrow factor we have chosen the expression:

$$J(r) = \alpha e^{-r^2/r_j^2} \tag{4.4.3}$$

where α and r_j are two parameters that have to be optimized in order to minimize ground state energy estimate. The practical advantage of this particular form is that it has a simple analytical Fourier transform:

$$J(G) = \frac{\alpha}{\Omega}\pi^{\frac{3}{2}} r_j^3 e^{-G^2 r_j^2/4}. \tag{4.4.4}$$

In Fig. 2 a variational Jastrow simulation is presented; in this case $\alpha = 1.0$ and $r_j = 2.5$. In a previous variational Jastrow approach, performed by a Monte Carlo algorithm, we found $E_0 = -1.151 \pm 0.001$ a.u. for H_2 molecule in the Born-Oppenhaimer approximation, to be compared with the exact result: $E_0 = -1.1745$ a.u.[18]. In that case about 2% of the total energy was neglected by a variational approach. In our small energy cutoff situation, we are able to recover, as Fig. 2 illustrates, the "exact" ground state energy and, moreover, by spending much less time than by using previous exact method (Fig. 1). In fact we obtain $E_0 = -0.365 \pm 0.008$ and the required CPU time was about 13 seconds.

In section 1.5 we asserted that a variational Jastrow auxiliary field approach can

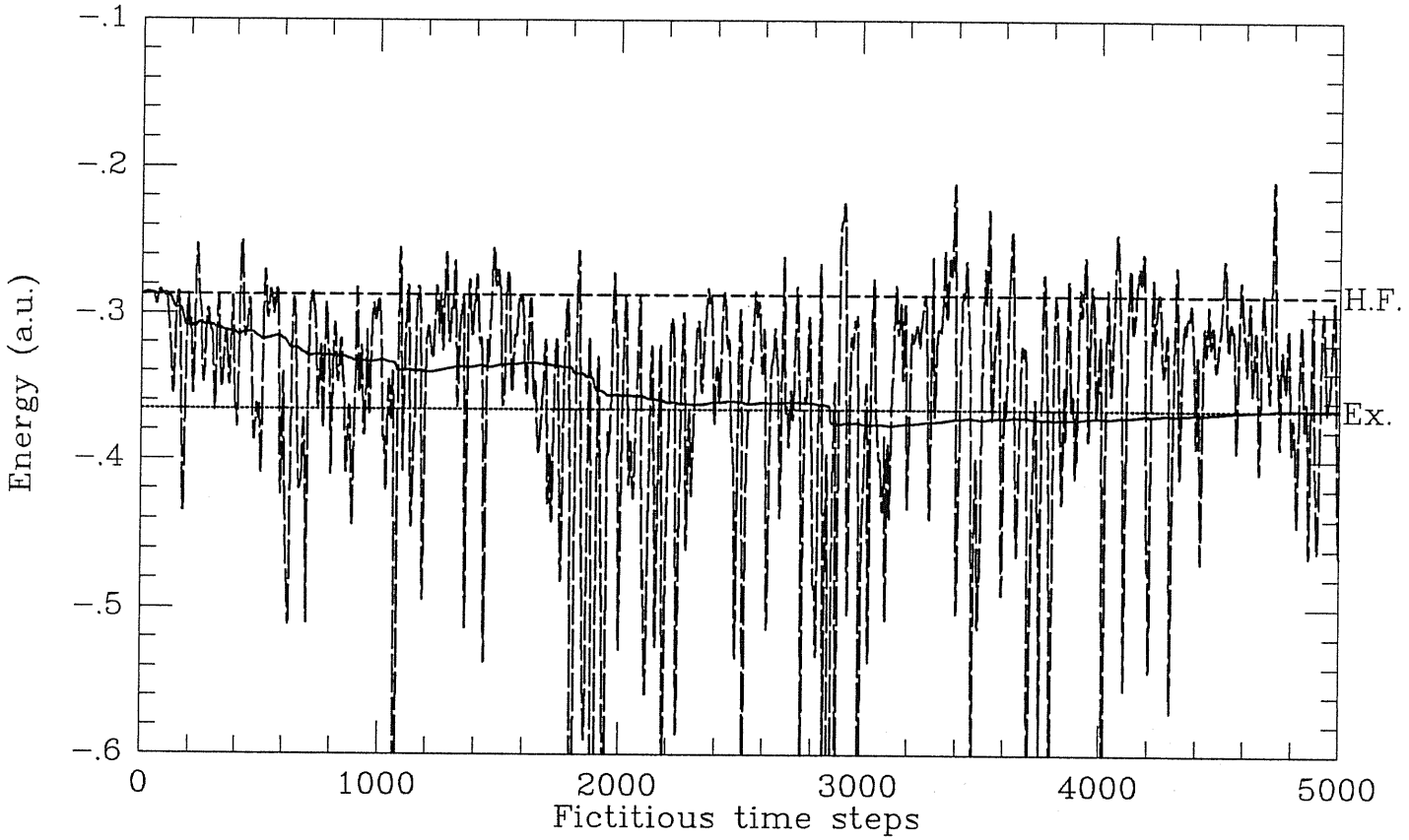

Fig. 2: Fictitious time evolution for H_2 at E_{cut}=0.5 Ryd's in the Hybrid MD scheme by using a variational Jastrow approach with α=1.0 and r_j=2.5.

be also used to produce a trial wave function better than usual Hartree-Fock determinants, and therefore to save a certain amount of computer time since a shorter imaginary time propagation (a smaller β value) can be performed. To verify this expectation we have tested an Auxiliary Field algorithm where the first "forth" and "back" propagation steps were variational-Jastrow-like while the remaining ones were the ordinary imaginary time propagation steps. In practice

we used a partition function Q:

$$Q = \langle \psi_J | \, e^{-\beta \hat{H}} \, | \psi_J \rangle = \langle \psi_T | \, \hat{U}_J \, e^{-\beta \hat{H}} \hat{U}_J \, | \psi_T \rangle \tag{4.4.5}$$

ψ_T being the usual Hartree-Fock determinant. The α and r_j parameters were chosen in such a way ($\alpha = 1.0$, $r_j = 2.3$) to produce, by a simple variational calculation, a ground state estimate, $E_0 = -0.346 \pm 0.005$ a.u., a little higher than optimal one. In this situation we found that only 6 imaginary time propagation steps, amounting to $\beta = 0.18$ a.u., were necessary to obtain, within the statistical error, the "exact" ground state energy: $E_0 = -0.360 \pm 0.008$ a.u.. In comparison with usual procedure, without introducing Jastrow trial wave functions, the improvement is evident, since a total of 8 propagation steps (about 60 seconds) are required in place of 64. This is very promising for the general situation when a variational method can only give a good approximate ground state energy estimate.

As far as auxiliary field imaginary time-dependence is concerned, some comments are opportune. If one studies the Fourier spectra of the auxiliary fields as a function of τ, there are as many Fourier components as there are time slices, so smaller $\Delta\tau$ in effect introduces higher frequencies. It has been demonstrated [30], in model calculations, that very high frequency fluctuations in the fields have very little effect on the states being propagated. In fact the high components are strictly Gaussian in their distribution, showing that the determinant of states reacts back on them with very weak forces and the amplitudes of the lower components do not vary much when higher components are introduced through smaller $\Delta\tau$. All this supports the idea that the highest components are not very important to the development of the projected many-body state.

In the following table we report ground state energy data obtained by the usual 64 time slice propagation, but with successively reduced Fourier components

which are used in propagating trial wave function.

Fourier components	Energy (a.u.)
64	-0.368 ± 0.011
32	-0.365 ± 0.009
16	-0.363 ± 0.008
8	-0.366 ± 0.013
4	-0.357 ± 0.012
2	-0.340 ± 0.008
1	-0.255 ± 0.003

As we can see the exact ground state value, $E_0 = -0.366$ a.u., is contained within the error bars even by taking into account only 4 Fourier components. Our conclusion from these observations is that a small $\Delta\tau$ is important to obtain accuracy from the Trotter approximation, even though the Trotter formula and a correct treatment of the many-body effects are not inexorably linked. In fact most of the computational work entailed by small $\Delta\tau$ is spent by doing the trivial part of the problem, the one-electron part, with sufficient accuracy. Probably a similar behaviour happens when Fourier coefficients $\sigma(G)$ are considered. In this case, from a physical point of view, we expect that only intermediate frequency components of σ contribute significantly to the evolution. In fact high-G components should be not very important since a physical density is not expected to fluctuate on a small scale, while low-G components are probably not necessary, since, in most of interesting electronic systems, correlation length is not too long. At our small energy cutoff we could not give a definite answer about this expectation.

Unfortunately, when one imposes an higher energy cutoff, in order to obtain meaningful quantitative results, problems arise. In fact, with E_{cut} greater than about 1.5 Ryd's, very large, on the scale of correlation energy, fluctuations in ground state energy estimator take place. They make the statistical error prohibitively huge, actually preventing to get acceptable results in a reasonable com-

puter time. Therefore a considerable effort was spent in order to understand what these fluctuations depend on. Essentially we found that they depend on the following factors:

1) The number N_G of auxiliary field Fourier component which are considered, as we have just reported. We note that $N_G \propto E_{\rm cut}^{\frac{3}{2}}$. To illustrate this N_G-dependence we have used the variational Jastrow algorithm, at $E_{\rm cut} = 6.0$ Ryd's, with $\alpha = 1.0$ and $r_j = 1.0$, but with only the $N_G^{\rm eff} (< N_G)$ lowest G Fourier components which are effectively taken into account in the calculation. As we can see in Fig. 3 the fluctuations, and the consequent error, are still acceptable with $N_G^{\rm eff} = 60$ but they make the results meaningless already for $N_G^{\rm eff} = 200$ (this not very high energy cutoff would require about 2000 σ Fourier components).

2) The strength γ of electron-electron interaction. In fact we performed, at small energy cutoff, some simulation runs with electrons interacting through a γ/r potential (in our previous tests $\gamma = 4$), and found an approximately linear dependence on γ, as far as the statistical error is concerned. For example, if $\gamma = 1$, we obtained $\Delta E_0 = 0.003$ a.u., to be compared with $\Delta E_0 = 0.011$ a.u., we got with $\gamma = 4$.

3) The imaginary time β. In Fig. 4 we show a simulation run with the same parameter of Fig. 1, but $\beta = 0.48$ a.u. (only 16 time slices in place of 64). Fluctuations are evidently much smaller - the statistical error being only $\Delta E_0 = 0.002$ a.u. - even though ground state estimator average converges to a result far from the exact one.

In this case β dependence is also approximately linear and we observe that fluctuations depends on β imaginary time and not on the way it is Trotter-decomposed, that is the time slices number. In the variational Jastrow approach the same arguments hold: if the Jastrow factor $J(r)$ weakly correlates electrons, fluctuations

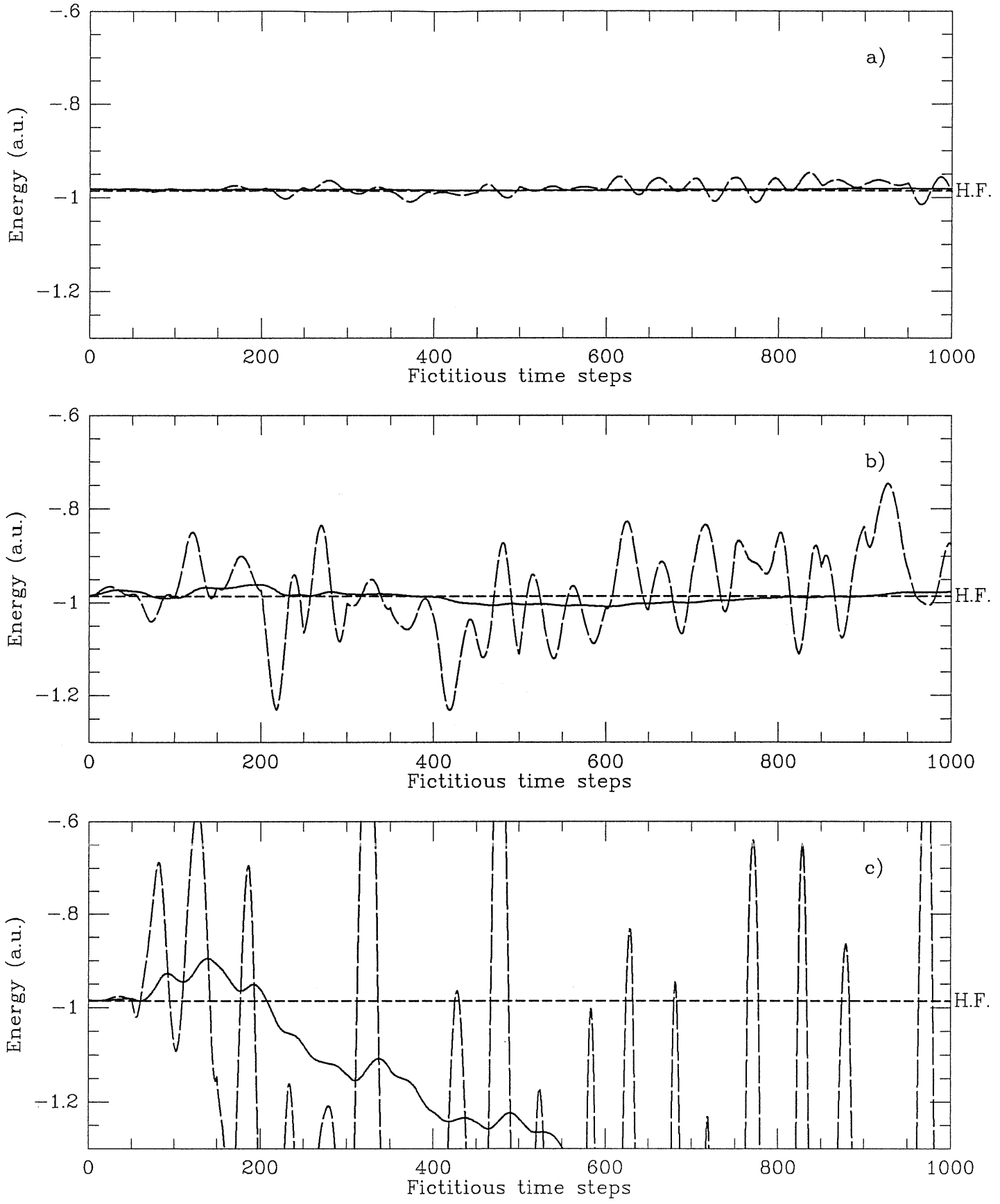

Fig. 3: Variational Jastrow test, at $E_{\rm cut}$=6.0 Ryd's, with only the $N_G^{\rm eff}$ lowest G Fourier components used. In Fig. 3a $N_G^{\rm eff}$=20 and ΔE_0=0.002 a.u.; in Fig. 3b $N_G^{\rm eff}$=60 and ΔE_0=0.017 a.u.; in Fig. 3c $N_G^{\rm eff}$=200 and ΔE_0=0.308 a.u. .

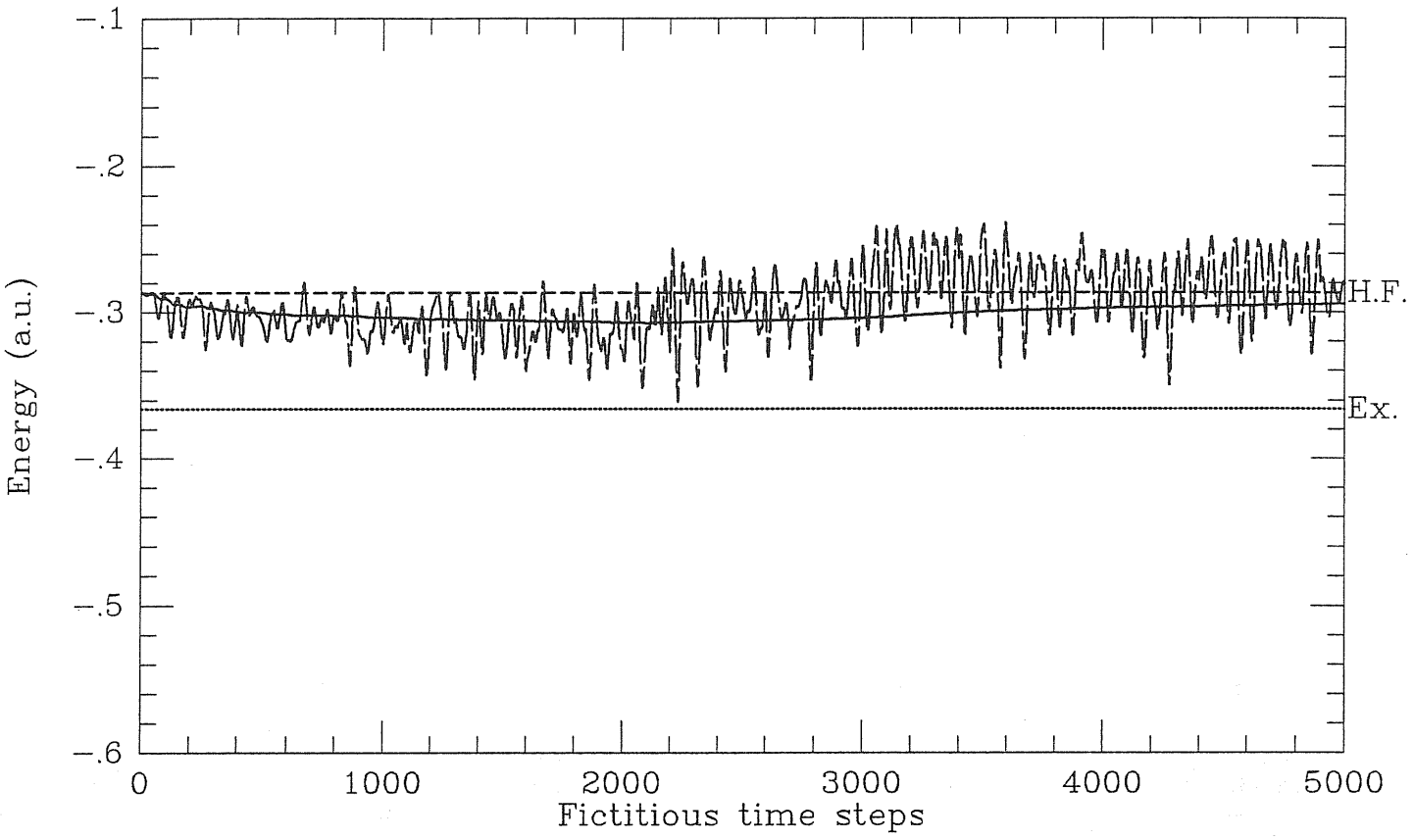

Fig. 4: As in Fig. 1 but with β=0.48 a.u. in place of β=1.92 a.u..

and statistical errors are small, but the result is poor; on the contrary if a suitable correlation is introduced we obtain fluctuations which are comparable with the usual ones when a long enough imaginary time is used (compare Fig. 1 and Fig. 2).

4) The λ parameter. In Chap. 2 we introduced a λ parameter which was necessary in order to obtain a two-body interaction matrix suitable for performing the

Hubbard-Stratonovich transformation. In principle this λ is a simple mathematical trick which should not affect the physical results, but, actually, its presence enhance the fluctuation problem. In fact the effective one-body potential, which governs wave function propagation, has Fourier coefficients given by - see section 2.1 - :

$$V_{\rm eff}(\mathbf{G}) = V_{\rm ext}(\mathbf{G}) - \left(\lambda - \frac{4\pi}{G^2}\right)\sigma^d(\mathbf{G}) \pm \lambda\sigma^m(\mathbf{G}). \qquad (4.4.6)$$

We observe that, since $V_{\rm ext}(\mathbf{G})$ is proportional to $1/G^2$ and $\lambda \geq 4\pi/G^2_{\rm min}$, then for $G \gg G_{\rm min}$ the effective potential becomes:

$$V_{\rm eff}(\mathbf{G}) \simeq -\lambda\left[\sigma^d(\mathbf{G}) \pm \sigma^m(\mathbf{G})\right]. \qquad (4.4.7)$$

This factor introduces two immediately evident negative and undesirable consequences.

First of all most of the σ field components evolve in a way that is completely independent on the physical system we are considering, the minimum allowed λ being fixed only by the form of electron-electron interaction.

Second, λ is usually a large enough constant. In fact $\lambda_{\rm min} = 4\pi/G^2_{\rm min} = a^2/\pi$, with a, the length of our cubic box side, which has to be chosen sufficiently large to make our system really isolate (we have used $a = 10$ a.u.). Therefore it is reasonable that λ, which is present in the one-body propagation and in the auxiliary field evolution, actually introduces a considerable "white noise" in our numerical calculations. Obviously all these negative effects increase when energy cutoff grows.

To confirm our previous assertions we have done two kinds of tests. First we performed two simulation runs at $E_{\rm cut} = 6.0$ Ryd's, by using a variational Jastrow approach. In these two tests all the parameters (α and r_j included) were the same but, in one case the sign of the Jastrow factor was "wrong" (the electrons

would be forced to come closer to each other) and this made the introduction of a λ factor useless. We found that, when λ was not present, the statistical error (and therefore the fluctuations which it depend on) in the ground state energy was about an order of magnitude smaller than in the other case.

Then, always by using a variational Jastrow method at $E_{\text{cut}} = 6.0$ Ryd's, we simply introduced a λ factor which was 5 times greater than the minimum allowed one. In principle this should be of no consequence in final results since a correct Hubbard-Stratonovich transformation only requires to introduce a sufficiently large ($\lambda \geq \lambda_{\text{min}}$) λ factor. Nevertheless the statistical error was about 4 times greater.

To summarize we can reasonably assert that, in our present AFQMC algorithm, if a λ factor has to be introduced, ground state estimator fluctuations are essentially proportional to $\beta\gamma N_G\lambda$ and, therefore, they generally become too large when those parameters assume suitable values to achieve precise quantitative results for ground state properties in realistic physical systems.

Conclusions and Outlook

In this thesis we have described in detail a method for the simulation of realistic many-electron systems. In this approach the Hubbard-Stratonovich transformation allow us to replace direct electronic interactions by coupling to auxiliary fields. Then, sums over these fields are performed statistically using the determinantal and Gaussian weights to guide the importance sampling by means of a force biased algorithm.

As in any other statistical method the most important problem is the minimization of the statistical error. At present our method seems to be not really efficient (especially in comparison with other QMC techniques) since, when we apply it to compute Hydrogen molecule ground state properties, large fluctuations in estimator values actually prevent us from obtaining physically interesting results except that in very small energy cutoff situations.

In order to solve this serious difficulty, we are studying several possible improvements, all of them being based on the "trick" to build into the method as much as possible of the physics without biasing the results by limiting the degrees of freedom of the system. For instance, our preliminary numerical tests show that, actually, only a small number of Fourier components are strictly necessary to obtain correct results, even though, at present time, a precise criterion to select these essential degrees of freedom is missing. Another promising solution is to reduce the auxiliary field degrees of freedom by performing a kind of "spatial importance sampling", that is by suitably neglecting field sampling in space regions, which for example are far enough from the centre of our molecule, where we expect field evolution does not affect physical properties. All these ideas surely require a deeper

investigation and a substantial amount of further numerical tests.

Nevertheless we are confident enough that it is feasible to obtain good results for a simple molecular system, such as H_2, at a reasonable energy cutoff, by using an improved version of our AFQMC algorithm. Then the problem of introducing very high energy cutoffs to achieve a good accuracy in calculated properties should not be an insuperable difficulty. In fact we expect that high energy cutoff corrections are essentially due to one-body properties and therefore they can easily be attained, for example, by a Local Density approach.

In conclusion we have demonstrated that application of the AFQMC method to a continuous system is feasible, even though the possibility of obtaining truly meaningful results for realistic systems depends basically on the solution of the auxiliary field fluctuation problem.

Appendix A

Derivation of Hubbard Stratonovich Transformation

We must prove the following identity for multidimensional integrals over real variables:

$$[\det(\beta A)]^{-\frac{1}{2}} e^{\frac{\beta}{2}\sum_{ij} A^{-1}_{ij}\rho_i\rho_j} = \frac{1}{(2\pi)^{\frac{n}{2}}}\int \mathrm{d}x_1 \ldots \mathrm{d}x_n e^{-\frac{\beta}{2}\sum_{ij} A_{ij}x_i x_j + \beta\sum_i x_i\rho_i} \tag{A.1}$$

where A is a real, symmetric, positive definite, $n \times n$ matrix.

This identity is straightforwardly established by changing variables to reduce it to diagonal form and using the familiar Gaussian integral:

$$\sqrt{\frac{\pi}{a}} = \int_{-\infty}^{+\infty} \mathrm{d}x e^{-ax^2}. \tag{A.2}$$

First of all let us perform the transformation:

$$y_i = x_i - \sum_j A^{-1}_{ij}\rho_j. \tag{A.3}$$

By using the relation $\sum_k A_{ik}A^{-1}_{kj} = \delta_{ij}$ and the symmetry of A we can rewrite the integral in the R.H.S of eq. $(A.1)$:

$$\int \mathrm{d}x_1 \ldots \mathrm{d}x_n e^{-\frac{\beta}{2}\sum_{ij} A_{ij}x_i x_j + \beta\sum_i x_i\rho_i} =$$

$$= \int \mathrm{d}y_1 \ldots \mathrm{d}y_n e^{-\frac{\beta}{2}\sum_{ij} A_{ij}y_i y_j + \frac{\beta}{2}\sum_{ij} A^{-1}_{ij}\rho_i\rho_j}. \tag{A.4}$$

Then we introduce the variables $z_k = \sum_i O_{ki}y_i$, where O is the orthogonal transformation which diagonalizes A:

$$\sum_{ij} = O_{ki}A_{ij}O^{-1}_{jm} = \alpha_m\delta_{km}. \tag{A.5}$$

With this transformation the R.H.S of eq $(A.4)$ becomes:

$$e^{\frac{\beta}{2}\sum_{ij} A^{-1}_{ij}\rho_i\rho_j}\int \mathrm{d}y_1\ldots\mathrm{d}y_n e^{-\frac{\beta}{2}\sum_{ij} A_{ij}y_iy_j} =$$

$$= e^{\frac{\beta}{2}\sum_{ij} A^{-1}_{ij}\rho_i\rho_j}\int \mathrm{d}z_1\ldots\mathrm{d}z_n e^{-\frac{\beta}{2}\sum_{l} z_l^2\alpha_l} \qquad (A.6)$$

where we used the fact that O is a unitary transformation, $\sum_k O_{ki}O_{kj} = \sum_k O^{-1}_{ik}O_{kj} = \delta_{ij}$, and α_l are the eigenvalues of A.

Now we can directly apply the well known eq.$(A.2)$:

$$e^{\frac{\beta}{2}\sum_{ij} A^{-1}_{ij}\rho_i\rho_j}\int \mathrm{d}z_1\ldots\mathrm{d}z_n e^{-\frac{\beta}{2}\sum_{l} z_l^2\alpha_l} = e^{\frac{\beta}{2}\sum_{ij} A^{-1}_{ij}\rho_i\rho_j}\prod_l\sqrt{\frac{2\pi}{\alpha_l\beta}}. \qquad (A.7)$$

Finally we can write

$$\prod_l\sqrt{\frac{2\pi}{\alpha_l\beta}} = \frac{(2\pi)^{\frac{n}{2}}}{[\det(\beta A)]^{\frac{1}{2}}} \qquad (A.8)$$

and therefore we have shown that:

$$\int \mathrm{d}x_1\ldots\mathrm{d}x_n e^{-\frac{\beta}{2}\sum_{ij} A_{ij}x_ix_j+\beta\sum_i x_i\rho_i} = [\det(\beta A)]^{-\frac{1}{2}}(2\pi)^{\frac{n}{2}} e^{\frac{\beta}{2}\sum_{ij} A^{-1}_{ij}\rho_i\rho_j} \qquad (A.9)$$

and hence identity $(A.1)$ is proved.

Note that the positivity of all eigenvalues α_l of A, that is the fact that A is a positive definite matrix, is essential for convergence of Gaussian integrals and, therefore, a crucial condition for the validity of the proof.

Appendix B

Higher order correlation function estimator

Here we want to show that (see Chap.2):

$$\left\langle c_i^\dagger c_j c_m^\dagger c_n \right\rangle = \left\langle c_i^\dagger c_j \right\rangle \left\langle c_m^\dagger c_n \right\rangle + \left\langle c_i^\dagger c_n \right\rangle \left\langle c_j c_m^\dagger \right\rangle . \tag{B.1}$$

Let us consider the quantity:

$$\left\langle c_j c_n c_i^\dagger c_m^\dagger \right\rangle \equiv \frac{\left\langle c_n^\dagger c_j^\dagger \hat{U}_\sigma (t,\beta)\, \psi_T \middle| c_i^\dagger c_m^\dagger \hat{U}_\sigma (t,0)\, \psi_T \right\rangle}{\left\langle \hat{U}_\sigma (t,\beta)\, \psi_T \middle| \hat{U}_\sigma (t,0)\, \psi_T \right\rangle}. \tag{B.2}$$

This involves the scalar product of two $(N+2)$-state determinants and we can write:

$$\left\langle c_j c_n c_i^\dagger c_m^\dagger \right\rangle = \frac{\det \tilde{A}\,(jn,im)}{\det A} \tag{B.3}$$

where A is the usual overlap matrix:

$$A_{pq} = \langle \tilde{\varphi}_p^< | \tilde{\varphi}_q^> \rangle \tag{B.4}$$

and

$$\tilde{A}_{pq}\,(jn,im) = \begin{pmatrix} \delta_{jm} & \delta_{nm} & \dots & \tilde{\varphi}_q^>(\mathbf{r}_m) & \dots \\ \delta_{ji} & \delta_{ni} & \dots & \tilde{\varphi}_q^>(\mathbf{r}_i) & \dots \\ \vdots & \vdots & & & \\ \tilde{\varphi}_p^<(\mathbf{r}_j) & \tilde{\varphi}_p^<(\mathbf{r}_n) & & A_{pq} & \\ \vdots & \vdots & & & \end{pmatrix}. \tag{B.5}$$

Let us introduce the quantity:

$$B\,(j,m) = \sum_{pq} \tilde{\varphi}_p^>(\mathbf{r}_m) A_{pq}^{-1} \tilde{\varphi}_q^<(\mathbf{r}_j). \tag{B.6}$$

Now, since a determinant remains unchanged if one adds to a column any linear combination of the others, we may add to the *first column* of the matrix $\tilde{A}$ a linear combination of the other columns in order to make vanishing all the elements of the first column but the ones in the *first two rows*:

$$\det\tilde{A} = \det\begin{pmatrix} \delta_{jm} - b_0\delta_{nm} - \sum_q b_q\tilde{\varphi}_q^{>}(\mathbf{r}_m) & \dots & \dots \\ \delta_{ji} - b_0\delta_{ni} - \sum_q b_q\tilde{\varphi}_q^{>}(\mathbf{r}_i) & \dots & \dots \\ \vdots & & \\ \tilde{\varphi}_p^{<}(\mathbf{r}_j) - b_0\tilde{\varphi}_p^{<}(\mathbf{r}_n) - \sum_q b_q A_{pq} & \dots & \dots \\ \vdots & & \end{pmatrix}. \qquad (B.7)$$

We choose $b_0 = 0$ and $b_q = \sum_{q'} A^{-1}_{qq'}\tilde{\varphi}_{q'}^{<}(\mathbf{r}_j)$. Then we obtain:

$$\det\tilde{A} = \det\begin{pmatrix} \delta_{jm} - B(j,m) & \delta_{nm} & \dots & \tilde{\varphi}_q^{>}(\mathbf{r}_m) & \dots \\ \delta_{ji} - B(j,i) & \delta_{ni} & \dots & \tilde{\varphi}_q^{>}(\mathbf{r}_i) & \dots \\ \vdots & \vdots & & & \\ 0 & \tilde{\varphi}_p^{<}(\mathbf{r}_n) & & A_{pq} & \\ \vdots & \vdots & & & \end{pmatrix}. \qquad (B.8)$$

Now we can repeat the same procedure in order to make vanishing all the elements of the *second column* but the ones in the *first two rows* and we have:

$$\det\tilde{A} = \det\begin{pmatrix} \delta_{jm} - B(j,m) & \delta_{nm} - B(n,m) & \dots & \tilde{\varphi}_q^{>}(\mathbf{r}_m) & \dots \\ \delta_{ji} - B(j,i) & \delta_{ni} - B(n,i) & \dots & \tilde{\varphi}_q^{>}(\mathbf{r}_i) & \dots \\ \vdots & \vdots & & & \\ 0 & 0 & & A_{pq} & \\ \vdots & \vdots & & & \end{pmatrix} = \qquad (B.9)$$

$$= \det\begin{pmatrix} B_{(2\times 2)} & \vdots & C_{(2\times N)} \\ \dots & \vdots & \dots \\ 0_{(N\times 2)} & \vdots & A_{(N\times N)} \end{pmatrix} = \det B \cdot \det A. \qquad (B.10)$$

Therefore by using definition (2.35):

$$\left\langle c_j c_n c_i^{\dagger} c_m^{\dagger} \right\rangle = \det B =$$

$$= [\delta_{jm} - B(j,m)][\delta_{ni} - B(n,i)] - [\delta_{nm} - B(n,m)][\delta_{ji} - B(j,i)] =$$

$$= \langle c_j c_m^\dagger \rangle \left\langle c_n c_i^\dagger \right\rangle - \langle c_n c_m^\dagger \rangle \left\langle c_j c_i^\dagger \right\rangle . \qquad (B.11)$$

Finally, by usual anticommutation rules for fermion operators c,$c^\dagger$, we obtain:

$$\left\langle c_i^\dagger c_j c_m^\dagger c_n \right\rangle = - \left\langle c_j c_n c_i^\dagger c_m^\dagger \right\rangle + \delta_{in} \langle c_j c_m^\dagger \rangle - \delta_{ij} \langle c_n c_m^\dagger \rangle + \delta_{nm} \left\langle c_i^\dagger c_j \right\rangle =$$

$$= \left\langle c_i^\dagger c_j \right\rangle \langle c_m^\dagger c_n \rangle + \left\langle c_i^\dagger c_n \right\rangle \langle c_j c_m^\dagger \rangle . \qquad (B.12)$$

Appendix C

Ground state energy and forces in reciprocal space

Let us consider the plane wave expansion

$$\varphi_p(\mathbf{r}) = \sum_{\mathbf{G}} C_p(\mathbf{G}) e^{i\mathbf{G}\cdot\mathbf{r}} \tag{C.1}$$

with Fourier coefficients given by:

$$C_p(\mathbf{G}) = \frac{1}{\Omega} \int \mathrm{d}\mathbf{r} \varphi_p(\mathbf{r}) e^{-i\mathbf{G}\cdot\mathbf{r}}. \tag{C.2}$$

The estimator of total ground state energy, evaluated at a particular auxiliary field configuration σ and at a fixed imaginary time t is:

$$E^t_{\hat{H}}(\sigma) = E^t_{\hat{K}\mathrm{in}}(\sigma) + E^t_{\hat{V}^{\mathrm{ext}}}(\sigma) + E^t_{\hat{V}^{\mathrm{ee}}}(\sigma) + E_{\mathrm{ion}}. \tag{C.3}$$

Then, by using definitions $(C.1 - C.2)$ and relations $(2.2.16 - 2.2.18)$ we can write the various components in the following way.

$$E^t_{\hat{K}\mathrm{in}}(\sigma) = \frac{1}{2} \sum_{\mu} \sum_{pq} (A^{\mu})^{-1}_{pq} \sum_{\mathbf{G}} G^2 \tilde{C}^{*<}_q(\mathbf{G}) \tilde{C}^{>}_p(\mathbf{G}) \tag{C.4}$$

$$E^t_{\hat{V}^{\mathrm{ext}}}(\sigma) = \sum_{\mu} \sum_{pq} (A^{\mu})^{-1}_{pq} \sum_{\mathbf{G}\neq 0} V^{\mathrm{ext}}(\mathbf{G}) \tilde{f}^*_{qp}(\mathbf{G}) \tag{C.5}$$

$$\begin{aligned} E^t_{\hat{V}^{\mathrm{ee}}}(\sigma) = {} & \frac{2\pi}{\Omega} \sum_{\mu\mu'} \sum_{pqp'q'} (A^{\mu})^{-1}_{pq} (A^{\mu'})^{-1}_{p'q'} \sum_{\mathbf{G}\neq 0} \frac{1}{G^2} \tilde{f}^{*\mu}_{qp}(\mathbf{G}) \tilde{f}^{*\mu'}_{q'p'}(\mathbf{G}) - \\ & - \frac{2\pi}{\Omega} \sum_{\mu} \sum_{pqp'q'} (A^{\mu})^{-1}_{pq} (A^{\mu'})^{-1}_{p'q'} \sum_{\mathbf{G}\neq 0} \frac{1}{G^2} \tilde{f}^{*\mu}_{q'p}(\mathbf{G}) \tilde{f}^{*\mu}_{qp'}(\mathbf{G}) + \\ & + N \left(\frac{2\pi}{\Omega} \sum_{\mathbf{G}\neq 0} \frac{1}{G^2} - \frac{1}{\pi} G_{\mathrm{cut}} \right). \end{aligned} \tag{C.6}$$

$$E_{\text{ion}} = 2\pi\Omega \sum_{\mathbf{G}\neq 0} \frac{|\rho_{\text{Gauss}}(\mathbf{G})|^2}{G^2} + \frac{1}{2}\sum_{I\neq J} Z_I Z_J \frac{\text{erfc}\left(|\mathbf{R}_I - \mathbf{R}_J|\sqrt{\frac{2}{\alpha}}\right)}{|\mathbf{R}_I - \mathbf{R}_J|} - \sqrt{\frac{\alpha}{2\pi}}\sum_I Z_I^2. \tag{C.7}$$

where:

$$A_{pq} \equiv \sum_{\mathbf{G}} \tilde{C}_p^{*<}(\mathbf{G})\tilde{C}_q^{>}(\mathbf{G}) \tag{C.8}$$

$$\tilde{f}_{qp}(\mathbf{G}) \equiv \frac{1}{\Omega}\int \mathrm{d}\mathbf{r}\tilde{\varphi}_q^{<}(\mathbf{r})\tilde{\varphi}_p^{>}(\mathbf{r})e^{-i\mathbf{G}\cdot\mathbf{r}} \tag{C.9}$$

$$V^{\text{ext}}(\mathbf{G}) \equiv \frac{1}{\Omega}\int \mathrm{d}\mathbf{r}V^{\text{ext}}(\mathbf{r})e^{-i\mathbf{G}\cdot\mathbf{r}}. \tag{C.10}$$

The last term in eq. (C.6), with $G_{\text{cut}} = \sqrt{2E_{\text{cut}}}$, is due to the fact that a periodically repeated system is considered. Therefore, in order to obtain electron-electron interaction per unit cell, one has to formally compute interaction between *all* the electrons of *all* the cells, by avoiding to take self-interaction into account, and then divide by the (infinite) number of cells.

The ion-ion interaction energy, produced by repulsion of unit point charges, is conveniently computed by adding and subtracting the interaction between Gaussianly shaped charge distributions:

$$\rho_{\text{Gauss}}(\mathbf{r}) = \left(\frac{\alpha}{\pi}\right)^{\frac{3}{2}}\sum_I Z_I e^{-\alpha(\mathbf{r}-\mathbf{R}_I)^2} \tag{C.11}$$

where α parameter, which determines Gaussian charge radius $R_{\text{Gauss}} = 1/\sqrt{\alpha}$, has to be suitably chosen.

We note that, in principle, $E^t_{\hat{V}^{\text{ext}}}(\sigma), E^t_{\hat{V}^{\text{ee}}}(\sigma), E_{\text{ion}}$ all contain $\mathbf{G} = 0$ terms and, therefore, they are separately divergent due to the form of the Coulomb potential Fourier transform. Anyway, all these divergent contributions cancel each other as we expect since the entire system is neutral.

As far as computation of forces, in auxiliary fields dynamics, is concerned, we can write the total energy $E_{\text{tot}}(\sigma, p)$ by considering real and imaginary parts of

Fourier coefficients

$$\sigma(\mathbf{G}) = \frac{1}{\Omega}\int \mathrm{d}\mathbf{r}\sigma(\mathbf{r})e^{-i\mathbf{G}\cdot\mathbf{r}}. \tag{C.12}$$

as independent variables:

$$\begin{aligned} E_{\mathrm{tot}}(\sigma,p) = \frac{1}{2}\sum_{l=1}^{P}\sum_{G>0}\left(|p^d(\mathbf{G})|^2 + |p^m(\mathbf{G})|^2\right) + \\ + \Delta\tau\Omega\sum_{l=1}^{P}\sum_{G>0}\left(|\sigma^d(\mathbf{G})|^2 W(G) + |\sigma^m(\mathbf{G})|^2\lambda\right) - \\ - \ln\langle\psi_T|\,\hat{U}\,|\psi_T\rangle + \text{const.} \end{aligned} \tag{C.13}$$

where

$$\lambda = \frac{4\pi}{G_{\mathrm{min}}^2} \tag{C.14}$$

$$W(G) = 4\pi\left(\frac{1}{G_{\mathrm{min}}^2} - \frac{1}{G^2}\right) = \lambda - \frac{4\pi}{G^2} \tag{C.15}$$

and we consider only the positive G Fourier coefficients as independent variables since we keep our *sigma* fields real and therefore:

$$\sigma(-\mathbf{G}) = \sigma^*(\mathbf{G}). \tag{C.16}$$

At each "heath-bath" step (see Chap. 3) we impose the condition:

$$\langle E_{\mathrm{kin}}\rangle = \frac{1}{2}N_d = 2PN_G \tag{C.17}$$

with N_d, the total number of degrees of freedom, which is obtained by multiplying the number N_G of positive G vectors by the number P of imaginary time slices, a factor 2 for the real and imaginary components of complex Fourier coefficients and, finally, a factor 2 for the two different kinds of fields we have to take into account.

By differentiating eq. ($C.13$) we obtain the following formulae for the forces:

$$F^d(\mathbf{G},l) \equiv -\frac{\partial V(\sigma)}{\partial \sigma^d(\mathbf{G},l)} = 2\Omega\Delta\tau \left[-\sigma^d(\mathbf{G},l) + h^d(\mathbf{G},l)\right] W(G) \qquad (C.18)$$

$$F^m(\mathbf{G},l) \equiv -\frac{\partial V(\sigma)}{\partial \sigma^m(\mathbf{G},l)} = 2\Omega\Delta\tau \left[-\sigma^m(\mathbf{G},l) + h^m(\mathbf{G},l)\right] \lambda \qquad (C.19)$$

with:

$$h^d(\mathbf{G},l) = \sum_{p\uparrow q\uparrow} (A^{\uparrow}_{qp})^{-1} f^{\uparrow}_{pq}(\mathbf{G},l) + \sum_{p\downarrow q\downarrow} (A^{\downarrow}_{qp})^{-1} f^{\downarrow}_{pq}(\mathbf{G},l) \qquad (C.20)$$

$$h^m(\mathbf{G},l) = \sum_{p\uparrow q\uparrow} (A^{\uparrow}_{qp})^{-1} f^{\uparrow}_{pq}(\mathbf{G},l) - \sum_{p\downarrow q\downarrow} (A^{\downarrow}_{qp})^{-1} f^{\downarrow}_{pq}(\mathbf{G},l) \qquad (C.21)$$

and:

$$f_{qp}(\mathbf{G},l) \equiv \frac{1}{\Omega} \int \mathrm{d}\mathbf{r} \varphi^{<}_{q}(\mathbf{r},l) \varphi^{>}_{p}(\mathbf{r},l) e^{-i\mathbf{G}\cdot\mathbf{r}}. \qquad (C.22)$$

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